TSINGHUA-PRINCETON-COMBUSTION INSTITUTE

2021 SUMMER SCHOOL ON COMBUSTION

Advanced Laser Diagnostics in Combustion Research

Mark Linne
The University of Edinburgh
July 11−17, 2021

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Advanced Laser Diagnostics for Combustion Research

Lecture 1: Overview and Introduction

Mark Linne

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Topics

Overview

Examples of Laser Diagnostics

- Absorption
- Laser induced fluorescence (LIF)
- Rayleigh and Raman scattering
- Particle image velocimetry (PIV)
- Four-wave mixing spectroscopies

Synthesis of this review

- Synthesis
- Course contents
- Other resources

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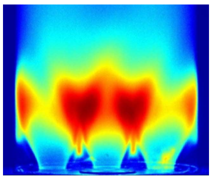
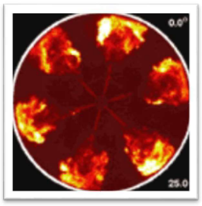
Why laser diagnostics?

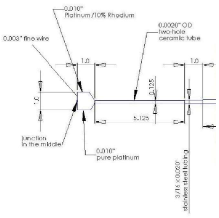


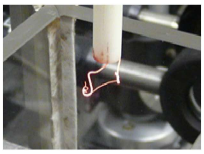


Do not use a laser diagnostic technique unless you really have to use it

- Physical probes can be inexpensive and easier to use.
- Passive imaging techniques like chemiluminescence from a molecule or luminescence from soot are much simpler and they are less expensive.
- They can be combined with high speed imaging systems and used in very challenging environments like IC engines.

Why laser diagnostics?





Do not use a laser diagnostic technique unless you really have to use it

- If the flow is steady, one can simply use a fine-wire thermocouple to detect temperature.
- Be aware, however that it will be necessary to apply a radiation correction to the measurement.
- The radiation correction introduces uncertainty, more than the uncertainty of CARS (for example); but it is so much simpler!

Why laser diagnostics?

Do not use a laser diagnostic technique unless you really have to use it

- One can use a white light to illuminate a flow (e.g. spray) from the front for "backscatter imaging" (aka "dark field imaging").
- Alternatively, backlighting with white light provides shadowgrams or schlieren images (aka "light field imaging").
- Here, incoherent white light provides much better image quality and spatial resolution than one would get with a laser.

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Why laser diagnostics?

But laser diagnostics can obtain detailed information

- They can detect minor species, temperatures, 3-D velocity etc.
- They can be used to make measurements at single point, in a plane, or even in 3-D.
- They can create high speed image sets, with appropriate statistical moments, for LES development.
- Short pulses freeze even the fastest events.

Moreover -

- They don't disturb the flame, if done correctly (they are "non-intrusive").
- These measurements can be done simultaneously, so that physics and chemistry can be correlated.

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Laser diagnostics

Ways to categorize laser diagnostics-

- Spectroscopic ('resonant'[1]) vs. non-spectroscopic ('non-resonant') techniques.
- Line-of-sight, single point (sort of), planar, or volumetric.
- Continuous, pulsed, or high-speed pulsed.
- Linear vs. nonlinear.
- The technique: absorption, laser induced fluorescence etc.

Various kinds of lasers-

- Continuous wave (cw) or pulsed (short pulse (ps - fs) or long pulse (ns -100 ns)).
- Narrow bandwidth or broad bandwidth.
- Infrared (IR), visible, or ultraviolet (UV).

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[1] Matching an atomic or molecular transition.

Some example laser diagnostics

- In what follows I will briefly describe several laser diagnostic techniques.
- There are many techniques and it is not possible to present all of them.
- Since this is an introduction we will discuss several of the most common techniques.
- We will also cover the range of classifications given above.
- This discussion will introduce a lot of new concepts and terms; but we will use the rest of this course to discuss them in detail.
- Don't panic if something seems unfamiliar; we are setting the stage for the week.

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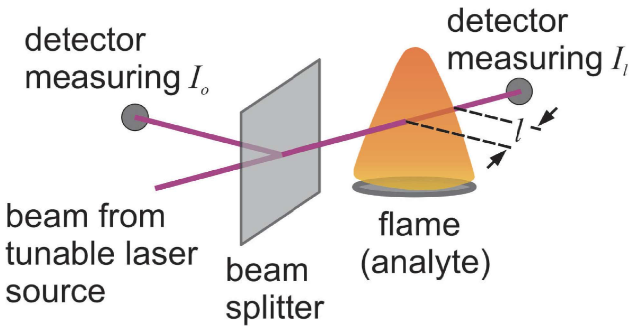
Absorption



Absorption

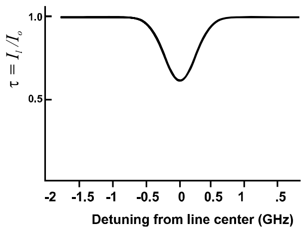
- Pass a tunable laser beam at frequency ν_L (resonant with an atomic or molecular transition) across the flow.
- Observe fractional reduction in beam irradiance (e.g. beam transmission τ) as a function of ν_L (scan the laser frequency).
- Use Beer's law to extract the number density of absorbers:

  $\tau(\nu) = I_l/I_o = e^{-N\sigma_\nu l}$, where:

  N is the number density of absorbers

  σ_ν is the absorption cross section

  l is the absorption path length through the flame



Absorption

Facts about this technique

- There are several ways to present Beer's law; this is just one of them.
- Beer's law applies only when the absorber is uniform across the path length (ok in many cases; e.g. shock tubes, exhaust pipes etc.).
- This is a line-of-sight (path integrated) technique.
- It is necessary to know σ_ν in advance.

Absorption

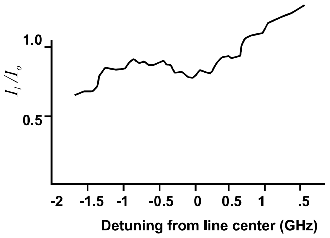
Facts about this technique continued

- When used in an appropriate experiment, the result is an absolute determination of number density.
- Combining two resonances (two absorption lines) can also provide temperature (via Boltzmann statistics).
- If one uses many beams at various angles, and applies the equation of radiative transfer instead of Beer's law, one can perform absorption tomography and extract a 3-D field of species and/or temperature from a steady flow.

Absorption

Experimental difficulties

- Most absorption techniques use diode lasers that are tuned by scanning current (that heats the diode and changes the laser frequency a small amount). That also makes the laser power change with laser frequency.
- Lasers can have a large amount of amplitude noise. The oscillations in amplitude can look similar to an absorption profile, and they set the detection limit of this technique.



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Absorption

Signal processing

- A balanced detector can background-subtract some of the change in power with current and some of the noise.
- Modulation/demodulation techniques (e.g. 'wavelength modulation spectroscopy' or 'frequency modulation spectroscopy') can force the experiment out to frequencies where the laser noise is minimal, filter, and then mix back down to normal frequencies.
- Cavity-enhanced techniques (e.g. 'multi-pass cells', 'cavity ringdown spectroscopy', or 'integrated cavity output spectroscopy') cause a big increase in ℓ (up to 100 km) which gives much higher sensitivity.

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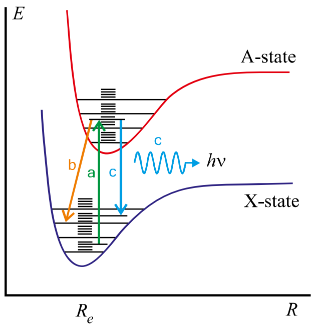
Absorption

In summary, absorption is -

- A resonant technique.
- Line-of-sight.
- Continuous mostly, but can be pulsed (e.g. CRDS).
- A linear technique (the signal scales with I).
- Across all infrared, visible, and ultraviolet, spectral regimes.
- Often narrow bandwidth but can be broad bandwidth ('hyperspectral').
- Absorption is fully quantitative if applied properly.

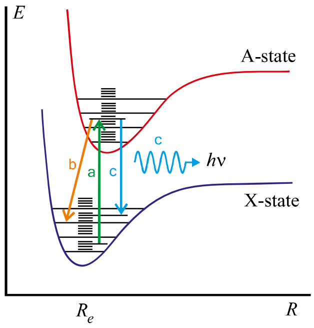
Laser induced fluorescence (LIF)

- This image depicts a lower electronic state (the 'X-state') for a diatomic molecule, together with the first excited electronic state (the 'A-state').
- We will discuss this curve in more detail later, but it is important to point out that statistical thermo dictates that at normal temperatures some of the ro/vibrational levels in the X-state are populated, but usually not those in the A-state.
- In LIF, the laser is tuned to overlap an allowed electronic- vibrational- rotational transition in the molecule; some laser light is absorbed (process a) and the absorbing molecules then occupy the A-state.



Laser induced fluorescence

- Once a molecule is in the A-state it can stay for a moment because that state has a natural lifetime, although that is not where statistical thermo wants it to be in equilibrium.
- During that lifetime, the energy can be redistributed across the other vibrational- rotational levels in the A-state (called the 'upper manifold'). It can also give up its energy to a collision partner during a collision (called 'quenching' and it's a function of the collider molecule, process **b**).



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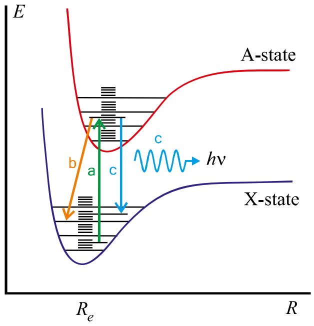
Laser induced fluorescence

- Molecules remaining in the A-state can relax back to the X-state by giving off fluorescence light (process **c**).
- The fluorescence quantum yield $\Phi \equiv$ (fluorescence photons)/(laser pump photons) is very small (order of 0.1%).



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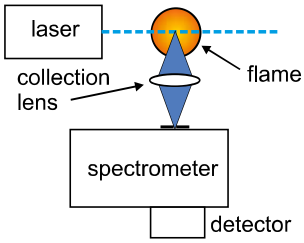
Laser induced fluorescence

LIF at single point

- Initially, people made LIF measurements at single point as shown.
- It wasn't really at a single point; it had a sample volume defined by the lens and the laser beam.
- Such an approach can still be used if the signal level is low, or if a researcher wants to study the spectrum.
- It is possible to make LIF more quantitative if one measures the quenching partners at the same time via Raman scattering.



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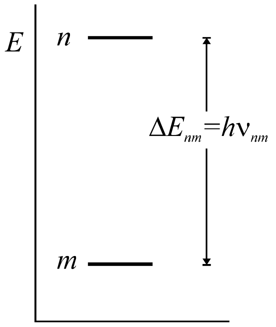
Laser induced fluorescence

Quantifying LIF

- Consider a highly oversimplified 2-level spectroscopic system (common in LIF).
- Assuming the laser is broadband (so we can ignore spectral overlaps for now) we can write the molecular-photon dynamics using Einstein rate coefficients:

$$S_F = \eta B_{mn} I_L \tau_L N_m \Phi \frac{\Omega}{4\pi} V$$

where S_F is the fluorescence signal.



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Laser induced fluorescence

$$S_F = \eta B_{mn} I_L \tau_L N_m \Phi \frac{\Omega}{4\pi} V$$

For the record

- η is a system efficiency (including losses in optics etc.),
- B_{mn} is the Einstein coefficient for absorption,
- I_L is the laser irradiance,
- τ_L is the laser pulsewidth,
- N_m is the number density in level m (the level that absorbs),
- Φ is the LIF quantum yield (including things like quenching),
- Ω is the optics collection solid angle, and
- V is the sample volume.

- Or, alternatively, many people just calibrate LIF.

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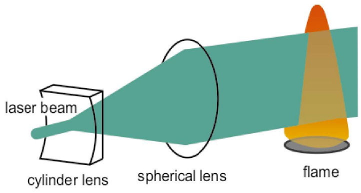
Planar LIF (PLIF) imaging



- Spread a laser beam into a sheet by first expanding it in the vertical direction only, by using a cylinder lens.
- Then collimate the vertical and focus the horizontal with a spherical lens. Alternatively, one or two cylinder lenses can be used instead of the spherical lens.
- This is basically how all planar laser imaging techniques produce the planar laser-flame interaction.

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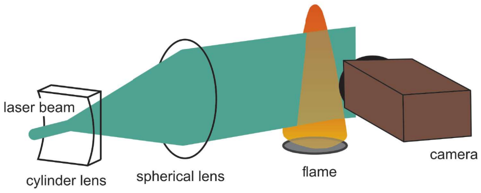
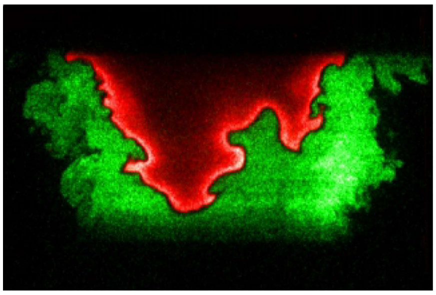
Planar LIF (PLIF) imaging



- The camera views the laser plane at 90° to the plane.
- PLIF cameras have to be able to sense low light levels (e.g. use an image intensifier, a back-illuminated CCD, or an electron multiplying CCD).
- High-speed systems use an image intensifier.

A PLIF example



- PLIF in a low swirl burner at the University of Lund.
- Green indicates unburned acetone used as a fuel tracer.
- Red is post-flame OH.

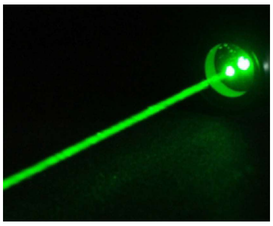
In summary, LIF is -

- A resonant technique.
- Spatially resolved (not line-of-sight) - and it allows imaging.
- Normally a pulsed technique.
- A linear technique (the signal scales with I).
- Normally performed in the visible and UV spectral regions.
- LIF is background-free; no fluorescence means no signal, the sensor is not looking into a large amount of of laser amplitude noise. This makes LIF much more sensitive than absorption.
- LIF can be made quantitative if applied properly, but usually that means a calibration.
- Some important molecules can not be measured by LIF for a number of reasons (e.g. Φ is too small). Often an absorption technique will sense them.

Scattering from a laser beam

- What you see in the photo is elastic scattering (i.e. the scattered light is at the same wavelength as the laser beam).
- It's called "elastic" because it describes the outcome of a collision between a photon and an object. It's elastic when the photon departs with the same energy ($E = h\nu$) it had when entering.

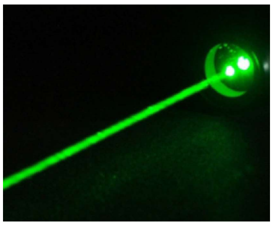
You have seen this:



Scattering from a laser beam

- You see some strong points of light that move around. That is Mie scattering from dust in the air.
- There is also a weaker, uniform volume of light. That is Rayliegh scattering from molecules in the air.
- Rayleigh scattering is proportional to density (if the chemical composition remains constant) and if pressure is uniform it can be used to image temperature.

You have seen this:



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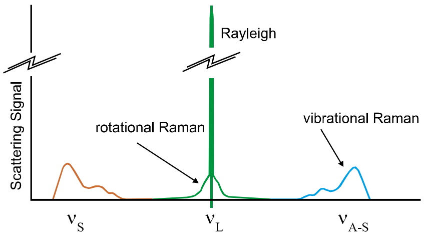
Rayleigh and Raman scattering



- Your eye detects only the elastically scattered Rayleigh light but there is a much weaker inelastic Raman scattering process.
- If you think like an electrical engineer, it is analogous to an RF mixer; the interaction puts sidebands on the carrier (the carrier is the Rayleigh response here).
- The carrier mixes with ro-vibrational modes of a molecule to make sidebands.

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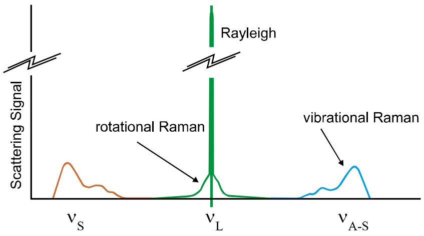
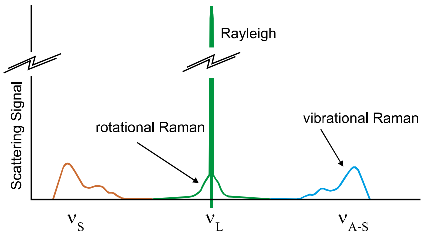
Rayleigh and Raman scattering



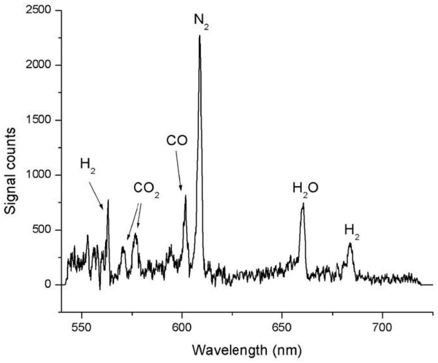
- The Raman signature comes from all of the rotational-vibrational transitions in all of the 'Raman active' molecules, so it is possible to detect a number of species simultaneously.
- The Raman response is very weak so it is possible to detect only major species, and those only at a single point or along a line (not often in a plane).
- If one resolves an entire vibrational manifold, one can infer temperature from the shape.

Rayleigh and Raman scattering



- When frequencies are shifted lower (more red) the Raman bands are called 'Stokes', and when higher the bands are called 'Anti-Stokes'.
- One can calibrate the system using known species (e.g. N_2) signatures that are built into the same spectrum.
- When combined with LIF of a minor species, Raman can provide LIF quenching information.

Rayleigh and Raman scattering



Single-shot Stokes Raman spectrum from a spray flame excited by a laser beam at 532 nm, from a project evaluating the effects of droplets and high hydrocarbon concentrations on the diagnostic.

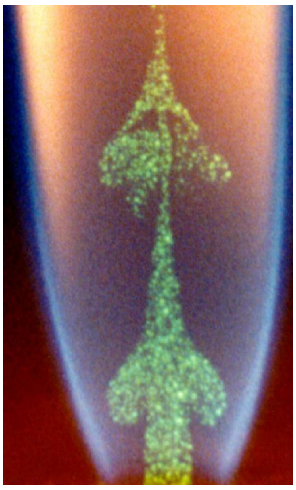
In summary, Rayleigh scattering is -

- A non-resonant, elastic ($\nu_{\mathrm{Rayleigh}} = \nu_{\mathrm{laser}}$) scattering technique.
- Spatially resolved (not line-of-sight) - and it allows imaging.
- Normally a pulsed technique but can also use cw.
- A linear technique (the signal scales with I).
- Like LIF it is background-free.
- A direct measure of density. If pressure is constant and the sample is uniform, an image of density can be used to infer an image of temperature.

In summary, Raman scattering is -

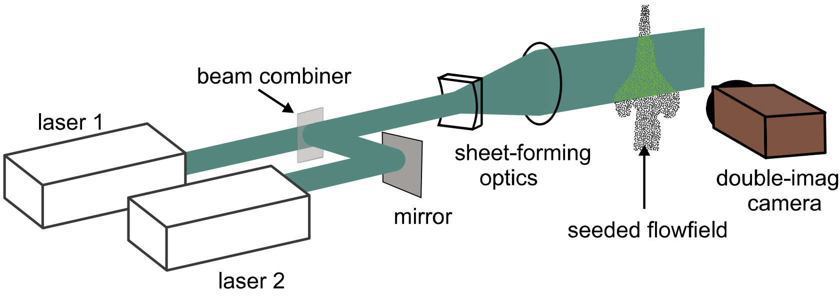
- A non-resonant, in-elastic ($\nu_{\text{Raman}} \neq \nu_{\text{laser}}$) but spectroscopic scattering technique.
- Spatially resolved (not line-of-sight) - but too weak to allow imaging.
- Normally a pulsed technique for the gas phase.
- A linear technique (the signal scales with I).
- It is not background-free because the Rayleigh signature is very close in wavelength and therefore challenging to suppress. Moreover, fluorescence and laser induced incandescence of particles can interfere.
- A way to detect multiple major species and temperature in a single shot.

Particle image velocimetry (PIV)



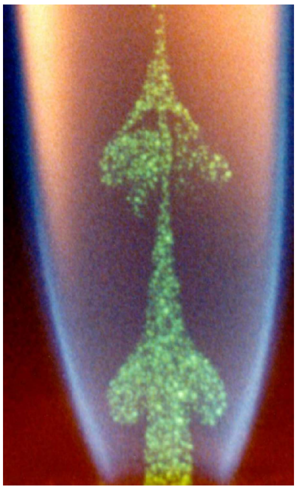
- As the name implies, it is necessary to seed the flow with particles (usually 1 μm oil drops or ceramic particles).
- The flow is illuminated with two frequency-doubled Nd:YAG laser pulses (at 532 nm, green light) in rapid succession, both shaped into a plane.
- Mie scattered light from the particles is imaged at 90° to the planes with a double-image camera.

PIV



An example complete system.

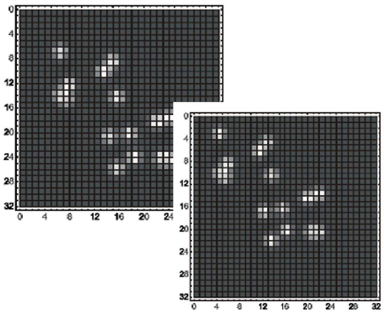
PIV



- To achieve good spatial resolution the flow must be densely seeded.
- One can't just follow individual particles between the two frames (that's called 'particle tracking velocometry').
- Instead, the image is divided into many small interrogation cells.
- The interrogation cell from frame 1 is correlated with the cell from frame 2.

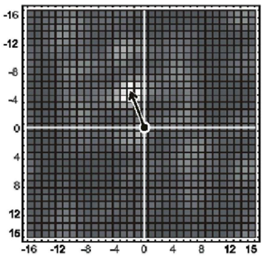
PIV image processing

- Two interrogation cells from images taken with a known time separation Δt.
- The correlation between the two is taken using FFT's.



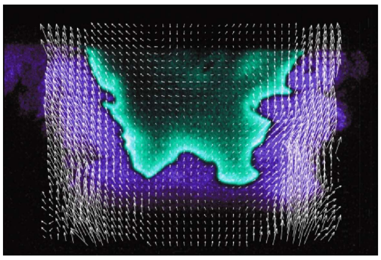
PIV image processing

- Two interrogation cells from images taken with a known time separation Δt.
- The correlation between the two is taken using FFT's.
- The correlation produces a cell-averaged offset $\Delta \ell$ and velocity is then $\Delta \ell / \Delta t$.
- Notice the background noise in the correlation; the correlation peak has to rise above it or the vector is not legitimate.



A correlation result.

PIV example



- Here a PLIF image of acetone fuel tracer (blue) and OH (green) similar to slide 24 is combined with PIV in a simultaneous frame.
- Simultaneous PLIF and PIV allow one to investigate interaction between the flow and the flame.
- This can be done even at very high image rates if one has sufficient funding.

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PIV

- 'Stereoscopic' PIV uses two double-image cameras viewing the laser plane at an angle (with camera lenses in the 'Scheimpflug' arrangement).
- This allows one to extract an out-of-plane velocity component; hence stereoscopic PIV provides a 2-D image of 3-D velocity.
- Holographic and volumetric PIV use sophisticated image processing to acquire a volume of velocity vectors, but with more limited spatial dynamic range.

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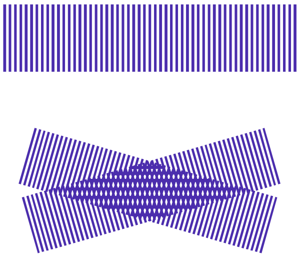
In summary, PIV is -

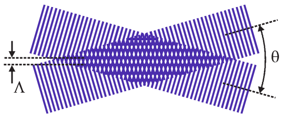
- A non-resonant technique.
- Spatially resolved (not line-of-sight).
- Normally a pulsed technique for the gas phase.
- A linear technique (the signal scales with I).
- Like LIF it is background-free (but scattered light from surfaces can present a problem).
- A way to detect velocity vectors even at high speed.
- It is a bit intrusive because seeding particles are added to the flow.

Laser induced grating spectroscopy (LIGS)



- A laser beam can be considered a sequence of plane waves.
- If we split a beam into two and cross them they will interfere with each other.
- If the laser is tuned to an absorption resonance, the interference pattern will be absorbed, producing a population grating.

Laser induced grating spectroscopy (LIGS)

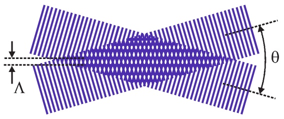


- If we know the 'pump' beam crossing angle θ we can get the fringe spacing Λ from:

$$\Lambda = \frac{\lambda_{pu}}{2\sin(\theta/2)}$$

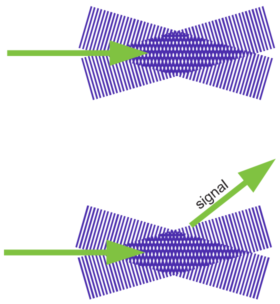
  where λ_{pu} is the pump laser wavelength.
- This population grating quickly thermalizes to produce a fringe pattern of hot and cool molecules (a thermal grating). Since the index of refraction is temperature dependent, this index fringe can scatter light like a transmission grating.

Laser induced grating spectroscopy (LIGS)



- In addition, molecular collisions between hot molecules and the surrounding gas will generate two counter-propagating acoustic (low pressure) waves. Matched counter-propagating waves will generate a standing wave structure.
- This acoustic grating also represents an index wave and it can also scatter light.
- If we use a laser pulse around 8 ns in width, the time-dependence of this grating will be observable.

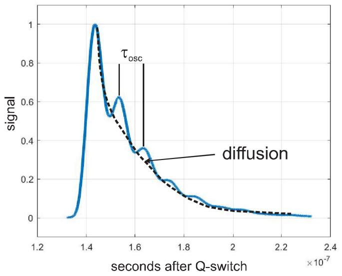
Laser induced grating spectroscopy (LIGS)



- Now bring in a third cw beam (the 'probe' beam) at a different wavelength.
- That beam will partially 'Bragg scatter' off of the gratings, producing a fourth, signal beam.
- The Bragg angle (θ_B) for scattering is given by $2\Lambda\sin(\theta_B) = n\lambda_{pr}$ where n is an integer (the scattering order) and λ_{pr} is the probe laser wavelength.

Laser induced grating spectroscopy (LIGS)

- LIGS is thus a 'four-wave mixing technique'.
- The measured waveform contains a decay caused by thermal and mass diffusion, combined with the signature of the standing acoustic wave.
- The speed of sound is directly measured as $v_{sound} = \Lambda/\tau_{osc}$.
- A more complex hydrodynamic model can be used to extract other parameters, including temperature.



Laser induced grating spectroscopy (LIGS)

In summary, LIGS is -

- A resonant technique.
- A nonlinear technique because the signal scales with three input laser beam intensities (it's a 3^{rd} order technique).
- Spatially resolved, and it works along a line so long as the detectors are fast enough.
- A pulsed+cw technique.
- A direct way to detect sound speed but other parameters are indirect.
- A high precision temperature measurement, but it does not have high accuracy unless the species in the sample volume (colliders) are known.

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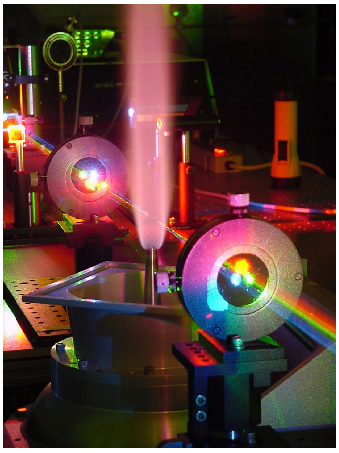
Coherent anti-Stokes Raman spectroscopy (CARS)



- CARS is a four-wave mixing technique in which beams at several wavelengths (often several lasers) are crossed in the flame to define a sample point.
- The beams excite 'Raman coherences' in a nonlinear fashion and a probe beam reads them out.
- A fourth signal beam exits the flame, carrying an entire nonlinear Raman spectrum.
- This technique produces a strong signal because the beams keep exciting the Raman coherences.

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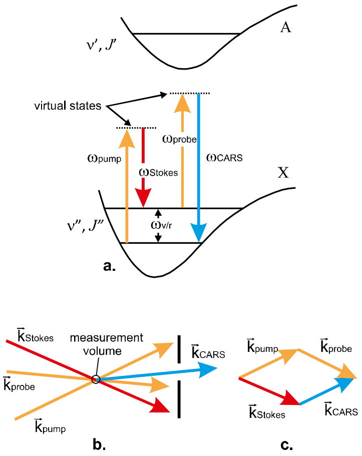
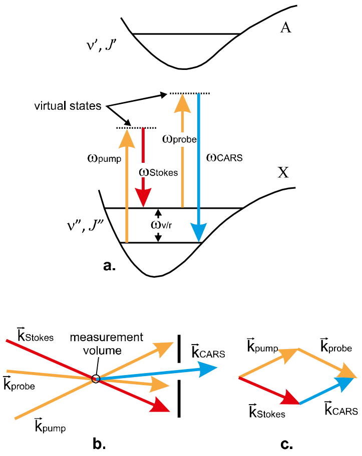
CARS



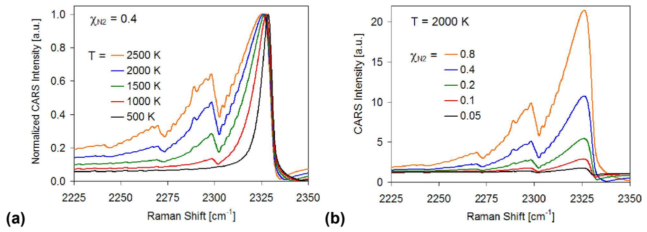
- The difference between two of the input beams (the Pump and Stokes beams) is matched in energy to actual ro-vibrational transitions.
- This two-beam input (two-photon excitation) does not directly change populations across $\omega_{v/r}$, but it does excite Raman coherences (more on that later in the class) within the probe volume.

CARS



- The probe beam then scatters off of the coherences to produce the CARS signal beam.
- The three input beams have to be arranged at specific angles relative to each other ('phase matching') and then the signal beam comes out at a known location and angle.

CARS



- Typical CARS spectra of nitrogen (synthesized in this case).
- The vibrational spectral fit is strongly temperature dependent (good thermometer), and
- CARS is also concentration dependent.

In summary, CARS is -

- A resonant technique - in a different context.
- Spatially resolved (a crossed-beam technique).
- Normally a pulsed technique for the gas phase.
- A non-linear technique (the signal scales with I^3).
- It is background-free.
- A way to detect temperature and some species concentrations.

CARS

- There has been a recent renaissance in CARS research based on the use of short pulse (pico- and femto-second) lasers.
- Perhaps the most exciting aspect of short-pules CARS is that pressure no longer corrupts the signals.
- Short pulse CARS generates very high signal levels and it has been used in line and planar imaging formats for species detection.
- It can also be used to study population and orientation transfers during chemical reaction.
- We will discuss recent developments in short pulse CARS later in the course.

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Synthesis

- This short review has identified a number of subjects in physics that are applied when making laser diagnostics measurements.
- Concepts in classical optics are applied to manipulate and collect light (I assume you have studied this).
- The equation of radiative transfer is used to describe how the intensity of light is manipulated to produce and propagate diagnostic signals.
- Often we have to use physical optics and the wave equation to describe an optical interaction e.g. light scattering from particles or drops, interference, and nonlinear interactions for example.
- Species and temperature measurements rely upon statistical thermodynamics, spectroscopy and quantum mechanics.
- That's a lot!

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This set of lectures

Monday	**Tuesday**
Introduction / Eqn. Rad. Transfer / Physical optics	Scattering / PIV, wOFV /SLIPI,BI
Wednesday	**Thursday**
Intro to quantum / Spectroscopy & OH / Stat. thermo, resonance,	Lasers / Absorption & lineshape / LIF
Friday	
Raman / Nonlinear optics / CARS	

Other resources

Laser diagnostics

- W. Demtröder, “Laser spectroscopy: basic concepts and instrumentation”, Springer, 1998.
- A.C. Eckbreth, “Laser diagnostics for combustion temperature and species”, Gordon and Breach, 1996.
- R.K. Hanson, R.M. Spearrin, and C.S. Goldstein, “Spectroscopy and Optical Diagnostics for Gases”, Springer, 2016.
- K. Kohse-Höinghaus and J.B. Jeffries, “Applied combustion diagnostics”, Elsevier, 2002.
- M. Linne, “Spectroscopic Measurement: an Introduction to the Fundamentals”, Academic Press, 2002.
- A. Steinberg, and S. Roy, editors, “Optical Combustion Diagnostics for Propulsion and Power Systems: Theory and Application”, American Institute of Aeronautics and Astronautics, (anticipated 2022)

Other resources

Optics

- E. Hecht, "Optics", Addison-Wesley, 2015.
- M. V. Klein and T. E. Furtak, "Optics", John Wiley and Sons, 1986.
- R. W. Boyd, "Nonlinear Optics", Academic Press, 1992.

Electricity and magnetism

- J. D. Jackson, "Classical Electrodynamics", John Wiley and Sons, 1999.
- R. K. Wangsness, "Electromagnetic Fields", John Wiley and Sons, 1986.

Lasers

- A. Siegman, "Lasers", University Science Books, 1986.

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Other resources

Quantum mechanics

- I. N. Levine, "Quantum Chemistry", Prentice Hall, 1991.
- J. J. Sakurai, "Modern Quantum Mechanics", Addison-Wesley, 1995.

Raman scattering

- D. A. Long, "The Raman Effect: A Unified Treatment of the Theory of Raman Scattering by Molecules", John Wiley and Sons, 2002.

Particle/droplet scattering

- C. F. Bohren and D. R. Huffman, "Absorption and Scattering of Light by Small Particles", John Wiley and Sons, 1983

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Other resources

Classics

- S.S. Penner, “Quantitative molecular spectroscopy and gas emissivities”, Addison-Wesley, 1959.
- G. Herzberg, “Atomic spectra and atomic structure”, Dover, 1944.
- G. Herzberg, “Spectra of diatomic molecules”, Krieger Publishing Co., 1950.
- G. Herzberg, “Molecular spectra and molecular structure, volume II, Infrared and Raman Spectra of Polyatomic Molecules”, Krieger Publishing Co., 1945.
- G. Herzberg, “Molecular spectra and molecular structure, volume III, Electronic spectra and electronic structure of polyatomic molecules”, Krieger Publishing Co., 1966.

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Next topic

The equation of radiative transfer

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Advanced Laser Diagnostics for Combustion Research

Lecture 2: Light and the Equation of Radiative Transfer

Mark Linne

University of Edinburgh

Tsinghua-Princeton-CI Summer School on Combustion
July 11 - 17, 2021

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Topics

Light

Equation of Radiative Transfer

- Definitions
- Development of the ERT
- Rate equations

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Introduction

- This lecture will begin with some optical concepts that are important for diagnostics.
- Next we will discuss how one performs calculations on a diagnostic from a classical viewpoint.
- The lecture will focus more on topics like absorption and fluorescence, but the same formalism is typically used to deal with chemiluminescence, other forms of luminescence like that emanating from soot, and other forms of optical emission/absorption in flames.

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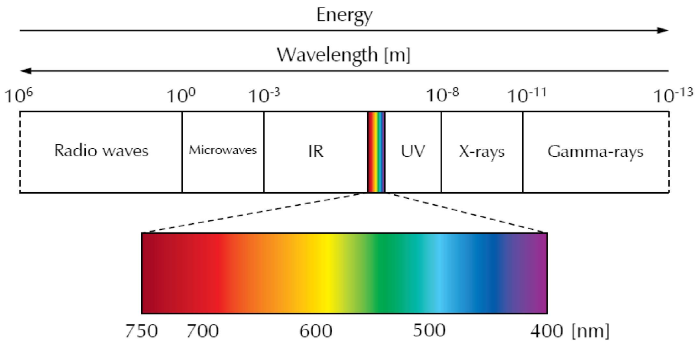
Light



- Light is an electromagnetic wave and these waves are typically characterized by their position in the electromagnetic spectrum.
- Note that Energy $= h\nu$ (h is Planck's constant), so frequency (ν) increases to the right while wavelength (λ) increases to the left.

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Light

- The wavelength (λ, nm) and frequency (ν, 1/s or Hz) of light are related by $\nu = u/\lambda$, where u is the speed of light in a material. As an aside - spectroscopists often use wavenumbers, $\check{\nu} = \nu/c$ in cm^{-1} where $c =$ speed of light in vacuum.
- $u = c/n$ where $n =$ material index of refraction.
- ν is a constant ($\nu = u/\lambda = c/\lambda_\circ$ where $\lambda_\circ$ is the wavelength in vacuum); as light passes through various materials u and λ change with the index (n) of the material, but ν doesn't because energy ($E = h\nu$) is conserved.
- Light always has bandwidth, and frequency bandwidth can be written in terms of wavelength bandwidth as:

$$|\mathrm{d}\nu| = \left|-\left(\frac{c}{\lambda_\circ^2}\right)\mathrm{d}\lambda_\circ\right| = \left|-\left(\frac{c}{n\lambda^2}\right)\mathrm{d}\lambda\right|.$$

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Light

Light can be described two different ways:

Classical optics

- In an optics course, one usually focuses on the redirection of light (e.g. ray tracing for imaging).
- The rays of light really represent energy flow, but for many optics calculations the energy is not important. For imaging, for example, the way in which light is redirected by optical elements is more important.
- In part, therefore, classical optics has to do with energy conservation (although it was hidden), and one way to represent that is by the equation of radiative transfer (ERT).
- For diagnostics; classical optics and the ERT are used to understand techniques like absorption, fluorescence, PIV etc.

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Light

Light can be described two different ways:

Physical optics

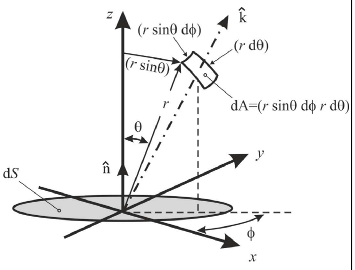
- Physical optics describe electromagnetic waves with the wave equation.
- This formalism is necessary to describe interference, diffraction, ultimate image resolution, lasers and so forth.
- For diagnostics; physical optics is used for laser beam propagation, interferometry (FTIR), particle scattering, holography, nonlinear optics, and fundamental classical/quantum optics.

Physical and classical optics are parallel formalisms, linked by the Poynting theorem in which the electric field strength is related to irradiance (energy).

Start with classical optics and the Equation of Radiative Transfer

Some definitions:

- $I \equiv$ Irradiance $= \frac{power}{unit\,area}\left(\frac{W}{m^2}\right)$
- $J \equiv$ Radiance $= \frac{power}{unit\,area-sr}\left(\frac{W}{m^2 sr}\right)$ where sr denotes a steradian defined as :
  - ▷ $\Omega \equiv \frac{area}{distance^2} = \frac{\mathrm{d}A}{r^2}$
- $\rho \equiv$ Energy density $\frac{energy}{unit\,volume}\left(\frac{J}{m^3}\right)$
- $E_p \equiv$ energy/photon $= h\nu$ where h is Planck's constant $h = 6.63 \times 10^{-34} J - s$



Equation of Radiative Transfer

Further definitions, now on a per-unit bandwidth basis:

- $I_\nu \equiv$ Spectral irradiance $= \frac{power}{(unit\,area)(unit\,bandwidth)} \left(\frac{W}{m^2 Hz}\right)$
- $J_\nu \equiv$ Spectral radiance $= \frac{power}{(unit\,area)sr(unit\,bandwidth)} \left(\frac{W}{m^2 sr Hz}\right)$
- $\rho_\nu \equiv$ Spectral energy density $\frac{energy}{(unit\,volume)(unit\,bandwidth)} \left(\frac{J}{m^3 Hz}\right)$
- And then -

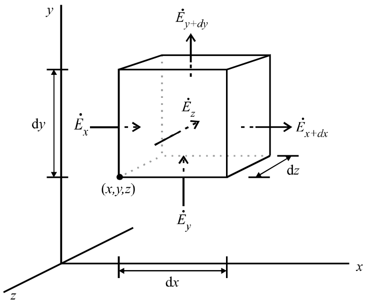
  $I_\nu = \rho_\nu c;\ J_\nu = \frac{\rho_\nu c}{\Omega};\ I = \int_{-\infty}^{+\infty} I_\nu \mathrm{d}\nu;\ J = \int_{-\infty}^{+\infty} J_\nu \mathrm{d}\nu$
- Finally, the number of photons per unit volume is then

  $N_p = \frac{\rho_\nu}{h\nu}\mathrm{d}\nu.$

Equation of Radiative Transfer

A conservation expression

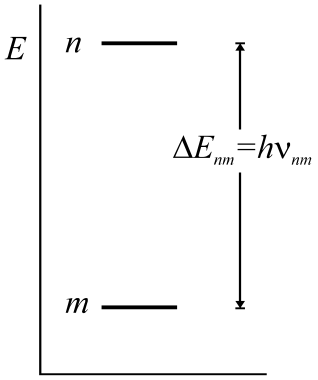
- The ERT is just energy conservation, but including special terms related to light.
- Similar to other energy bookkeeping approaches;



$$\frac{\partial E_{cv}}{\partial t} = \dot{E}_x + \dot{E}_y + \dot{E}_z$$
$$-\dot{E}_{x+\mathrm{d}x} - \dot{E}_{y+\mathrm{d}y} - \dot{E}_{z+\mathrm{d}z}$$
$$+creation - loss$$

Equation of Radiative Transfer

- For creation and loss terms; assume the interactions are spectroscopic for this development (they don't have to be - they could focus instead on black body interactions for soot, as one example).
- Spectroscopic interactions occur between two allowed quantum levels, so it is common to assume a two-level system as shown, with upper level n and lower level m.



Equation of Radiative Transfer

- The spectroscopic version of the ERT is then:

$$\frac{\partial}{\partial t}\Big(\rho_\nu \, \mathrm{d}\nu\Big) + \vec{\nabla}\cdot\Big(\rho_\nu \vec{c} \, \mathrm{d}\nu\Big) \tag{1}$$
$$= h\nu N_n A_{nm} Y_\nu \, \mathrm{d}\nu + h\nu (N_n B_{nm} - N_m B_{mn}) \rho_\nu Y_\nu \, \mathrm{d}\nu \quad (\mathrm{W/m^3})$$

where:

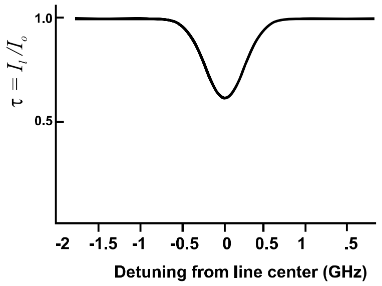
N_n is the number density of atoms/molecules in energy level n,
N_m is the number density of atoms/molecules in energy level m,
A_{nm} is the Einstein coefficient for spontaneous emission $(1/s)$,
B_{nm} is the Einstein coefficient for stimulated emission $(m^3/J-s)$,
B_{mn} is the Einstein coefficient for stimulated absorption $(m^3/J-s)$, and
Y_ν is the interaction lineshape function $(1/Hz)$.

- The terms associated with the Einstein coefficients are sources and sinks for optical energy.

Equation of Radiative Transfer

Line shape function Y_ν

- The transitions between m and n don't happen at just one precise frequency (ν_{nm}), there is some bandwidth to the phenomenon:



- And lineshape functions are normalized: $\int_{-\infty}^{+\infty} Y_\nu \mathrm{d}\nu = 1.$
- More about this topic will be presented later on.

Equation of Radiative Transfer

Further development:

- It is quite common to assume steady state (especially relative to the rates of molecular processes§); so $\partial/\partial t \to 0$,and then the the $\mathrm{d}\nu$ terms cancel out across equation (1).
- Assume the light travels along an optic axis z, with relatively small solid angle Ω so that $\partial/\partial x = \partial/\partial y \simeq 0$.
- Recall that the spectral radiance is $J_\nu = c\rho_\nu/\Omega \ \ (W/m^2 sr Hz)$.
- And the spectroscopic ERT becomes:

$$\frac{\mathrm{d}J_\nu}{\mathrm{d}z} = \frac{h\nu}{4\pi} N_n A_{nm} Y_\nu + \frac{h\nu}{c}(N_n B_{nm} - N_m B_{mn}) J_\nu Y_\nu \qquad (2)$$

§ If not, one must consider using the density matrix equations of quantum mechanics.

Equation of Radiative Transfer

Define:

- Volume emission coefficient per steradian:
  $\epsilon_\nu(z) \equiv \frac{h\nu}{4\pi} N_n A_{nm} Y_\nu \ (W/m^3 sr Hz)$.
- Volume absorption coefficient:
  $\kappa_\nu(z) \equiv \frac{h\nu}{c}(N_m B_{mn} - N_n B_{nm}) Y_\nu \ (1/m)$.
- And the spectroscopic ERT becomes:

$$\frac{\mathrm{d}J_\nu}{\mathrm{d}z} = \epsilon_\nu(z) - \kappa_\nu(z) J_\nu \qquad (3)$$

More definitions:

- Source function: $S_\nu(z) \equiv \frac{\epsilon_\nu}{\kappa_\nu}$.
- Optical depth: $\tau_\nu(\ell) \equiv \int\limits_0^\ell \kappa_\nu(z')\mathrm{d}z'$.

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Equation of Radiative Transfer

- It's possible to leave the ERT as it is, but researchers often assume the medium is homogeneous (no dependence on z).
- To get to the expressions frequently used in diagnostics we will assume the medium is homogeneous going forward, but that assumption can be seriously in error within a flame.
- If we assume homogeneity:
  $S_\nu(z) = S_\nu = \frac{\epsilon_\nu}{\kappa_\nu}$
  $\tau_\nu(\ell) = \kappa_\nu \ell$
- And the spectroscopic ERT can be integrated across dz to give:

$$J_\nu = \underbrace{J_\nu(0)e^{-\kappa_\nu \ell}}_{\text{absorption}} + \underbrace{S_\nu\left[1 - e^{-\kappa_\nu \ell}\right]}_{\text{emission}} \qquad (4)$$

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Equation of Radiative Transfer

Emission

- If the medium is emitting (e.g. via chemiluminescence, or the light emitted by LIF) and there is no light source being absorbed, the ERT can be written:

$$J_\nu(\ell) = S_\nu \left[1 - e^{-\kappa_\nu \ell}\right] \tag{5}$$

- If τ_ν is small we can linearize the expression to give:

  $J_\nu(\ell) = S_\nu \left[1 - (1 - \kappa_\nu \ell)\right] = \epsilon_\nu \ell = \frac{h\nu}{4\pi} N_n A_{nm} Y_\nu \ell$
- The $1/4\pi$ appears because J is on a per-unit-solid-angle basis and molecules emit in all directions. To convert to irradiance I multiply J by the solid angle of the collection optics Ω:

  $I_\nu(\ell) = h\nu \frac{\Omega}{4\pi} N_n A_{nm} Y_\nu \ell$

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Equation of Radiative Transfer

Absorption

- If the medium is not emitting but it is illuminated by a light source that can be absorbed, the ERT can be written:

$$J_\nu(\ell) = J_\nu(0) e^{-\kappa_\nu \ell} \tag{6}$$

  which is one form of the Beer-Lambert law
- Usually Ω does not change with distance in such a case, and then:

  $I_\nu(\ell) = I_\nu(0) e^{-\kappa_\nu \ell}$
  which is the most common form of the Beer-Lambert law.
- If the medium is optically thin and $N_n \sim 0$ (e.g. the upper state is not populated, thermally or otherwise):

  $I_\nu(\ell) = I_\nu(0) \left[1 - \frac{h\nu}{c} N_m B_{mn} Y_\nu \ell\right]$
  an expression that is no longer used very much.

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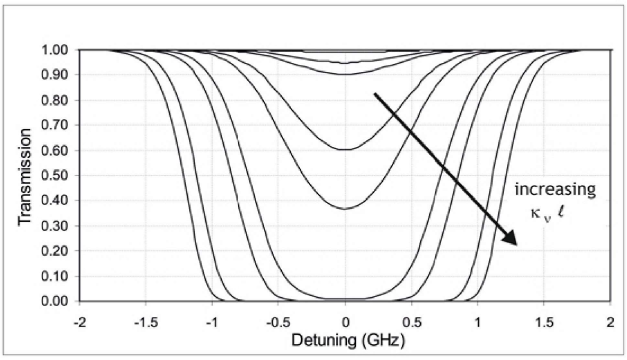
Equation of Radiative Transfer

The effect of optical depth $\tau_\nu = \kappa_\nu \ell$ on absorption:



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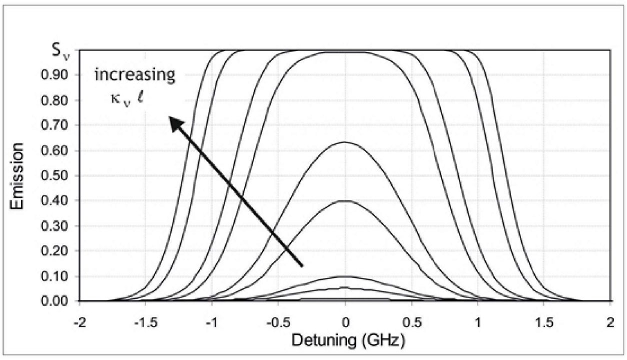
Equation of Radiative Transfer

The effect of optical depth $\tau_\nu = \kappa_\nu \ell$ on emission:



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Rate equations

- The ERT contains relationships for the rate of exchange of populations to various energy levels associated with optical interactions.
- Going back to the original formalism, in order to keep track of the populations in the two levels we write:

  $\frac{\mathrm{d}N_m}{\mathrm{d}t} = -N_m(t)B_{mn}\int_\nu \rho_\nu Y_\nu \mathrm{d}\nu +$
  $N_n(t)\left[B_{nm}\int_\nu \rho_\nu Y_\nu \mathrm{d}\nu + A_{nm}\int_\nu Y_\nu \mathrm{d}\nu + Q_{nm}\right]$

  where Q_{nm} is the rate at which collisions remove population from level n ('collisional quenching') and

  $\frac{\mathrm{d}N_n}{\mathrm{d}t} = N_m(t)B_{mn}\int_\nu \rho_\nu Y_\nu \mathrm{d}\nu -$
  $N_n(t)\left[B_{nm}\int_\nu \rho_\nu Y_\nu \mathrm{d}\nu + A_{nm}\int_\nu Y_\nu \mathrm{d}\nu + Q_{nm}\right]$
- These expressions help define what the Einstein coefficients are, but the Einstein coefficients can also be developed using quantum mechanics.

Rate equations

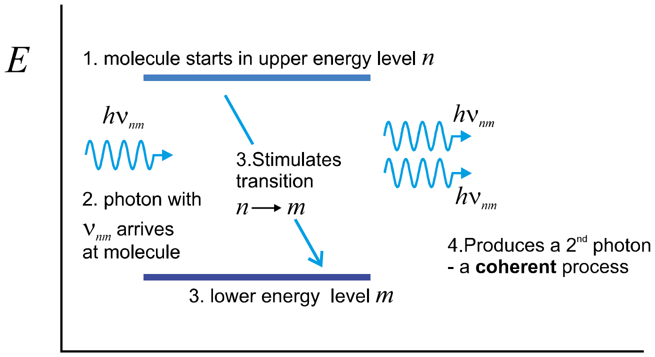
- It is common to make the following definitions:

  - stimulated absorption rate
  $W_{mn} \equiv B_{mn}\int_\nu \frac{I_\nu}{c} Y_\nu \mathrm{d}\nu$

  - stimulated emission rate
  $W_{nm} \equiv B_{nm}\int_\nu \frac{I_\nu}{c} Y_\nu \mathrm{d}\nu$
- And then:
  $\frac{\mathrm{d}N_m}{\mathrm{d}t} = -N_m(t)W_{mn} + N_n(t)\left[W_{nm} + A_{nm} + Q_{nm}\right]$
  (remember the lineshape function is normalized which is why the Y_ν integral disappeared from the A_{nm} term)
  and
  $\frac{\mathrm{d}N_n}{\mathrm{d}t} = N_m(t)W_{mn} - N_n(t)\left[W_{nm} + A_{nm} + Q_{nm}\right]$
- For spontaneous emission (e.g. chemiluminescence) for example:
  $\frac{\mathrm{d}N_n}{\mathrm{d}t} = -N_n(t)A_{nm}$

Rate equations

- Absorption and spontaneous emission may seem clear.
- But stimulated emission is a little bit more complex:



E

1. molecule starts in upper energy level n

$h\nu_{nm}$

2. photon with ν_{nm} arrives at molecule

3.Stimulates transition $n \longrightarrow m$

$h\nu_{nm}$

$h\nu_{nm}$

4.Produces a 2nd photon - a **coherent** process

3. lower energy level m

- This is where laser gain comes from.

Rate equations

Saturation

- For measurements like laser absorption we usually neglect the stimulated emission terms because $N_m >> N_n$, but as the energy of the laser beam increases, N_n grows.
- It's possible to analyze that. To make it simple we can assume that ρ_ν is so spectrally broad that it has no spectral dependence within Y_ν and so we can pull it out of integrals and then the integrals go to 1.
- It's a two level system and mass conservation can be expressed as:
  $N_n + N_m = N_{\text{total}}$
- If N_n reaches its maximum, the system is called saturated. There is no time dependence and we write:
  $N_m B_{mn} \rho_\nu = N_n \left[B_{nm} \rho_\nu + A_{nm} + Q_{nm} \right] \,)$

Rate equations

Saturation

- Use conservation to remove N_m:

  $\frac{N_n}{N_{\text{total}}} = \frac{B_{mn}\rho_\nu}{(B_{nm}+B_{mn})\rho_\nu + A_{nm} + Q_{nm}}$

- Recall that $I_\nu = \rho_\nu c$ and so:

  $\frac{N_n}{N_{\text{total}}} = \frac{B_{mn}}{(B_{nm}+B_{mn})} \frac{1}{1+\frac{I_{\nu,\text{sat}}}{I_\nu}}$

  with

  $I_{\nu,\text{sat}} \equiv \frac{(A_{nm}+Q_{nm})c}{(B_{nm}+B_{mn})}$

- When $I_\nu >> I_{\nu,\text{sat}}, N_n/N_{\text{total}} \rightarrow 1/2$.
- Do not confuse an optically thick situation ($\kappa_\nu \ell$ very large) with saturation - they are totally different limiting situations.

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Next topic

Physical optics and the wave equation

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Advanced Laser Diagnostics for Combustion Research

Lecture 3: Some concepts in electromagnetism

Mark Linne

University of Edinburgh

Tsinghua-Princeton-CI Summer School on Combustion
July 11 - 17, 2021

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Topics

E & M

- Maxwell's equations and the wave equation
- Interaction of light with matter
- The Lorentz atom

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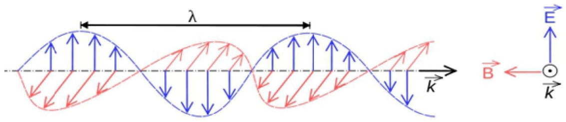
Introduction

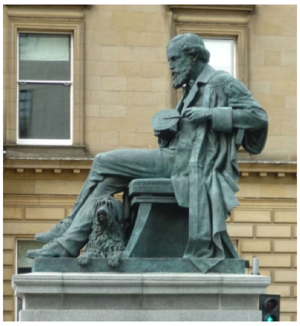
- This lecture will discuss physical optics.
- It will focus on topics like propagation of electromagnetic waves (light) and their interaction with matter including a classical picture of an atom (the Lorentz atom) upon which many concepts are based.
- An understanding of physical optics is necessary to understand nonlinear optics, light scattering and diffraction, and to understand how light can be coupled to quantum mechanics via the density matrix equations.

Light



- Light is an electromagnetic wave (as are x-rays, microwaves etc.).
- The electric permittivity ($\epsilon_\circ$) and the magnetic permeability ($\mu_\circ$) allow the electric field ($\vec{E}$) to sustain the magnetic field ($\vec{B}$) and vice versa as light propagates through vacuum ('free space', the sub-$\circ$ denotes free space).

Light and electromagnetism (E & M)



- The connection between light and electromagnetic waves was discovered by James C. Maxwell. This statue of him and his dog sits at the end of George Street in the Newtown district of Edinburgh.

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E & M

- Maxwell's equations describe electromagnetic fields, including optical radiation. For propagation through free space they are written (in MKS units):

$$\vec{\nabla} \cdot \vec{E} = \frac{\varrho_\mathrm{f}}{\epsilon_\circ} \tag{7}$$

$$\vec{\nabla} \cdot \vec{B} = 0 \tag{8}$$

$$\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \tag{9}$$

$$\vec{\nabla} \times \vec{B} = \mu_\circ \vec{J}_\mathrm{f} + \mu_\circ \epsilon_\circ \frac{\partial \vec{E}}{\partial t} \tag{10}$$

  Here: ϱ_f is the free charge density, and $\vec{J}_\mathrm{f}$ is the free charge current.

- Be aware that E & M uses 3 different units schemes and these equations can look quite different from one scheme to the next. In these lectures everything is written in MKS (actually MKSA).

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E & M

- Make the following assumptions:
  - ▷ Optical interactions are electronic (non-magnetic)
  - ▷ Optical measurements happen in locations where $\varrho_{\mathrm{f}} = 0$ and $\vec{J}_{\mathrm{f}} = 0$.
- Apply vector calculus to get:

$$\nabla^2 \vec{E} = \mu_\circ \epsilon_\circ \frac{\partial^2 \vec{E}}{\partial t^2} \tag{11}$$

$$\nabla^2 \vec{B} = \mu_\circ \epsilon_\circ \frac{\partial^2 \vec{B}}{\partial t^2} \tag{12}$$

- Equations 11 and 12 are both wave equations, and the speed of the waves is given by $c = 1/\sqrt{\mu_\circ \epsilon_\circ}$.
- Independent measurements of $\mu_\circ$, $\epsilon_\circ$ and the speed of light in vacuum (c) confirm this finding.

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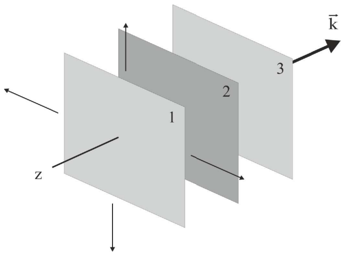
E & M

- The following expressions:

$$\vec{E} = Re\left[\vec{E}_\circ e^{i(\vec{k}\cdot\vec{r}-\omega t)}\right],\ \vec{B} = Re\left[\vec{B}_\circ e^{i(\vec{k}\cdot\vec{r}-\omega t)}\right] \tag{13}$$

are one set of solutions to the wave equation, with $|\vec{k}| = 2\pi/\lambda$ and $\omega = 2\pi\nu$ (rad/sec).



- They describe a simple arrangement of plane waves as shown.

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E & M

- The wave equation is linear, so equation 13 can form a basis set of solutions (with various values for $\vec{E}_\circ$, $\vec{k}$, and ω for example) that are combined to form more complex solutions to the wave equation.
- The plane wave solution (equation 13) is thus much more important than it may seem at first; it is the building block for physical optics solutions.
- Now, if we plug equation 13 into equations 7 and 8, we get:

$$\vec{\nabla}\cdot\vec{E} = -i\vec{k}\cdot\vec{E} = 0$$
$$\vec{\nabla}\cdot\vec{B} = -i\vec{k}\cdot\vec{B} = 0$$

meaning that $\vec{E}$ and $\vec{B}$ are both normal to $\vec{k}$, and $\vec{k}$ points in the direction of plane wave propagation (we didn't prove that here but look in the references if you want to see it); so $\vec{E}$ and $\vec{B}$ oscillate transverse to the direction of propagation.

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E & M

- Now plug equations 13 into equation 9:

$\vec{B} = \frac{\vec{k}\times\vec{E}}{c|\vec{k}|}$

Since $\vec{E}$ is normal to $\vec{k}$, $\vec{E}$ and $\vec{B}$ are normal to each other.
- The three vectors $\vec{E}$, $\vec{B}$ and $\vec{k}$ form a right-handed coordinate system.
- Note that the amplitude terms $\vec{E}_\circ$ and $\vec{B}_\circ$ are actually vectors; they are polarized. In optics, 'polarization' denotes the electric terms since optical interactions are nearly always electronic.
- Because the $\vec{E}$ field oscillates normal to $\vec{k}$, it can potentially oscillate at any angle within the plane wave (so long as $\vec{B}$ follows around and stays normal to $\vec{E}$).
- This means that any polarization state can be decomposed into two states.

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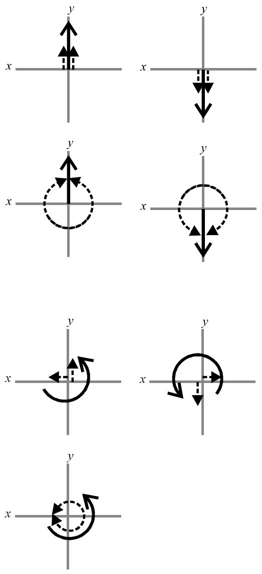
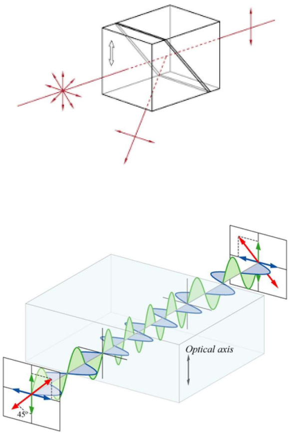
E & M



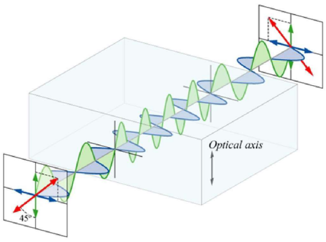
- Linear polarization (solid vectors) decomposed into two polarization states (dotted vectors).
- Circular polarization (solid vectors) decomposed into two polarization states (dotted vectors).

E & M



- Optical devices can be used to manipulate polarization. For example, a simple polarizer separates mixed polarization into two linear components.
- A birefringent material has a different index of refraction along the optical axis than it does normal to the optical axis (recall from Lecture 2 that $u = c/n$).

E & M

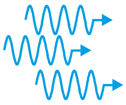


- In the image, linearly polarized light (red) enters the waveplate. We decompose it into two waves - parallel (green) and perpendicular (blue) to the optical axis. The parallel wave propagates slower than the perpendicular one because the indices are different. At the exit, the parallel wave is delayed by half a wavelength (in this "half wave plate"), and the resulting combination (red) has been rotated $90°$.

E & M

Coherence

- Coherence describes a situation where the various components (i.e. a collection of plane waves that make up the total light field) from a light source remain within a fairly narrow bandwidth (almost the same wavelength) and in a fixed phase relationship with each other:



- Coherence makes constructive and destructive interference possible (e.g. to generate interference patterns more easily). It also generates phenomena like laser speckle (e.g. from a pointer).
- Even light from the sun has some coherence (not much!), while lasers are highly coherent.

Interaction of light with matter

- Now we discuss in more detail what happens as light traverses a gas or other material (e.g. glass).
- As mentioned already, electric interactions dominate optics.
- Material polarization - the collection of active polar molecules - can interact with an electromagnetic wave.
- Material polarization is formally defined as the volume averaged dipole moment (occurring any number of ways):

$$\vec{P} \equiv \lim_{\Delta \mathrm{v} \to 0} \frac{1}{\Delta \mathrm{v}} \sum_{i=1}^{N \Delta \mathrm{v}} \vec{\mu}_i$$

  where $\Delta \mathrm{v}$ is a volume element, N is the number density of dipoles, and $\vec{\mu}_i$ is the dipole moment of individual atoms or molecules (unfortunately μ is also used for magnetic permeability).
- Don't confuse material polarization with optical polarization!
- Material polarization is a macroscopic property defined in terms of microscopic phenomena.

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Interaction of light with matter

- Material polarization can be induced by the electric field of the optical wave, as described by:

$$\vec{P} = \epsilon_\circ \chi_e \vec{E} \qquad (14)$$

  where χ_e is the electric susceptibility (often just called 'the susceptibility' when discussing optical techniques).
- It is then necessary to rewrite Maxwell's equations to account for extra interactions, but making the same assumptions as before (e.g. $\varrho_{\mathrm{f}} = 0$ and $\vec{J}_{\mathrm{f}} = 0$):

$$\vec{\nabla} \cdot \vec{E} = 0, \; \vec{\nabla} \cdot \vec{B} = 0$$

$$\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}, \; \vec{\nabla} \times \vec{B} = \mu\epsilon \frac{\partial \vec{E}}{\partial t}$$

  where $\epsilon = \epsilon_\circ(1 + \chi_{\mathrm{e}})$ and $\mu = \mu_\circ(1 + \chi_{\mathrm{m}})$ - here χ_{m} is a magnetic susceptibility equal to zero for optical interactions (in which case then $\mu = \mu_\circ$).

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Interaction of light with matter

- New Maxwell's equations for material interactions then lead to a new wave equation:

  $$\nabla^2 \vec{E} = \mu\epsilon \frac{\partial^2 \vec{E}}{\partial t^2}$$

  and a new speed of light in the material $u = 1/\sqrt{\mu\epsilon}$,

  now providing a formalism for the index of refraction

  $n \equiv c/u = \sqrt{\mu\epsilon/\mu_\circ\epsilon_\circ}$

  or $n^2 = (1 + \chi_\mathrm{e}) = \kappa_\mathrm{e}$ (the so called 'dielectric constant').
- At this point it is common to drop the e-subscript because we assume the interaction is electric.

Interaction of light with matter

- The new wave equation can also be written:

  $$\nabla^2 \vec{E} - \mu_\circ\epsilon_\circ \frac{\partial^2 \vec{E}}{\partial t^2} = \mu_\circ \frac{\partial^2 \vec{P}}{\partial t^2} \tag{15}$$

  On the left side is the normal wave equation in vacuum while on the right side is a source term originating in the material polarization; but the material polarization arises from an electromagnetic interaction with the light wave - the light leapfrogs across dipoles.
- Notice that the right hand side of equation 15 represents the acceleration of electrons in the material. Electromagnetic radiation arises from the acceleration of electrons.
- The susceptibility (and thus n) is built into the source term via $\vec{P}$.

Nonlinear interaction of light with matter

- Going back to equation 14, if the electric field of the light wave is strong enough it can induce a nonlinear material interaction described generally (including the linear term) by:

$$\vec{P} = \epsilon_\circ \left[\chi^{(1)}\vec{E} + \chi^{(2)}\vec{E}^2 + \chi^{(3)}\vec{E}^3 ...\right]$$

  where each of the nonlinear susceptibilities (the $\chi^{(n>1)}$ terms) is a physical constant associated with various nonlinear optical interactions.
- Now we can use a nonlinear polarization in the wave equation:

$$\nabla^2 \vec{E} - \mu_\circ \epsilon_\circ \frac{\partial^2 \vec{E}}{\partial t^2} = \mu_\circ \frac{\partial^2 \vec{P}_{\mathrm{NL}}}{\partial t^2} \tag{16}$$

  so $\vec{P}_{\mathrm{NL}}$ is a source for a totally new wave (different color, different direction etc.). Absorption and fluorescence are $\chi^{(1)}$ processes, second harmonic generation (a laser 'doubling crystal') uses a $\chi^{(2)}$ process, and CARS is $\chi^{(3)}$.

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The Lorentz atom

- Returning to linear optics, we now look in more detail at material polarization, but we use a classical model for the interaction between a dipole and an electromagnetic wave.
- It is not fully correct because it ignores quantum mechanics, but it can reveal a lot about material interactions and much of the language we use is based on this model.
- Assume a dilute, nonpolar (in advance), nonmagnetic gas.
- For a single molecule j we can describe a single dipole via:

$$\mu_j = \alpha_j \vec{E}_m(\vec{r}) \tag{17}$$

  where μ_j is the induced dipole moment and α_j is called the polarizability of the individual atom or molecule interacting with the electric field. α_j is a microscopic version of the macroscopic term $\epsilon_\circ\chi$. $\vec{E}_m(\vec{r})$ is the localized, microscopic electric field and we assume it doesn't change around the molecule.

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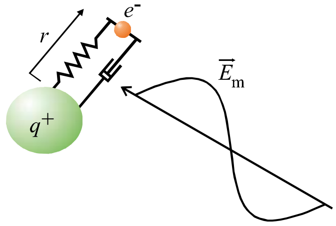
The Lorentz atom

- We model the atom or molecule as shown:



- The electric field drives a classical damped oscillator with an equation of motion given by:

$$m_e \frac{\mathrm{d}^2\vec{r}}{\mathrm{d}t^2} = -k_s\vec{r} - \frac{m_e}{\tau}\frac{\mathrm{d}\vec{r}}{\mathrm{d}t} + \vec{F}, \quad \vec{F} = q_e\vec{E}_m$$

where k_s is the spring constant and τ is the characteristic damping time.

The Lorentz atom

- We know the solution to that problem already:

• The system has a natural oscillation frequency given by:

$\omega_\circ = \sqrt{k_s/m_e}$

• If we assume harmonic behavior:

$\vec{r} = \frac{q_e/m_e}{\omega_\circ^2 - \omega^2 + i\omega/\tau}\vec{E}_m$

• The solution for $\vec{r}$ leads to a solution for the polarization of the atom or molecule, and that leads to a volume-averaged, complex polarizability (generalized by removing j):

$\tilde{\alpha} = \frac{q_e^2/m_e}{\omega_\circ^2 - \omega^2 + i\omega/\tau}$

where the tilde denotes a complex number $\tilde{\alpha} = \alpha^R + i\alpha^I$.

The Lorentz atom

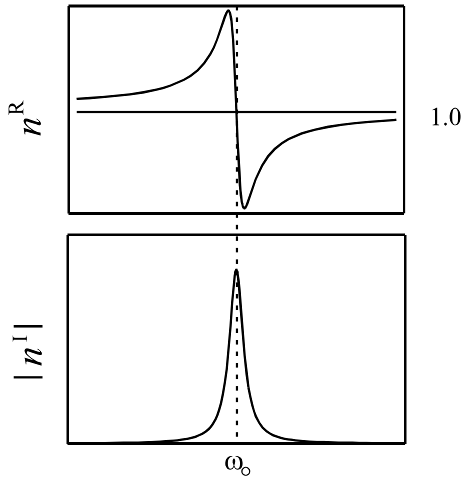
- After some manipulation:
  $\alpha^R = \left(\frac{q_e^2}{m_e}\right) \frac{(\omega_\circ^2-\omega^2)}{(\omega_\circ^2-\omega^2)^2+\omega^2/\tau^2}$; $\alpha^I = -\left(\frac{q_e^2}{m_e}\right) \frac{\omega/\tau}{(\omega_\circ^2-\omega^2)^2+\omega^2/\tau^2}$
- This result can be expressed several ways. The index of refraction, for example, is related to α and after manipulation we find:

$$n^R - 1 = \left(\frac{Nq_e^2}{2\epsilon_\circ m_e}\right)\left[\frac{\omega_\circ^2-\omega^2}{(\omega_\circ^2-\omega^2)^2+\omega^2/\tau^2}\right] \tag{18}$$

$$n^I = -\left(\frac{Nq_e^2}{2\epsilon_\circ m_e}\right)\left[\frac{\omega/\tau}{(\omega_\circ^2-\omega^2)^2+\omega^2/\tau^2}\right] \tag{19}$$

  notice that n^I is negative.
- These notes skipped over a lot, but it was mostly definitions and algebra. See *Spectroscopic Measurement* (in the reference list) for more details.

The Lorentz atom



- The real index has positive and negative phases on either side of $\omega_\circ$.
- The imaginary index has a Lorentzian profile, owing to the energy decay term τ.
- Just as a reminder, $\omega(\text{radians/sec}) = 2\pi\nu$ where the units of ν are (1/sec).

The Lorentz atom

- Now we can describe how light propagates through a collection of Lorentz atoms:

  • If we put the plane wave expression $\vec{E} = \vec{E}_\circ e^{i(\vec{k}\cdot\vec{r}-\omega t)}$ into the wave equation, we find that

  $|\vec{k}| = \frac{n\omega}{c}$
  • Hence, put $n = n^R + in^I$ into the plane wave expression:

  $$\vec{E} = \vec{E}_\circ e^{n^I \frac{\omega}{c}\hat{k}\cdot\vec{r}} \; e^{i\left(n^R \frac{\omega}{c}\hat{k}\cdot\vec{r}-\omega t\right)} \tag{20}$$

  where $\hat{k}$ is the unit vector for $\vec{k}$.

The Lorentz atom

- There are two parts to equation 20.
- The first exponential $e^{n^I \frac{\omega}{c}\hat{k}\cdot\vec{r}}$ is real, and as mentioned n^I is negative, meaning that the magnitude of E (and therefore I because $I \propto E^2$) decreases with distance r if n^I is non-zero.
- The imaginary index is thus related to the absorption coefficient in Beer's law $I(\ell) = I(0)e^{-\kappa_\nu \ell}$:

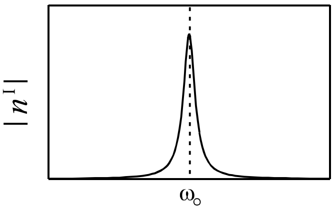
$$\kappa_{\text{Lorentz}} = 2|n^I|\frac{\omega}{c}$$

- The Lorentz atom formalism involves many simplifications and it is not quantum mechanically correct, but it gives a nice level of understanding and so it is common to relate κ_{Lorentz} to the real (perhaps measured) κ_ν using an "oscillator strength" $f_\circ$:

$$\kappa_\nu = f_\circ \kappa_{\text{Lorentz}}$$

The Lorentz atom

- The Lorentzian profile now illustrates the idea of a lineshape function Y_ν, which was introduced in the lecture on the ERT. Indeed, any phenomenon that involves a lifetime (e.g. the 'dephasing time' or 'fluorescence lifetime' etc. of an atom or molecule) will have a Lorentzian lineshape $\left[\frac{\omega/\tau}{(\omega_\circ^2-\omega^2)^2+\omega^2/\tau^2}\right]$.
- Real lineshape functions involve several different physical processes and so Y_ν is described by a convolution of several functional forms (often Lorentzian and Gaussian).



The Lorentz atom

- The second part of equation 20 is the second exponential $e^{i\left(n^R\frac{\omega}{c}\hat{k}\cdot\vec{r}-\omega t\right)}$ and it involves imaginary terms in the exponent. In fact, it looks just like the wave propagation expressions we have already discussed.
- n^R is therefore what we normally just call the index of refraction. When we use that name in optical discussions, it is shorthand for 'the real part of the index of refraction'.
- The main problem with this formalism is that the Lorentz atom can take any value of $\omega_\circ$, based on the spring constant, but real atoms and molecules have discrete frequencies where an energy transition occurs, the frequencies can not take just any value.
- In the Lorentz atom, the E field dumps energy into a harmonic oscillation but in the actual case, atoms and molecules make energy transitions only between two well defined quantum states.

Next topic

Scattering of light from molecules and particles and/or drops

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Advanced Laser Diagnostics for Combustion Research

Lecture 4: Laser light scattering - Rayleigh and Mie

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Tsinghua-Princeton-CI Summer School on Combustion
July 11 - 17, 2021

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Topics

Rayleigh scattering from molecules

- Polarizability and scattering
- Solution for Rayleigh scattering and geometry of the scattered light

Mie scattering from particles and/or drops

- Simple explanation of Lorenz-Mie-Debye theory
- Available solutions

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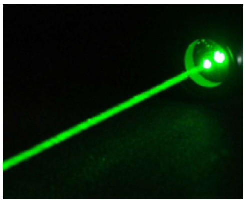
Introduction

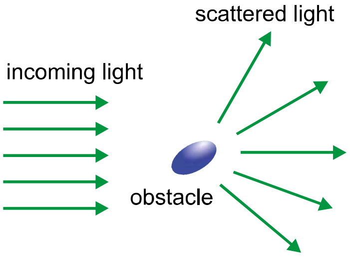
- As mentioned in the course introduction, laser light can scatter from molecules, drops, or particles (all of them called "obstacles" here).
- The form of scattering we discuss in this lecture is "elastic", meaning that the light is scattered at the same wavelength as the laser light.
- In contrast, Raman scattering is called "inelastic" because it shifts the wavelength.
- The terms elastic and inelastic have to do with photons and the energy they have ($E = h\nu$) after a collision with an obstacle.



Introduction

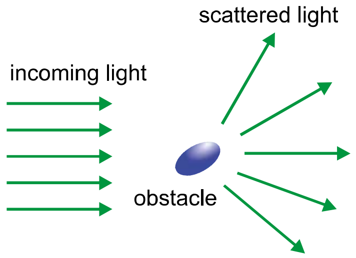
- Matter always consists of charged elements; electrons and protons.
- When a material obstacle is illuminated by an electromagnetic wave, the electromagnetic wave sets the electrons in the material into oscillatory motion.
- Accelerating charges give off electromagnetic radiation (called "secondary radiation", or "reradiated light" in this case).
- So:

  Scattering = excitation + reradiation



Introduction

- But - in comparison to absorption, what do we mean by “excitation”?.
- The obstacle does not occupy a different quantum state when the light arrives; the light is not resonant with a transition.
- Instead, the rapidly oscillating electronic field deposits energy into the one thing that can respond as rapidly - the electron by itself.
- The oscillating electron then emits ('re-radiates') instantaneously (more to follow).
- This kind of excitation is what defines the “virtual energy levels” we discuss in topics like Raman scattering.



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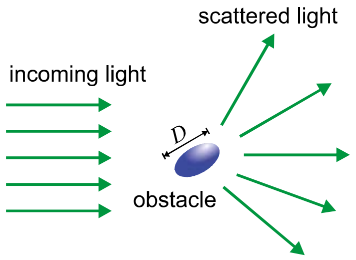
Introduction

- Scattering theory is separated into several regimes by a scattering parameter defined by:

  $x \equiv \pi D/\lambda$

  where D is the size of the obstacle.
- Molecular Rayleigh scattering applies when $x < 1$ (wavelength much bigger than the circumference of the obstacle). It is the weak, completely uniform scattered light you see in a laser beam.



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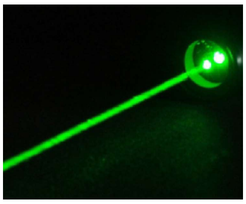
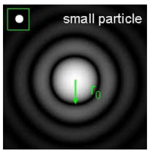
Introduction

- So called “Mie” scattering applies when $x \geq 1$ (the name Mie is often applied to any kind of elastic scattering from particles or drops, although that’s not entirely correct). Mie scattered light in a laser beam sparkles from individual dust particles as they drift about in the air. If you look somewhat towards the laser (never look directly into a laser beam!) the Mie scattered light will look stronger than if you look in the opposite direction. Rayleigh scattering does not do that, and this difference will be explained in the lecture.



Introduction

- When $x >> 1$ the obstacle falls into the geometric optical regime.
- This literally means we analyze the obstacle the same way we would large optical objects.
- For transparent obstacles (e.g. fuel drops) we treat each drop like a spherical lens.
- For an opaque particle we use diffraction from the edge.
- Those topics are taken up in a normal optics class and we will not discuss them further in this class.



Rayleigh scattering

- Rayleigh scattering originates from the aggregate of all molecular scatterers in the measurement volume. It represents a species-averaged density.
- If pressure is uniform (i.e. not a highly compressible flow) and known, then a measurement of density gives a measurement of temperature. Rayleigh scattering is often used to measure (and image) temperature.
- In some cases Rayleigh scattering is stronger for one species than another and the technique can be used to image mixing. Fuel often has a much stronger Rayleigh scattering response than air, for example.

Rayleigh scattering

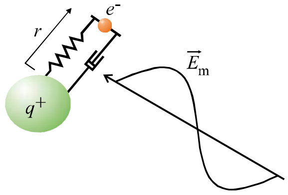
- Rayleigh scattering is caused by an interaction between the optical electromagnetic field and the equilibrium polarizability of the molecule (we introduced the concept of polarizability in the Lorentz atom discussion, equation number 17).
- So we begin similar to the Lorentz atom, except that we will not change populations now (it is a non-resonant interaction). Equation 17 defined the polarizability α via:

  $\mu = \alpha \vec{E}_m(r)$
- But for a scattering process we have to worry about the orientation of the dipole relative to the incoming field polarization. Polarizability is actually a second ranked tensor and we write:

  $\vec{\mu} = \vec{\alpha} \cdot \vec{E}_m(r)$

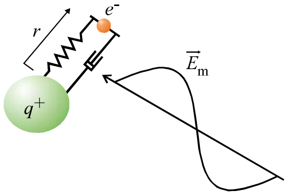
Rayleigh scattering

- This Lorentz atom image was somewhat specialized:
- Note that the $\vec{E}$ field is aligned with the dipole. If the dipole were 90° sideways there would be no interaction.
- In the Lorentz atom we did a simplified model to see how the atom could take up light. Now we have to be more sophisticated.
- In addition, the Lorentz atom assumed energy would be deposited in the atom (or molecule); which describes absorption.
- Here we are discussing scattering, and there are some very important differences.



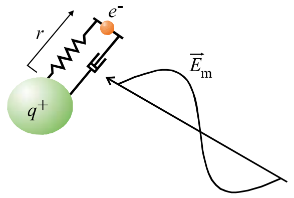
Rayleigh scattering

- Absorption occurs at specific frequencies ν_{nm} (wavelengths λ_{nm}) to match quantum-mechanically allowed transitions. Once the atom or molecule has absorbed a photon at ν_{nm} and occupied an upper energy level, it can stay that way during a fluorescence lifetime (averaging from several ps to 100 ns or more depending on the situation) or until a collision causes non-radiative energy exchange.
- Atoms and molecules can scatter any wavelength of light. There is no required ν_{nm} and no change of energy level for elastic scattering. There is no lifetime; scattering occurs almost instantaneously.



Rayleigh scattering

- We ended the Lorentz atom treatment with a simplified answer because the correct answer for absorption requires quantum mechanics. Scattering, however, is solved classically.
- Recall that the polarizability is really a second rank tensor - we need to pay attention to orientation of the dipole.



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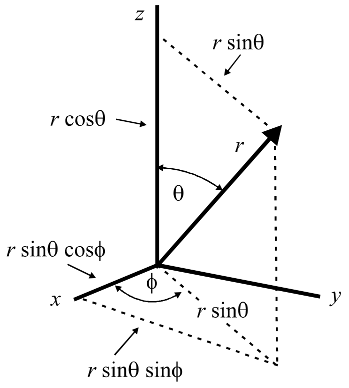
Rayleigh scattering

- This requires defining a coordinate system as shown. It's a right handed system but with z as the vertical because that is often how spectroscopists show it (here z is sometimes the polarization orientation of the incoming electromagnetic field).
- The molecular dipole is then oriented along r, at an angle θ with respect to the polarization of the electromagnetic field.



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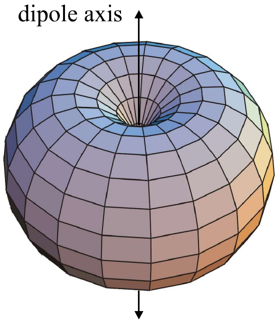
Rayleigh scattering

- Polarized light can interact with a natural dipole, set it in motion and cause secondary radiation (scattering) because electron in motion will emit radiation; think in terms a tiny RF antenna for example.
- Polarized light can also separate the electron and nucleus in a nonpolar molecule and cause scattering, although it will not be as strong (different polarizability).
- If θ is less than 90°, then incoming linear optical polarization (along z) can be decomposed along r and a direction normal to r, ensuring that there will be a response (along r) even if it is weakened by orientation.
- The total Rayleigh signal will always be an ensemble average of all the contributions from a specific location, so individual orientations are not detected.
- The classical approach is to solve something like the Lorentz atom, paying close attention to orientations, and then to model the light emitted by the dipole once activated.

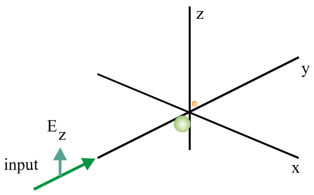
Rayleigh scattering

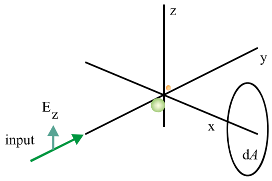
- Can such an explanation make sense when we know a quantum mechanically correct explanation does not allow an electron to be stuck on a spring with a damper? Yes - in the end we measure polarizability.
- The polarizability α describes how the molecule responds to the light, and its value along 3 axes is a function of the specific molecule.
- Like an antenna, the radiation pattern will depend on the emitter structure and size, but for atoms and molecules they generally look like this.



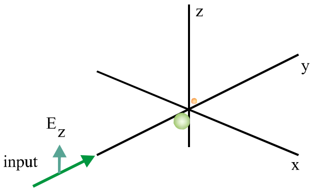
Rayleigh scattering

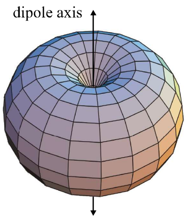
- The complete approach is to work out the scattering intensity for a single molecule fixed in space, and then take an average over many molecules with random orientation.
- The image represents a space-fixed scatterer with incoming light polarized along z.
- The plane containing the optical input path (y) and the observation path (let's use x) is called the "scattering plane".
- The amount of light we sense (with a detector, camera etc.) also depends on the collection solid angle $\mathrm{d}\Omega \equiv \mathrm{d}A/x^2$.





Rayleigh scattering





- The power scattered along x includes contributions from the induced dipole $\vec{\mu}$ along z and y (think in terms of decompositions along all 3 axes; the polarizability is a tensor after all).
- We don't include $\vec{\mu}$ along x because that would be to look down the dipole axis where there is no signal.

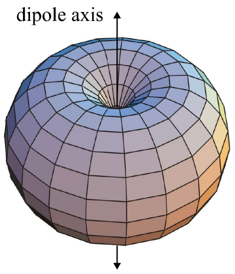
Rayleigh scattering

- The first process (excitation) is quite a bit like the Lorentz atom solution, but we use direction cosines to sort out the dipole and polarization orientations.
- The second process (reradiation) involves a time consuming solution in E&M:
  ▷ It starts by recasting Maxwell's equations into two equations written terms of scalar and vector potentials
  ▷ This set of equations is then solved out beyond the Lorentz atom to produce a series of spherical wave functions
  ▷ For boundary conditions one writes an expression for the oscillating electronic charge (assuming the nucleus does not move), written in terms of the scalar and vector potentials
  ▷ This then produces a spatial electromagnetic field distribution and Poynting's theorem is used to convert that to spatially dependent irradiance

---

Rayleigh scattering

- That solution produces the torus, now for an ensemble of scattering atoms or molecules.
- The final outcome is written in terms of the power per unit area emitted $\mathrm{d}P/\mathrm{d}A$, but in the end the $\mathrm{d}A$ ends up $\mathrm{d}A/r^2 = \mathrm{d}\Omega$.



Rayleigh scattering

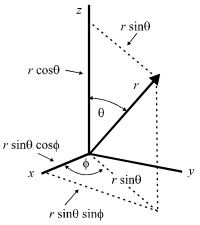
- The solution is:

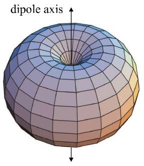
$$\frac{\mathrm{d}P}{\mathrm{d}\Omega} = \frac{4\pi^2\nu^4(n-1)^2}{N^2}(\sin^2\theta)\ I \tag{21}$$

where:

ν is frequency expressed in wavenumbers in this case,
n is the real index of refraction,
N is the number density of scatterers, and
I is the irradiance of incoming light.

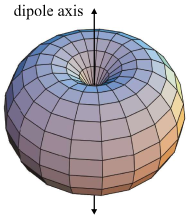
- Note that there is a dependence on θ but not on ϕ



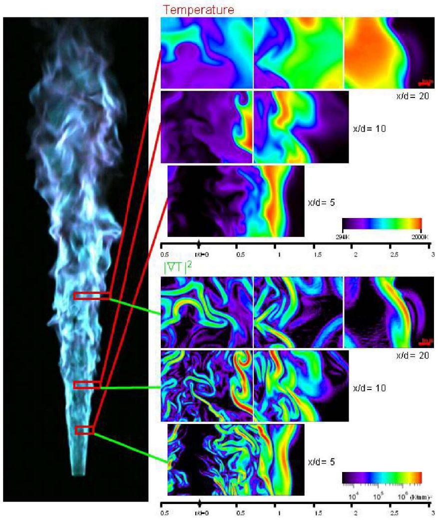


Rayleigh scattering

- The dependence on ν^4 is why the sky is blue and sunsets are red.
- This development took a lot of short-cuts but it introduced some concepts, and the 3-D scattering pattern (the torus) can be drawn in 2-D. We can't do that with Mie scattering.



Rayleigh scattering



An example

- Rayleigh scattering images of temperature in a turbulent flame, with highly resolved turbulent structures (image from Jonathan Frank at Sandia Labs).

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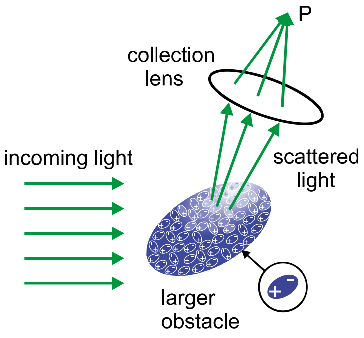
Mie scattering



- The name Mie scattering is typically applied when $x \geq 1$, but the Mie solution doesn't hold in all such cases (e.g. very big obstacles are in the geometric optics regime).
- If the obstacle is large with respect to the wavelength, there are far more dipoles present than in the Rayleigh case. This cartoon shows a distribution of dipole structures across the obstacle surface.

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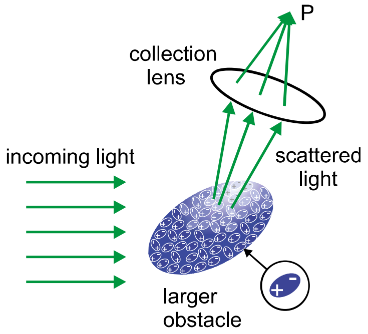
Mie scattering



- The reradiated light emitted by the dipoles is coherent with the input light. That means there will be interference structures around the scattering angles making very complex scattering patterns.
- The scattering patterns will also depend on the polarization of the incoming light. The dipoles across the surface are not all aligned with each other.
- The amplitudes and phases of each induced dipole moment also depend on the material (polarizability again).

Mie scattering

- The Lorenz Mie Debye solution applies only to a spherical obstacle.
- The solution to this problem is written in terms of a series of plane wave functions.
- A simple electromagnetic plane wave can be expressed as described in equation 13:

  $\vec{E} = \mathrm{Re}[\vec{E}_\circ e^{i(\vec{k}\cdot\vec{r}-\omega t)}]$.

  where: $\vec{E}_\circ$ is the amplitude of the wave (a vector because of polarization), $i = \sqrt{-1}$, $\vec{k}$ is called the wave vector pointing in the direction of propagation, $\vec{r}$ is the position vector in space, and ω is the radial frequency of the light. This expression (plus one for $\vec{B}$) is a solution to the wave equation and to Maxwell's equations.
- Because Maxwell's equations are linear, an infinite summation of plane wave solutions is also a solution.
- A separation of variables along θ, ϕ and r is used.

Mie scattering

- The irradiating plane wave and the scattered field are expanded in spherical vector wave functions (with a $1/r$ times the amplitude).
- The irradiating field induces an internal field in the obstacle (on the surface), and the internal field is expanded into spherical vector wave functions.
- The scattered field is written in terms of a series of spherical wave functions.
- The solution is written in terms of infinite series (e.g. Bessel functions).
- Boundary conditions on the spherical surface allow the expansion coefficients of the scattered field to be computed.
- The internal field thus produces the external field that propagates away - summing the infinite series as a function of angle and polarization.

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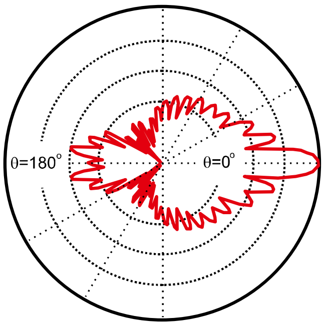
Mie scattering

- One of the first published computer programs was written in early Fortran at Bell Labs to prove how valuable computers could be. It was a Mie scattering calculator and it can be found many places. A printed copy is in the book by Bohren and Huffman (see the reading list called "Other sources" in Lecture 1).
- There is no specific code for Mie scattering, but there is a free-standing version called "Mie plot" at http://www.philiplaven.com/mieplot.htm.
- It produces plots like this.
- But what is that?



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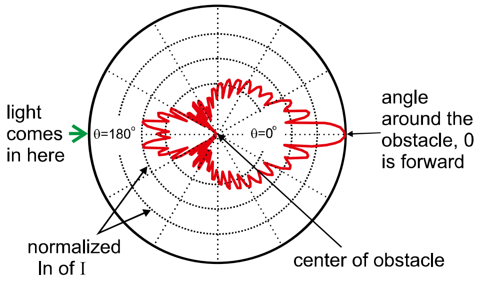
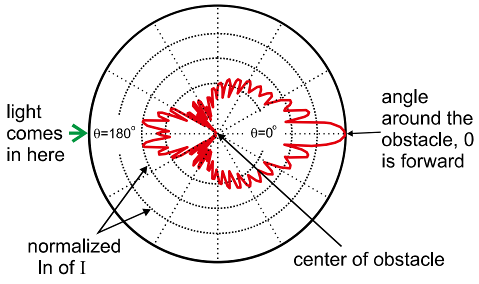
Mie scattering



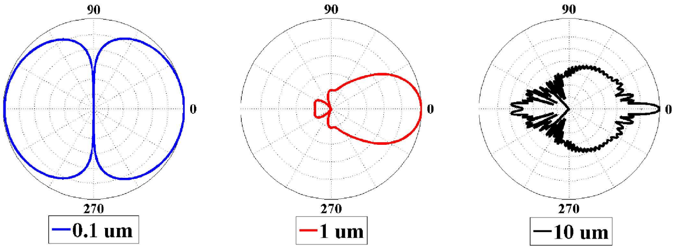
- The result is too complex to plot in 3-D, so we make one polar plot for light that is polarized perpendicular to the scattering plane and one plot for polarization that is in the scattering plane.
- You are looking at the scattering plane now.

Mie scattering



- This is a polar plot for normalized natural log of scattered irradiance vs. angle around the obstacle.
- This one is for a 5 μm fuel drop in air, with polarization perpendicular to the scattering plane (called "perpendicular polarization"), irradiated by 532 nm (green) light.

Mie scattering



- These are normalized polar plots for three different sizes, using polarization in the plane (called “parallel polarization”).
- The smallest obstacle (to the left) is in the Rayleigh regime (remember the torus).
  For perpendicular polarization we would get just a circle.
- Note how the forward lobe grows with particle size (really with x). That is why the dust in a laser beam is brighter when you look towards the laser.

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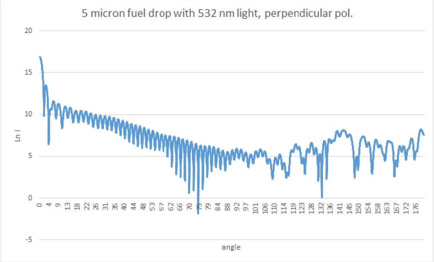
Mie scattering



- For detailed work it is better to generate plots like this (generated by Mie plot).
- But be careful. There are various approaches to the Mie scattering problem. Some make assumptions that lead to simpler infinite series but the solution does not apply to all cases. Some truncate the infinite series early for computational speed (without saying so).

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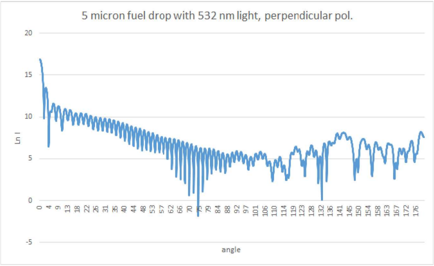
Mie scattering



- It is OK to use a source just to compare polar plots.
- But if you plan to do quantitative analysis, be sure you understand the uncertainties in your calculations for the scattering problem. Don't just grab and use any code from the web.

Mie scattering

- Mie scattering can be used in various ways.
- It is what contributes optical signal when one takes a backscattered light image of a spray, or a laser plane image of drops, for example.
- It is also what gives particle images for particle image velocimetry (PIV), and signal for phase Doppler interferometry (PDI).
- Mie scattering vs. angle can be used to measure particle size; soot size for example. It has been used to calibrate laser induced incandescence imaging of soot.
- When the size distribution causes blurring of the polar distribution, several different laser wavelengths can be used. Multiple wavelength extinction and scattering experiments are a reliable way to get particle or drop sizes at one sample volume. The technique has often been supplanted by PDI.

Next topic

PIV, tomographic PIV, and Optical Flow.

Advanced Laser Diagnostics for Combustion Research

Lecture 5: Particle Image Velocimetry

Mark Linne

University of Edinburgh

Tsinghua-Princeton-CI Summer School on Combustion
July 11 - 17, 2021

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Topics

PIV basics
- Techniques and rules of thumb
- Stereoscopic PIV

Tomographic PIV

Optical Flow

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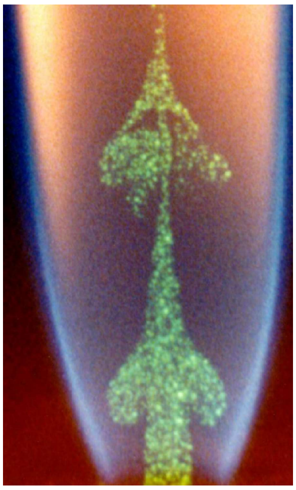
PIV basics



- For PIV (and laser Doppler anemometry, a single-point technique) the flow has to be seeded with oil droplets or particles.
- Oil droplets are fairly easy to seed because one can use a nebulizer (unless the flow volume is high). Oil droplets do not survive a flame front, however, so they can not image post-flame.
- Ceramic particles are harder to seed into a flow but they survive the flame.
- Seeding is one of the hardest parts of PIV.

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PIV

- The choice of particle size and type depends on how fast the flow is (particle frequency response). This table provides some guidance:

Particle	ρ_p (kg m^{-3})	Gas (10^5 Pa)	Density ratio s	Viscosity ν (m^2 s^{-1})	f_c (kHz)	Sk_c	d_p (μm)
TiO_2	3500	Air	2950	1.50×10^{-5}	1	0.0295	1.44
		(300 K)			10		0.45
Al_2O_3	3970	Flame	20250	3.00×10^{-4}	1	0.0113	2.46
		(1800 K)			10		0.78
Glass	2600	Air	2190	1.50×10^{-5}	1	0.0342	1.67
		(300 K)			10		0.53
Olive oil	970	Air	617	1.45×10^{-5}	1	0.0645	3.09
		(220 K)			10		0.98
Microballoon	100	Air	84.5	1.50×10^{-5}	1	0.1742	8.50
		(300 K)			10		2.69

From A. Melling, Meas. Sci. Technol., **8**, 1406–1416, (1997).

Here: ρ_p is the particle density, f_c is the particle response frequency (1 or 10 KHz, which do you want?), S_k is the Stokes number for a particle and d_p is the particle diameter ($S_k \equiv \sqrt{\omega/\nu}\, d_p$, where ω is the angular frequency of the turbulent motion and ν is the kinematic viscosity).

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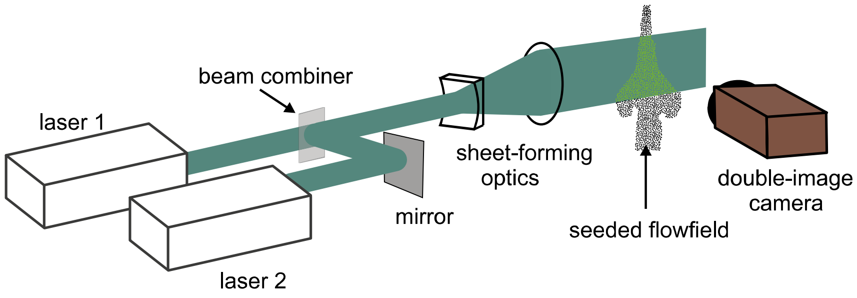
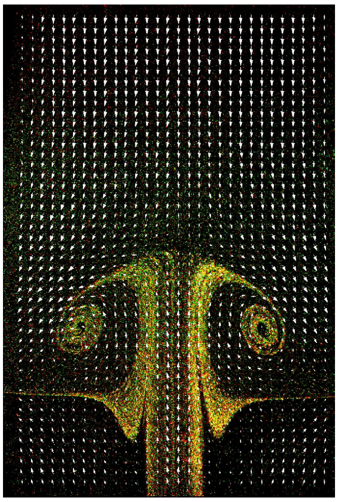
PIV



An example complete system.

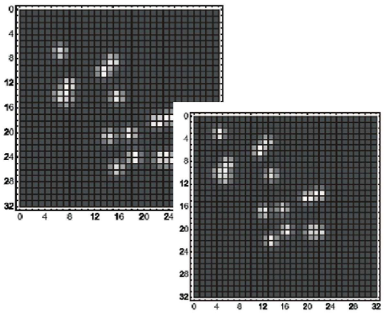
PIV



- To achieve good spatial resolution the flow must be densely seeded.
- One can't just follow individual particles between the two frames (that's called 'particle tracking velocometry').
- Instead, the image is divided into many small interrogation cells (typically around 1 mm square in the flow).
- The interrogation cell from frame 1 is correlated with the cell from frame 2.

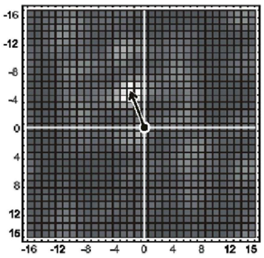
PIV image processing

- Two interrogation cells from images taken with a known time separation Δt.
- The correlation between the two is taken using FFT's.



PIV image processing

- Two interrogation cells from images taken with a known time separation Δt.
- The correlation between the two is taken using FFT's.
- The correlation produces a cell-averaged offset $\Delta\ell$ and velocity is then $\Delta\ell/\Delta t$.
- Notice the background noise in the correlation; the correlation peak has to rise above it or the vector is not legitimate (not 'validated').



A correlation result.

PIV details

- There are actually a lot of details hiding inside the commercial PIV processing instrumentation. Most of the time it is fine to just use the instrument, but it is good to know what is going on.
- R. Adrian◇ published a number of guidelines for high quality PIV. First, he said that the imaging system produces a spot image (via Mie scattering) corresponding to every particle. If we assume the imaging system is diffraction limited, the particle image size d_i at the chip can be estimated by:

  $d_i = \left(M^2 d_p^2 + d_s^2\right)^{1/2}$, where d_s is the diffraction-limited point response function of the lens given by

  $d_s = 2.44(1+M)f/\#\lambda$

  here M is the magnification and $f/\#$ is the lens F-number defined by (lens focal length)/(diameter) (you set that with the camera aperture).

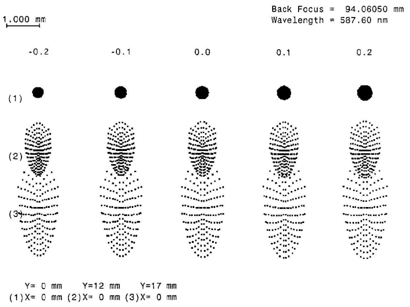
◇ see e.g. "Particle Imaging Techniques for Experimental Fluid Mechanics", R.J. Adrian, Annu. Rev. Fluid Mech., 23, 261-304, (1991).

PIV details

- Real systems are not diffraction limited so the spot size will be bigger.
- The Adrian spot size estimate is controlled by diffraction. Diffraction limited spots are smaller if the diameter of the lens is larger, which is why $d_s \propto f/\#$ in the expression.
- Real lenses have aberrations (which are not included in the estimate) and if you use a small $f/\#$ (open the aperture a lot) you may suffer from them.
- The goal is to achieve the smallest spot size possible with the optical system so that the correlations are crisp.

PIV details

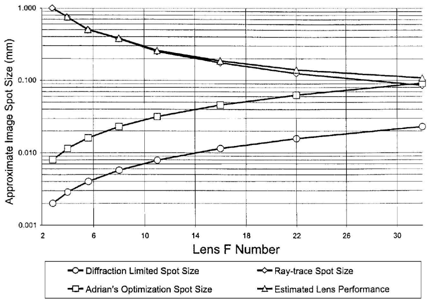
- Long ago[†] we analyzed the spots generated by a publicly-available camera lens design, using ray tracing.
- This spot diagram is for a 55-mm lens at $f/\#2.8$, imaging 1:1.
- The horizontal rows are for sources along the axis, and the columns are for displacements from the axis in a plane.



[†] "Optical Alignment Tolerances and Techniques for Particle Image Velocimetry", T. Drouilliard, P. McCarthy and M. Linne, AIAA Journal, 38, No. 9, 1659-1668, (2000).

PIV details

- This plot compiles all of the ray trace results for the 55-mm lens.
- These results are for 1:1 imaging; images are for spots originating at (0, 12, 17 mm) in the object plane.
- Other lenses (100-mm and zoom) are evaluated in that article.



PIV details

- In our work we found that a 100-mm lens provides superior performance, but our 55-mm design was quite old. More modern designs are probably better (but they are proprietary).
- Aberrations are the dominant source of distortion for lower $f/\#$, and diffraction effects dominate at higher $f/\#$.
- We believe that a fixed spot size criterion (such as an upper limit of $30\,\mu m$ for any $f/\#$) is the most useful tolerance, based on minimum absolute error in the subpixel peak location.
- Sometimes (e.g. tomographic PIV) it is important to have a long depth of field, which means using a large $f/\#$.

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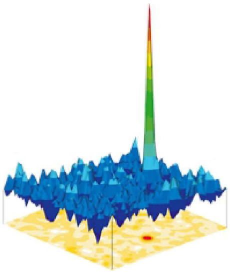
PIV details

Back to Adrian

- The quality of the correlation peak (height of the peak compared to the sub-peaks caused by noise) determines the error in part, and if the system decides the ratio between the main peak and the next peak is too low it will discard the data (they will not be 'validated vectors' in the language of PIV).



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PIV details

- To get a decent quality correlation peak one needs to have 10 - 15 particle pairs inside each interrogation cell. That need controls spatial resolution in the flowfield because if the seeding density is low, one has to use bigger interrogation cells.
- Relative particle displacement (controlled by the time delay between laser pulses Δt for a given flow) is also important. If the particles are too close then it will be hard to correlate them, and if Δt is too big then the second particle image will be over in an adjacent interrogation cell.
- The minimum in-plane displacement should be about twice d_i and the maximum displacement should be less than 1/4 of the interrogation cell size d_c, or:

  $\sqrt{u^2+v^2}\Delta t < \frac{d_c}{4M}$ (just a "rule of thumb").
- Also, keep $d_i < 0.1 d_c$.

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PIV details

- For turbulent flow, the out-of-plane motion can be a problem; the second particle image could be lost because the particle left the laser plane. A good rule of thumb is to hold:

  $\frac{w\Delta t}{\Delta z_\circ} \leq 0.25$

  where w is the out of plane velocity and $\Delta z_\circ$ is the laser sheet thickness. Adjusting the camera so that the depth of field matches or exceeds the sheet thickness (when possible) is a good idea.
- If there are velocity gradients (Δu) inside an interrogation cell the correlation peak can smear out, which lowers the height of the peak. Rules of thumb for that problem are:

  $\frac{\Delta u d_c}{u d_i} \leq 4$ and $\frac{M\Delta u \Delta t}{d_i} \leq 1$
- Do these things really matter?

  If you start to get data you don't trust, start to think about these things.

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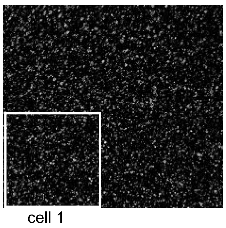
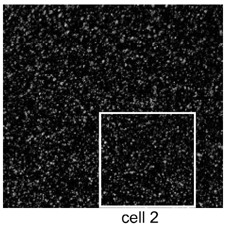
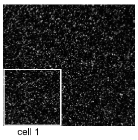
PIV details

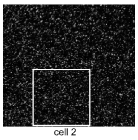


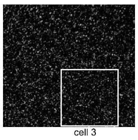


- That is just an introduction to the kinds of issues people must concern themselves with, especially if they wish to study a challenging flow or extend the technique. Many other tricks are performed.
- For example, instead of this
  Going to this

PIV details



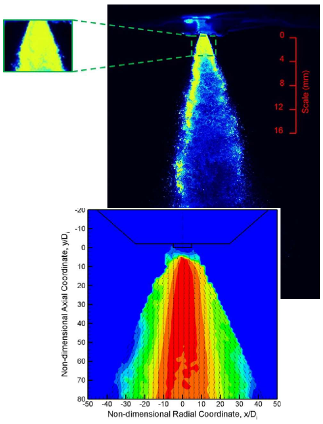




- Modern systems overlap interrogation cells (usually by a reported percentage)
  Going to this
  Going to this, and that gives some averaging for better noise while improving resolution.
- There are also tricks for locating correlation peaks at a sub-pixel level despite pixellation of the images.
- Most of this goes on in software without the user interacting.

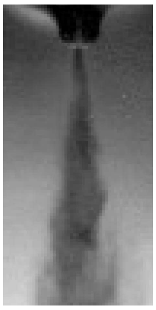
PIV

- Why, then, did I say all of that?
- In the last 10 years some people seem to have started to think they can do anything with PIV.
- They seem to think they can just point a camera and laser and then let the software sort it out, and there are times when it is obvious that their data can't be correct.
- Some people have even tried to extract velocities in structures like this using their PIV systems.
- The features in such a flow are not point scatterers; the PIV correlations will not work properly. The software will invent vectors.



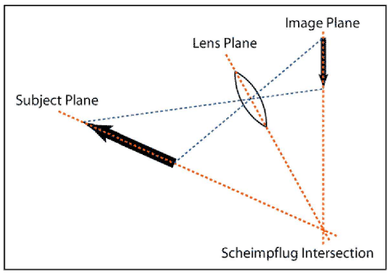
PIV

- Another example - a Diesel spray.
- These are so dense that the light scatters around inside, undergoing as many as 10 droplet scattering events before exiting the spray. It is not possible to correctly correlate multiply scattered light. It will have high errors.



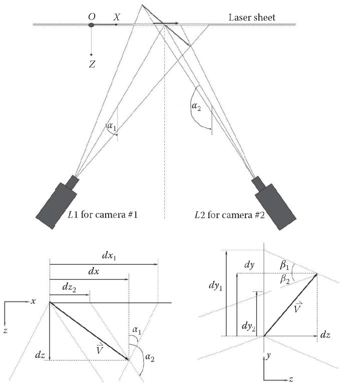
Stereoscopic PIV

- 'Stereoscopic' PIV uses two double-image cameras viewing the laser plane at an angle (with camera lenses in the 'Scheimpflug' arrangement).
- There is simply a geometrical transformation that maps a tilted object plane to an image plane.

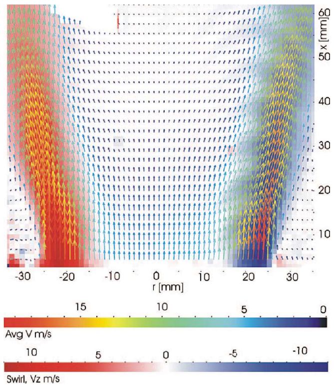


Stereoscopic PIV

- This allows one to extract an out-of-plane velocity component.
- The camera alignments have to be matched before starting because the out of plane motion will be extracted by geometrically comparing the interrogation cell vector from camera 1 to that of camera 2. This alignment is done by placing a grid in the same location as the laser plane and then real-time image processing is used to match the 2 cameras up.
- Stereoscopic PIV then provides a 2-D image of 3-D velocity.

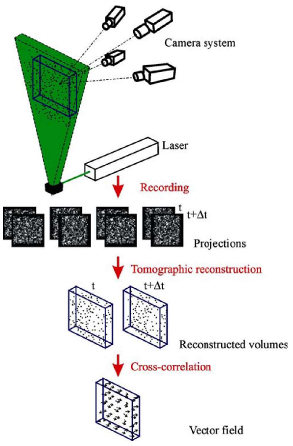


Stereoscopic PIV



- One example from a low-swirl burner.
- The vectors indicate in-plane velocities and the colors indicate out of plane velocities.
- All the manufacturers sell this style with setup equipment and guidance, but it costs more.

Tomographic PIV

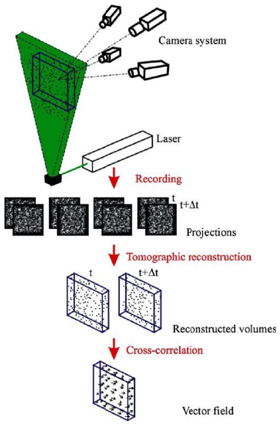


Much of this discussion is based on “Tomographic particle image velocimetry”, G.E. Elsinga, F. Scarano, B. Wieneke and B.W. van Oudheusden, Expt. Fluids, 41, 933-947, (2006).

- Tomographic PIV is a serious extension of Stereoscopic PIV.
- More cameras are used and they are not located in a single plane. Their lenses are all in the Scheimpflug arrangement.
- The cameras have to be aligned similar to Stereoscopic PIV but more carefully.

Tomographic PIV

- The laser sheet is expanded into a very thick plane of light and the camera lenses are stopped down to give long depth of field.
- The alignment grid now has to be scanned from one side to the other, doing camera alignment and calibration at many positions.
- A properly aligned system is used to capture 2 flow-field images per camera from different angles relative to the center plane of the laser sheet.



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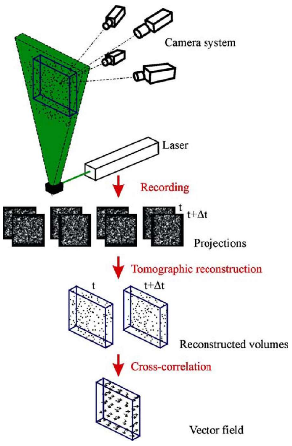
Tomographic PIV



- A tomographic inversion is used to identify all the particle pairs in the volume.
- The particle pairs are then subjected to a 3-D correlation.
- A 3-D field of velocity vectors is extracted from the correlation.

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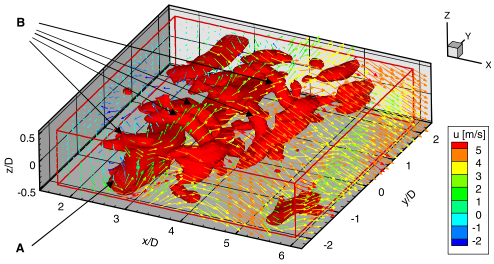
Tomographic PIV



- Here is a nice result from Elsinga et al. The image shows every third vector, and the iso-surface is a vorticity magnitude ($|\omega| = 2.3 \times 10^3 s^{-1}$). 'A' labels a Karman vortex and 'B' labels secondary, streamwise vortex structures. This was a fairly slowly moving flow.

Tomographic PIV

- The tomographic inversion that works best for point images is an algebraic method (vs. Fourier or back-projection).
- The technique requires iterations, starting with an assumed volumetric intensity distribution (uniform in this case) and then trying to reconstruct the signal at each pixel $I(x, y)$ from the distribution based on:

  $I(x_i, y_i) = \sum_{N_i} w_i E(X, Y, Z)$

  where N is the number of voxels along the line of sight, w_i is a weighting coefficient for each voxel i (could include differences in image intensity owing to scattering direction, changes in pixel sensitivity etc.), and E is a voxel intensity (ultimately the distribution of E's will give the particles).

Tomographic PIV

- Convergence and error minimization are controlled by a multiplicative algebraic reconstruction technique (MART) in which the next guess (guess $k+1$) for E is given by:

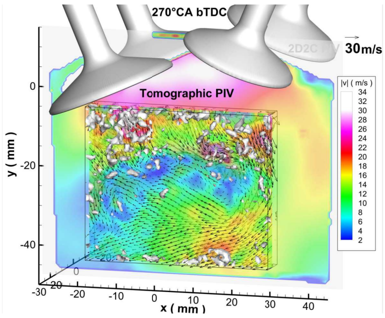
  $$E(X,Y,Z)^{k+1} = E(X,Y,Z)^{k}\left(\frac{I(x_i,y_i)}{\sum_{N_i} w_i E(X,Y,Z)^{k}}\right)^{\mu w_i}$$

  where μ is a relaxation parameter that is less than or equal to 1.
- Convergence is typically reached with 10 - 20 iterations.

Tomographic PIV

- There are additional issues to be considered, as detailed by Elsinga et al.
- The quality of the reconstruction goes up with the number of cameras, but for more than 5 cameras the benefits are not great.
- The cameras should be at an angle to the plane between 15° and 45°. Steeper angles do not sample enough of the volume but wider angles sample too much of it and the inversion starts to make too many "ghost" images.
- If 4 - 5 cameras are used one can load the flow with more particles for better spatial resolution. Otherwise they can cause too many ghost particles to be generated.
- Calibration errors should be held below 0.4 pixel (in location). There are ways to get to 0.1 pixel, so this is possible but takes care.
- The large depth of field and requirements of the inversion schemes produce spatial resolution that is not as good as 2-D PIV.

Tomographic PIV



- ▶ Despite the difficulties, this technique has been applied to an optical IC engine at TU Darmstadt (E. Baum, B. Peterson, C. Surmann, D. Michaelis, B. Böhm, A. Dreizler). These results were checked against 2-D PIV and the agreement was excellent.

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Wavelet-based Optical Flow Velocimetry (wOFV)

- ▶ wOFV is an image processing technique that can extract velocities from two sequential images, but it is not correlation-based.
- ▶ It can be used to interrogate PIV images, although the imaging process has different requirements than the Adrian figures of merit.
- ▶ Particles are not required for wOFV however, any conserved scalar can be used.
- ▶ It can generate velocity vectors at each camera pixel, for significantly better spatial resolution than PIV, and it can have the same accuracy as PIV if done well.
- ▶ wOFV is not simple; the math is complex, there are a number of variants, and great care is necessary to avoid just making up numbers.

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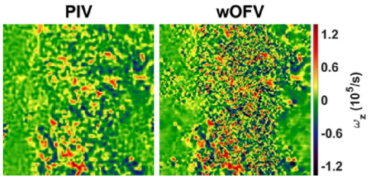
wOFV

- Optical flow was originally designed for machine vision, to track the motion of a work piece during production.
- It was introduced by Horn and Schunck‡.
- Flow-fields incorporate divergence and vorticity, so they require more complex treatments than the original form of OF used to estimate rigid-body motion.



Results from B. Schmidt, A. Skiba, J. Driscoll, S. Hammack, C. Carter and J. Sutton, "High-resolution velocimetry in turbulent premixed flames using a wavelet-based optical flow technique", Proceedings of the 11th US National Combustion Meeting, Pasadena, CA, (2019).

NB: It was the group of Jeff Sutton who introduced this topic to the community.

‡ "Determining optical flow", B. Horn and B. Schunck, Artificial Intelligence, 17, 185-203, (1981).

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wOFV

Experimental

- For an experiment, we simply take sequential images (PIV-type images, high-speed shadowgraphy, high-speed Rayleigh or PLIF of a conserved scalar etc.).
- For reasons that will become clear, it is important to make the excitation light level equal across the images - it's best to use just one laser (unlike PIV).
- Spatial resolution of the imaging system becomes more important so that moving interfaces or scalar gradients can be resolved by the wOFV software.

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wOFV

The data term

- We assume the overall image 'brightness' (or intensity value $I(x, y)$ in the image) is conserved from one frame to the next.

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wOFV

The data term

- We assume the overall image 'brightness' (or intensity value $I(x, y)$ in the image) is conserved from one frame to the next.
- We then write a brightness conservation expression linking the object motion:

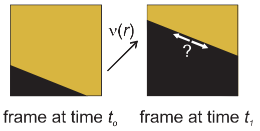
$$\frac{\partial I}{\partial x}\frac{\partial x}{\partial t} + \frac{\partial I}{\partial y}\frac{\partial y}{\partial t} + \frac{\partial I}{\partial t} = 0 \tag{22}$$

- Unfortunately, Equation 22 is ill posed because it is one equation with two unknowns; the velocities $u = \partial x/\partial t$ and $v = \partial y/\partial t$.
- Equation 22 makes it possible to calculate only the displacement of an image feature along the brightness gradient vector, leaving its other motion component ambiguous.

wOFV

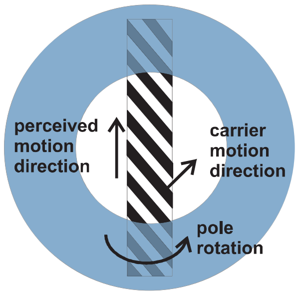
The data term

- This ill-posedness is known as the aperture problem.



Aperture problem

- It's also called the 'barber pole illusion'.



The barber pole illusion

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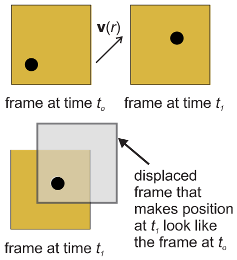
wOFV

The data term

- As another problem, experimental data can violate the assumption of brightness conservation, because of variations in light level from frame-to-frame for example.
- For this reason we do not just set Equation 22 equal to zero. We begin by integrating it across the frames to get:

$$I_1(\vec{r}) - I_2(\vec{r} + \mathbf{v}(\vec{r})) = 0 \qquad (23)$$

  where $\mathbf{v}(\vec{r})$ is the inter-frame displacement.
- Equation 23 is called the "displaced frame difference" (DFD) equation.



Displaced frame
(in a PIV context)

wOFV

The data term

- We then numerically *minimize* the DFD equation (Equation 23) - but to do that we write it as a penalty function. Various forms are used, but here we show a Lorentzian penalty function to minimize the sensitivity of OF to imaging variations:

$$J_D = \int_\Omega \log \left[1 + \frac{1}{2} \left(\frac{I_1(\vec{r}) - I_2(\vec{r} + \mathbf{v}(\vec{r}))}{\sigma} \right)^2 \right] \qquad (24)$$

  where Ω denites the image domain, and σ sets a threshold at which an observation is considered an outlier.
- The goal is then to minimize J_D, but before we can do that we must deal with the ill-posedness problem.
- To address this problem, it is necessary to impose a constraint on the recovered motion. One way to do that is with a *regularization* term (a smoothness constraint).

wOFV

Regularization

- The first order regularizer (J_R) originally proposed by Horn and Schunck is:

$$J_R = \int_\Omega \left[\left(\frac{\partial u}{\partial x}\right)^2 + \left(\frac{\partial u}{\partial y}\right)^2 + \left(\frac{\partial v}{\partial x}\right)^2 + \left(\frac{\partial v}{\partial y}\right)^2 \right] dr \qquad (25)$$

- In effect, minimizing Equation 25 states that neighboring pixels will tend to move together.
- Many other types of regularizers are used, depending on the nature of the flow-field studied. Equation 25 works well for a displaced solid (or moving liquid interface).
- More advanced regularizers are used when the flow incorporates divergence and/or vorticity. Sutton and co-workers apply the third derivative in an equation like Equation 25, to avoid penalizing divergence and vorticity.

wOFV

- When using wavelets, one is not *required* to use a regularizer. Wavelets can be truncated at a user-determined size and that performs a similar function, but use of a formal regularizer offers more flexibility in terms of spatial resolution.

Minimization

- A regularization term can be added to the data term with an associated weighting parameter λ to form the objective function which must be minimized to estimate the velocity field $\hat{v}$:

$$\hat{v} = \operatorname{argmin}\left[J_D(I_1, I_2, \mathbf{v}) + \lambda J_R(\mathbf{v})\right] \qquad (26)$$

- λ controls the extent to which the regularization term can deviate the estimated velocity field from the brightness constraint in the data term.
- Choice of λ is key to uncertainty control, once the regularizer form has been chosen to match the type of flow-field under study.

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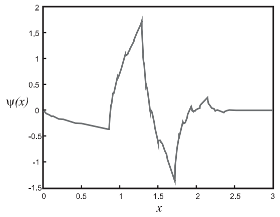
wOFV

Wavelets

- Wavelets are somewhat similar to windowed Fourier transforms.
- Many wavelet families are orthonormal, so they can be used to decompose an image into wavelet coefficients (Θ).
- The wavelet shown here is what we use on ballistic images.
- The nature of the flowfield also determines which wavelet family to use.



A Daubechies 4-tap (db2) wavelet function ($\psi(x)$). Here "x" denotes any 1-D input signal (position, time etc.), and it can be scaled. The mean value of a wavelet is zero, so it must exhibit oscillatory behaviour.

wOFV

- The discrete wavelet transform (DWT) can be applied recursively to its own output wavelet coefficients up to n times for a 1-D signal of length 2^n. The result is a complete wavelet domain representation of the image at different scales of resolution, also known as multi-resolution analysis (MRA). This attribute supports the entire set of turbulent length scales.
- We don't actually minimize Equation 26. We perform minimization over the coefficient set for the wavelet transform Θ:

$$\hat{\Theta} = \operatorname{argmin}\left[J_D(I_1,\, I_2,\, \Theta) + \lambda J_R(\Theta)\right] \tag{27}$$

- Equation 27 is optimally solved by starting at the coarsest scales and then proceeding in steps to the finest scales. Large displacements can thus be captured while retaining numerical stability and resolving all scales.

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wOFV

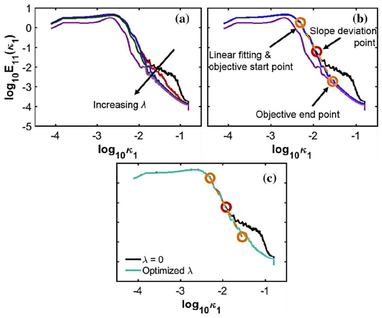
Error control

- Many decisions and judgments are involved in the development of a wOFV algorithm. One must choose the form of penalty function used in the data term (J_D), the form of regularizer (J_R) if using one, the wavelet family, and so forth. Following that, one must decide how to set λ. There is a danger of just inventing numbers.
- Error control is typically performed by comparing the wOFV code to something that is known and then adjusting λ to minimize the root mean squared error (RMSE).
- If, after all that, the errors are high then it may be time to consider a different wavelet family or regularizer.
- The specific approach is adapted to the flow-field being studied.

wOFV

Error control

- When working with PIV-like images in a turbulent flame (a single-phase, compressible flow), the group of Sutton and co-workers§ found the λ affected the inferred turbulence frequency spectrum.
- If they can find "ground truth" data on the spectrum of such a flow (e.g. by LDV measurements, LES/DNS computations, or the like) they can adjust λ to get minimum RMSE and then use that value for their images.



§"High-resolution velocimetry from tracer particle fields using a wavelet-based optical flow method", B. E. Schmidt and J. A. Sutton, Experiments in Fluids, 60:37, (2019).

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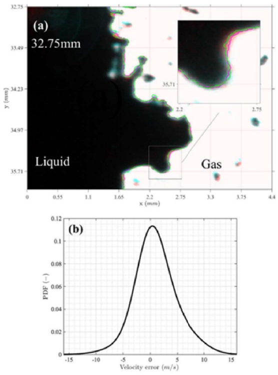
wOFV

Error control

- In our work on spray breakup (two-phase incompressible and irrotational flow) with sequential ballistic images, we find that the liquid-gas interface moves in an easily identified way (vs. e.g. a gas phase flowfield that dilates and rotates).
- This allows us to use the wOFV offset vectors to displace the second image backwards, and then compare it to the first image. We then evaluate the mean-squared-error (MSE) between the actual first image and the one based on the wOFV displacements. We then select the value of λ that generates a minimum MSE.



(a) BI with overlaid liquid-gas boundaries: green: liquid-gas interface at t; pink: liquid-gas interface at $t + \Delta t$ warped to time t using wOFV flow-field; (b) PDF of velocity uncertainty

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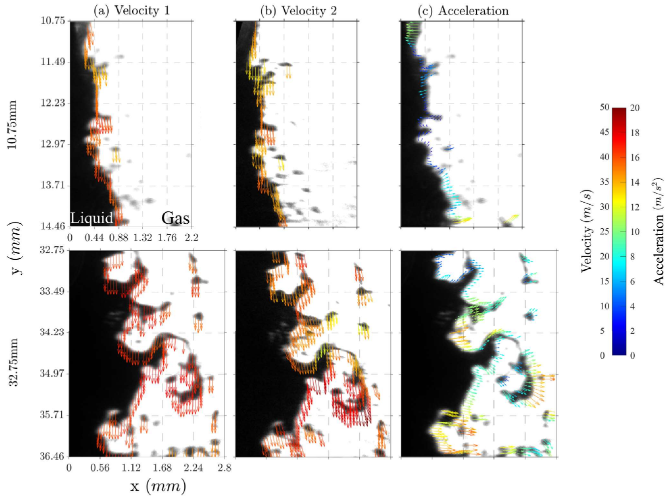
wOFV

Ballistic imaging example



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Next topic

New spray diagnostics: structured laser illumination planar imaging (SLIPI), ballistic imaging (BI), and Two-photon PLIF.

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Advanced Laser Diagnostics for Combustion Research

Lecture 6: New Spray Diagnostics

Mark Linne

University of Edinburgh

Tsinghua-Princeton-CI Summer School on Combustion
July 11 - 17, 2021

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Topics

The spray problem

- Optical depth and scattering in sprays

Time-gated imaging

- Ballistic imaging (BI)

Planar imaging

- Structured laser illumination planar imaging (SLIPI)
- Two-photon PLIF (2P-PLIF)

- Note that the techniques discussed in this lecture are explained in extreme detail in a chapter of "Optical Combustion Diagnostics for Propulsion and Power Systems: Theory and Application", A. Steinberg, and S. Roy, editors, American Institute of Aeronautics and Astronautics, (anticipated 2022).

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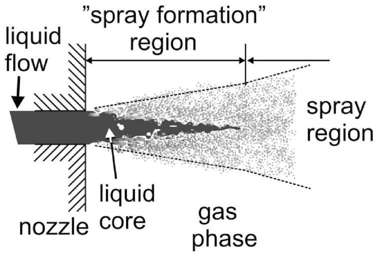
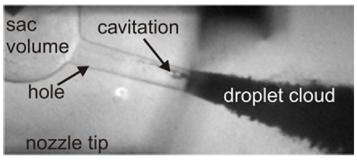
The spray problem

- To burn a liquid fuel it is necessary to break a flow of fuel into drops that break up further, mix with air, vaporize, and mix to produce a combustible fuel/air mixture.
- The "spray" is the collection of drops, not the rest of it.
- We can measure what happens downstream - in the spray - using imaging techniques (e.g. PLIF, Mie, SLIPI) together with PDI at single point.
- Serious problems are encountered in the spray formation region.



The spray problem

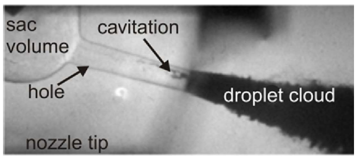
- The flow in the nozzle has a significant effect on the flow exiting the nozzle and so it has a significant effect on spray formation.
- In the nozzle – x-ray phase contrast imaging or optically transmissive tips can be used; here an optical tip shows that the liquid cavitates inside the nozzle.
- In dense spray formation region one can measure total liquid mass (including drops) with x-ray radiography, or map it in 1-D with x-ray fluorescence (all phase averaged).



From M. Blessing, G. König, C. Krüger, U. Michels, V. Schwarz, SAE Technical Paper Series, paper no. 2003-01-1358 (2003).

The spray problem

- Until recently it has been impossible to see interfaces (e.g. surface structures, ligaments, breakup dynamics) when the liquid leaves the nozzle in highly atomizing sprays, in the spray formation region, because a dense droplet cloud hides what is happening.
- Ballistic imaging can see into that region by minimizing image corruption caused by droplet scattering off-axis.
- SLIPI and 2P-PLIF can see into a spray that is not as dense as the spray shown here.



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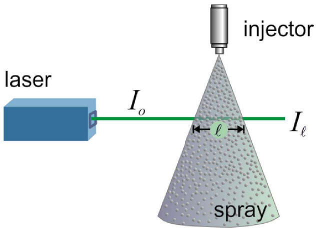
Optical depth and scattering in sprays

- Optical depth was introduced in Lecture 2. It is commonly written into Beer's law by spray people in terms of the transmissivity of light through the spray (τ) as follows:

  $\tau = \frac{I_\ell}{I_o} = e^{-OD}$

  and $OD = N\sigma_e\ell$

  where: N = number of interactions per unit volume, σ_e is the extinction cross section ($\sigma_e = \sigma_{\text{absorption}} + \sigma_{\text{scattering}} \simeq \sigma_{\text{scattering}}$ for a spray), and ℓ is the path length through the spray.



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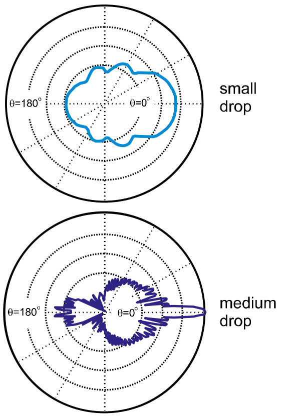
Optical depth and scattering in sprays

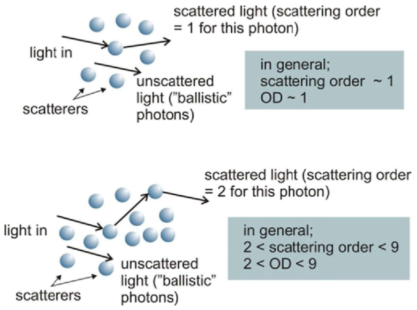
- As an aside - trying to measure OD in a spray is very messy.
- The measurement will depend on what the drop size distribution is, and it will depend on what solid angle was collected by the measurement optics.
- We normally talk about the number of interactions instead. Monte Carlo modeling has shown that in the range of drop sizes, the OD is similar to the number of interactions (called the "scattering order").



These are logarithmic (ln) plots

Optical depth and scattering in sprays

- In the "single-scattering regime": the ave. no. scattering events < 1 and one can use classic scattering formalisms (e.g. Lorentz-Mie).
- In the "intermediate-scattering regime" (applies to dense sprays): the ave. no. scattering events is between 2 & 9, classic single-scattering formalisms do not describe what exits and this is a difficult regime to handle. It's necessary to use Monte-Carlo (M-C) techniques.


scattered light (scattering order = 1 for this photon)

light in

unscattered light ("ballistic" photons)

scatterers

in general;
scattering order ~ 1
OD ~ 1

scattered light (scattering order = 2 for this photon)

light in

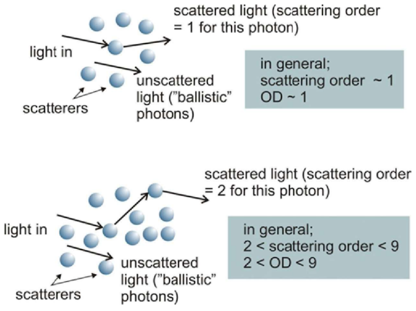
unscattered light ("ballistic" photons)

scatterers

in general;
2 < scattering order < 9
2 < OD < 9

Optical depth and scattering in sprays

- In the "multiple-scattering regime": the ave. no. scattering events > 9. The relative contribution from each scattering order is the same and the process can be described by diffusion approximation (assume a continuum).
- Very dense sprays cover the range from the intermediate-scattering regime to the dense regime. We apply a M-C simulation to all of it.



light in

scatterers

scattered light (scattering order = 1 for this photon)

unscattered light ("ballistic" photons)

in general;
scattering order ~ 1
OD ~ 1

light in

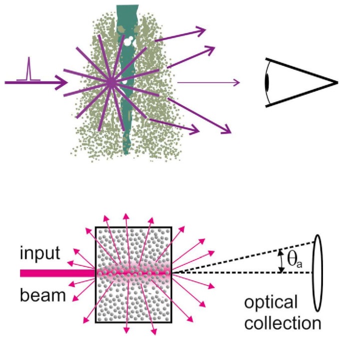
scatterers

scattered light (scattering order = 2 for this photon)

unscattered light ("ballistic" photons)

in general;
2 < scattering order < 9
2 < OD < 9

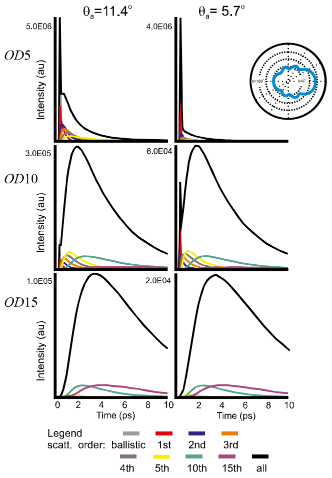
Optical depth and scattering in sprays



- Edouard Berrocal at the University of Lund has developed a Monte Carlo code for transit of photons through a spray[†].
- This code allows us to predict how light going through a spray will come out; in position and time.

[†] "Multi-Scattering software: part I: online accelerated Monte Carlo simulation of light transport through scattering media", J. Jönsson and E. Berrocal, Optics Express, Vol. 28, No. 25, (2020).

Optical depth and scattering in sprays



Small scatterers

- Here is the light that comes out in the forward direction after passing 10 mm through monodisperse collection of scatterers with $x = 3.6$ (small scatterers).
- Note how the MC code gives scattering orders; that information is not available from experiments.
- Here, much of the light is scattered to the side, especially at high OD. Some of it comes back into the forward direction but it arrives late because it has a long optical path.

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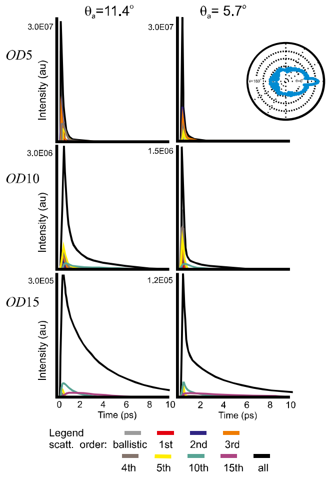
Optical depth and scattering in sprays



Bigger scatterers

- Here is the light that comes out in the forward direction after passing 10 mm through monodisperse collection of scatterers with $x = 17.9$ (fuel drop size).
- The scattering patterns have gone through a change of regime.
- Here, the strong forward scattering lobe keeps much of the scattered light on a forward path (if collected by a small solid angle).

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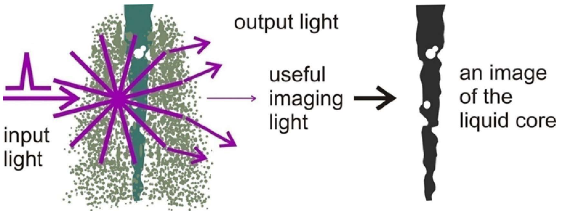
Ballistic imaging



- This technique was originally developed in 2000 by the Linne group based on a medical imaging technique that did not work (for tissue).
- Use what we know about light traversing a turbid medium:
  ▷ Most of it is just spatial noise that corrupts the image – because it was scattered off-axis by drops
  ▷ A very small amount of it contains useful image information about structures (e.g. intact liquid) buried inside – it was refracted by the larger structures.

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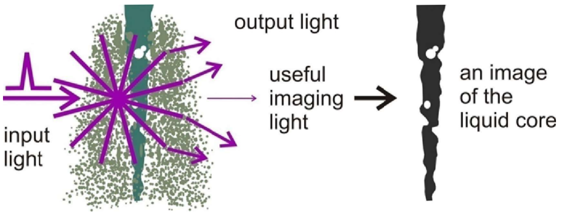
Ballistic imaging



- We reject most of the light exiting the spray, minimize the amount of corrupted light, and collect as much useful imaging light as possible (not very much of it).

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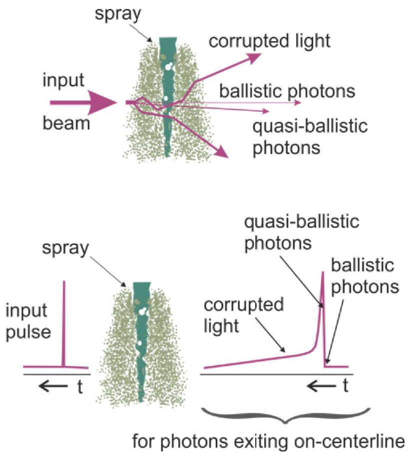
Ballistic imaging



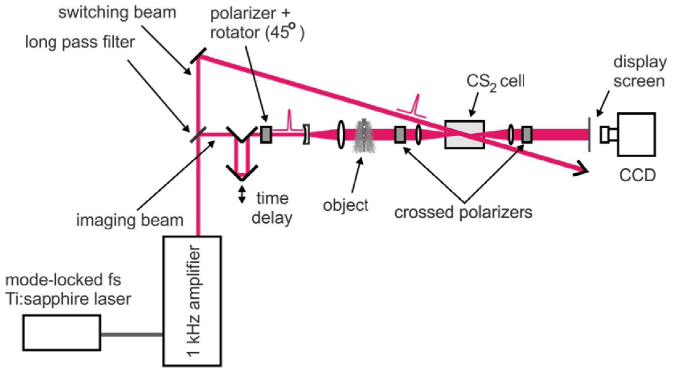
- Even in turbid media, some photons do not scatter, passing directly through the medium – called "ballistic photons". Photons scattered into the droplet's forward lobe (quasi-ballistic) can behave almost exactly the same way – all of them together are called useful imaging light.
- Because they do not scatter at significant angles, useful imaging photons have the shortest path length and exit first.

Ballistic imaging

- In a shadowgram type arrangement, useful imaging photons can be used to image the liquid core – if one can sufficiently minimize the contribution of the much more prevalent corrupted light.
- This can be done by emphasizing signatures of the useful imaging light:
  ▷ Directional orientation – useful light is coincident with the input beam (some form of spatial filtering)
  ▷ Preservation of polarization (polarization filtering)
  ▷ First to exit (time gating)
  ▷ Ballistic photons themselves are coherent with the input beam (coherence gating – interferometry, holography etc.). We don't use coherence because too many coherent photons are lost in a very dense spray, and emphasizing coherence emphasizes diffractive background interference.

Ballistic imaging

Typical BI system



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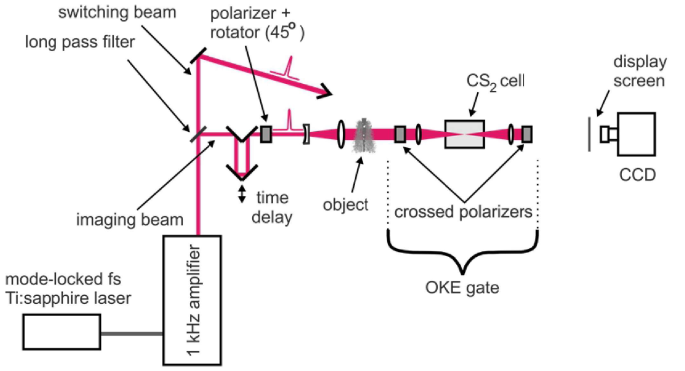
Ballistic imaging

Typical BI system



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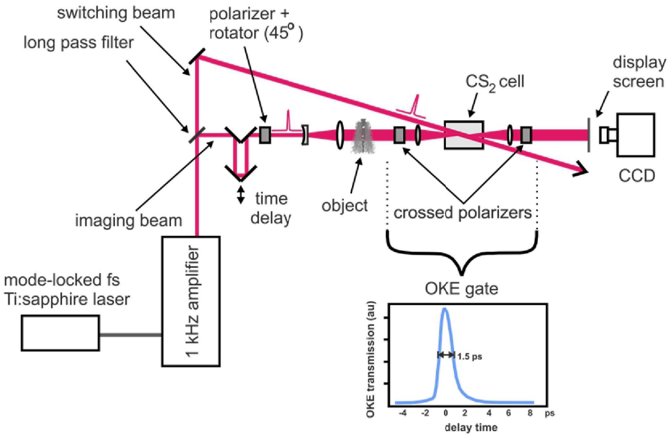
Ballistic imaging

Typical BI system



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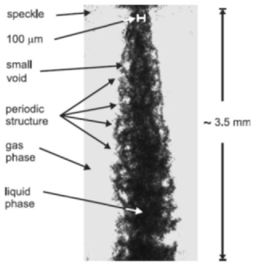
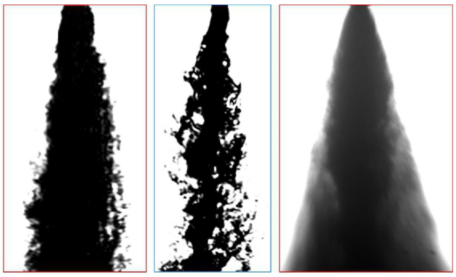
Ballistic imaging

Diesel sprays by 2 different groups



CSM[§], Diesel fuel spray into 1 atm at We = 7.6x105 & Re = 1.6x104



CNRS/CORIA[‡] steady period

late in injection

shadowgram of spray

CNRS – UNIVERSITE et INSA de Rouen

§ M. Linne , M. Paciaroni, T. Hall, and T. Parker, Experiments in Fluids, 40, 836-846, (2006).

‡ S. Idlahcen, J.-B. Blaisot, T. Girasole, C. Rozé and L. Méès, 14th Int Symp on Applications of Laser Techniques to Fluid Mechanics Lisbon, Portugal, 07-10 July, (2008).

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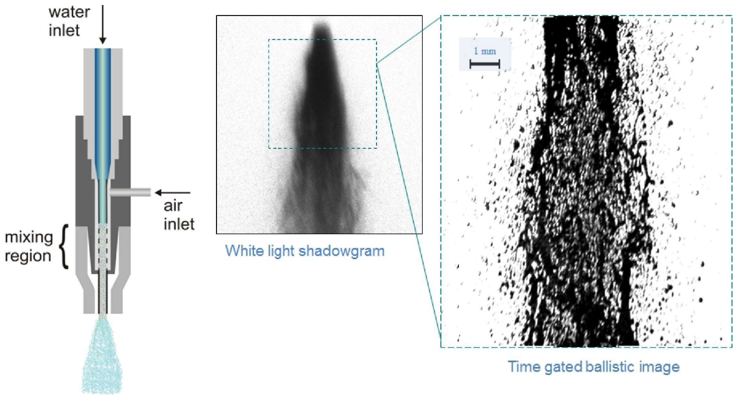
Ballistic imaging

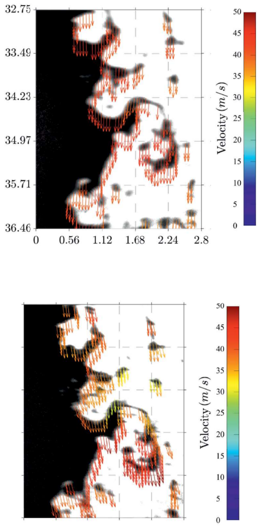
An aerated ("effervescent") jet



White light shadowgram

Time gated ballistic image

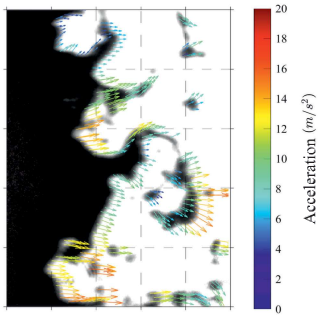
Ballistic imaging



Multi-pulse BI

- wOFV was applied to two BI taken in rapid succession (e.g. $\Delta t = 5\mu s$) to extract velocities of liquid/gas interface, of ligaments, or of large refractive drops.
- This one is taken from a steady water jet undergoing turbulent primary breakup, with the edge of the jet magnified.
- With a three-pulse system, it is possible to get a second velocity image.

Ballistic imaging



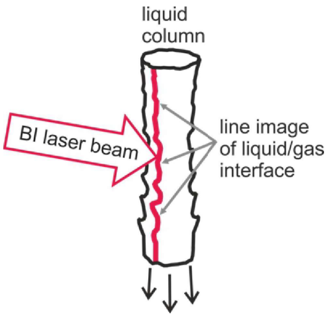
Multi-pulse BI

- Two velocity images can be subtracted to extract acceleration (for known image time separation).
- Many such images make it possible to extract statistics as a function of axial distance and flow conditions.

Ballistic imaging

Attributes of BI

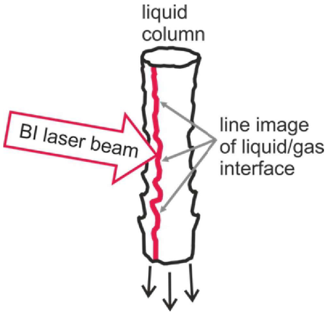
- Meant only for very dense sprays.
- It looks like a line-of-sight technique, but the OKE gate actually captures a 450 μm plane in space that's normal to the imaging axis, with the axial location selected by the gate timing.
- BI captures the liquid/gas interface with good spatial resolution (from 20 to 30 μm; FWHM of the PSF).
- Images all refractive structures, but it's not a drop sizing technique.
- Can go up to $OD = 12$.



Ballistic imaging

Attributes of BI

- Can extract statistics on:
  - Ligament size distributions
  - Void size distributions
  - Surface curvature distributions
  - Surface wave spectra
  - Interface velocity
  - Interface acceleration



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SLIPI

- Structured laser illumination planar imaging (SLIPI) is a moderately new technique developed by E. Berrocal and E. Kristensson at the University of Lund. It is also based on techniques from the community of biological microscopy.
- As the name indicates, SLIPI is a planar spray imaging technique.
- SLIPI works well for $OD \leq 6$. For this reason it complements BI, which is intended for $OD \geq 6$.

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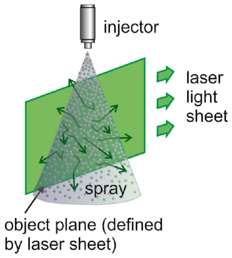
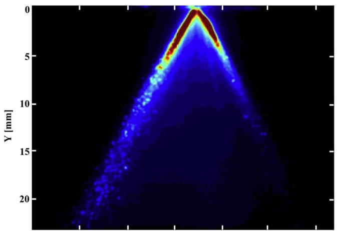
SLIPI

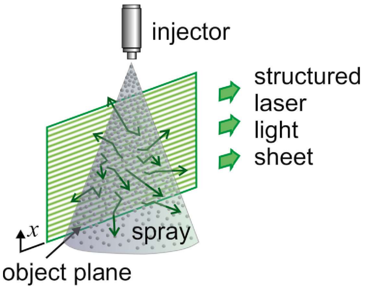
- SLIPI addresses a serious problem for imaging in sprays: once the planar signal is generated it is scattered multiple times before it gets to the camera. Multiple scattering corrupts the image.
- Here is a planar image based on elastic scattering from inside a hollow cone spray. The center is supposed to be free of drops and yet there is a lot of image signal there. It's caused by multiple scattering from the drops in the laser plane. Light goes sideways, through the rest of the spray, and finally it scatters into the camera collection optics.





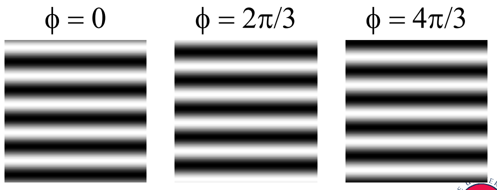
SLIPI

- The idea behind SLIPI is to imprint the signal light from the laser plane with a pattern that will be lost as the photons scatter around the spray. Image elements that retain the imprint came from the plane, while those that do not can be segregated and removed. Here the imprint is a sequence of horizontal bars.
- The problem here is that there will be empty spaces between the bars.



SLIPI

- To solve that problem, one can acquire 3 images with bar patterns that are shifted. The patterns are actually clean spatial sinusoids in the vertical (x) direction, and they are shifted in spatial phase as shown.
- The most common approach is to take average images for the three phases and then manipulate the three average images. For good time resolution, a fast system (freezing the motion) three-laser setup can be used for a 3-pulse burst, but a sufficiently fast camera system is also needed.



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SLIPI

- If we call the three images I_0, $I_{2\pi/3}$, and $I_{4\pi/3}$, and then call the final processed image I_s, the necessary image manipulation to remove the non-structured (corrupted) light is done via a root-mean-square:

$$I_s = \frac{\sqrt{2}}{3}\left[(I_0 - I_{2\pi/3})^2 + (I_0 - I_{4\pi/3})^2 + (I_{2\pi/3} - I_{4\pi/3})^2\right]^{1/2} \quad (28)$$

- A conventional planar image (I_c) can be reconstructed from the three by a simple average:

$$I_c = \frac{I_0 + I_{2\pi/3} + I_{4\pi/3}}{3}$$

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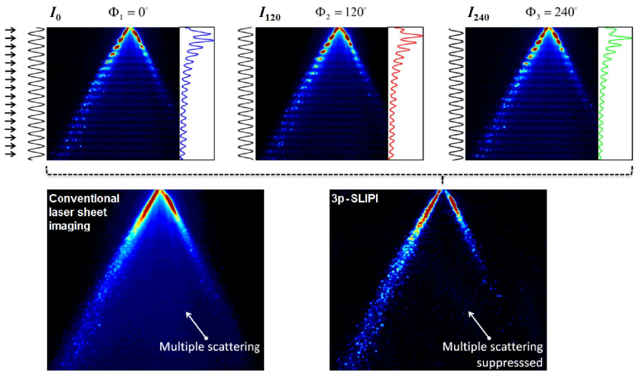
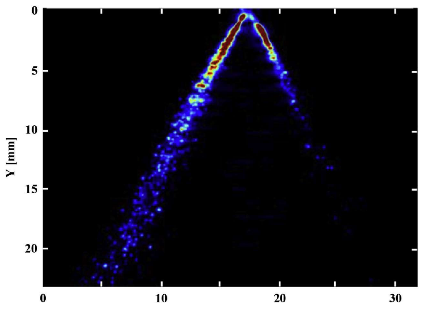
SLIPI



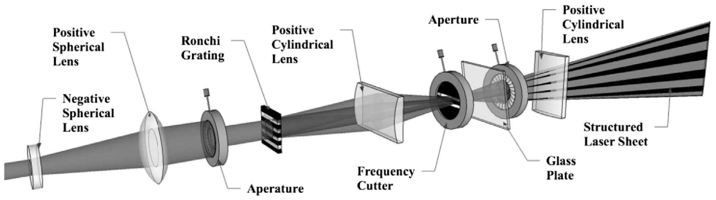
- Lower left: a corrupted hollow cone spray image constructed by taking the average if three structured images (upper row).
- Lower right: apply equation 28 to the same three images.
- Image corruption has been removed; the SLIPI image of a hollow cone spray is now hollow in the center.

SLIPI

- This spray was a good test case but it is actually not seriously dense.
- Unfortunately, this technique fails for continuous liquid structures because they refract the bar pattern structure and corrupt it. SLIPI works only when the drop size is smaller than the spatial modulation of the beam.
- BI and SLIPI are thus highly complementary techniques.



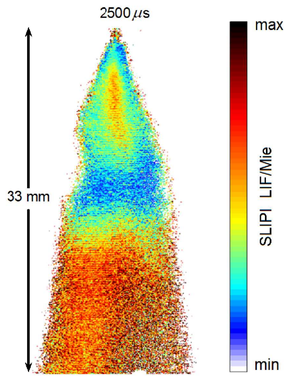
SLIPI



- Here is a SLIPI optical setup. A fast system (freezing the motion) requires three of these properly aligned.
- “Can it be done with 2 pulses instead?” There is an approximation that requires very small stripes and specialized averaging across the bare spots (E. Kristensson, E. Berrocal, M. Aldén, Optics Letters, 39, (9), 2584 - 2587, (2014)).

SLIPI

- There is a technique called LIF/Mie imaging that generates an image of the droplet Sauter mean diameter across a spray.
- The rough idea is that LIF is volume dependent and Mie scattering is surface area dependent, so if we divide a PLIF image by a Mie scattering image we should get the diameter.
- There are many potential problems with this approach. It works only if one:
  ▷ is careful about the imaging,
  ▷ uses SLIPI to remove multiple scattering, and
  ▷ calibrates with phase Doppler interferometry.
- Here is an example.



2-photon PLIF

- Planar laser induced fluorescence (PLIF) was discussed briefly during the introduction. We will discuss it in more detail later, but for now we can discuss PILF in a special format for sprays.
- For *linear* (1-photon) LIF, one laser photon at the correct wavelength is absorbed by a molecule. As a result, the molecule occupies an excited state and after a short period of time some of the molecules return to the lower energy state by releasing a photon (at a wavelength that is red-shifted from the laser wavelength).
- We then locate a camera normal to the laser plane and image this fluorescence.
- In sprays, the goal usually is to image the liquid components within a plane inside the flow. Often a dye or tracer is doped into the liquid for good fluorescence yield.

2-photon PLIF

- Two-photon LIF is a nonlinear process because two photons are required to induce it. Here, two photons with half the necessary energy (twice the wavelength) for a specific transition come together at the molecule at the same time. If the sum of their frequencies matches the required transition frequency, they can also be absorbed by the same molecule.
- This process is much less effective than 1-photon LIF because this convergence of 2 photons at the molecule is highly unlikely. To enhance 2-photon LIF, one uses a very short laser pulse with high pulse energy. In so doing we increase the chances that two photons will land at the molecule within the necessary time frame.
- We also have to ensure that the two photons have twice the wavelength of the 1-photon transition.

2-photon PLIF

- Why go to all this trouble?
- For PLIF of a spray: when the laser sheet enters a spray the drop cloud will scatter much of it out of the plane of the sheet. That scattered light can induce 1-photon LIF in drops that are outside the laser plane, and that light acts as a serious interference for PLIF from within the intended plane.
- Photons at twice the wavelength of the transition will also scatter out of plane, but the chances of two photons arriving at the same place at the same time out of the laser plane is so low that 2-P PLIF from photons scattered out of plane does not occur (in effect).
- Furthermore, 2-P PLIF can be used in larger fluid structures that refract the input light (avoiding the SLIPI liquid refraction problem).

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2-photon PLIF

- Recently, a combined group[‡] has demonstrated 2-P PLIF in a 6-hole gasoline direct injection (GDI) nozzle using water doped with fluorescein.
- The 2-P process was excited by a 25 fs Ti:sapphire laser pulse (which had the necessary wavelength) with 2.5 mJ of energy.
- A comparison was made between shadowgraphy, planar elastic scattering, 1-P PLIF (the laser was frequency doubled), and 2-P PLIF.

A dark field image of a GDI spray.

[‡] "Two-photon fluorescence laser sheet imaging for high contrast visualization of atomizing sprays", E. Berrocal, C. Conrad, J. Püls, C. L. Arnold, M. Wensing, M. Linne, and M. Miranda, OSA Continuum, 2(3), 983-993, (2019).

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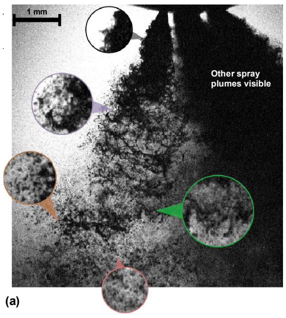
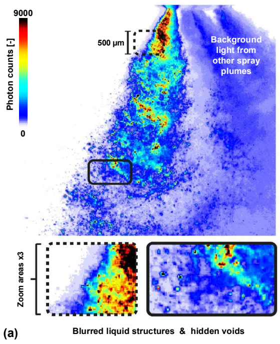
2-photon PLIF

- This shadowgram (light field image) of the GDI spray makes clear that the flow looks optically dense to the eye.
- Owing to the line-of-sight configuration, the shadowgram is strongly affected by liquid structures and droplets located outside the image plane established by the camera lens.



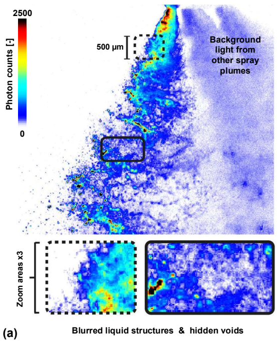
2-photon PLIF

- Planar elastically scattered image of the GDI spray (created by a laser sheet).
- A large amount of background light corrupts the image. It is generated by multiple scattering. The 5 other spray plumes scatter strongly even though they are not in the laser plane; this is evidence of strong multiple scattering.



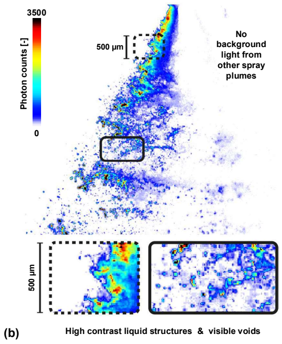
2-photon PLIF

- A 1-photon PLIF image of the same spray.
- This image is an improvement, but LIF arising from out-of-plane light is clearly present.
- The other spray plumes are also apparent, even though they don't lie in the laser plane. The light they produce is LIF from scattered laser light.



2-photon PLIF

- A 2-photon PLIF image of the same spray.
- This image is a significant improvement. No signals from out of the laser plane are detected and this approach provides much higher fidelity imaging.
- The disadvantage is that 2P PLIF requires access to a high energy, short pulse laser.



Next topic

Some concepts in atomic/molecular physics.

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Advanced Laser Diagnostics for Combustion Research

Lecture 7: Atomic/molecular physics and ro-vibrational transitions

Mark Linne

University of Edinburgh

Tsinghua-Princeton-CI Summer School on Combustion
July 11 - 17, 2021

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Topics

Atomic and molecular physics

- Simple introduction to quantum mechanics
- Energy levels and transitions
- Nuclear solutions

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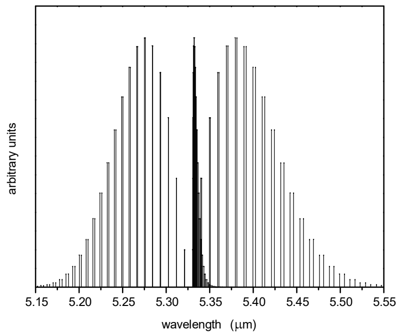
Introduction

- In this lecture we will begin to discuss atomic and molecular structure from an introductory quantum mechanical viewpoint.
- For spectroscopic measurements the spectral location of a resonance (horizontal axis in the figure), the strength of the response (vertical axis), and line broadening (not present in the figure) are all important.
- This lecture is related just to the spectral location (horizontal axis). The rest will follow.



Simulated IR ro-vibration spectrum of nitric oxide for the fundamental vibrational band ($\Delta v = 0 \leftrightarrow 1$)

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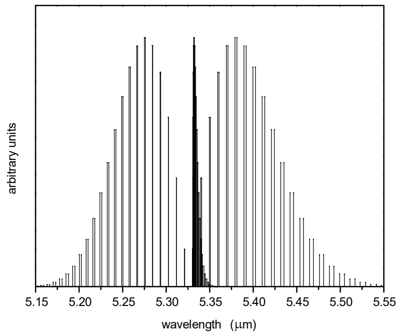
Introduction

- A spectral line location corresponds to a *change* in energy state of the molecule.
- The energy difference between two allowed quantum states is related to the frequency of the light coupling the two energy levels, by $\Delta E_{nm} = h\nu_{nm}$ (and $\nu_{nm} = c/\lambda_{nm}$).
- For this reason, we will focus on ΔE_{nm} in this lecture, which means analyzing atomic and then molecular structure, because energy is related to electric charge (+ and -) distribution.



Simulated IR ro-vibration spectrum of nitric oxide for the fundamental vibrational band ($\Delta v = 0 \leftrightarrow 1$)

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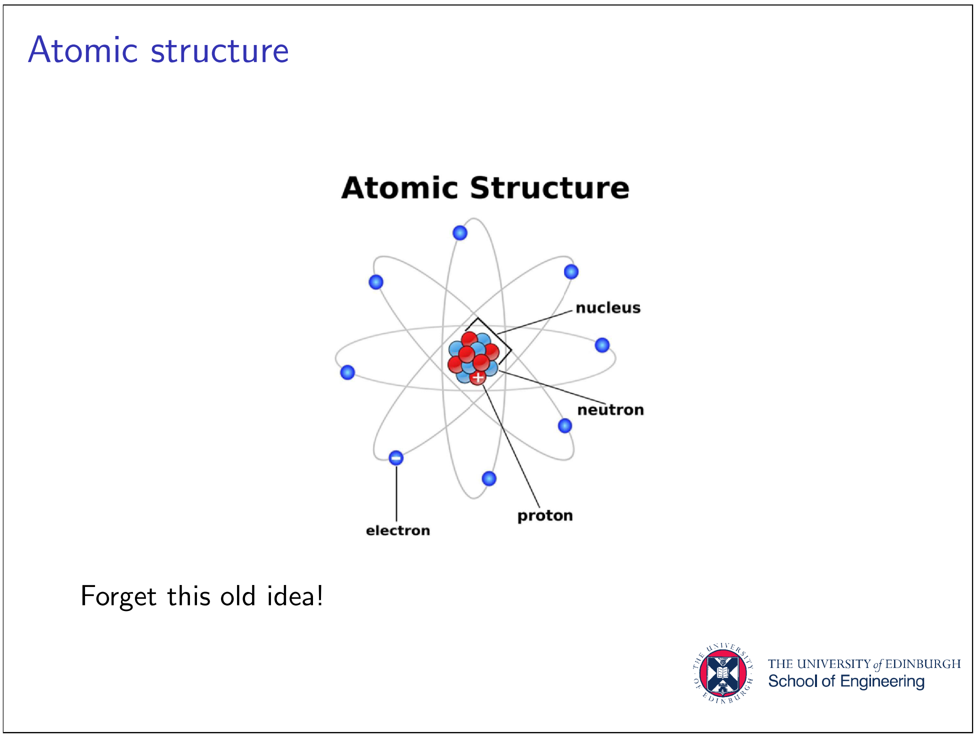
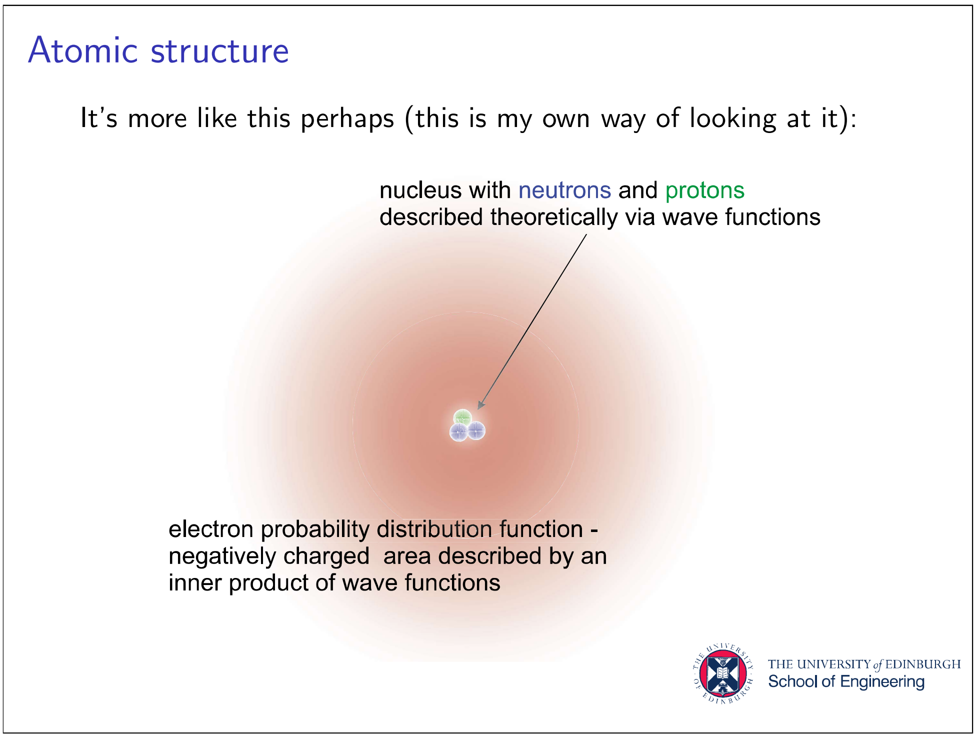


Atomic structure

Forget this old idea!



Atomic structure

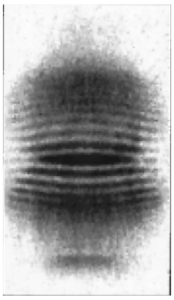
It's more like this perhaps (this is my own way of looking at it):

nucleus with neutrons and protons
described theoretically via wave functions

electron probability distribution function -
negatively charged area described by an
inner product of wave functions

Atomic structure

- Do you accept the idea of material waves?
- de Broglie postulated that a particle could have a wavelength given by: $\lambda = h/p$ where p is the particle momentum.
- The image shows two atoms that were trapped, highly cooled (low momentum) and manipulated to be near each other. They produce an interference fringe; material produces interference patterns!



From "Observation of Interference Between Two Bose Condensates", M. R. Andrews, C. G. Townsend, H.-J. Miesner, D. S. Durfee, D. M. Kurn, W. Ketterle, Science, Vol. 275 no. 5300, pp. 637-641, (1997).

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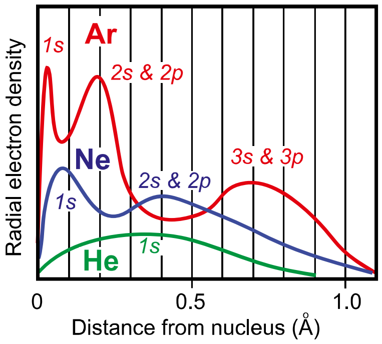
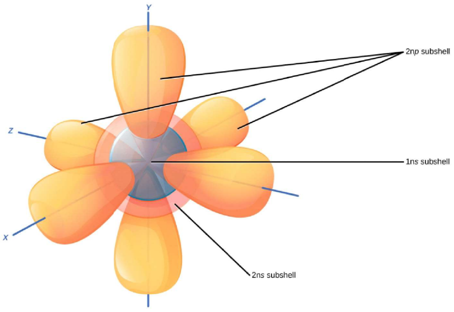
Atomic structure

- The various electrons in an atom organize themselves in ways that satisfy the Schrödinger equation (a wave-like equation) of quantum mechanics, within electromagnetic boundary conditions specific to the structure:





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Schrödinger equation

- The full Schrödinger equation is written as:

$$-\frac{\hbar}{2m}\nabla^2\Psi(r,t) + \hat{V}\Psi(r,t) = i\hbar\frac{\partial}{\partial t}\Psi(r,t) \qquad (29)$$

  where: $\hbar = h/2\pi$
  Ψ is the wave function (of position and time, and Ψ^2 is a probability density)
  $\hat{V}$ is the potential energy distribution (i.e. based on the presence of protons and electrons).
- The Schrödinger equation is spatially similar to a wave equation (in the ∇^2; it's a boundary value problem) but it has a first order time dependence which describes transitions.

Schrödinger equation

- The time dependence of equation 29 can be removed via separation of variables, and what remains is a stationary Schrödinger equation:

$$\left[-\frac{\hbar}{2m_a}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r}) \qquad (30)$$

  where:

  m_a is a generic mass (depending on the problem being solved),
  ψ is the stationary wave function,
  $V(\vec{r})$ is the potential energy distribution again, and
  E is the energy of the system.
- This is an eigenvalue problem where ψ is the eigenfunction, E is the eigenvalue, and the terms $\left[-\frac{\hbar}{2m_a}\nabla^2 + V(\vec{r})\right]$ are an *operator* called the Hamiltonian. In quantum mechanics, solutions to eigenvalue problems produce an observable like energy.

Schrödinger equation

- In what follows, we mention the idea of operators that commute.
- Dirac stated that "A measurement always causes the system to jump into an eigenstate of the dynamical variable that is being measured."
- If we wish to observe some variable A to arbitrary precision, and if ψ is an eigenfunction of the A-related operator $\hat{A}$, we can show that the measurement outcome will be $A = a$ where a is the related eigenvalue.
- If we wish to observe another quantity, call it B, to equally arbitrary precision, then ψ must be an eigenfunction of $\hat{B}$ as well. That happens when $\hat{A}$ and $\hat{B}$ commute:
  $\hat{A}\hat{B}\psi - \hat{B}\hat{A}\psi = 0$
- Point being - if operators commute, several variables (observables) can be determined at the same time.

Schrödinger equation

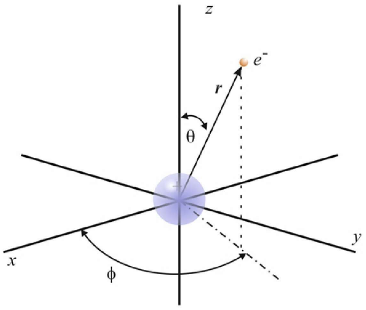
- In related news, the Schrödinger equation can be a little confusing because there are several outcomes built into the one equation:
  ▹ If we solve for the eigenvalue E then we have expressions for the various quantized levels of energy.
  ▹ It turns out we can also solve for momentum, because momentum squared commutes with the Hamiltonian (an energy operator).
  ▹ In classical terms, if we have momentum squared we can divide it by $2m_a$ to get kinetic energy. So that one solution gives us several results already.
  ▹ It is worth mentioning that because momentum and the Hamiltonian commute, they share the same eigenfunction ψ.
  ▹ If we solve for the eigenfunction ψ then we also have the probability amplitude, and using that we can solve for the probability density (ψ^2) of things like the electron vs. position (i.e. the shell structure), or we can find the expectation values of things like the spectroscopic transition dipole moment (resonance response) using an inner product (more on that in the lecture on resonance).

The one-electron atom

- The potential energy function (in the Hamiltonian) for a one electron atom is:

  $V(r) = -\frac{Ze^2}{4\pi\epsilon_o r}$

  where we have assumed it is not time dependent but is dependent on position r. Here Z denotes the number of positive charges in the nucleus, and e is the charge on one electron.



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The one-electron atom

- It is necessary to solve the stationary Schrödinger equation (number 30) in steps via separation of variables. There are three coordinates (r, θ, and ϕ) and as it turns out there are three quantities that commute with one another in this problem: the energy E, the square of the electronic orbital angular momentum (often called c in atomic physics), and one component of electronic orbital angular momentum (often called b in atomic physics) along one of the three cartesian coordinates (we use z).
- I used the word "orbital". The electron has two forms of angular momentum - orbital and spin. We will ignore spin for a bit.
- Since the atom is symmetric about the origin, z is not really defined, but if we put a magnetic field across the atom the moving electron will respond to it and we call the direction of the magnetic field z.
- One can not solve directly for E using the expression for $V(r)$ just provided. $V(r)$ is the potential energy. The electron also has kinetic energy, which can be had from the square of the electronic orbital angular momentum (c).

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The one-electron atom

- The solution to the one electron atom goes together in a way that is reminiscent of a Russian doll.
- The first solution is small and relatively simple. It enters into the next solution, which is a bit bigger. That solution then enters into the next and bigger solution - and so forth.
- If you wish to see this done in detail, consult the sources mentioned at the beginning of this course. What follows is taken from *Spectroscopic Measurement: An Introduction to the Fundamentals*, M.A. Linne, Academic Press, London, UK, ISBN 0-12-451071-X, (2002).

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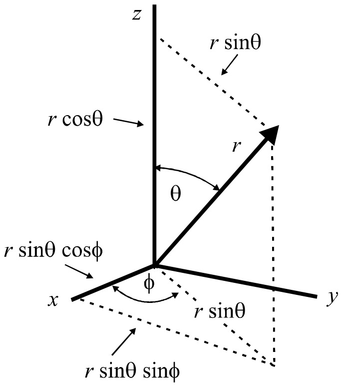
The one-electron atom

- The solution starts by separating the Schrödinger equation, and the simplest first solution is for Φ, the ϕ-dependent wave function (the eigenfunction of this sub-problem). The necessary condition on Φ is that it will close on itself each time it comes around 360°, and that produces:

  $\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$

  where m is the magnetic quantum number, called that because it responds to the magnetic field aligned along z.
- This is the right hand rule - rotation around ϕ points along z.



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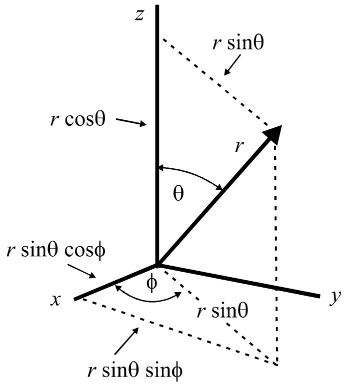
The one-electron atom

- The component of the electronic orbital angular momentum aligned along z (the eigenvalue of this sub-problem) is found to have magnitude:

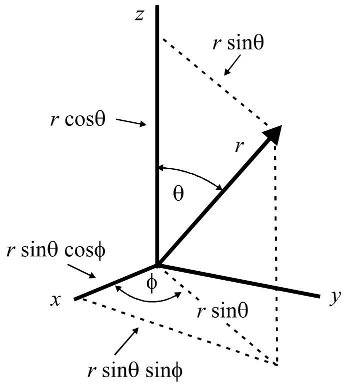
  $b = m\hbar.$
- Now the solution for Φ is put into the full orbital electronic Schrödinger equation written in terms of an angular wave function $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$, producing an eigenvalue of:

  $c = l(l+1)\hbar^2$ for $l = 0, 1, 2, 3...$
- The expression for the eigenfunction $Y(\theta, \phi)$ is complicated and not related to this discussion so we don't include it.



The one-electron atom

- We also find that $l \geq |m|$.
- In fact, m is renamed m_l and it is then equal to $-l, -l+1, ...0... l-1, l$
- That means that the square of the electronic orbital angular momentum (c), with quantum number l, has quantized components of $\sqrt{c}$ along z given by b with quantum number m_l.
- There are thus $2l+1$ values of b and of m_l. We will encounter $2l+1$ type expressions many times.



The one-electron atom

- Now the ϕ and θ solutions are plugged into the stationary Schrödinger equation (equation 30) to produce an expression for the internal energy (eigenvalue of equation 30) in a 1-electron atom:

$$E_n = -\left(\frac{Ze^2}{h\epsilon_\circ}\right)^2 \frac{\mu}{8n^2} \tag{31}$$

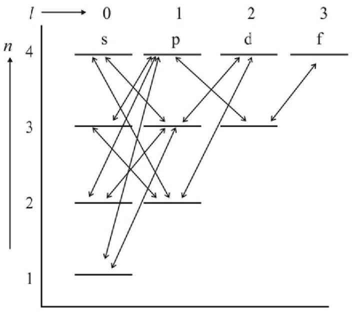
where:
μ is the reduced mass given by $\mu \equiv \frac{m_n m_e}{m_n + m_e}$
n = principal quantum number; n takes integer values starting at 1.

- Again, the solution for eigenfunction ψ is complex and not really related to the discussion at hand so we leave it out of the presentation.
- The ϕ and θ solutions went into producing equation 31 even though it is not obvious. One outcome is that $l \leq n - 1$, so there are relationships between all three quantum numbers.

The one-electron atom

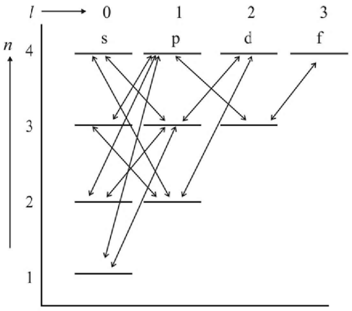
- The electronic energy is quantized (via n); the allowed energy of the system exists only in specific levels given by equation 31.
- Changes in the energy stored in the atom have to occur between quantum states.
- There are also "selection rules" that determine whether or not a transition is "allowed" (allowed transitions are those one can detect, "forbidden" transitions are not detectable):

$\nabla n = 0, 1, 2, ...$
$\nabla l = \pm 1$
$\nabla m_l = 0, \pm 1$



The one-electron atom

- Some states have the same energy even though they have different quantum numbers (e.g. different l, m_l). Levels that are physically different from each other but have the same energy are called “degenerate”. That name applies to the same situation for multi-electron atoms and for molecules.

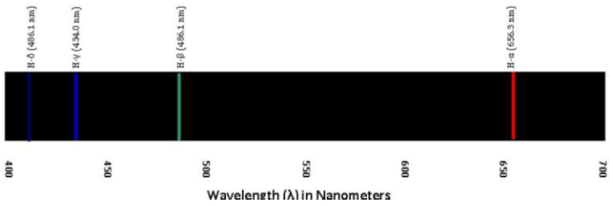


The one-electron atom

- Now we need to include electron spin. Spin was discovered because some fine splitting of spectral lines (small $\delta\nu$ separation) occurs in a magnetic field and it was postulated that electrons themselves are spinning (hence they would have a magnetic moment). That’s not the case, but it behaves almost like an intrinsic rotation.
- The postulate was that there was a spin angular momentum similar to c, or $S^2 = s(s+1)\hbar^2$ where S would be the total spin momentum and s woud be the spin quantum number (analogous to l). Then there would be an $S_z = m_s\hbar$ as well, with $m_s = 0, \pm s$ just like the case for b.
- It is not uncommon to draw analogies like that in quantum mechanics. The only experimental discovery that altered this analogy is that s can only take the value $\frac{1}{2}$.
- The selection rule is $\Delta m_s = 0$.

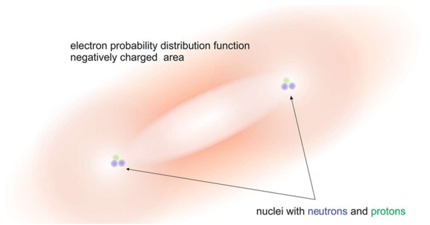
The one-electron atom

- When a transition occurs from one quantum state to the next, and when it is an optical interaction (e.g. absorption or emission), then the energy difference between the two states is related to the frequency (related to wavelength) of the light by: $\Delta E = h\nu$ where h is Planck's constant again.
- An example spectrum (the "Balmer series" of the Hydrogen atom):

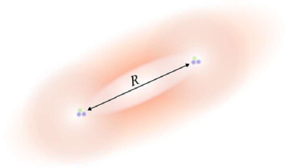


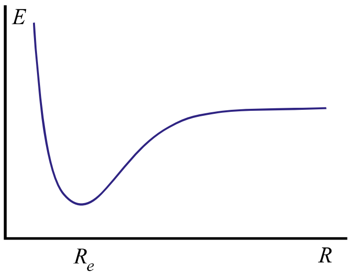
Molecular structure

- Those results were just for single electron atom (H is one).
- Multi-electron atoms have more complex energy level structure and spectra.
- Molecules are even more complex. Diatomic molecules are nice examples because there are just two nuclei and the coordinate connecting the two can act as the z-axis. They are also critically important in combustion.



Molecular structure





- Think in terms of an electronic probability density distribution (i.e. an electronic ψ^2) that surrounds the nuclei and holds them inside a potential well.
- This kind of image of a potential well is possible only because we are discussing a diatomic molecule with a defined, linear internuclear axis which allows us to show a 2-D plot of potential energy vs. R.

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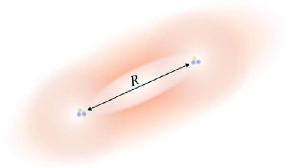
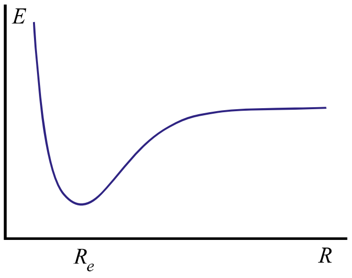
Molecular structure





- The potential well is responsible for bonding.
- It also provides a resilient, extensible boundary (I like to think of a thick membrane) inside which the nuclei can vibrate.

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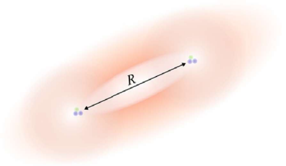
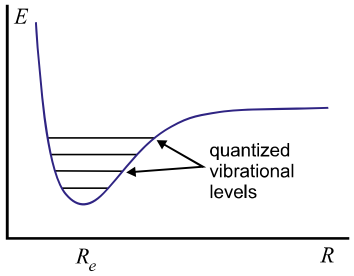
Molecular structure

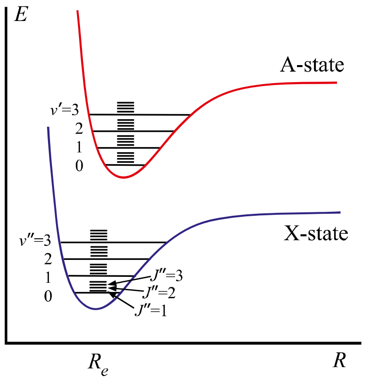




- Energy in a molecule is quantized, and so vibrational energy is quantized. At one of the quantized vibrational energy levels, the two nuclei can literally oscillate within the potential well. At the small R end of the vibration they are coming too close and repel each other and at the long R end the electron cloud pulls them back together.
- If we add too much vibrational energy the molecule can climb levels to the point where it dissociates and $R \to \infty$.

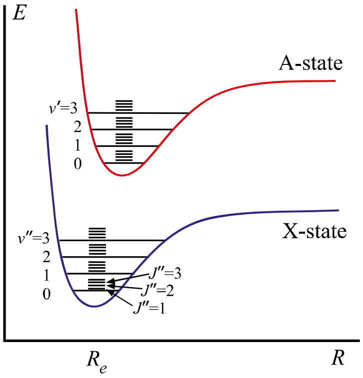
Molecular structure

- This shows two electronic energy states for the valence electron (blue and red curves) with other, intermediate energy states represented as well.
- The valence electron hops to a different configuration going from X to A (or from A to X).
- The vibrational energy is characterized by quantum numbers: v" is the vibrational quantum number of the lower electronic level (X-state) and v' is the vibrational quantum number of the upper electronic level (A-state).



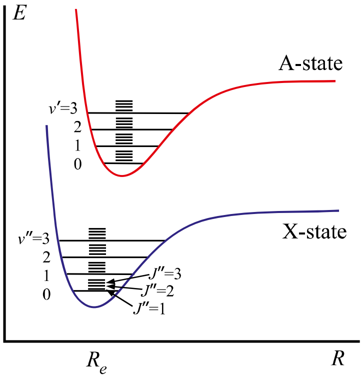
Molecular structure

- The entire molecule can also rotate, and rotational energy is also quantized:
  J" is the rotational quantum number of the lower electronic level (X-state)
  J' is the rotational quantum number of the upper electronic level (A-state).
- A huge number of energy levels are possible, and transitions occur between them according to selection rules.
- As always, if the transitions are optical, the energy difference is related to the optical frequency $\Delta E = h\nu$.



Molecular structure

- Typically, a molecule undergoes several vibrations (about 5-100) during a single rotation.
- The characteristic times involved are:
  ▷ electronic motion 10^{-16} sec
  ▷ vibration 10^{-13} sec
  ▷ collision interaction 10^{-12} sec
  ▷ rotation 10^{-10} sec
  ▷ radiative lifetime $10^{-6} - 10^{-8}$ sec

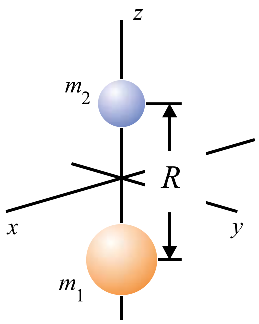


Molecular structure

- Now consider more detail about this diatomic molecule. Just the nuclei are depicted here.
- We can separate the various "term energies" for electronic, vibrational, and rotational states, where term energies are defined by:

  $T \equiv \frac{E}{hc} = T_e + G_v + F_J \, (cm^{-1})$

  here:
  T_e is the electronic term energy
  G_v is the vibrational term energy, and
  F_J is the rotational term energy.



Schrödinger equation for a diatomic molecule

- The stationary Schrödinger equation for a diatomic molecule (with nuclei numbered 1 and 2) is written (without calling out the positional dependence):

$$\left[\underbrace{-\frac{\hbar}{2\mu}\nabla^2}_{\text{nuclear}} \underbrace{- \frac{\hbar}{2m_e}\sum_{i=1}^{N}\nabla_i^2}_{\text{electronic}} + \hat{V} \right] \psi = E\psi \qquad (32)$$

where:

μ is the reduced nuclear mass ($\mu \equiv \frac{m_1 m_2}{m_1 + m_2}$),
m_e is the electronic mass with N as the number of electrons, and
$\hat{V}$ represents three different potential interactions: electron-electron repulsion, electron-nuclear attraction, and nuclear-nuclear repulsion.

Schrödinger equation for a diatomic molecule - solutions

- The Born-Oppenheimer approximation says that the nuclei can be considered stationary compared to how fast the electrons move, so we can separate electronic solutions from nuclear solutions. The internuclear separation R still enters into the electronic Schrödinger equation but as a parameter, not a variable.
- Just like a 1-electron atom, the energy of an electron in a molecule can not be solved just using potential energy related to charge separation. The electron also has orbital kinetic energy. Again, the best approach for the electrons and for the nuclei is to solve the problem of orbital angular momentum squared first because it enters into the rest of the formalism.

Schrödinger equation for a diatomic molecule - solutions

- It turns out that it is quite difficult to calculate electronic states; wave functions and energies. It can be done using specialized ab-initio approaches and that is done more commonly nowadays. Mostly, however, electronic energy levels are measured using spectroscopy. We usually assume the lowest electronic state (the X state) has zero electronic energy and use the measured ΔE for each higher state.
- It is still necessary to analyze electron interactions with the nuclei, in ways we will discuss.
- For a diatomic molecule it is possible to solve for rotational and vibrational states of the nuclei to varying degrees of accuracy.
- We will thus begin by discussing nuclear solutions and transitions, and then discuss transitions between electronic, vibrational, and rotational states combined (in lecture 8).

Nuclear solutions

- The nuclear Schrödinger equation is written :

  $$\left(-\frac{\hbar^2}{2\mu}\nabla^2 + E(R)\right)\chi(\vec{R}) = E_{\text{total}}\,\chi(\vec{R})$$

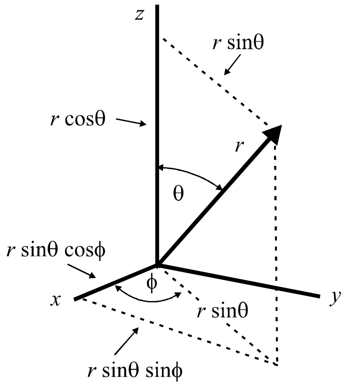
  where χ is the nuclear wavefunction and $E(R)$ is the electric potential distribution, the eigenvalue of the *electronic* Schrödinger equation.
- This equation looks almost identical to the one electron atom Schrödinger equation except that $V(r)$ has been replaced by $E(R)$, which is the potential field introduced by the electron cloud. This makes sense; the one electron atom problem was about two bodies in a field, as is this one.
- The nuclear solution goes together in the same Russian doll pattern, from the ϕ solution to the θ solution to the full solution.

Nuclear solutions

- Return to the coordinate system, where the internuclear axis is aligned along z.
- As before, the solution starts by separating the nuclear Schrödinger equation, and the simplest first solution is for Φ, the ϕ dependent wave function. The necessary condition on Φ is that it will close on itself each time it comes around 360°, and that produces:

  $$\Phi(\phi) = \frac{1}{\sqrt{2\pi}}e^{iM\phi}$$

  where M is the nuclear magnetic quantum number.

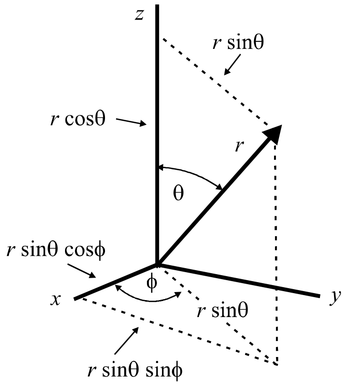


Nuclear solutions

- Warning - with molecules we discuss both nuclear and electronic orbital angular momentum!
- One can also solve for the component of nuclear orbital angular momentum along z :

  $L_Z = M\hbar.$

  (if you think this sounds familiar, it should).
- As before, the sub-Z on the symbol L appears because the solution was for the angular component around ϕ and by the right hand rule the momentum points along z.

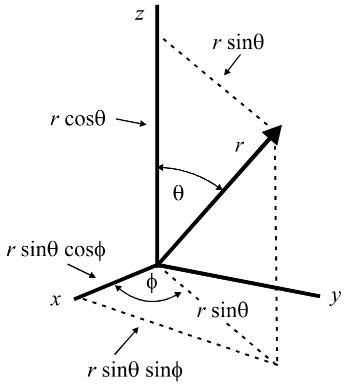


Nuclear solutions

- M is called the magnetic quantum number because a rotating charge around ϕ interacts with a magnetic field along z causing a shift in energy (spectral location) and the shift depends on the orientation of the field along z.
- The ϕ solution can then be inserted into the combined Schrödinger equation in θ and ϕ to get:

  $L^2 = \mathcal{J}(\mathcal{J}+1)\hbar^2$

  where L is the total nuclear orbital angular momentum, and $\mathcal{J}$ is the nuclear angular momentum quantum number (for θ and ϕ).



Nuclear solutions

- A special font is used for the nuclear rotational quantum number $\mathcal{J}$ because the rotational states for a complete molecule involve coupling between the nuclear orbits and the electronic orbits. We use J to denote a coupled-state molecular rotational quantum number.
- The θ/ϕ momentum solution is then be inserted into the nuclear Schrödinger equation to produce a radial Schrödinger equation.
- The radial Schrödinger equation is then solved for rotational motion under various sets of assumptions. If we assume R remains fixed under rotation we get the simplest formalism; a "rigid rotator":

  $E_{\mathcal{J}} = \frac{\hbar^2}{2I_e}\mathcal{J}(\mathcal{J}+1),\ \mathcal{J} = 0, 1, 2, 3...$

  where I_e is the moment of inertia, and we use the nuclear orbital quantum number.
- In the microwave region of the spectrum it is possible to detect changes in purely rotational levels, and here we have enough to discuss a simple model for that process.

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Nuclear solutions

- Selection rules determine which transitions are allowed. This has to do with the transition dipole moment mentioned previously (the strength of the resonant response). It can go to zero under specific conditions discussed in the next lecture. If that is the case it is usually not possible to observe a spectral response and so the transition is called forbidden. Simply put, a forbidden transition means one that is not experimentally observable.
- For the rigid rotator model, under purely rotational transitions, the selection rule is:

  $\Delta\mathcal{J} = \mathcal{J}_{\text{final}} - \mathcal{J}_{\text{initial}} = \pm 1.$
- As an example, absorption can be described by:

  $\nu = \frac{E_{\mathcal{J}\text{upper}} - E_{\mathcal{J}\text{lower}}}{h} = 2B_e(\mathcal{J}_{\text{lower}} + 1)$

  and emission by: $\nu = 2\mathcal{J}_{\text{upper}}B_e$ where $B_e \equiv \frac{\hbar^2}{2I_e h}$.
- These formulas predict evenly spaced rotational lines but it's just a first order approximation.

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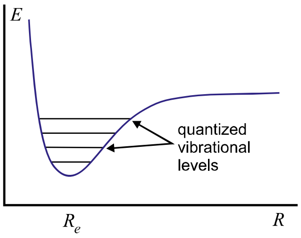
Nuclear solutions

- Before adding some sophistication to the rotational solution, it would be good to discuss vibration because there is an interaction between the two (vibration affects I_e).
- The potential well can be modeled (approximated) various ways, but the function is typically written as an expansion about R_e and the first term ends up being parabolic, i.e. a harmonic oscillator.



Nuclear solutions

- The vibrational solution uses some mathematical-physical arguments about a recursion relation. It is a bit messy but the outcome for a "simple harmonic oscillator" is:

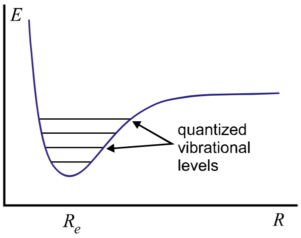
  $$E_v = (v + 1/2)h\nu_e, \; v = 0, 1, 2, 3...$$

  where v is the vibrational quantum number,
  ν_e is analogous to an oscillator frequency given by:

  $$\nu_e \equiv \frac{1}{2\pi}\sqrt{\frac{k_e}{\mu}} \; ,$$

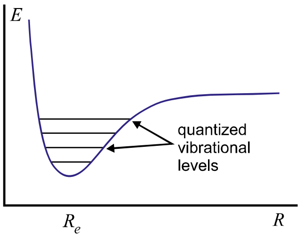
  μ is the reduced nuclear mass, and
  k_e is an analog to the spring constant:

  $$k_e \equiv (\mathrm{d}^2E/\mathrm{d}R^2)_{R_e}.$$



Nuclear solutions

- Notice that the $(v + 1/2)$ means vibrational energy doesn't go to zero.
- Under the harmonic oscillator assumption the selection rule is $\Delta v = \pm 1$, and for an electronic transition Δv can also be zero. The harmonic oscillator assumption is not accurate, however, and "overtones" of $\Delta v = \pm 2$ can also be found.



Nuclear solutions

- More realistic expressions for rotation include terms for centrifugal distortion (I changes with $\mathcal{J}$), and vibration/rotation interaction where we use a quantum mechanical expectation value for R_e that depends on v. This is just a start, and it produces the following expression for the rotational term energy ($F_{\mathcal{J}} = E_{\mathcal{J}}/hc$):

$$F_{\mathcal{J}} = \frac{B_v}{c}\mathcal{J}(\mathcal{J}+1) - \frac{D_v}{c}\mathcal{J}^2(\mathcal{J}+1)^2 + \frac{H_v}{c}\mathcal{J}^3(\mathcal{J}+1)^3 \qquad (33)$$

  where: B_v is a vibrationally corrected form of B_e, the term with D_v is a vibrationally corrected rotational distortion term, and the H_v is a third rotational correction.

Nuclear solutions

- More realistic expressions for vibration include terms for anharmonicity. Typically, terms are added to the expansion of the potential energy function $E(R)$ about R_e. As one example, it produces the following 3-term expression for the vibrational term energy ($G_v = E_v/hc$):

$$G_v = \omega_e\left(v+\frac{1}{2}\right) - \omega_e x_e\left(v+\frac{1}{2}\right)^2 + \omega_e y_e\left(v+\frac{1}{2}\right)^3 \qquad (34)$$

  where: $\omega_e \equiv \nu_e/c$, $\omega_e x_e$ is the first anharmonic constant and $\omega_e y_e$ is the second.
- Most often these anharmonic coefficients are extracted by fitting an experimental spectrum.
- The total nuclear term enery is then $G_v + F_{\mathcal{J}}$.

Nuclear solutions

- The vibrational levels are no longer evenly spaced; the spacing decreases with v.
- The rotational lines are no longer evenly spaced as well; the minus sign on the second term containing D_v means that the energy spacings can be reduced at high $\mathcal{J}$ (depending on the value of D_v). This negative term can produce a “band head”, to be discussed later.
- Most often these spectroscopic coefficients are extracted by fitting an experimental spectrum.

“Ro-vibrational” transition selection rules

- We have already discussed some of this, but for completeness:

  ▷ Transitions that are forbidden (have no resonance response, the transition dipole moment = 0) will not be observed. For purely ro-vibrational transitions the molecule must have a permanent dipole moment; i.e. homonuclear molecules like O_2 and N_2 have no IR active transitions.
  ▷ For ro-vibrational transitions, $\Delta\mathcal{J} = \pm 1$ if the electronic state is a Σ state (see below), otherwise $\Delta\mathcal{J} = 0, \pm 1$.
  ▷ Rotational and ro-vibrational transitions occur only between states of “opposite parity” (the wave function ψ changes upon reflection across the molecular center of mass for such states).
  ▷ There is no strict transition rule for vibrational transitions but the strongest resonance response is for $\Delta v = \pm 1$.

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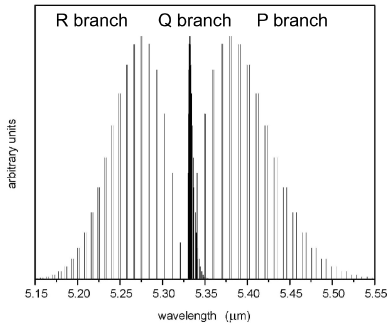
Ro-vibrational transitions

- For every ro-vibrational transition in which $\Delta\mathcal{J} = -1$, the collection of lines is called a “P branch” of the vibrational transition while $\Delta\mathcal{J} = +1$ produces an “R branch”, and $\Delta\mathcal{J} = 0$ is called a “Q branch”.
- Note the pairs of lines (this spectrum is for NO). The pairs are caused by “lambda doubling” which will be discussed later.



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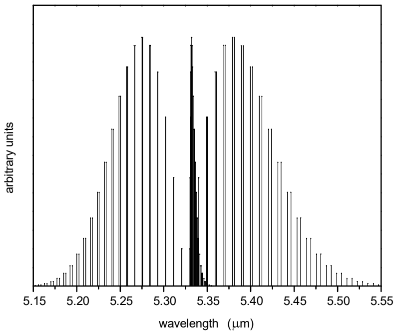
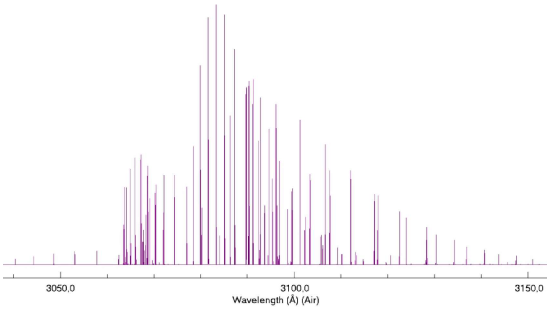
Molecular structure



- Vibrational and "ro-vibrational" transitions occur in the infrared.

Molecular structure



Simulated UV spectrum of OH for the first electronic transition and fundamental vibrational band, from the Lifbase database (http://www.sri.com/engage/products-solutions/lifbase).

- There can also be ro-vibrational transitions during an electronic transition, and because $E(R)$ changes between electronic levels the situation becomes much more complex. In addition, the rules for electronic transitions enter but they depend on each molecule (how the various modes couple to each other). It's not possible to generalize.

Next topic

Electronic transitions, and then an OH example.

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Advanced Laser Diagnostics for Combustion Research

Lecture 8: Electronic transitions and OH

Mark Linne

University of Edinburgh

Tsinghua-Princeton-CI Summer School on Combustion
July 11 - 17, 2021

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Topics

Spectroscopy

- Electronic states and coupling between electronic and nuclear modes

An important example: the OH UV spectrum

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Introduction

- This lecture is a continuation of Lecture 7 where we briefly discussed the one electron atom and then spent a good deal of time on nuclear solutions for a diatomic molecule.
- Here we continue that discussion by going into how the electronic states are dealt with. As a reminder, in Lecture 7 we said, "It turns out that it is quite difficult to calculate electronic states; wave functions and energies. It can be done using specialized ab-initio approaches and that is done more commonly nowadays. Mostly, however, electronic energy levels are measured using spectroscopy. We usually assume the lowest electronic state (the X state) has zero of energy and use the measured ΔE for each higher state."
- We also said, "There can also be ro-vibrational transitions during an electronic transition, and because $E(R)$ changes between electronic levels the situation becomes much more complex. In addition, the rules for electronic transitions enter but they depend on each molecule (how the various modes couple to each other). It's not possible to generalize."

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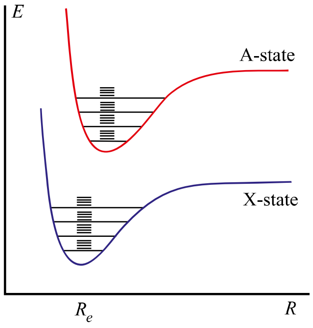
Electronic transitions

- The lowest valence electronic state is called the "X-state", and from there they are called the $A-, B-, C-$ ... states going up in energy.
- Each electronic level has a different potential well shape.
- That means $E(R)$ is different for the two states and that means the vibrational and vibrationally dependent rotational coefficients are different between X and A.



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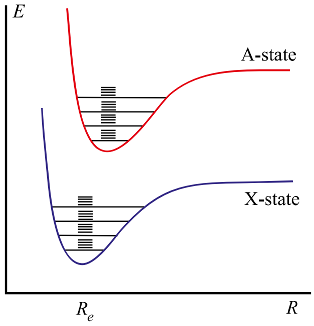
Electronic transitions

- As before, the total term energy for the molecule is:

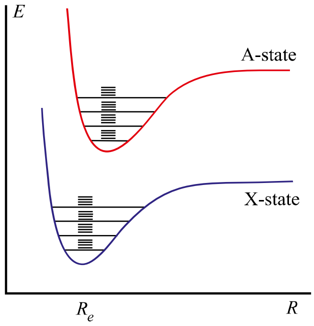
  $T = \frac{E}{hc} = T_e + G_v + F_J.$

  Now that we are involving the electronic transitions, the expressions for G_v and $F_{\mathcal{J}}$ will change.
- Most importantly, $F_{\mathcal{J}}$ will now have to include the orbital contribution of the high speed electron (hence becoming F_J).



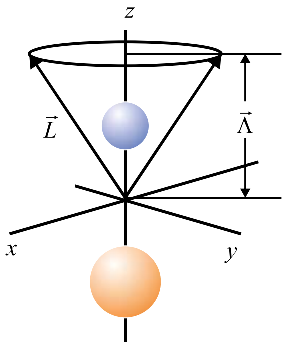
Electronic transitions

- You may recall that in Lecture 7 we discussed solutions for the one electron atom, including the component of the electronic orbital angular momentum along z (with magnetic quantum number m_l), and total electron orbital angular momentum (quantum number l). The atomic shells are called s, p, d, f... for $l = 0, 1, 2, 3$.... Both m_l and l enter into selection rules. There will be similar but not entirely analogous terms for the electrons in a molecule.



Electronic transitions

- The molecule has many electrons and it is necessary to combine their contributions into an aggregate electronic behavior. We will not discuss the math, but we have to discuss electronic states and how they couple.
- Mismatched nuclei form a natural charge distribution along the internuclear axis, making it a natural z axis.
- There is an aggregate electronic orbital angular momentum we denote by $\vec{L}$ (with quantum number L).



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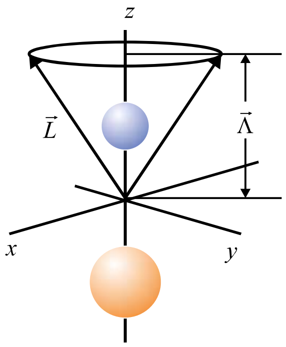
Electronic transitions

- As $\vec{L}$ precesses around z (around angles ϕ) it gives rise to a component along z that we call $\vec{\Lambda}$ (with magnetic quantum number M_L - note that often the molecular counterpart uses capitalized and/or Greek letters that are actually the same as the smaller letters used for an atom).
- The magnitude of $\vec{\Lambda}$ is given by $|M_L|\hbar$, where $M_L = L, L-1, L-2..0.., -L$.



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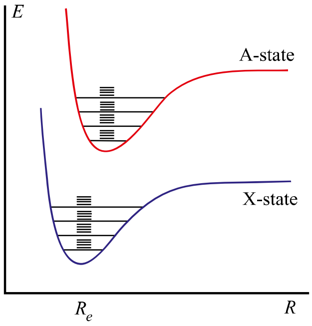
Electronic transitions

- Similar to the atomic solution $(s, p, d, f, ...)$, electronic states are designated by $\Sigma, \Pi, \Delta, \Phi, ...$ for $|M_L| = \Lambda = 0, 1, 2, 3, ...$
- The energy will change with $|\vec{\Lambda}|$. It helps to establish the energies of the X and A states for example.



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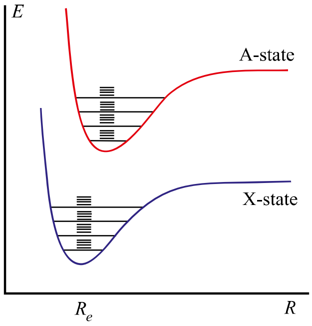
Electronic transitions

- Since $|M_L| = \Lambda = 0, 1, 2, ...L$ there are $L + 1$ distinct states with different energies for each value of L.
- This makes it sound like there are many electronic states like the ones in the image, but in reality there are just a few of use to us (2 for OH, and 4 for NO and CH for example).
- $\vec{\Lambda}$ will also control how the electronic and nuclear rotation affect (couple to) each other.



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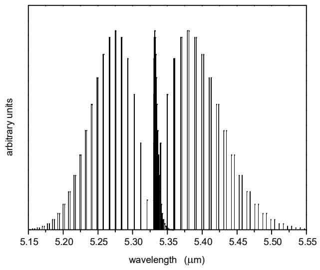
Electronic transitions

- Notice we used $|M_L|$. Depending on the directionality of the electron oribt, M_L can point up or down (switch sign). The two states are usually degenerate or nearly degenerate. This phenomenon is called lambda doubling, and the spectroscopic lines can sometimes be separated by a small amount as shown for NO (charge motion like nuclear rotation can set up a small magnetic field that splits the two states in energy).
- Note that Σ states $(\Lambda = 0)$ have no Λ doubling degeneracy.
- Line broadening and instrument broadening often obscure such features, at which point we deal with them as though they are degenerate.



Electronic transitions

- Electron spin was discovered because some fine splitting of spectral lines occurs in addition to phenomena like lambda doubling. Since the rotation of the electron in orbit explains the lambda doubling, it was postulated that electrons themselves are spinning. That's not the case, but the name stuck.
- There is one spin quantum number $(1/2)$ and a spin component along z with magnetic quantum number $m_s = \pm 1/2$ for each electron. To populate shells we add spin in unmatched $(\pm)$ pairs.
- The resultant spin S of the electrons in a molecule will be integral if there are an even number of electrons, and half-integral if odd.

Electronic transitions

- The component of total spin along the internuclear axis is designated Σ. It is very unfortunate that we use the same symbol for $\Lambda = 0$ and for the total spin along the z axis. Here we will use Σ_s to denote the total spin along the z axis but that is not the normal notation.
- Σ_s is then $\Sigma_s = S, S-1, S-2, ... - S$. There are thus $2S+1$ possible values for Σ_s.
- To find the total electronic orbital plus spin angular momenta one must sum along the z axis with $\Omega \equiv |\Lambda + \Sigma_s|$.
- That was for the electrons. It is necessary to analyze how the nuclear and electronic orbits couple and that is done via angular momenta.

Electronic transitions

- In an unusual case during purely ro-vibrational transitions, when the electron orbital has a significant effect on the moment of inertia about z, the rotational term energy is commonly modeled by:

  $$F_{\mathcal{J}} = \frac{B_v}{c}\mathcal{J}(\mathcal{J}+1) - \frac{D_v}{c}\mathcal{J}^2(\mathcal{J}+1)^2 + \frac{1}{c}(A - B_v)\Lambda^2$$

  where $(A - B_v)\Lambda^2$ is the so-called "symmetric top correction".
- When the electronic orbit couples to the internuclear axis it affects the rotational contributions to an electronic spectrum.
- This phenomenon is described in terms of Hund's coupling cases. There are many such cases but the diatomics important to combustion usually fall into Hund's cases a and b.
- Combining nuclear and electronic solutions causes a problem because we used similar notation in each case, e.g. L was used for orbital angular momentum for the nuclei and for electrons. In this presentation we will use R to designate the nuclear term just to keep them separate for a moment (again, this goes against normal notation).

Electronic transitions

Hund's case a

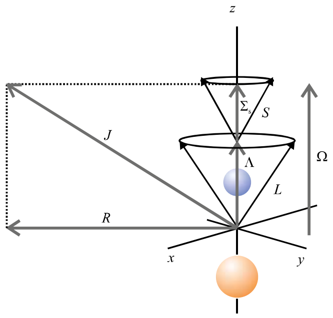
- Assume:

  ▷ Interaction between nuclear rotation and electronic angular momentum is weak.

  ▷ Electronic angular momentum is strongly coupled to z.

  ▷ $\vec{L}$ and $\vec{S}$ precess independently about z.

  ▷ Their projections Λ and Σ_s simply add to give Ω, a well defined quantum number that can be used for electronic motion instead of Λ.



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Electronic transitions

Hund's case a

- In this case the total angular momentum is:

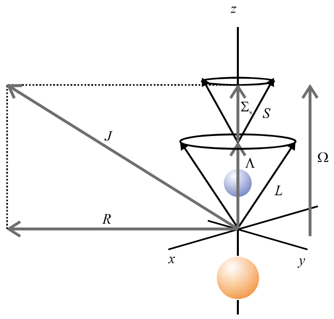
  $\vec{J} = \vec{R} + \vec{\Omega}$

  with a quantum number $J = R + \Omega$.

- The rotational energy for Hund's case a is usually given by:

  $F_J = \frac{B_v}{c} J(J+1) - \frac{B_v}{c}\Omega^2$

  or for a more symmetric top molecule $F_J = \frac{B_v}{c} J(J+1) - \frac{(A - B_v)}{c}\Omega^2$



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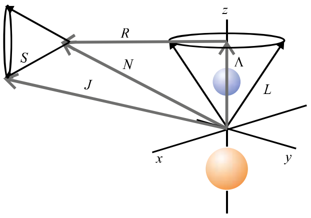
Electronic transitions

Hund's case b

- Assume:
  - ▷ Spin and electronic orbital angular momenta do not couple.
  - ▷ Instead, spin couples to R.
  - ▷ S does not precess about z. It remains fixed in space and adds to $\vec{R}$.



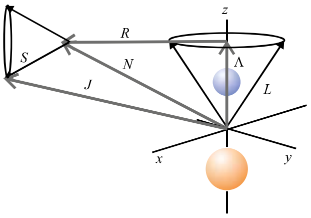
Electronic transitions

Hund's case b

- In this case the a new angular momentum vector combines nuclear and electronic orbitals:

  $\vec{N} \equiv \vec{R} + \vec{\Lambda}$
- Then total rotation is described by:

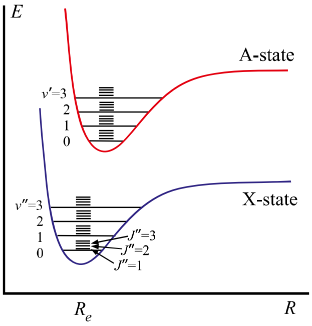
  $\vec{J} = \vec{N} + \vec{S}$
- Hund's case b is very common in the kind of free radicals that appear in flames.
- Energy formulas for Hund's case b molecules differ from one to the next; they are similar to expressions we have already discussed but no single expression can be quoted.



Electronic transitions

- Energies add and so the spectral lines for electronic transitions can be found by summing term energies (in terms of wavenumbers):

  $\breve{\nu} = \frac{\nu}{c} =$
  $(T'_e - T''_e) + (G'_v - G''_v) + (F'_J - F''_J).$



Selection rules

- The selection rules for diatomic molecules in Hund's cases a and b are:

  ▷ $\Delta J = 0, \pm 1$, but $J = 0 \nleftrightarrow J = 0$. Actually, $\Delta J = \pm 2$ is also allowed but these O and S transitions are very weak relative to the P, Q and R branches.
  ▷ There is no restriction on Δv, but Franck-Condon principles apply (to be discussed under resonance response).
  ▷ Parity must change during a molecular electronic transition (i.e. the wave function must transition from symmetric when reflected through the center of mass to antisymmetric, or vice versa).
  ▷ For the electron, $\Delta \Lambda = 0, \pm 1$ and $\Delta S = 0$. In addition;
    in Hund's case a $\Delta \Sigma_s = 0,\ \Delta \Omega = 0, \pm 1$
    and in Hund's case b $\Delta N = 0, \pm 1$ except $\Delta N = 0$ for transitions of $\Sigma \leftrightarrow \Sigma$

Degeneracy

- It is important to keep track of degeneracy because it affects how one calculates the Boltzmann fraction in each level and it affects the strength of the resonance response. It can be calculated according to:

▷ Electronic degeneracy can be described by $g_e = (2S+1)\phi$, where $\phi = 1$ for $\Lambda = 0$ and $\phi = 2$ for $\Lambda \neq 0$ (e.g. a non-resolved lambda doubled level: if the levels are actually resolved then $\phi = 1$ again).
▷ Vibrational levels are not degenerate.
▷ For rotation;
  in Hund's case a $g_N = 2N + 1$ (if we include lambda doubling as above)
  and in Hund's case b $g_J = 2J + 1$
▷ For heteronuclear molecules, nuclear spin (not talked about until now) degeneracy is $g_I = (2I_1 + 1)(2I_2 + 1)$, for homonuclear molecules there is not simple formula for nuclear spin degeneracy: it's necessary to find it for the molecule under study.

Notation

- Spectroscopic notation is fairly straightforward for diatomic molecules. An electronic state is described by:

$\Diamond^{(2S+1)}\triangle^{\diamond}_{\mho}$, where

$\Diamond$ represents the letter designating which valence electronic level (i.e. $X, A, B, C, ...$ for the ground state, first excited electronic state, second, third and so forth),

$(2S+1)$ is the multiplicity,

$\triangle$ represents the designation for the value of Λ (i.e. $\Sigma, \Pi, \Delta,$ ... for Λ = 0,1,2 ...),

$\diamond$ is a parity designator; "+" for a symmetric ψ and "-" for an asymmetric ψ, and

$\mho = (\Lambda + \Sigma_s)$ when there is spin coupling to the internuclear axis.

Notation

- For example:

  ▷ The first excited electronic state of OH is designated by $A^2\Sigma^+$. The succeeding subscript is sometimes left off, but it is irrelevant in a Hund's case b molecule, and the OH A state is Hund's case b.

  ▷ The ground electronic state of OH is designated by $X^2\Pi$. There is no succeeding superscript (+ or -) because this state is lambda doubled and the two Λ components have different parity (+ and -).
- Transitions are labeled using these designators with the lower level to the right and an arrow indicating in which direction the transition goes. For example,

  $A^2\Sigma^+ \leftarrow X^2\Pi$

  indicates absorption from the ground to the first electronic state of OH.

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Notation

- Vibrational band notation (for a transition) is written as (v', v'').
- Rotational notation is more complex as we have to think about coupling. Rotational transition notation goes as:

  $\triangle\Diamond_{\alpha,\beta}(J''\mathrm{or}N'')$, where

  $\triangle = S, R, Q, P, O$ for $\Delta N = +2, +1, 0, -1, -2$; but when $\Delta J = \Delta N$ or when ΔNmakes no sense for the coupling case, the $\triangle$ is left off.

  $\Diamond = S, R, Q, P, O$ for $\Delta J = +2, +1, 0, -1, -2$.

  α, β are related to Hund's case b. α is used for the upper level; $\alpha = 1, 2, 3...$ for $J' = (N+S), (N+S-1), (N+S-2)...$ and β is for the lower level; $\beta = 1, 2, 3...$ for $J'' = (N+S), (N+S-1), (N+S-2)...$ When $\alpha = \beta$ only one value is written.

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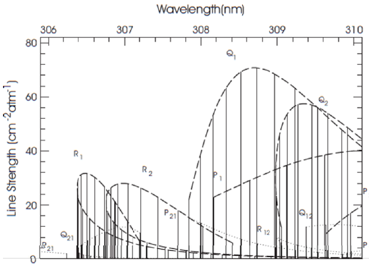
Notation

- For example, one could say that "the $P_1(8)$ line of the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ electronic transition in OH was observed." Note that all the necessary information for describing the states is included.
- These details are different for each molecule so it is not possible to provide strict guidelines for all molecules. In fact, many of the models we have discussed already are simplifications that can be violated or made much more complex in real molecules.
- There are many articles on how to perform LIF under various conditions, for example, and if you are following established procedures it is not absolutely necessary to bury yourself in the subtle details of a particular molecule. If you need to depart from established practice, however, you will need to study the physics of the specific molecule in detail.

OH $A^2\Sigma^+ \leftarrow X^2\Pi$



Selected region of the OH $A^2\Sigma^+ \leftarrow X^2\Pi(0,0)$ band at 2000K, in absorption. Remember that the P, Q and R stand for $\Delta J = -1, 0, +1$ and the subscripts are related to Hund's case b coupling.

- Here we will discuss the major UV (~ 300 nm) transitions for OH.
- It is important to emphasize that every molecule is different; it is not possible to assume that other important diatomic molecules (e.g. NO, CH etc.) will have the same energy level structures or spectral characteristics. This is just one example that will show some of the complexity of spectroscopy.

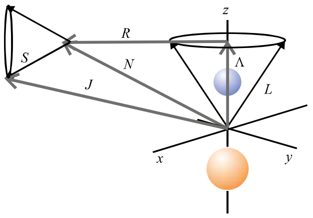
OH $A^2\Sigma^+ \leftarrow X^2\Pi$

- The information on OH (e.g. spectroscopic constants, line strengths etc.) is published in several locations:

  ▷ G. Herzberg, *Spectra of diatomic molecules*, Krieger Publishing Co., (1950),
  ▷ G.H. Dieke and H.M. Crosswhite, "The Ultraviolet Bands of OH; fundamental data", Journal of Quantitative Spectroscopy and Radiative Trasfer, Vol. 2, pp. 97 - 199, (1962),
  ▷ J. Luque and D.R. Crosley, "LIFBASE (version 1.5)", SRI report No. MP 99-009, (1999) - look in the handouts,
  ▷ and the references cited on those three.
- The electronic term energies are measured, and vibration is straightforward, so we dispense with them first.
- The full expression for vibrational term energy is given in equation 34:
  $G_v = \omega_e \left(v + \frac{1}{2}\right) - \omega_e x_e \left(v + \frac{1}{2}\right)^2 + \omega_e y_e \left(v + \frac{1}{2}\right)^3.$
- Next rotations and coupling.

OH $A^2\Sigma^+ \leftarrow X^2\Pi$

the $A^2\Sigma^+$ excited state

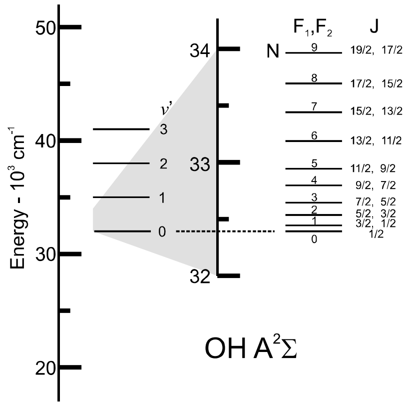


- The OH A state follows Hund's case b coupling:
  ▷ $N = 0, 1, 2, ... = R$ because $\Lambda = 0$ (Σ state)
  ▷ $S = 1/2$
  ▷ $J = N \pm 1/2$
- Rotational term energies are spin split, denoted: $F_1(N)$ for $(N + 1/2)$ and $F_2(N)$ for $(N - 1/2)$.
- Here we use:

  $F_1(N) =$
  $B_v N(N + 1) - D_v N^2(N + 1)^2 + \gamma_v N$

  $F_2(N) =$
  $B_v N(N+1) - D_v N^2(N+1)^2 - \gamma_v(N+1)$

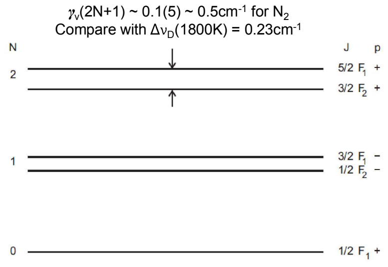
OH $A^2\Sigma^+ \leftarrow X^2\Pi$



$A^2\Sigma^+$

- This is an energy diagram for the $A^2\Sigma^+$ excited state of OH.
- As shown, the spin splitting of the lines is very weak.

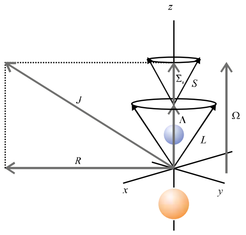
OH $A^2\Sigma^+ \leftarrow X^2\Pi$



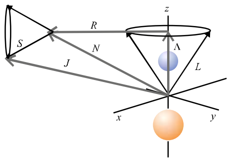
$A^2\Sigma^+$ - finer detail

- The term γ_v in the equations for F_1 and F_2 is a spin splitting constant with a value around 0.1 cm^{-1} for the OH $A^2\Sigma^+$ state.
- The spin-splitting that occurs is $\gamma_v(2N+1)$; it is a function of the vibrational state v and it increases with N.
- In the image, 'p' is the parity we have already discussed.

OH $A^2\Sigma^+ \leftarrow X^2\Pi$



Hund's case a



Hund's case b

the $X^2\Pi$ ground state

- For the ground state, the electronic term energy is spin-split, expressed as:
  $T_e = T_0 + A\Lambda\Sigma_s$
  where A is a spin-orbit coupling constant $(A \sim -140\,cm^{-1}$ for OH) but the splitting is a constant value.
  ▷ And $\Lambda = 1$, $S = 1/2$
- The OH X state follows Hund's case a at low N and Hund's case b at high N (but it is common to use case b notation)

OH $A^2\Sigma^+ \leftarrow X^2\Pi$

$X^2\Pi$

- Here the rotational term energies are:

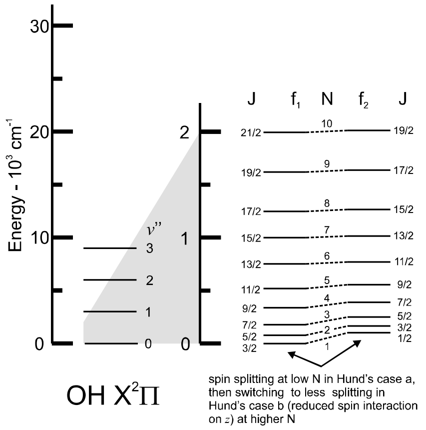
$$f_1(N) = B_v\left\{(N+1)^2 - \Lambda^2 - \tfrac{1}{2}[4(N+1)^2 + Y_v(Y_v-4)\Lambda^2]^{1/2}\right\} - D_v[N(N+1)]^2$$

$$f_2(N) = B_v\left\{N^2 - \Lambda^2 + \tfrac{1}{2}[4N^2 + Y_v(Y_v-4)\Lambda^2]^{1/2}\right\} - D_v[N(N+1)]^2$$

where $Y_v \equiv A/B_v \; < 0$ for OH.

Note $f_1(N) < f_2(N)$.

OH $A^2\Sigma^+ \leftarrow X^2\Pi$



- For the ground state, Hund's case a at low N and Hund's case b at high N.
- These lines are also Λ doubled, but often it goes undetected, the splitting is weak and so it is most often considered a degeneracy.

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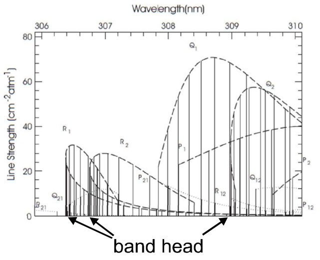
OH $A^2\Sigma^+ \leftarrow X^2\Pi$

- Notice that the progression of lines along the horizontal axis doesn't look like the IR ro-vibrational spectrum for NO in Lecture 7. Bandheads are formed.
- The line positions are set by:

  $$\breve{\nu} = \frac{\nu}{c} = (T_e' - T_e'') + (G_v' - G_v'') + (F_J' - F_J'')$$

  and the formulas for F_J can change significantly between the X and A states. As the value of J increases, a progression towards higher $\breve{\nu}$ can switch and reverse towards lower $\breve{\nu}$ because of the differences between the two formulas for F_J. That creates the bandheads.



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OH $A^2\Sigma^+ \leftarrow X^2\Pi$

- The main message is that the simple models presented earlier have to be made more complex and involve more details to effectively reproduce the spectral locations of each transition.
- If you plan to depart from established practice, or if you are interested in a molecule that has not already been measured in flames, you should investigate the details of that particular molecule.

Other molecules

- Molecules with more than two atoms (called “polyatomics”; often very important in combustion) become much more complex, meaning there are many more lines but in general each one is weaker.
- Some of them are detected directly using absorption-based techniques.
- Others are used as fuel tracers (e.g. keytones like acetone or pentanone) in engine research. These have a strong response and so they can be imaged with LIF.
- Their spectrum is so complex and dense that it looks more like a very broadband hump, but in some cases the hump shifts with temperature so the tracer can also be used to image temperature (until, of course, it starts to burn).

Other molecules

- For very big molecules like PAH (soot precursors) it is better to extract a sample and use a mass spectrometer or go to a synchrotron and use wide-angle, small-angle x-ray scattering.
- As more lines appear and more species become involved the spectrum becomes crowded, especially for ro-vibrational transitions in the IR.
- As lines broaden and the optical field becomes thick, the Planck black body distribution replaces discrete spectral lines.
- In fact, if we combine the ERT, what we have learned here, and statistical thermodynamics it is possible to model the Planck distribution and its dependence on temperature.

Next topic

Statistical thermo, resonance response, and lineshapes.

Advanced Laser Diagnostics for Combustion Research

Lecture 9: Some concepts in stat thermo, resonance response, and line shapes

Mark Linne

University of Edinburgh

Tsinghua-Princeton-CI Summer School on Combustion
July 11 - 17, 2021

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Topics

Quick review of statistical thermo

Resonance response

- The Einstein A-coefficient
- All the rest

Line shapes

- Lotentzian and Gaussian processes
- Voigt profiles

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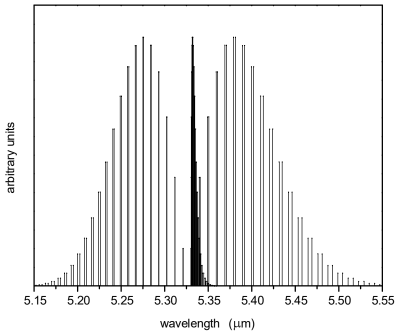
Introduction

- Statistical thermo will give us the fraction of molecules (population) in each of the individual energy levels under thermal equilibrium.
- That is important because if we use a spectroscopic technique to measure concentration it often just detects how many are in one energy level and we have to calculate the total concentration from that.
- Resonance response has to do with how strongly a molecule reacts to incoming light (i.e. the imaginary index).
- Those 2 determine the height of the peaks in the spectrum (the y axis).



Thermal equilibrium

- Recall from Thermodynamics that temperature is a representation of internal energy 'u'.
- At a particular temperature the molecule does not occupy all possible energy levels, but the internal energy is distributed among a number of them.
- Energy in the molecule is partitioned among various modes available for energy storage (kinetic energy of the molecule, vibration, rotation etc.).

Thermal equilibrium

- To start with, the kinetic energy of the molecule as it moves through space is not quantized. It can take continuous values depending on the temperature. The Maxwellian velocity distribution (a Gaussian distribution) is given by:

$$f(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{mv^2}{2k_B T}\right) \tag{35}$$

where:

$f(v)$ = the fraction of molecules with velocity amplitude $|\vec{v}|$,
m = molecular mass,
k_B = Boltzmann's constant (an ideal gas constant per molecule) = 1.38×10^{-23} J/(K-molecule).

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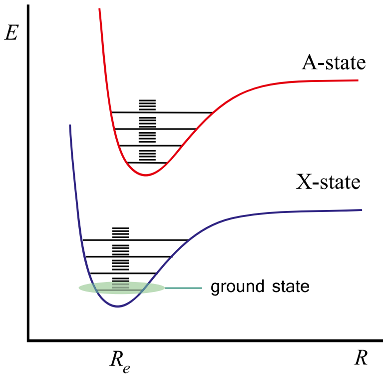
Thermal equilibrium

- The internal modes (electric, vibrational, rotational) are quantized, and the "ground state" is defined as the collection of modes that are normally occupied when the molecule is in thermal equilibrium at room temperature.



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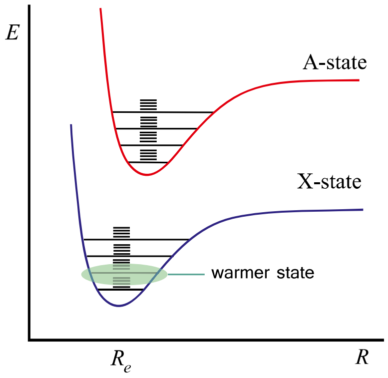
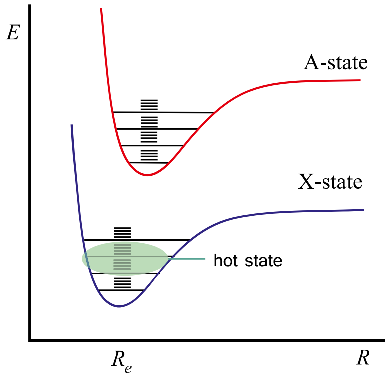
Thermal equilibrium

- As temperature rises, so does the state distribution.



Thermal equilibrium

- As temperature rises, so does the state distribution.
- And the distribution widens.
- At room temperature (and often at flame temperatures) the upper electronic states are not populated in most cases because the A state is well above the X state in energy.



Thermal equilibrium

- The distribution of energy across internal modes (electronic, vibrational and rotational) is given by Boltzmann statistics.
- The Boltzmann energy distribution function is:

$$f_i = \frac{N_i}{N} = \frac{g_i e^{\left(-\frac{E_i}{k_B T}\right)}}{Q} \tag{36}$$

where:

f_i = the fraction of molecules in energy level i,
N_i = the number of molecules in energy level i,
N = total number of molecules,
g_i = degeneracy of level i,
E_i = energy of level i,
Q = partition function ('partitioning' energy among the possible energy states).

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Thermal equilibrium

- The partition functions are given by:

$$Q_{\text{electronic}} = \sum_n g_n e^{\left(-\frac{E_n}{k_B T}\right)}$$

where n is the principal quantum number and g_n is the degeneracy of the electronic state. The absolute value of E_n depends on what we chose to call the zero of energy. It is most common to say $E_1 = 0$ and go up from there.

$$Q_{\text{vibrational}} = \sum_v e^{-\left(\frac{E_v}{k_B T}\right)}, \; E_v = (v + \frac{1}{2})h\nu_e$$

(or E_v from e.g. equation 34) where v is the vibrational quantum number and ν_e is the vibrational frequency.

The fraction of molecules in a particular vibrational energy level is then: $f_v = \frac{e^{\left(-\frac{E_v}{k_B T}\right)}}{Q_{\text{vibrational}}}$

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Thermal equilibrium

- The partition functions are given by (cont.):

$$Q_{\text{rotational}} = \sum_{\text{rot}} g_I(2J+1)e^{\left(-\frac{E_J}{k_BT}\right)},\ E_J = \frac{\hbar^2}{2I_e}J(J+1)$$

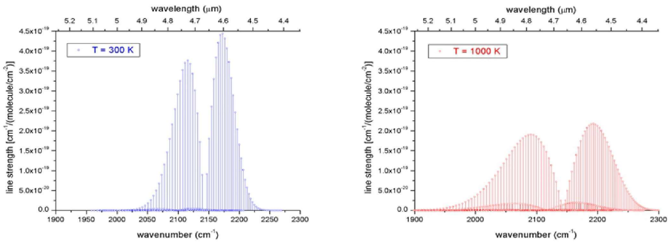
(or E_J from e.g. equation 33) where g_I is the rotational (rigid rotator) level degeneracy, J is the rotational quantum number, and I_e is the equilibrium rotational moment of inertia.

The fraction of molecules in a particular rotational energy level is then: $f_J = g_I(2J+1)\frac{e^{\left(-\frac{E_J}{k_BT}\right)}}{Q_{\text{rotational}}}$

The fraction of molecules in a particular rotational/vibrational energy level is:

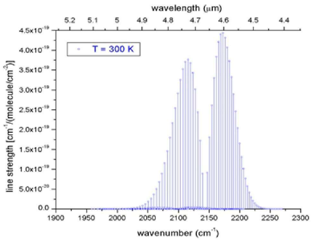
$f_{\text{ro/vib}} = f_v f_J = \frac{g_I(2J+1)e^{\left(-\frac{E_J}{k_BT}\right)}}{Q_{\text{rotational}}}\frac{e^{\left(-\frac{E_v}{k_BT}\right)}}{Q_{\text{vibrational}}}$

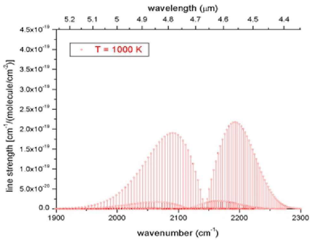
Thermal equilibrium



- CO molecular line strength spectrum - a sequence of optically induced (absorption) rotational level changes for one vibrational level change (v goes from 0 to 1; no electronic transition in this case).
- The heights of the various lines have to do with their spectral response (remember the imaginary index) but more significantly they have to do with the populations in the states that are addressed. If there are more molecules in a level that is being targeted by a laser, for example, the amount of absorption will go up.

Thermal equilibrium





- The spectrum changes shape with temperature (note also that a "hot band" appears at 1000 K) and this change is a visual representation of Boltzmann statistics.
- This change in shape (including change in the heights of various lines) makes it possible to use a spectroscopic technique to measure temperature.

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Resonance response

- 'Resonance response' means how strongly an atom or molecule will react if it is illuminated by light at a wavelength that corresponds to a transition (e.g. $\nu_{nm} = \Delta E_{nm}/h$).
- We have already discussed resonance response in several lectures:

  ▷ In Lecture 1 the absorption cross section σ_ν was introduced within Beer's law.

  ▷ In the same lecture (number 1) the Einstein coefficient for absorption B_{mn} was introduced during a discussion of LIF.

  ▷ Lecture 2 contains the development of the ERT, and the three Einstein coefficients [the A_{nm} coefficient for spontaneous emission, the B_{nm} coefficient for stimulated emission, and the B_{mn} coefficient for absorption] were first introduced in equation 1, while a volume absorption coefficient κ_ν was introduced several slides later.

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Resonance response

- We have already discussed resonance response in several lectures (continued):
  - ▷ In Lecture 3 the solution to the Lorentz atom produced an expression for the volume absorption coefficient κ_ν in terms of the absolute value of the imaginary part of the refractive index n^I.
  - ▷ That treatment showed that the imaginary part of the refractive index is also related to the oscillator strength f_o, the polarizability α, the susceptibility χ, and a dielectric constant κ_e.
  - ▷ So far we have said nothing about the line strength S (written in terms of partial pressures), or the band strength $f_{v''v'}$, which are also popular ways to describe resonance response.
- You would be justified in asking why there are so many different ways to describe the same thing.
- And you will be glad to know there are ways to relate them all to each other, but it starts with yet one more item - the transition dipole moment.

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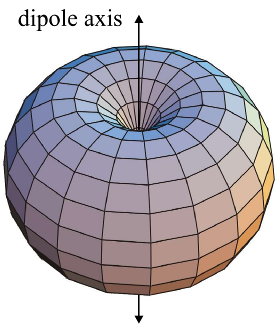
Resonance response

- The classical approach is nearly identical to the Rayleigh scattering treatment, but here the energy levels actually change (populations shift).
- Assume the Lorentz atom is oscillating (electron relative to the nucleus) for some reason [maybe it was excited by a collision (e.g. thermal exchange), or it absorbed light for example].
- An electron in motion will emit radiation and the radiation pattern will depend on the emitter structure and size, but for atoms and molecules they generally have the torus structure.



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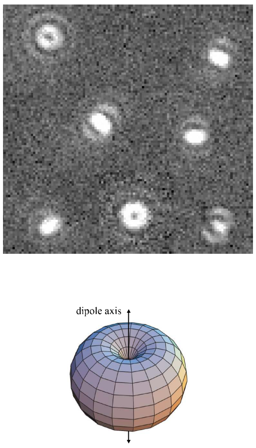
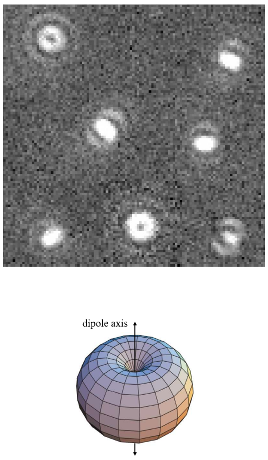
Resonance response

- Here is an image taken by a single molecule microscope; the individual dipoles are dye molecules that absorbed light and then emitted fluorescence.
- Just as in Rayleigh scattering, these patterns from individual molecules depend upon the orientation of the molecular dipole moment.
- The images with a dark spot in the center have the electron oscillating in and out of the plane (looking down the dipole axis)..
- The others are being viewed from the side.



Resonance response

- An aside - note that the emission patterns are polarized along the dipole axis.
- Emission from individual atoms and molecules in a gas can be polarized as well, but if the molecule has occupied an excited state via optical pumping, the excited state has a lifetime and so a gas-phase molecule can rotate away from the excitation polarization.
- Molecular scattering (e.g. Rayleigh or Raman) causes no population change and thus very little chance to rotate polarizarion; Rayleigh and Raman are more cleanly polarized.

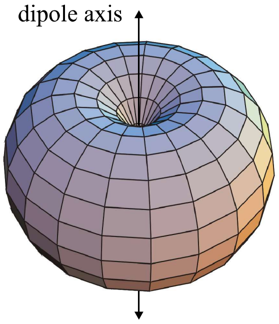


Resonance response

- The classical theoretical approach to the problem of dipole emission is to treat the dipole almost like an antenna.
- Maxwell's equations are written and then recast in terms of scalar fields and potentials.
- Vector calculus is applied to generate expressions for $\vec{E}$ and $\vec{B}$.
- Poynting's theorem is applied and then the basic definitions from the ERT are used to get:

$$A_{nm} = \frac{\omega^2 |\mu_{\rm ed}|^2}{6h\epsilon_{\rm o} c^3} \qquad (37)$$

where $\mu_{\rm ed}$ is a classical electric dipole moment.



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Resonance response

- We know that the classical Lorentz atom solutions are limited and not fully accurate.
- To develop a quantum mechanically correct expression for A_{nm} we have to consider the transition dipole moment.
- The quantum mechanical matrix element of the dipole moment is written:
  $\vec{\mu}_{nm} \equiv \langle \psi_n | \hat{\mu} | \psi_m \rangle$
  but what does all that mean?
- The 'bra' $\langle|$ and 'ket' $|\rangle$, when arranged like that are short hand for the inner product (a scalar product in vector calculus). The wave functions ψ are probability amplitudes, so the expression is an expectation value for a transition dipole moment between states ψ_n and ψ_m.
- $\vec{\mu}_{nm}$ is called a matrix element because the states along the diagonal of the $n, m, \ldots$ matrix ("…" to indicate that there are more than just 2 levels in a molecule) denote actual energy level populations.

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Resonance response

- The quantum mechanical expression for A_{nm} is then:

$$A_{nm} = \frac{2\,\omega_{nm}^3 |\vec{\mu}_{nm}|^2}{3\,h\,\epsilon_\circ c^3 g_n} \tag{38}$$

- Discerning students would ask, “What happened to all of that orientational math from Rayleigh scattering?” This treatment was only for atoms and molecules that were properly oriented to receive radiation at ν_{nm} and thus induce a population change. The $1/3$ in equation 38 is the outcome of orientational changes as the excited state species rotates before emitting.
- In this respect there is a major difference between scattering and absorption/fluorescence. In scattering the excitation + reradiation process is instantaneous but in absorption/fluorescence they are two distinct processes separated in time.
- Equation 38 is just for the fluorescence part.

Resonance response

- One outcome of this development is that there are cases where $\vec{\mu}_{nm}$ goes to zero. That happens when the symmetries of the wave functions n and m are the same. That happens, for example, for ro-vibrational transitions in homo-nuclear molecules like O_2 and N_2. O_2 and N_2 have no resonance response in the IR; they can't be observed via absorption, for example.
- Equation 38 could be used for, say, a vibrational transition if we had an expression for, or somehow knew, $\vec{\mu}_{nm}$. The expression has to do with knowing a specific transition dipole matrix element.

Resonance response

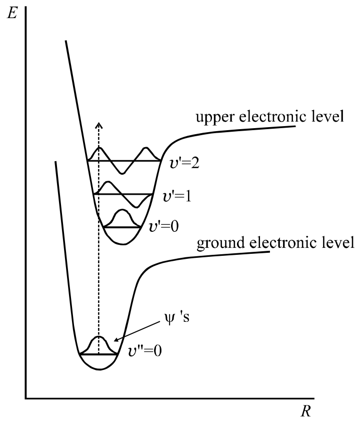
- We can also use equation 38 for an electronic transition, but we have already said that electronic transitions also involve simultaneous ro-vibrational transitions. We could try to bundle all of that physics into one $\vec{\mu}_{nm}$ for each possible transition, but that would produce a large, complex collection of many different $\vec{\mu}_{nm}$'s.
- Instead we take advantage of the separation of variables allowed by the Born-Oppenheimer approximation and we find a *electronic* matrix element of the dipole moment given by $\vec{\mu}_e = \langle \psi_{n,e} | \hat{\mu}_e | \psi_{m,e} \rangle$. Then we need to deal with the contributions of vibration and rotation.
- To start, consider a case where all of the rotational transitions within a manifold occur. Perhaps we hit the molecule with a very broadband laser, for example. This way it is possible to consider just the vibrational transition to start.

Resonance response

- The vibrational part is then written: (here the bra and ket are replaced by the integration they represent):

  $\int \psi_{n,v}\, \psi_{m,v} \mathrm{d}R$

  which is an overlap integral between the wave function of the vibrational state in the ground electronic level and the wave function of the vibrational state in the upper electronic level. As shown, when the overlap is strong the transition probability is strong, and vice versa.
- Note the effect of horizontal displacement between the electronic states.



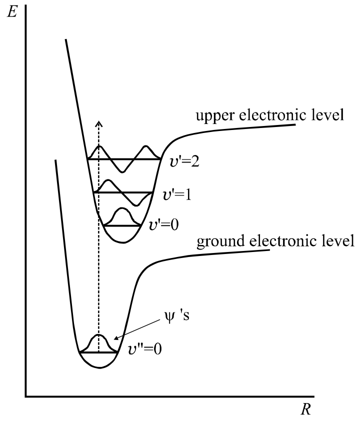
Resonance response

- In terms of irradiance, we write the Franck-Condon factor as:

  $S_{v'v''} = |\int \psi_{n,v}\, \psi_{m,v} \mathrm{d}R|^2$
- Now if we want to consider individual rotational transitions as well, we write the Hönl-London factors as:

  $S_{J'J''} = |\int \psi_r^{*'}\, \psi_r^{''} \mathrm{d}\tau|^2$

  where $\mathrm{d}\tau$ is a volume element. It doesn't really matter; these things can usually be found in the literature for a molecule of interest.



Resonance response

- Summarizing all of that:

$$A_{nm} = \frac{2\omega_{nm}^3 |\vec{\mu}_e|^2 S_{v'v''} S_{J'J''}}{3h\epsilon_\circ c^2 g_n} \tag{39}$$

- These data can be found published for important molecules, although they may be in slightly different form.
- From A_{nm} we can get the other Einstein coefficients by:

  $g_n B_{nm} = g_m B_{mn}$
  $B_{nm} = \frac{2\pi^3 c^3}{h\omega^3} A_{nm}$

Resonance response

- From equation 39 everything else can follow. In the ERT we inferred a spectral absorption coefficient:

  $\kappa_{\text{actual}} = \frac{h\nu}{c} N_m B_{mn} Y_\nu$

  and from the Loretnz atom we had a classical absorption coefficient. We said the two were related by an oscillator strength. If we assume we have the Einstein coefficients in a quantum-mechanically correct way, then the oscillator strength is:

  $f_{mn} = \frac{4\epsilon_\circ m_e h\nu_{nm}}{e^2} B_{mn}$

  The absorption cross section was written as a spectral property, so it becomes:

  $\sigma_\nu = \frac{h\nu}{c}\left(\frac{N_m}{N_{tot}} B_{mn} - \frac{N_n}{N_{tot}} B_{nm}\right) Y_\nu$

  Sometimes people prefer a spectrally integrated cross section:

  $\sigma_\circ = \int \sigma_\nu \, \mathrm{d}\nu = \frac{h\nu_{nm}}{c} \frac{N_m}{N_{tot}} B_{mn}$

  Cross sections are useful when there are other processes going on, e.g. scattering from particles.

Resonance response

- Resonance relationships continued:
  "Band strength" is a system for using a spectrally integrated oscillator strength with individual Franck-Condon and Hönl-London factors.

  Start by defining an electronic oscillator strength:

  $f^{el}_{mn} = \frac{8\pi^2 m_e \nu_{nm}}{3hq_e^2 g_m} |\vec{\mu}_e|^2$

  Then the band strength (a vibrational oscillator strength) is:

  $f_{v''v'} = f^{el}_{mn} S_{v''v'}$

  These are often directly measured (e.g. with an FTIR).

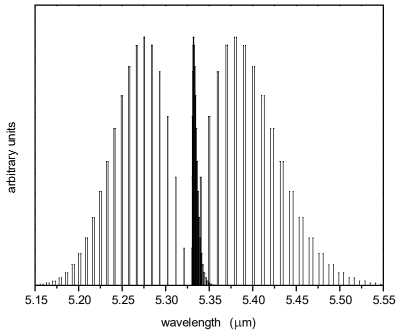
  Then the oscillator strength for an isolated transition is:

  $f_{J''J'} = f_{v''v'} \frac{S_{J''J'}}{2J''+1}$

  Remember that you multiply these times the Lorentz atom absorption coefficient to get a true absorption coefficient.

Line broadening

- The spectrum shown in the introduction used "sticks" (straight vertical lines) to indicate transitions. If we use the expressions for A_{nm} and B_{mn} for example, they are written for just one value of ν_{nm} and so stick line spectra would be appropriate.
- Measurement, however, indicates that spectral transitions are not sticks. They have bandwidth formed in recognizable functional shapes $Y_\nu\ (1/Hz)$ as mentioned during the development of the ERT (equation 1).



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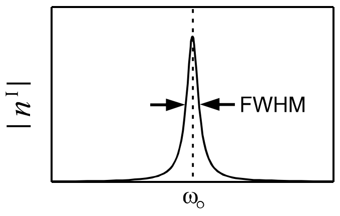
Line broadening

- You may recall this line profile for the Lorentz atom.
- Lineshape matters whenever the spectral resolution of the instrument is higher or about the same as the linewidth. Examples include a narrow-band laser scanned across an absorption line, or a Fabry-Perot etalon (a very narrow-band spectral filter) is scanned across an emission line.
- In such a case, as the lineshape broadens the peak falls (the integral across the function is a constant = 1) so the actual response one measures at a specific λ depends on the lineshape function.



The width of a spectral distribution is commonly quoted in terms of the "full width at half maximum" (FWHM).

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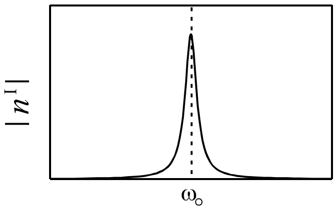
Line broadening

- For broadband instruments (e.g. a very broadband, smooth-spectrum laser exciting multiple transitions) one can integrate across the lineshape function and eliminate it from expressions. Since

  $$\int_{-\infty}^{+\infty} Y_\nu \mathrm{d}\nu = 1$$

  we normally recover the values for terms like B_{mn} without the spectral dependence.
- To develop a model for Y_ν one must understand the various processes that cause broadening.



Line broadening

Homogeneous broadening

- Whenever a time dependence is involved then the Lorentzian expression is appropriate. The Lorentz atom expression for n^I (equation 19) had a lineshape function built into it. Here it is written in terms of ν as:

$$Y_H(\nu - \nu_{nm}) = \frac{\Delta\nu_H}{2\pi} \frac{1}{(\nu - \nu_{nm})^2 + (\frac{\Delta\nu_H}{2})^2} \tag{40}$$

- The H on Y_H stands for "homogeneous", meaning that all atoms or molecules that are absorbing (all the same species) respond in the same way. Time-based spectral lineshape functions are homogeneous.
- In a real atom or molecule there are several time-based processes that lead to a Lorentzian lineshape function.

Line broadening

Homogeneous broadening

- So called "natural broadening" has to do with Heisenberg uncertainty, but the linewidth of a naturally broadened line is very small in combustion problems compared to the main process.
- Another time-based source of broadening we sometimes observe in very low pressure environments is called "lifetime broadening" and it has to do with the excited state lifetime of the molecule (the fluorescence lifetime). In that case, the $\Delta\nu_H$ in equation 40 is given by:

  $\Delta\nu_H = \frac{1}{2\pi} A_{nm}$
- Lifetime broadening is on the order of 1 MHz FWHM or less.

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Line broadening

Homogeneous broadening

- The main source of homogeneous broadening in combustion is a result of collisions with other molecules; so-called "pressure broadening", or "collisional broadening".
- If we think in terms of quantum mechanics: as the absorption of a photon (for example) is in process, the wave functions in the m and n states set up a coherence (coherent with the light in fact) that feeds the energy into the molecule and drives the transition from state m to state n. A collision will impulsively (in time) change the phase of the coherence and thus cause a broadening (in spectrum) because it has changed the response of the molecule to the frequency of light.

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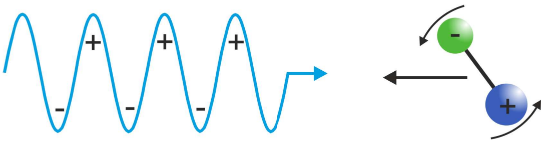
Line broadening

Homogeneous broadening



- A crude image of rotational coherence shows a molecular dipole with rotational "orbital energy" that matches oscillating polarity of the electromagnetic wave.
- It's easy to imagine that if this rotation got interrupted by a collision, it would change the interaction.
- It's a crude, unrealistic image, but changes in rotational coherences are a major contributor to collisional broadening.

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Line broadening

Homogeneous broadening

- The width $\Delta\nu_H$ in equation 40 is given by $\Delta\nu_H = \frac{1}{\pi}\gamma_{nm}$, where $\gamma_{nm} = \gamma/2$ is the rate of dephasing collisions and γ is the coherence decay rate.
- The rate of dephasing collisions can be written in terms of the collision rate and a dephasing cross section ($\sigma_{nm,w}$ where w indicates the collision partner).
- If we assume a Maxwellian velocity distribution and use that to model the collision rate we get:

  $$\gamma_{nm} = N_w \sigma_{nm,w}\sqrt{\frac{8k_BT}{\pi\mu}}$$

  where N_w is the number density of collisions partners w and μ is the reduced mass. For a mixture of collision partners the one must evaluate to contribution of each and it becomes quite complex.
- Collision broadened linewidths are on the order of 10 GHz FWHM at atmospheric pressure.

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Line broadening

Inhomogeneous broadening

- Inhomogeneous broadening applies when only specific classes of the target molecule respond at specific wavelengths near the central wavelength or frequency.
- There are various forms of inhomogeneous broadening but for combustion there is just one important class; Doppler broadening.
- If we pass a laser beam through a flame we define one Cartesian axis. Molecules that have a velocity component along that axis directed towards the laser will be Doppler shifted up in frequency. The laser frequency will seem as though it is above ν_{nm} in the rest frame of the molecule. To induce absorption, the laser has to be tuned a bit lower in frequency. The opposite is true for classes of molecules with velocity components going away from the laser.

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Line broadening

Inhomogeneous broadening

- To describe Doppler broadening we have to describe classes of molecules based upon their velocity along the laser axis, using the Maxwellian velocity distribution, which is Gaussian. For this reason the Doppler spectral lineshape is Gaussian:

  $$Y_D(\nu - \nu_{nm}) = \sqrt{\frac{4\ln 2}{\pi}}\frac{1}{\Delta\nu_D}\exp\left[-4\ln 2\left(\frac{\nu - \nu_{nm}}{\Delta\nu_D}\right)^2\right] \qquad (41)$$

  where the Doppler FWHM is given by

  $\Delta\nu_D = \nu_{nm}\sqrt{\frac{8\ln 2 k_B T}{mc^2}}$.
- The Doppler width is clearly a strong function of temperature, but it is typically narrower than the collision width.

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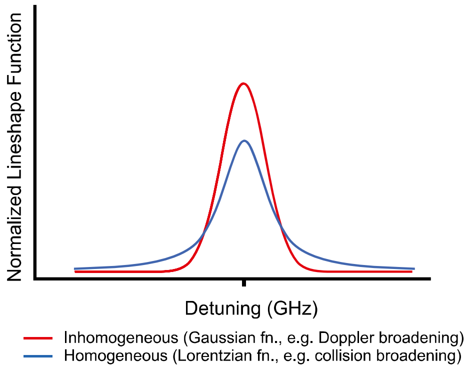
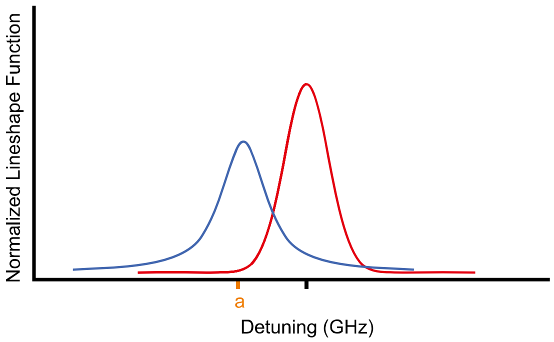
Line broadening



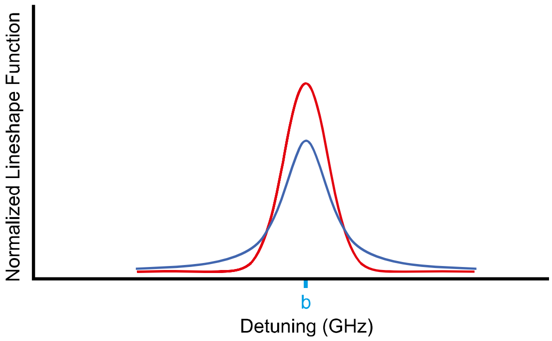
- When plotted together, one can see the two lineshapes are different. The Lorentzian (homogeneous) lineshape is broader, especially in the wings, and therefore lower in the peak (when normalized). The Gaussian (inhomogeneous) lineshape is narrower and more peaked.

Line broadening



- To combine the two processes, think this way: all along the Doppler profile, every spectral location going from left to right (from a to b to c) represents a velocity class of molecules; just a portion of all the molecules. Each of those classes is collisionally broadened. It is like sweeping the Lorentzian across the Gaussian; it is a convolution of the two.

Line broadening



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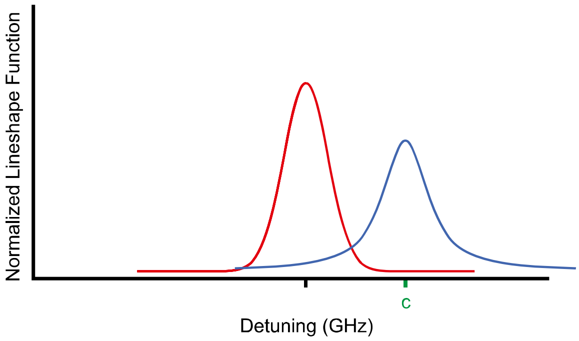
Line broadening



- To combine the two processes, think this way: all along the Doppler profile, every spectral location going from left to right (from a to b to **c**) represents a velocity class of molecules; just a portion of all the molecules. Each of those classes is collisionally broadened. It is like sweeping the Lorentzian across the Gaussian; it is a convolution of the two.

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Line broadening

Voigt profile

- The Voigt profile is a normalized convolution of the two broadening functions:

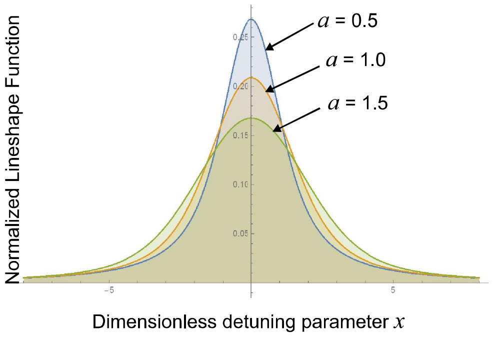
$$Y_V(x;a) = \sqrt{\frac{4\ln 2}{\pi}}\frac{V(x;a)}{\Delta\nu_D} \tag{42}$$

where the Voigt function $V(x;a)$ is given by:

$$V(x;a) \equiv \frac{a}{\pi}\int_{-\infty}^{+\infty}\frac{e^{-x'^2}}{(x-x')^2+a^2}\,\mathrm{d}x' \tag{43}$$

where the nondimensional detuning parameter x is:
$x \equiv \frac{\sqrt{4\ln 2}}{\Delta\nu_D}(\nu - \nu_{nm})$, and the nondimensional broadening parameter a is: $a \equiv \sqrt{\ln 2}\,\frac{\Delta\nu_H}{\Delta\nu_D}$

Line broadening



- Both Matlab and Mathematica have routines that calculate a Voigt profile if you input a value for a, and a range of detuning x that you wish to investigate. This one was made using Mathematica.

Line broadening

Using the Voigt profile

- If the line broadening parameters are known for the molecule you are studying (e.g. the γ_{nm} for collisional broadening, Doppler broadening is known if the temperature is known), one can simulate a realistic lineshape using Mathematica or Matlab.
- Often people don't know the broadening parameters and then it becomes necessary to measure them if one is trying to do quantitative measurements. To do that, it is necessary to:

▷ Recognize that the measured lineshape is a function of instrument broadening together with homogeneous and inhomogeneous broadening,

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Line broadening

Using the Voigt profile

▷ One usually tries to make the instrument broadening very narrow so that it is negligible compared to the lineshape (e.g. narrow bandwidth laser). When that is not possible, the instrument broadening usually contributes as an overlap integral with the lineshape. One measures the instrument broadening and then extracts the lineshape via nonlinear fitting. This can add significant uncertainty to the measurement of broadening parameters,

▷ To separate the homogeneous and inhomogeneous line functions (assuming temperature is known), one uses the convolution theorem - according to the convolution theorem the FFT of a Lorentzian times the FFT of a Gaussian is then inverse transformed to give a Voigt function. To separate a Voigt into the a Gaussian and Lorentzian one just does the opposite. Matlab and Mathematica can do that, and in the outcome yields a measured a which leads to a measured γ_{nm}.

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Stat thermo, line strength, and line shapes

- You may ask, how is all of this used? There are several ways one uses this formalism.
- If one wishes to model an absorption or fluorescence spectrum, it is necessary to model the spectral locations based upon the energy levels (lecture 7), and the peaks of the lines depend on populations in each energy level (stat thermo), the line strength (resonance response) and then broadening (which reduces the peak and spreads the response sideways).
- Such a model can also be fit to a measured spectrum via nonlinear fitting routines to return something like concentration (can use just one absorption line but several improve accuracy), temperature etc.

Stat thermo, line strength, and line shapes

- How to find data:
  ▷ For ro-vibrational transitions of molecules that matter in combustion, the HITRAN database (https://www.cfa.harvard.edu/hitran/) has line positions, line strengths, and line broadening parameters. Unfortunately, the database is mostly for atmospheric chemists and so data for high temperatures (called HITRAN HiTemp) is not as good,
  ▷ The books by G. Herzberg have a lot of data but it can drop the ball sometimes,
  ▷ As mentioned, LIFBASE (J. Luque and D.R. Crosley, "LIFBASE (version 1.5)", SRI report No. MP 99-009, (1999)) is good for UV transitions of selected molecules - look in the handouts,
  ▷ The book edited by K. Kohse-Höinghaus and J.B. Jeffries or the book edited by Steinberg and Roy (see references in Lecture 1) are excellent resources.

Next topic

Lasers

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Advanced Laser Diagnostics for Combustion Research

Lecture 10: Lasers

Mark Linne

University of Edinburgh

Tsinghua-Princeton-CI Summer School on Combustion
July 11 - 17, 2021

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Topics

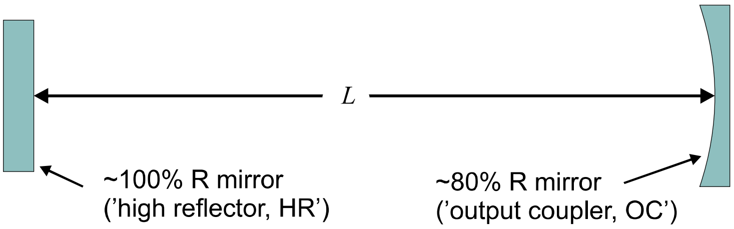
- Basic components of a laser
- Common lasers
  - ▷ Flashlamp-pumped, Q-switched Nd:YAG lasers
  - ▷ Diode-pumped solid-state lasers
  - ▷ Dye lasers
  - ▷ Short pulse lasers
  - ▷ Quantum cascade diode lasers

Basic components of a laser

- LASER = Light Amplification by Stimulated Emission of Radiation.
- Preceded by the MASER = Microwave Amplification by Stimulated Emission of Radiation.
- We will start with a classical layout: a Fabry-Perot, stable resonator, continuous wave (cw) laser. Then we will move on to other layouts.

Basic components of a laser

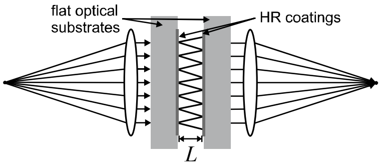
- Lasers are oscillators in the optical regime: gain + feedback.
- Optical feedback can be provided by a Fabry-Perot resonator:

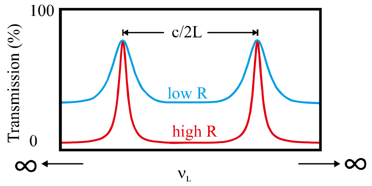


~100% R mirror
('high reflector, HR')

~80% R mirror
('output coupler, OC')

Basic components of a laser

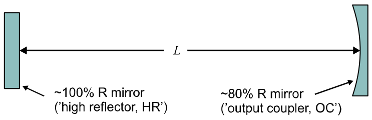


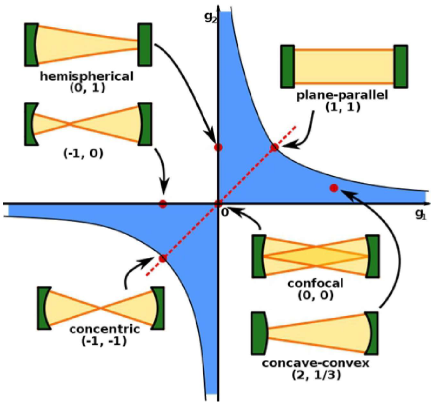


- A basic Fabry-Perot etalon is an optical "resonant tank".
- Spectral bandpass of a Fabry-Perot etalon.
- Stable laser cavities have a similar "longitudinal mode" structure with modes spaced by $c/2L$.

Basic components of a laser

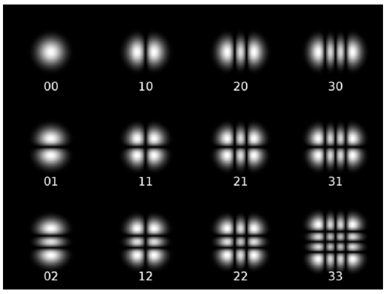
- And these resonators have cavity stability criteria.
  ▷ $g_2 \equiv 1 - L/R_2$ where R_2 is the radius of mirror 2.
  ▷ $g_1 \equiv 1 - L/R_1$ where R_1 is the radius of mirror 1.
- This one is almost hemispherical:





Basic components of a laser

- The stability criteria apply to the “lowest order spatial mode”, a radial Gaussian spatial intensity distribution.
- Resonators can support other spatial modes, and each spatial mode supports an array of longitudinal modes.
- The TEM$_{oo}$ mode is the highest quality, highest brightness mode. Often the cavity design, or an intra-cavity aperture, is used to kill off the higher order modes.



Hermite-Gaussian spatial modes.

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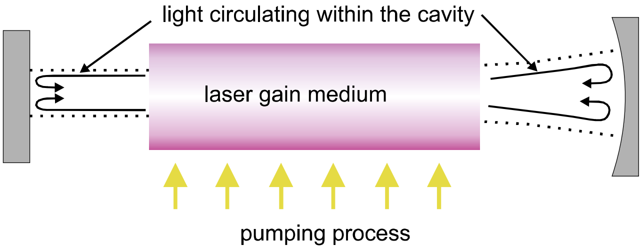
Basic components of a laser

- The essential elements of a laser also include optical gain.
- To create gain we have to use some kind of pumping process – lamps, another laser, electrical current etc.



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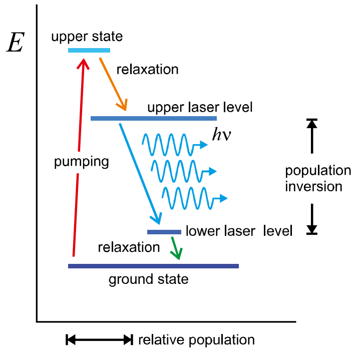
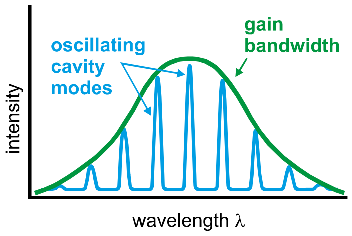
Basic components of a laser

- Gain in a 4-level system via stimulated emission from the upper laser level.
- Four levels are best so that the laser process does not collide with the pumping process or communicate with the ground state (avoids absorption of the beam by the gain medium).
- The stimulated emission process is coherent; the photons inside the cavity and exiting in the beam are coherent with each other.



Basic components of a laser

- Back to modes: assume we have a single, TEM$_{oo}$ spatial mode. The cavity will support an infinite number of longitudinal modes that are spaced by $\Delta\nu = c/2L$.
- But the gain medium has a fixed bandwidth (it's a spectroscopic transition) and so it overlays the modes.
- Only modes inside the gain bandwidth can oscillate.
- Beating between modes (longitudinal and spatial) is one source of laser amplitude noise.



Basic components of a laser

- The laser oscillates when there is optical gain above the lasing threshold in the system (the threshold is controlled by optical losses in the cavity; scattering, absorption etc.).
- Laser start-up is caused by “noise photons” (as they are called) inside the resonator (because of the pumping, the gain medium fluoresces and so there are more than enough noise photons available). The light inside the cavity has to fall within the allowed spatial and longitudinal electromagnetic mode system for the cavity, of course.
- As these initial photons pass through the gain medium, they are amplified by stimulated emission – they “sweep out the gain”.
- The optical modes build up to very high intensity within the resonator, but some of it leaks out because the output coupler is partially transmissive, and that forms the laser beam.

Basic components of a laser

Recap

- A laser consists of:
  - ▷ A gain medium taking advantage of a 4-level spectroscopic system (usually) to make a population inversion.
  - ▷ A feedback system like the Fabry-Perot cavity to allow buildup of stimulated emission; a coherent source.
- The transmission of the output coupler is chosen to maximize output power (intra-cavity gain sits just at threshold for a cw laser).
- High brightness scientific lasers contain as much of the gain as possible within the lowest order mode (TEM_{oo} for stable F-P cavities).
  - ▷ That’s hard to do with lamp-pumped systems.
  - ▷ It’s much easier with laser-pumped systems.
- For industrial lasers, extracting as much power as possible is often more important, and it’s then necessary to allow higher order spatial modes to oscillate.

Common lasers

Flashlamp-pumped, Q-switched Nd:YAG lasers

- The gain medium is Nd in a glass host (e.g. in YAG, or Nd^{3+}:$Y_3Al_5O_{12}$); a 4-level laser system.
- Pumped by broadband, pulsed "flashlamps" in a gold coated reflection chamber filled with circulating cooling water.
- The upper lasing level of Nd has a very long fluorescence lifetime; it is possible to store a lot of energy in the upper level.
- The energy can be stored only if the laser is not allowed to oscillate, so the "cavity Q" is destroyed using a "Q-switch" until the maximum energy has been stored in the gain medium and then the Q-switch opens the cavity.

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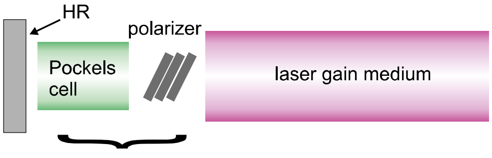
Common lasers

Flashlamp-pumped, Q-switched Nd:YAG lasers

- The Q-switch consists of a polarizer and a Pockels cell.
- The Pockels cell is an electroptic device; a crystal that can be made birefringent by putting high voltage across it; an optical switch.
- When the Q-switch is "closed" no light circulates because the Pockels cell (often in combination with a waveplate) rotates the intra-cavity polarization so that the light is rejected by the polarizer.
- When the Q-switch is "open" it aligns the intra-cavity polarization with the polarizer and so light now oscillates inside the cavity.



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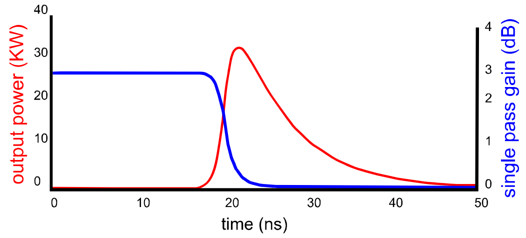
Common lasers

Flashlamp-pumped, Q-switched Nd:YAG lasers



- The lamps are on for longer than the fluorescence lifetime of Nd:YAG (230 μs), and the Q-switch can open in about 1 μs.
- When the cavity opens, fluorescence photons start the oscillation, and an intense pulse of coherent light builds up in the cavity until it has swept the gain down below threshold. The intracavity energy then dies away as a single exponential.

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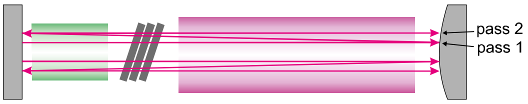
Common lasers

Flashlamp-pumped, Q-switched Nd:YAG lasers

- The intracavity energy is so high it can easily damage the gain medium.
- An "unstable resonator", with $\sim 5-10$ passes through the cavity, is used.
- The YAG rod is actually a GRIN lens because there is a thermal gradient caused by lamp pumping and water cooling.
- The curvature of the HR is chosen during manufacturing to give desired beam size and divergence at the pre-set pulse rate (10 – 30 Hz) so it is not possible to change the pulse rate by much.



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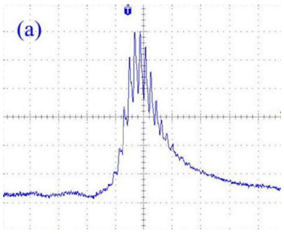
Common lasers

Flashlamp-pumped, Q-switched Nd:YAG lasers

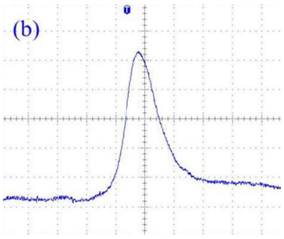
- The "pseudo Gaussian" spatial mode of an unstable resonator can be fairly complex.
- The longitudinal modes can beat against each other inside the pulse envelope, and the mode-beating changes from pulse to pulse.
- The outcome is a fairly broadband pulse with a lot of intensity variation from pulse to pulse.
- It affects everything else that happens downstream.



Common lasers

Flashlamp-pumped, Q-switched Nd:YAG lasers

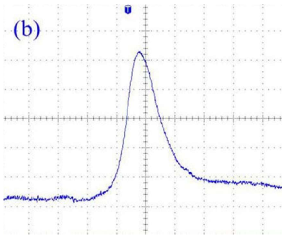
- The best way to remove this problem is a technique called "injection seeding".
- Light from a small, single frequency (single spatial and longitudinal mode) diode pumped YAG laser is injected into the big pulsed laser cavity along its axis. Low power lasers are easy to operate single mode while big pulsed systems are not.



Common lasers

Flashlamp-pumped, Q-switched Nd:YAG lasers

- The large laser modes are tuned in frequency (the HR is mounted on a piezoelectric stack) so that one of them overlaps the small laser mode. The large laser then oscillates single frequency because this mode sweeps out all the gain and suppresses oscillation by other modes.
- The system requires active feedback control to keep the modes overlapped.



Common lasers

Flashlamp-pumped, Q-switched Nd:YAG lasers

- The output light is at $\lambda = 1.064\mu m$, and to get other wavelengths we start by using nonlinear optical crystals.
- When operating with a lot of power (e.g. high energy and short pulse, the power at the peak is very high) one can induce nonlinear effects.
- Second harmonic generation: production of green ($532\ nm$) light from the $1.064\ \mu m$ laser light is a "Chi-2" process; $I_{532} = \chi^{(2)} I_{1064}^2$ (this idea was introduced in Lecture 3, equation 16).

▷ One uses a crystal inside an adjustable control box.
▷ It requires phase matching (angle of input photons relative to exit photons; a photon momentum conservation requirement) and temperature stabilization.
▷ Conversion efficiency is below 50%.
▷ Lasers can reach well over 1 $J/pulse$ at $532\ nm$ nowadays.

Common lasers

Flashlamp-pumped, Q-switched Nd:YAG lasers

- Third harmonic generation: production of blue ($355\ nm$) light is a "Chi-3" wavemixing process using both the $532\ nm$ and the $1.064\ \mu m$ light.
  - ▷ An "optical parametric process"; mixing two colors in a crystal to generate the third color.
  - ▷ Requires phase matching again and conversion efficiencies are low.
- Fourth harmonic generation means generation of UV ($266\ nm$) light from the laser light.
  - ▷ Just frequency double the 532 nm light.

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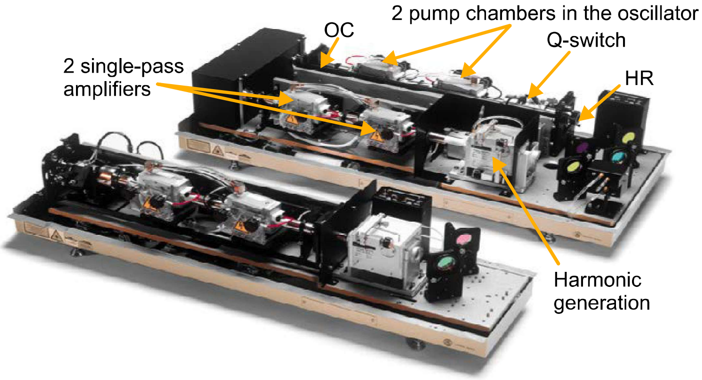
Common lasers

Flashlamp-pumped, Q-switched Nd:YAG lasers



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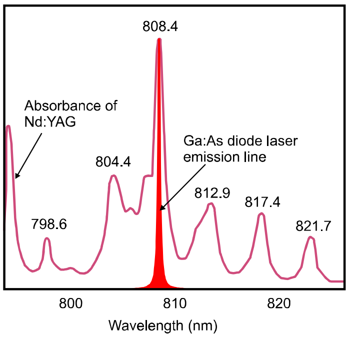
Common lasers

CW Diode-pumped Nd:YAG lasers

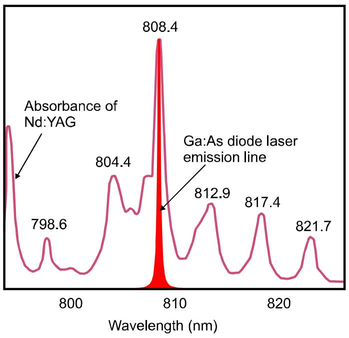
- The Nd:YAG absorption spectrum has a strong peak at about $808\ nm$.
- Ga:As diode lasers emit radiation in the same wavelength region, and the diode laser spectrum is very narrow compared to a flashlamp.
- The diode laser wavelength can be tuned by controlling its temperature (it sits on a thermoelectric cooler), so that the wavelengths match exactly.
- It is also possible to manipulate a coherent diode laser beam to "mode-match" the TEM$_{oo}$ spatial mode of the Nd:YAG laser when axially pumping (lower power lasers).



Common lasers

CW Diode-pumped Nd:YAG lasers

- It is thus possible to couple diode laser light into the gain medium with very high efficiency, with no water cooling in the laser head.
- The laser head is then all solid-state; with very high stability, lower amplitude noise, and incredibly stable beam pointing.
- Unfortunately the diodes can be very expensive, and in the past they were not super reliable.



Common lasers

CW Diode-pumped Nd:YAG lasers

Essential light tool.

You have the application. We have the DPY. If you're still looking for the diode-pumped laser that can meet *your* needs, look at Spectra-Physics. Our array of DPY options and accessories is unparalleled in the laser industry. With our modular system design, interchangeable laser heads, choice of wavelengths and solid-state materials, you'll have the flexibility to build a laser any way you need it.

Use more power, keep a cool head. Let your power grow without enlarging *or* overheating the laser head—the exclusive S-P Lasers fiber optic-coupled design makes it possible. Add extra power flexibility with our unique 2-diode pump module. Choose 200-mW, 500-mW, or 1-Watt pump configurations and increase your output power as your needs change.

You don't have to touch it (unless you want to). If you're an OEM manufacturer, you can have a customized, computer-interfaced DPY in a 19-in. rack mount that fits right into your system. If your work is scientific, you'll find all the manual controls you want. In either case, you'll possess a rugged, maintenance-free laser delivering highly reliable TEM_{00} output.

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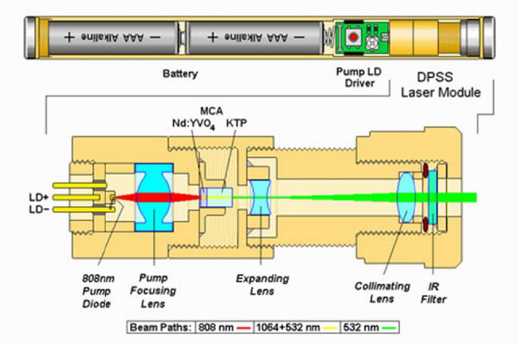
High-Power Diode Pumped Lasers

Spectra-Physics

- The first (1988) commercially available, Q-switched, diode-pumped solid state laser with 10 - 20 $\mu J/pulse$.
- It used an acousto-optic Q-switch and had a frequency doubler.

Common lasers

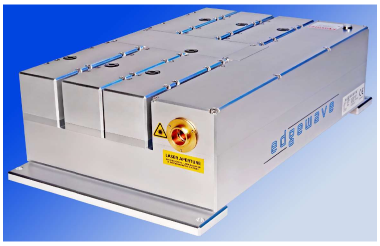
CW Diode-pumped Nd:YAG lasers



- Green laser pointers are small diode-pumped (axially) Nd:YVO$_4$ (neodymium vanadate) lasers with a frequency doubling crystal.

Common lasers

CW Diode-pumped Nd:YAG lasers



- Nowadays we do high speed imaging with diode-pumped lasers:
  - ▷ 60 $\mu J/pulse$ at 1.064 nm,
  - ▷ Pulsewidth = 4 ns (at 1.064 nm),
  - ▷ Max repetition rate = 150 kHz,
  - ▷ These lasers have so much energy circulating inside that they require a cooling system to stabilize everything.

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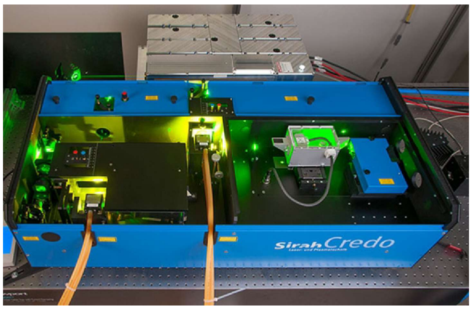
Common lasers

Dye lasers



- Solid state lasers have fixed wavelengths, it's hard to do spectroscopy with them (except for fuel tracers at 355 and 266 nm, and formaldehyde at 355 nm).
- For things like OH or CH PLIF, for example, we often (not always) use a tunable dye laser, most often at 10 Hz but not always.

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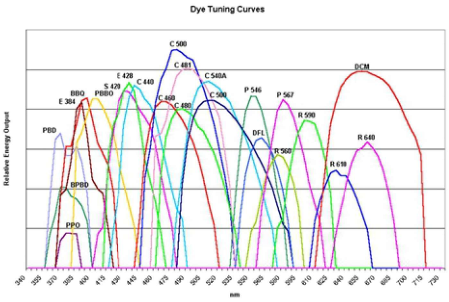
Common lasers

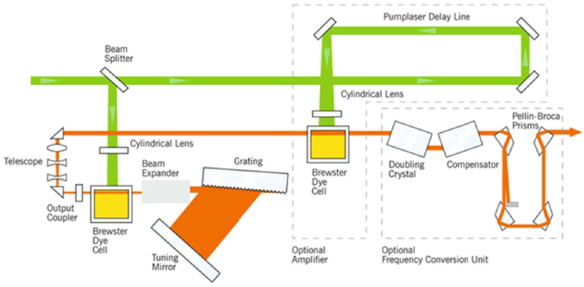
Dye lasers

- One can chose from among many dyes (in solution with methanol) for the laser gain medium, and there is broad spectral coverage.
- Each dye is very broadband and the dye laser tunes across the dye spectrum.
- The dye laser cavity controls the output bandwidth.



Common lasers

Dye lasers

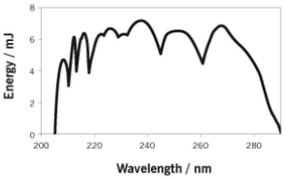


- This is one optical layout.
- Dye lasers perform best when pumped by an injection seeded pump laser.

Common lasers

Dye lasers

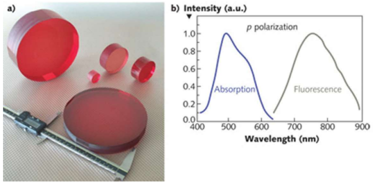
- It is also possible to generate harmonics of the dye fundamental wavelength using nonlinear crystals (doubling and mixing are both possibilities).
- Here is an example of a difficult region to reach - it's from a frequency doubled dye laser pumped by $375\ mJ/pulse$ with $355\ nm$ laser light. The region around 226 is for NO LIF, and it's necessary to get to about $10\ mJ/pulse$ at that wavelength.



Common lasers

Mode locked cw lasers

- One can generate very short pulses (below 40 fs) using a very broadband gain medium because there is an inverse Fourier transform relationship between gain bandwidth and pulsewidth - for a Gaussian shaped pulse the transform limit is given by $\Delta t \times \Delta\nu = 0.44$.
- Narrow bandwidth lasers are usually cw, and short pulse lasers must have broad bandwidth.
- The commonly used gain medium for short pulses is titanium in sapphire (Ti:sapphire).



Common lasers

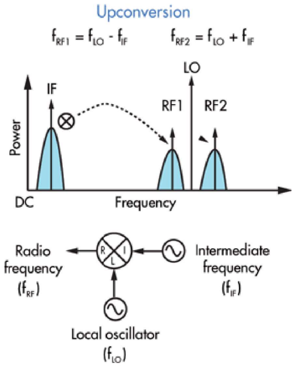
Mode locked cw lasers

- Think in terms of RF electronics and mixing:

  $$\cos(f_{If}t) \times \cos(f_{Lo}t) =$$

  $$\frac{1}{2}\cos[\underbrace{(f_{If} + f_{Lo})}_{\text{sum frequency}}t] + \frac{1}{2}\cos[\underbrace{(f_{If} - f_{Lo})}_{\text{diff. frequency}}t]$$

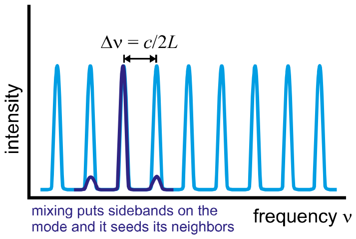
  It produces sum and difference frequency side-bands on the local oscillator.
- For mode-locking, the local oscillator is running at a frequency given by the $c/2L$ mode spacing of the longitudinal cavity modes.



Common lasers

Mode locked cw lasers

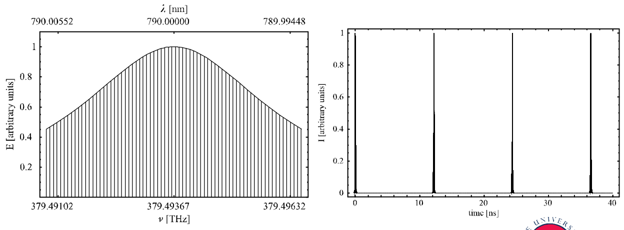
- The mode locker could be an acousto-optic device that modulates intracavity loss, for example.
- It produces side-bands on each longitudinal mode that, by design, are at the frequency of the next nearest modes.
- Each mode mixes with its neighbors, and in so doing they injection-seed each other all across the gain bandwidth.
- All of the longitudinal modes are locked to each other.



Common lasers

Mode locked cw lasers

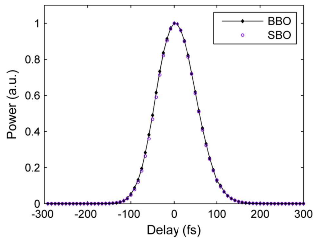
- This produces extremely quiet and stable laser output:
  ▷ Uncontrolled cw lasers produce mode beating noise because their modes rapidly shift in phase relative to each other as they add coherently.
  ▷ In a mode-locked laser, frequency stabilized modes add coherently.
- An infinite series of spikes in frequency can be Fourier transformed to give an infinite series of spikes in time.



Common lasers

Mode locked cw lasers

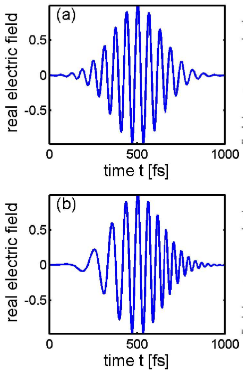
- Think of each pulse as a summation of a Fourier series across many frequencies to give a very short pulsewidth.
- A "transform limited pulse" has all of the colors piled uniformly into the pulse waveform.
- These pulses have to be measured via autocorrelation; no detector is fast enough.
- In summary, a mode-locked laser is basically a normal, stable cavity cw laser using a broad gain bandwidth and a modulator of some kind in the cavity operating at $\nu_{\text{modulation}} = c/2L$.



Common lasers

Pulse chirp

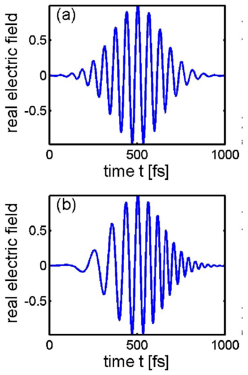
- Image (a) depicts the electric field of a transform limited pulse. Many wavelengths from within one laser oscillator have added coherently to produce the waveform shown, and they added uniformly across the pulse to produce a transform limited pulse.
- Image (b) depicts a pulse that is not transform limited. The waveforms did not add uniformly across the pulse and so we see "chirp" on the pulse. Pulse (b) is not transform limited although the effect is subtle in terms of the pulse envelope.



Common lasers

Pulse chirp

- If we send a very short transform limited pulse through glass (or even a gas at high pressure), the index of refraction of the material will vary slightly with wavelength. Blue colors typically slow down relative to the red colors. The pulse becomes chirped.
- Chirp can become important for time-dependent spectroscopic diagnostics like short pulse CARS.



Common lasers

Mode locked cw lasers

- Example; the laser I have used:
  - ▷ Average power $> 4.0W$ at 800 nm
  - ▷ Pulse rate of 82 MHz (same as the $c/2L$ mode spacing of the laser - think about it)
  - ▷ Pulsewidth from $< 30fs$ up to $\sim 180\,fs$ depending on the intracavity optics.
  - ▷ Around $50\,nJ/pulse$; not much energy per pulse but it is $\sim 500\,kW$ of power at the peak of the pulse.

Common lasers

Chirped pulse regenerative amplification

- What if you want more energy per pulse (e.g. for a nonlinear process like an OKE time gate, or for short pulse CARS)?
- It is possible to convert the 4 W of average power into much more pulse energy if we slow the pulse rate down (using the same pump power).
- A 1 kHz system can then generate up to $10\,mJ/pulse$ which is a lot (nearing a TW at the peak of the pulse).
- That much power at the peak would drill holes in the Ti:sapphire, so it is necessary to use “chirped pulse regenerative amplification”.

Common lasers

Chirped pulse regenerative amplification

- Chirped pulse regenerative amplification:

  ▷ Spread the pulse out in time (make it into a broadly chirped pulse) by separating the colors in a grating-based pulse stretcher, which brings down the peak power,
  ▷ Use a Pockels cell to select individual pulses at 1 kHz (like a Q-switch), and reject the others,
  ▷ Inject the selected pulse into a cavity containing a Ti:sapphire rod that is pumped by a pulsed laser, and let it pass back and forth gaining intensity (regenerative amplification),
  ▷ When the pulse has sufficient energy, switch it out of the cavity with a Pockels cell,
  ▷ Now re-compress the pulse to the transform limit.

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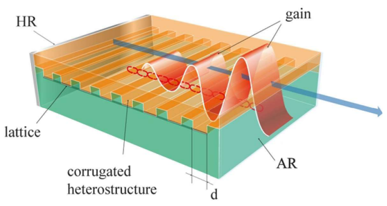
Common lasers

Distributed feedback

- To generate feedback we don't necessarily need two mirrors (that's called a "Fabry-Perot cavity").
- One can replace the output coupler with a grating that selects specific wavelengths for buildup inside the gain medium.
- This is called a "distributed feedback (DFB)cavity".
- In fact, a DFB dye laser pumps the dye cell with overlapping pump beams that interfere with each other and make a dye population grating in the gain medium. DFB dye lasers are tuned by changing the angle between the pump beams.



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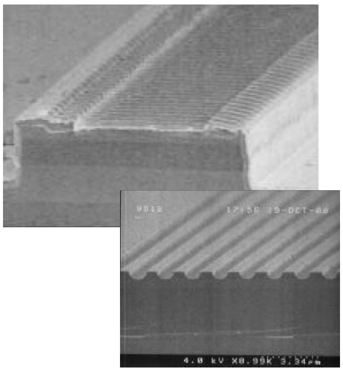
Common lasers

Quantum cascade diode lasers

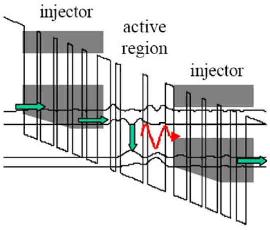
- Quantum cascade diode lasers are small IR sources with relatively high power.
- QC diode lasers use DFB.



Common lasers

Quantum cascade diode lasers

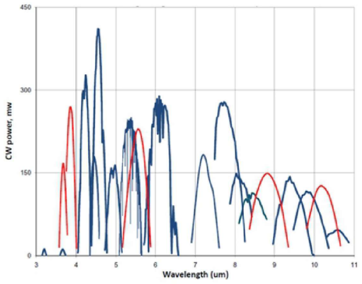
- QC diode lasers create gain differently from the 4-level system described above.
- They force electron confinement inside a quantum well structure, which can be tailored to different energy gaps (optical wavelengths) simply by changing the thickness of the constituent layers.
- The structure induces electron transitions to the next lower level, and the transition is photonic; it gives off light.
- Many quantum wells can be connected so that one electron can induce a number of photons, hence the high power.



Common lasers

Quantum cascade diode lasers

- QC diodes have very wide wavelength coverage (from $3.7 - 16\,\mu m$ at room temperature) and high power; perfect for studies of mid IR fundamental vibrational bands in molecules.
- Each individual laser emission spectrum is much narrower than this image, which shows all possible lasers.
- Each laser can be tuned over the laser's range by scanning current (heats the chip).



Next topic

Absorption-based techniques

Advanced Laser Diagnostics for Combustion Research

Lecture 11: Absorption-based techniques

Mark Linne

University of Edinburgh

Tsinghua-Princeton-CI Summer School on Combustion
July 11 - 17, 2021

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Topics

Absorption

- Direct line of sight absorption
- Wavelength-modulated absorption
- Frequency comb absorption
- Absorption tomography

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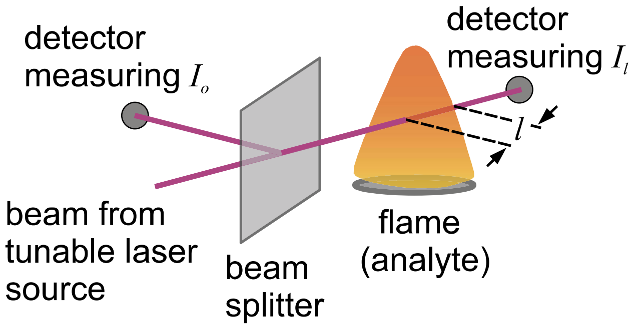
Absorption

Absorption is -

- A resonant technique.
- Line-of-sight.
- Continuous mostly, but can be pulsed (e.g. CRDS).
- A linear technique (the signal scales with I).
- Across all infrared, visible, and ultraviolet, spectral regimes.
- Often narrow bandwidth but can be broad bandwidth (e.g. frequency comb spectroscopy).
- Absorption is fully quantitative if applied properly.

Direct absorption



Direct absorption

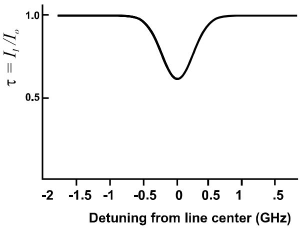
- Pass a tunable laser beam at frequency ν_L (resonant with an atomic or molecular transition) across the flow.
- Observe fractional reduction in beam irradiance (e.g. beam transmission τ) as a function of ν_L (scan the laser frequency).
- Use Beer's law to extract the number density of absorbers:

  $\tau(\nu) = I_l/I_o = e^{-N_m\sigma_\nu l}$, where:

  N_m is the number density of absorbers (molecules in the absorbing energy level)

  σ_ν is the absorption cross section

  l is the absorption path length through the flame



Absorption

- The measurement is a direct experimental detection of $\tau(\nu)$.
- If not using an established technique, one should model the absorption spectrum under the appropriate conditions (pressure and temperature) to decide how one can achieve the goal (detectivity, temperature sensitivity or insensitivity, avoidance of interferences etc.).
- The N that enters into Beer's law is the number density in the energy level that absorbs. The total number density, which is what we want, is related to the number density in the absorbing level m by inverting equation 36:

$$\frac{N_m}{N_{\text{total}}} = f_e f_v f_J = \frac{g_e e^{\left(-\frac{E_n}{k_B T}\right)}}{Q_{\text{elec}}} \frac{g_I(2J+1)e^{\left(-\frac{E_J}{k_B T}\right)}}{Q_{\text{rotational}}} \frac{e^{\left(-\frac{E_v}{k_B T}\right)}}{Q_{\text{vibrational}}}$$

Absorption

- The various energy expressions, degeneracies, and partition functions need to be found in books and in the literature. When following an established technique there are usually just a few papers containing all the necessary details.
- Next, the spectral absorption cross section is written:

$\sigma_\nu = \frac{h\nu}{c}\left(\frac{N_m}{N_{\text{total}}}B_{mn} - \frac{N_n}{N_{\text{total}}}B_{nm}\right)Y_\nu$

- Often $N_m >> N_n$ and we write:

$\sigma_\nu = \frac{h\nu}{c}\left(\frac{N_m}{N_{\text{total}}}B_{mn}\right)Y_\nu$

- Often one can't easily find the Einstein coefficient, but one can find an oscillator strength for example. We have already discussed how one can convert between formalisms, but be very careful about units.

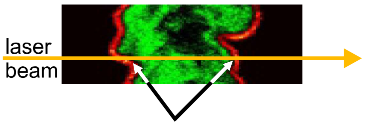
Absorption

- The lineshape function Y_ν is most often modeled as a Voigt profile, as already discussed.
- The necessary broadening parameter is a in the Voigt expression, equation 42. Usually one calculates the Doppler width (which is used in several locations within equation 42) and then finds a published measurement of γ_{nm} to provide a.
- Finally the absorption path length is needed and that is often measured another way:
  ▷ If an open flame, one can translate the flow sideways, make absorption measurements, assume the flow is rotationally symmetric and infer l,
  ▷ If an open flame, take a Schlierein image,
  ▷ If enclosed, use enclosure dimensions (if that makes sense) etc.
- It is actually not easy to get a good value for l, especially if the flow is nonuniform (e.g. has cold boundaries) which (via statistical mechanics) can contribute differently than the hotter core.

Direct absorption

Facts about this technique

- When used along one line of sight, Beer's law applies only to a homogeneous medium. We made that assumption in order to derive it from the ERT.
- If the medium is not homogeneous, then the complex coupling between local concentration (N_{total}, controlled by chemistry, mixing etc.) and temperature (the fraction of molecules in the absorbing level $f_m = N_m/N_{\text{total}}$ is exponentially temperature dependent via Boltzmann statistics) can not be disentangled.



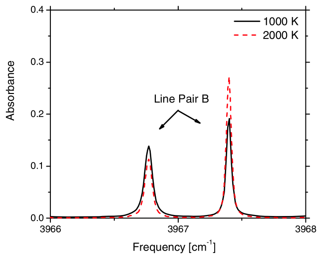
rapid changes in species concentrations (N_{total}) and temperature (hence $f_m = N_m/N_{\text{total}}$) along the laser line of sight

---

Direct absorption

Facts about this technique

- When used in an appropriate experiment, however, the result is an absolute determination of number density, which is actually unusual but very valuable.
- Combining two resonances (two absorption lines) can also provide temperature (via Boltzmann statistics), assuming, again, that the medium is homogeneous.



from: Farooq, Jeffries & Hanson, Meas. Sci. Technol. **19** (2008).

Direct absorption

Facts about this technique

- Quantitative detection requires the spectra to be normalized to variations in the baseline intensity (with no absorption). Baseline variation can include laser power changes with tuning, wavelength modulation by window "etaloning", and via uncontrolled processes (e.g. intermittent scattering from soot, index graduents steering the beam etc.).
- The quality of this normalization can control uncertainty. It is common to deal with the repeatable baseling variations by fitting a polynomial to the baseline and using that to divide out the baseline from an absorption spectrum.
- When scanning over a broad range to capture multiple species, or scanning through a dense field of lines, normalization can become highly uncertain.

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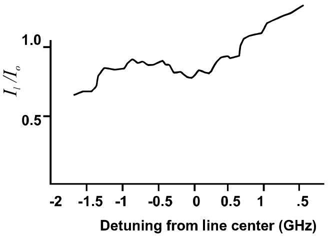
Direct absorption

Experimental difficulties



- Most absorption techniques use diode lasers that are tuned by scanning current. That also makes the laser power change with laser frequency.
- Lasers can have a large amount of amplitude noise. This is not a "background free" technique; the detector looks into an intense and noisy background. The oscillations in amplitude can look the same as an absorption profile, and they set the detection limit of this technique.
- Direct absorption has a high detection limit (one wants a low one) for this reason.

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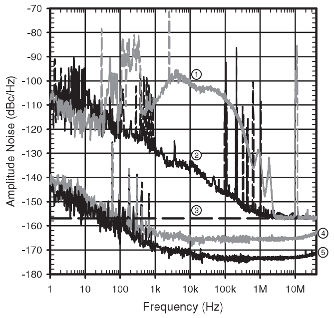
Laser amplitude noise

- An example laser amplitude noise spectrum, in dB/Hz.
- Zero in frequency is the cw laser dc and the technical noise (caused by pump laser noise, vibrations etc.) falls away slowly with frequency, almost like $1/f$ noise (also called 'pink noise').
- The noise hump in the Ar:Ion spectrum is probably from cooling water turbulence.
- Diode lasers are typically quieter than this, but this is the kind of noise that limits direct absorption. The mimimum fractional absorption one can detect within this much noise is about 0.05.



1. Ar:Ion laser, 2. Diode-pumped solid state laser, 3. shot noise limit,
4. Photodetector noise floor,
5. Measurement system noise floor.

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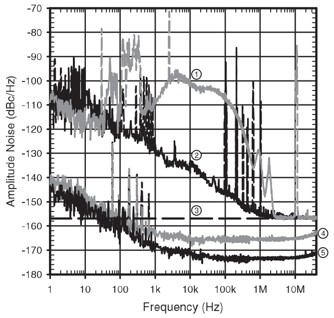
Absorption

Improving detection limits

- One approach to reach lower detection limits is to modulate the laser beam at high frequencies (where the noise is lower) and then extract the absorption signal at that same frequency using a lock-in amplifier. An even better way to do that is called "wavelength modulation spectroscopy" (WMS) or by a related technique called "frequency modulation spectroscopy" (FMS). Those techniques can detect fractional absorption on the order of $10^{-4} - 10^{-6}$. Collectively they are called "derivative techniques" for reasons that will become clear.



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Absorption

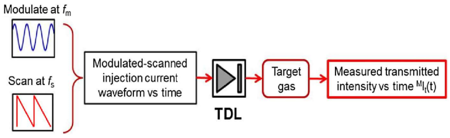
Improving detection limits

- Another approach is to place the sample in an optical cavity of highly reflecting mirrors, which causes the beam to make many passes and increases the path length l in Beer's law ($I_l/I_o = e^{-N_m \sigma_\nu l}$), which increases sensitivity. This approach includes cavity ring-down spectroscopy, integrated cavity output spectroscopy and others. Those techniques can detect fractional absorption on the order of $10^{-7} - 10^{-9}$. They are not discussed here.
- A new approach based on frequency comb spectroscopy takes advantage of "free induction decay" to eliminate the laser noise.

Wavelength modulation spectroscopy - a narrow bandwidth technique

- WMS is still a line of sight technique. The experiment looks very much like direct absorption, but it uses signal processing to get away from the laser noise.
- Diode laser wavelength is controlled by the temperature of the chip. A thermoelectric cooler usually holds the chip at near the correct temperature. Then the current through the chip is scanned to hit the correct wavelength via fine tuning. To scan back and forth across the absorption line in direct absorption, one introduces a repeated current ramp that causes the laser to repetitively scan across the line.
- That also causes the laser power to scan up and down but even in direct absorption there are ways to remove that ramp in output irradiance.

Wavelength modulation spectroscopy



from: Sun et al., Meas. Sci. Technol. 24 (2013)

- For WMS we add an extra current signal the modulates the wavelength using a sine wave, in addition to the slower ramp scan (to keep the two straight I will call them the 'scan' or sometimes 'ramp scan' and 'modulation' current signals).
- Here we will follow the notation of the Hanson group at Stanford so that we can use their images. The frequency for scanning will be called f_s and the frequency of modulation will be called f_m, both in units of Hz.

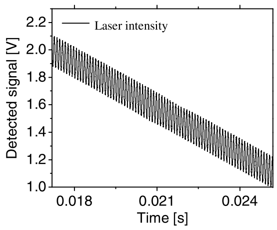
Wavelength modulation spectroscopy

- Warning - all these frequencies can be confusing; there are two types of frequency - optical and electronic signal frequencies

  ▷ The optical frequency of the laser beam itself (i.e. based on the actual wavelength of light) is usually denoted by ν (in Hz or 1/s) or by $\breve{\nu}$ (in wavenumbers, cm^{-1}); green light has a frequency around $\nu = 6 \times 10^{14}$ Hz, or $\breve{\nu} = 2 \times 10^{4} cm^{-1}$,
  ▷ The scan frequency f_s (a signal frequency, the rate at which we sweep ν) is quite low by comparison, often tens of Hz,
  ▷ The modulation frequency f_m (another signal frequency) is meant to avoid $1/f$ laser noise, so it should be in the range of 10 kHz to 1 MHz,
  ▷ The modulation signal at f_m is imposed on the diode current, so the laser output includes a sinusoidal optical frequency modulation induced by the modulated current, and here we will call the maximum in the modulation $\delta\nu_m$; so the laser output optical frequency oscillates between $\nu + \delta\nu_m$ and $\nu - \delta\nu_m$ at frequency f_m.

Wavelength modulation spectroscopy

- Here is a representation (measured laser output power onto a photodetector) where the current scan causes the output power to trend down linearly over the measurement period and the modulation is seen as a smaller sine wave on the ramp. The ramp scan rate was $f_s = 25$ Hz with an amplitude of 2 V while the modulation frequency was $f_m = 10$ kHz with a modulation amplitude of 0.1 V.
- The goal is not to modulate the power (i.e. amplitude), it is to modulate the frequency of the laser output over a small range around the central value of ν (which is drifting downward with the scan), but that also modulates power.

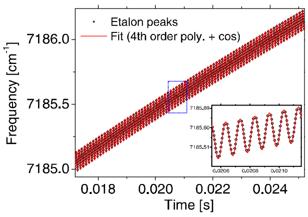


Wavelength modulation spectroscopy

- By sending the beam through a narrow optical filter (a Fabry-Perot Etalon) one can detect the laser optical frequency: $\breve{\nu}$ in cm^{-1}, including the modulated sweeping $\delta\breve{\nu}_m$.
- It is common to define a dimensionless frequency by:

  $x \equiv \frac{\nu}{\nu_{1/2}}$ where $\nu_{1/2}$ is <u>half</u> of the FWHM of the absorption line profile $Y(\nu)$ in $1/s$.

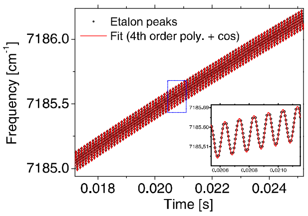
  The dimensionless modulated frequency would then be $x_m \equiv \frac{\delta\nu_m}{\nu_{1/2}}$.



Wavelength modulation spectroscopy

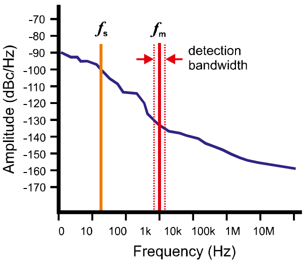
- We then express the instantaneous, dimensionless laser frequency as:

  $x(t) = x_o + x_m \sin(f_m t)$.
- If $X(x)$ is the Beer's law absorption function (including the lineshape), the detector signal $S(t)$ will be given by: $S(t) = X[x_o + x_m \sin(f_m t)]$.
- $S(t)$ can then be expressed in terms of a sequence of harmonics of f_m, and as it turns out the measured absorption shape for the n^{th} harmonic is proportional to the n^{th} derivative of the lineshape function. We don't have enough time in this class to develop that result.

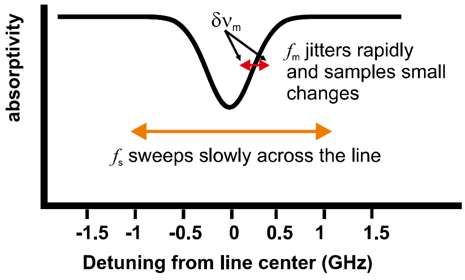


Wavelength modulation spectroscopy

- That result may be hard to accept.
- It is necessary to think in terms of the frequency spectra of the signals. The slowly varying sweep occurs at a low frequency while the modulation occurs at a high frequency; the two processes are separated by a big frequency difference.
- When doing phase sensitive detection like a lock-in amplifier, one also filters the high frequency signal with a user selected detection bandwidth. Specifically at f_m, then, the signal will ignore the other processes. Because f_s is so slow, it is as though the processing at f_m is completed for each small step from f_s.



Wavelength modulation spectroscopy



- In the spectrum we see that the sweep covers a very large span, it includes the entire absorption line (or several lines) and it creeps across the line when compared to f_m.
- The span of the modulated portion is $\delta\nu_m$, and it is not nearly as big as the sweep, but it jitters back and forth at high speed (f_m).

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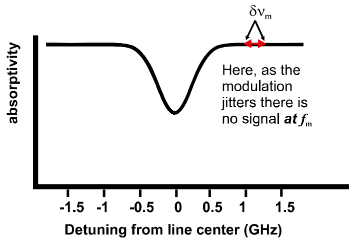
Wavelength modulation spectroscopy

- When thinking about this, remember that at f_m the signal processing is only going to recognize signals that fall within the detection bandwidth around f_m.
- In this image, no signal is generated at f_m because the curve is flat. The absolute value of that background level is noticed at f_s, not at f_m. Think in terms of AC coupling at high frequencies; the DC is not noticed at f_m.



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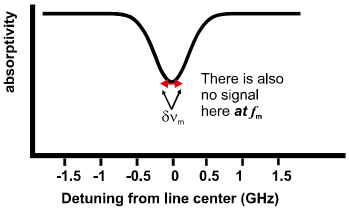
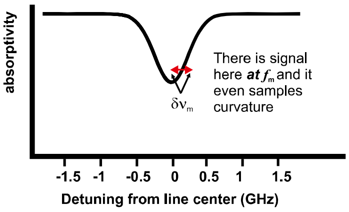
Wavelength modulation spectroscopy

- The same is true here; the higher absorption level is registered at f_s but in the vicinity of f_m not much is happening.

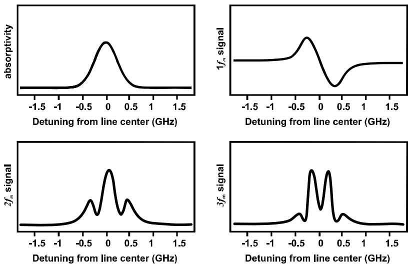


Wavelength modulation spectroscopy

- Here, however, there is signal at f_m.
- The signal detected at f_m now oscillates up and down, but it is not a clean sinusoid; the oscillations depend on the slope and curvature of the absorption profile. If we take the various Fourier components of that signal we will get the various derivatives mentioned earlier.



Wavelength modulation spectroscopy



- The various harmonics then look like derivatives.
- The established technique was to use a lock-in amplifier and demodulate at one of the harmonics while the ramp scanned (usually $2f_m$ because most lock-in amplifiers have a built in $2f$ demodulation and it has an easily detectable peak on line center).

Wavelength modulation spectroscopy

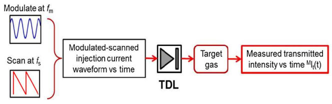
- This approach was not problem free:
  ▷ It was necessary to develop a fairly complex model (including the laser spectral properties) to extract a concentration from the measurement, and it depended on uncertain parameters.
  ▷ It became more common to calibrate the measurement, which is a bit of a step backwards.
  ▷ The scan and modulation process causes intensity to change and it adds an amplitude modulated noise signal at the same frequency where one is demodulating.
- The Hanson group at Stanford have developed a new approach that avoids many of these problems

  (e.g. K. Sun et al., Meas. Sci. Tech., 25, 125203, (2013); C.S. Goldenstein et al., Applied Optics, 53, no. 3, 356-367, (2014)).
- The technique involves capturing the entire signal and doing signal processing in a lab computer (no lock-in amplifier is used) so that many of the harmonics are available, not just one of them. This avoids the need to model the Fourier components of the absorption signal based on just one harmonic.

Wavelength modulation spectroscopy

The entire process

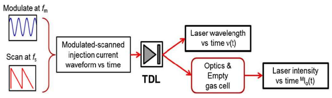
- Here we go through the entire process one step at a time.
- The actual measurement involves passing the scanned and modulated beam through the sample and measuring the irradiance I on the other side, as ${}^{M}I_t(t)$, where the preceding superscript M indicates "measured", and the succeeding subscript t indicates transmitted light.



Wavelength modulation spectroscopy

The entire process

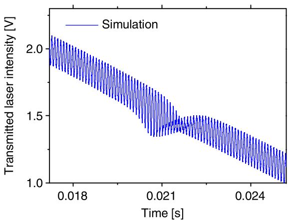
- Next the irradiance I must be detected in the same setup but without absorbers, as ${}^{M}I_0(t)$, where the preceding superscript M indicates "measured", and the succeeding subscript 0 indicates absence of absorbers.
- The extra top channel in the image detects laser frequency as a function of time using an etalon (as shown before in the red curve). The laser frequency data are then fit to a model for the laser output frequency as a function of scan and modulation.



Wavelength modulation spectroscopy

The entire process

- Now the absorption spectrum is synthesized from known spectral data (i.e. σ_ν, $Y(\nu)$ etc.; we needed all of that information before, the need for spectral data is nothing new).
- The measured laser frequency vs. time model (e.g. ${}^{M}I_0(t)$) is now passed through the absorption spectrum to generate a synthesized irradiance vs. time curve that would be landing on the detector, called ${}^{S}I_t(t)$ where the preceding superscript S means “simulated”.

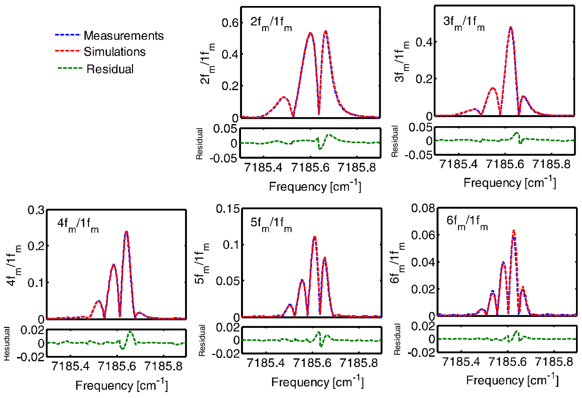


Wavelength modulation spectroscopy

The entire process

- Both ${}^{M}I_t(t)$ and ${}^{S}I_t(t)$ are processed with digital lock in amplifier software to simulate many of the harmonics.
- The center of the $1f_m$ curve is then used to normalize the others in order to remove laser amplitude variations.
- The two can then be compared and adjusted in a nonlinear fitting routine until the appropriate number density and temperature, (if fitting more than one line, otherwise temperature must be had another way), are correct.

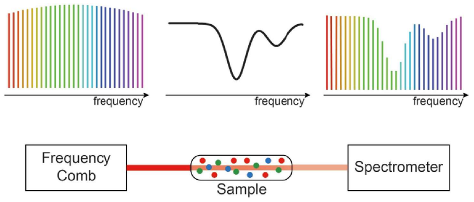
Wavelength modulation spectroscopy



- Example results for water vapor at room temperature.

Frequency comb absorption spectroscopy - a broad bandwidth technique

- Frequency combs are generated by mode-locked lasers (a comb in time generates a comb in frequency space). Each "tooth" of the frequency comb is a spectrally narrow frequency spike.
- Frequency combs can be though of as broadband, spectrally clean and low noise sources for absorption spectroscopy.
- This is a simple setup, but higher resolution can be found using "dual comb" absorption spectroscopy.



from N. Picque and T. Hänsch, "Frequency Comb Spectroscopy", Nature Photonics, 13, 146-157, (2019).

Frequency comb absorption spectroscopy

Attributes of frequency comb spectroscopy

- Frequency comb spectroscopy is "self referencing" (sometimes called "self calibrating"): the spikes appear in the signal spectrum and we know their frequency spacing to the resolution of a crystal oscillator (very high resolution). We automatically have the horizontal axis for the absorption spectrum.
- For some implementations the spectral instrument response function does not enter the analysis (e.g. "dual comb").
- Spectral resolution is given by the pulse repetition rate (frequency comb spacing), and it can be high.
- The laser is naturally spectrally broad so many species can usually be detected.
- Detection limits can be low, but the measurement is not highly time-resolved owing to the need for averaging.

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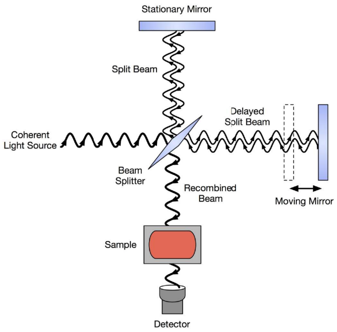
Frequency combs

Fourier Transform IR (FTIR)

- To discuss dual comb absorption spectroscopy, it might be best to start with a description of how an FTIR works:
  ▷ FTIR uses a broadband light source (usually a small lamp).
  ▷ The light beam passes through a Michelson interferometer which also contains the sample to be analyzed.
  ▷ One end mirror is scanned, and the *time-dependent* interferogram is acquired at the detector.
  ▷ If we take the Fourier transform of the detector signal we get the transmission spectrum.



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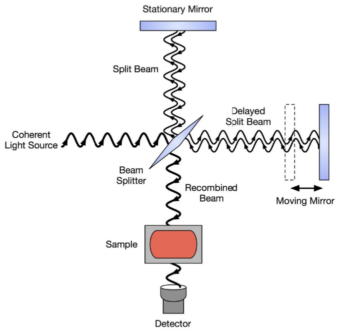
Frequency combs

Fourier Transform IR (FTIR)

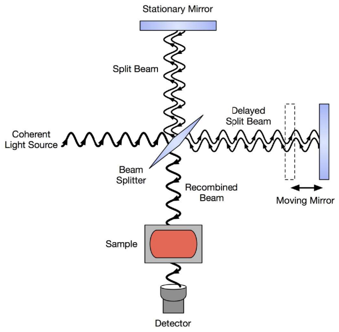
- Is that right?
  ▷ Imagine there is no sample and we send a single frequency laser though. One arm of the interferometer stays fixed while the other scans. We'd get a very clean sinusoid as the mirror is scanned because the two arms would interfere constructively and destructively as the scan proceeds.
  ▷ If we Fourier transform that signal, which is a single sine wave, we'd get a narrow spike in frequency space depicting the narrow bandwidth of the laser - right?



Frequency combs

Fourier Transform IR (FTIR)

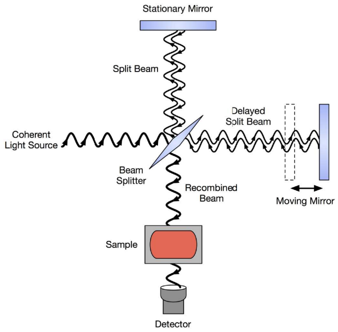
- continuing:
  ▷ Now imagine there is no sample and we send *two* single frequency lasers at two closely spaced frequencies through. We'd get sinusoids with beats as the mirror is scanned and if we Fourier transform that signal we'd get two narrow spikes in frequency.
  ▷ Now imagine you send broad-band light through. You'd get a much more complex set of interference patterns but if you Fourier transform it you'd get the spectrum of the light.



Frequency combs

Fourier Transform IR (FTIR)

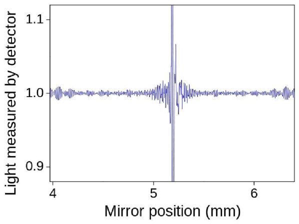
- continuing:
  - ▷ Now imagine you send a broad-band source into the interferometer but there is an absorbing sample in the final arm. The loss of signal at absorption lines would be imbedded in the scan signal and they'd be seen once it gets Fourier transformed.
  - ▷ If you are thinking about this you realize the scan rate (compared to detector speed) and scan length control spectral resolution.



Frequency combs

Fourier Transform IR (FTIR)

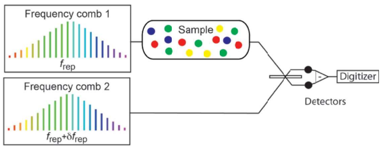
- continuing:
  - ▷ Here is a time-dependent interferogram for white light going through a sample.
  - ▷ Dual comb absorption spectroscopy is a way to do this without any moving parts.



Frequency combs

Dual comb spectroscopy

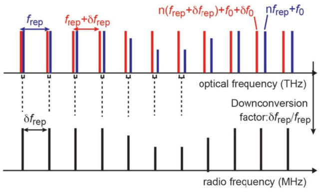
- One beam (a frequency comb, with broad bandwidth centered around the absorption lines of interest) at pulse repetition frequency of f_{rep} is sent through an absorbing sample.
- A second beam from the same type of laser (same center wavelength and bandwidth) at a slightly different pulse repetition frequency $f_{rep} + \delta f_{rep}$ is combined with the first beam at the detector.



Frequency combs

Dual comb spectroscopy

- As shown, the frequency difference causes the two pulse trains to “walk through” each other. Because the pulse train is effectively infinite, this process is identical to what would happen if we put the first comb through an FTIR interferometer with a scan time of $1/f_{rep}$. But we no longer need the interferometer mechanics.

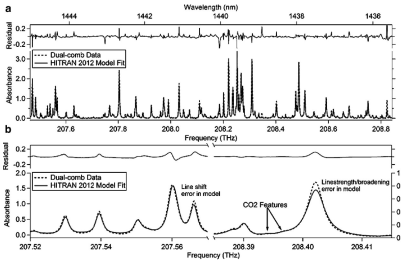


The beat notes between pairs of comb lines, one from each comb, generates a radio-frequency comb [Picque and Hänsch, Nature Photonics, 13, 146-157, (2019)]

Frequency combs

Dual comb spectroscopy

- We can think of $f_{rep} + \delta f_{rep}$ as a local oscillator frequency. That comb beats with the comb at f_{rep} which means the beat can be detected by normal digital electronics.
- Judicious choice of frequencies means we can set the beat frequency out past the laser $1/f$ noise.
- The beat signal is then Fourier transformed to give a spectrum.



From P. J. Schroeder, R.J. Wright, S. Coburn, B. Sodergren, K.C. Cossel, S. Droste, G.W. Truong, E. Baumann, F.R. Giorgetta, I. Coddington, N.R. Newbury, G.B. Rieker, “Dual frequency comb laser absorption spectroscopy in a 16 MW gas turbine exhaust”, ProCI, 36, (2017).

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Frequency combs

Cepstral analysis

- Rieker and co-workers§ have recently introduced a signal analysis technique (“cepstral analysis”) that removes the baseline problem from absorption measurements.
- It does not require frequency combs, but they introduced it as an enhancement to their dual comb work so we will discuss it in that context as well.
- It is based on a phenomenon called “free induction decay”, so it’s necessary to start the discussion there.

§ R. K. Cole, A. S. Makowiecki, N. Hoghooghi, and G. B. Rieker, “Baseline-free Quantitative Absorption Spectroscopy Based on Cepstral Analysis”, Optics Express, 27:26, 37920, (2019).

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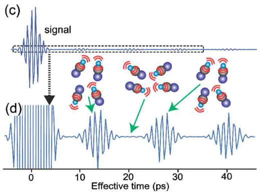
Frequency combs

Free induction decay

- When a laser beam is absorbed by a volume of molecules, those molecules will oscillate coherently, giving rise to coherent forward-scattered radiation (colinear with the laser beam).
- Because they are distributed volumetrically, this forward scattered light will go into and out of coherence, and it will decay over time. That's called free induction decay (FID).

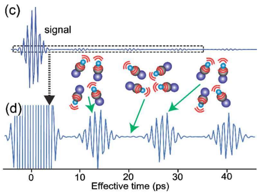


From I. Coddington, W. C. Swann, and N. R. Newbury, "Time-domain spectroscopy of molecular free-induction decay in the infrared", Optics Letters, 35:9, (2010).

Frequency combs

Cepstral analysis

- In between laser pulses, the weak FID can be observed.
- Notice that the FID is separated in time from the laser pulse; the baseline intensity in the absorption signal decays fast relative to the FID.
- A baseline-free measurement can be found by detecting just the FID.



Frequency combs

Cepstral analysis

- FID in time can be located by taking the inverse Fourier transform of the transmission signal, which is described by Beer's law:

  $I_l(\nu) = I_o(\nu)e^{-N_m\sigma_\nu l}$.
- Unfortunately, the source intensity is convolved with the signal:

  $I_l(t) = \mathcal{F}^{-1}[I_l(\nu)] = \mathcal{F}^{-1}[I_o(\nu)] * \mathcal{F}^{-1}[e^{-N_m\sigma_\nu l}]$.
- This convolution makes it hard to isolate the FID signal from the background ($I_o(\nu)$) because the baseline has a notable effect over a large part of the FID.

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Frequency combs

Cepstral analysis

- To get around that problem, we define a new term:

  $A(\nu) = -\ln(I_l(\nu)) = -\ln(I_o(\nu)) + (N_m\sigma_\nu l)$.
- Then:

  $A(t) = \mathcal{F}^{-1}[-\ln I_l(\nu)] = \mathcal{F}^{-1}[-\ln(I_o(\nu))] + \mathcal{F}^{-1}[N_m\sigma_\nu l]$.
- $A(t)$ produces a modified FID signal (called "m-FID"). It is called the cepstrum of $I(t)$.
- The baseline in the m-FID signal decays quite quickly, leaving the FID to be isolated (see Cole et al.).

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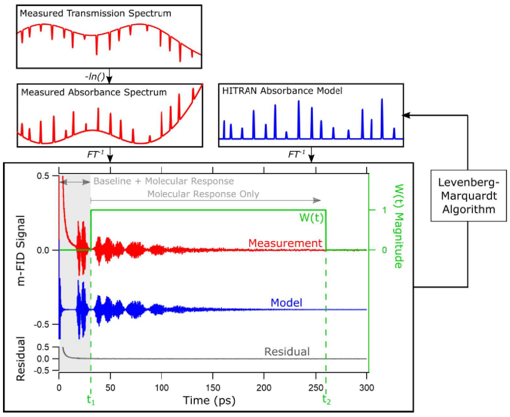
Frequency combs

Cepstral analysis - the details

- To analyze the frequency comb data:
  1. Measure the transmission spectrum and take the negative natural logarithm.
  2. Take the inverse Fourier transform to produce a cepstrum, and remove the early portion of the curve to eliminate the background.
  3. Generate a model for the m-FOD signal using spectroscopic information (see Cole et al.).
  4. Use nonlinear least squares fit of the model to the measured m-FID.
- See the diagram on the next page.

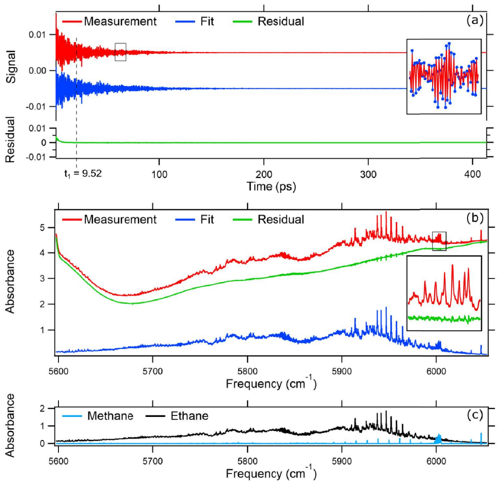
Frequency combs

Cepstral analysis - the details



From R. K. Cole, A. S. Makowiecki, N. Hoghooghi, and G. B. Rieker, "Baseline-free Quantitative Absorption Spectroscopy Based on Cepstral Analysis", Optics Express, 27:26, 37920, (2019).

Frequency combs

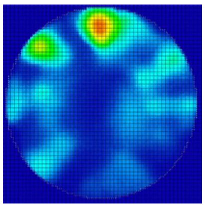


Cepstral analysis - results

An m-FID fit to an experimental spectrum taken from an ethane/methane mixture.

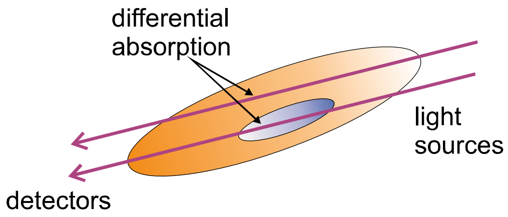
Laser absorption tomography

- We discussed the problems associated with a single line of sight going through a complex flow. One way to overcome many of the problems is to use many beams crossing the flow and apply tomographic inversion‡.



‡ e.g. Wright et al., App. Opt. 44 (2005) 6578 - 6592; Wright et al., Chem. Eng. J., 158 (2010) 2-10; Terzija et al., Meas. Sci. Technol. 19 (2008) 094007; Terzija and McCann, IEEE Sensors J. 11 (2011) 1885 - 1893.

Laser absorption tomography

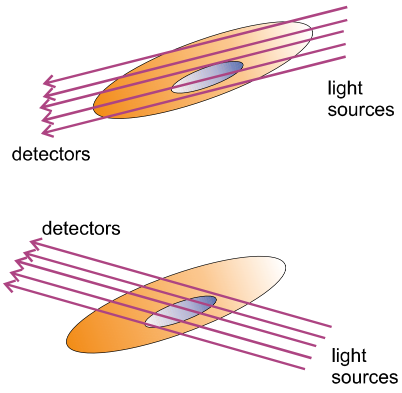


- For two absorbing beams (could be x-rays in humans or diode lasers in flames) there is a difference in the “path density integral” (PDI).
- It is necessary to integrate the ERT instead of using Beer’s law (with appropriate assumptions):

$$I_d = I_\circ \exp\left(-\int_L (N\sigma)_{x,y}\mathrm{d}l\right) = I_\circ \exp\left(-\int_L \mu(x,y)\mathrm{d}l\right)$$

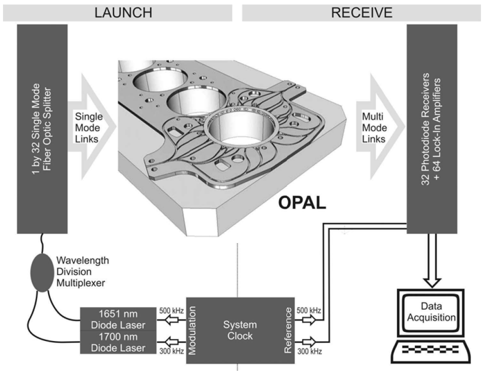
or: $-\ln\left(\frac{I_d}{I_\circ}\right) = \int_L \mu(x,y)\mathrm{d}l$

Laser absorption tomography



- For x-rays we take many projections.
- And we rotate the sources and detectors, ultimately producing $10^5 - 10^6$ PDI’s for a radon transform.
- Data inversion (image reconstruction) is ill posed and it requires iterative procedures which we do not have time to discuss here.

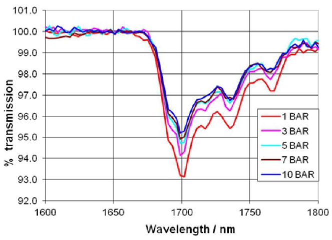
Laser absorption tomography



- Here we will show 2 examples based on engine research.
- A special engine head with input fibers and collection fibers, allows a metal engine to be run with tomography in one cylinder.

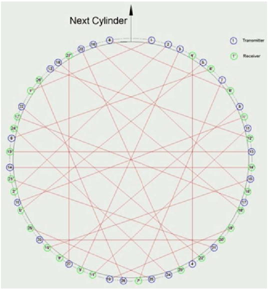
Laser absorption tomography

- They were interested in a map of fuel vapor so it is necessary to look at the fuel absorption spectrum.
- They did not scan frequency because they wanted high speed, so that they could cycle-resolve the absorption. Instead they used two diode lasers; one at 1651 nm to get the baseline and one at 1700 nm to get absorption.



Laser absorption tomography

- They use an optimized irregular 27-beam geometry.
- Angular coverage is critical, and under constraints presented by the engine fewer beams can be better.



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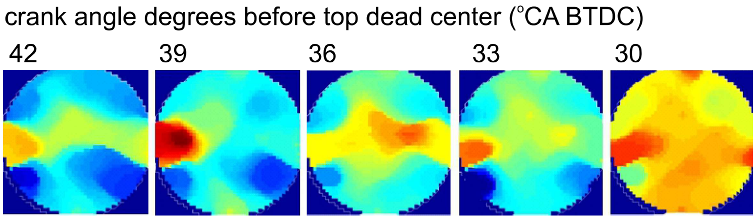
Laser absorption tomography



- First demonstration - instantaneous absolute values of fuel concentration in a plane at the head gasket in an all metal port injected engine. The engine was running at 1500 rpm, and at a low load.

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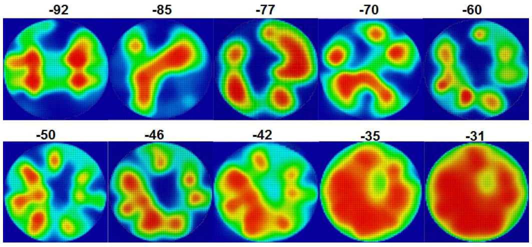
Laser absorption tomography

crank angle degrees after top dead center (°CA ATDC)



- Instantaneous absolute values of fuel concentration in a plane at the head gasket in light duty Diesel (direct injected) engine. Thirty one beams were used here. The engine was running at 1200 rpm, and at a low load.

Next topic

Laser induced fluorescence

Advanced Laser Diagnostics for Combustion Research

Lecture 12: Laser induced fluorescence

Mark Linne

University of Edinburgh

Tsinghua-Princeton-CI Summer School on Combustion
July 11 - 17, 2021

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Topics

LIF

- Basic equations
- Short pulse LIF
- Calibrated LIF
- Planar laser induced fluorescence
- PLIF with fuel tracers

Laser induced fluorescence (LIF)

LIF is -

- A resonant technique.
- Spatially resolved.
- Pulsed for combustion applications.
- A linear technique (the signal scales with I).
- Used mostly in the visible and ultraviolet spectral regimes.
- Often narrow bandwidth.
- LIF is a background-free technique; inherently more sensitive than absorption.
- LIF is difficult to make quantitative.

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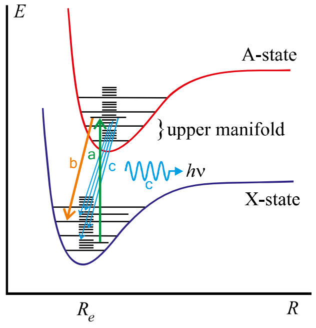
Laser induced fluorescence (LIF)

- In LIF, the laser is tuned to a resonance, some laser light is absorbed (process **a**), and the absorbing molecules occupy an energy level in an excited state (the A-state here).
- Once a molecule is in the A-state it can stay for a moment because that state has a natural lifetime.
- During that lifetime, the energy can be redistributed across the other vibrational- rotational levels in the A-state (called the 'upper manifold').



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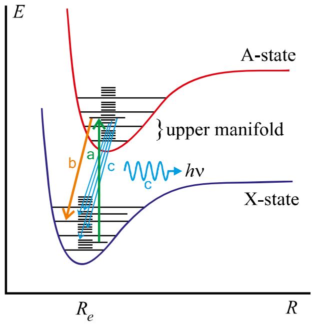
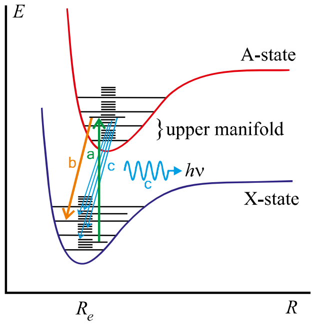
Laser induced fluorescence (LIF)

- It can also give up its energy non-radiatively to a collision partner during a collision (called 'quenching' and it's a function of the collider molecule, process **b**).
- Molecules remaining in the A-state (now occupying many ro-vibrational levels in the upper manifold) can relax back to the X-state by giving off fluorescence light from many transitions (process **c**).



Laser induced fluorescence

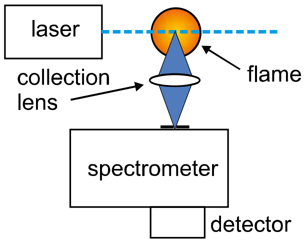
- Researchers take advantage of this process to separate the LIF spectrum from the Rayleigh scattered light at the laser wavelength (e.g. one can use a laser to 'pump' a a line in the (0,1) band but detect in the (0,0) band).
- The fluorescence quantum yield $\Phi \equiv$ (fluorescence photons)/(laser pump photons) is very small (order of 0.1%).



Laser induced fluorescence

LIF at single point

- Initially, people made LIF measurements at single point as shown.
- It wasn't really at a single point; it had a sample volume defined by the lens and the laser beam.
- Such an approach can still be used if the signal level is low, or if a researcher wants to study the spectrum.
- It is possible to make LIF more quantitative if one measures the quenching partners at the same time via Raman scattering.

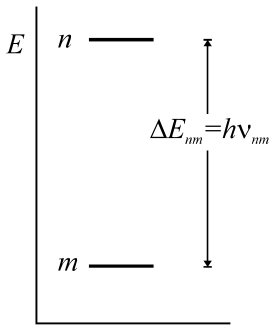


Laser induced fluorescence

Basic equations

- We start with the oversimplified 2-level spectroscopic system (common in LIF).
- During development of the ERT (Lecture 2) we described molecular-photon dynamics using Einstein rate coefficients:

$$\frac{\mathrm{d}N_n}{\mathrm{d}t} = N_m(t)W_{mn} - N_n(t)\left[W_{nm} + A_{nm} + Q_{nm}\right]$$



Laser induced fluorescence

Basic equations

- Where:
  - ▷ N_m is the number density in level m (the level that absorbs),
  - ▷ N_n is the number density in level n (the upper level that is ocupied by an absorption process),
  - ▷ $W_{mn} \equiv B_{mn} \int_\nu \frac{I_\nu}{c} Y_\nu \mathrm{d}\nu$ is the stimulated absorption rate,
  - ▷ $W_{nm} \equiv B_{nm} \int_\nu \frac{I_\nu}{c} Y_\nu \mathrm{d}\nu$ is the stimulated emission rate,
  - ▷ B_{mn} is the Einstein coefficient for absorption,
  - ▷ B_{nm} is the Einstein coefficient for stimulated emission,
  - ▷ A_{nm} is the Einstein coefficient for spontaneous emission,
  - ▷ Q_{nm} is the excited state collisional quenching rate,
  - ▷ I_ν is the spectral laser irradiance, and
  - ▷ Y_ν is the lineshape function.

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Laser induced fluorescence

Basic equations

- It is common to assume N_n is in steady state (the rates of change are much faster than a normal ns laser pulse), making $\mathrm{d}N_n/\mathrm{d}t = 0$.
- Then:

  $N_n = \frac{N_m(t) W_{mn}}{[W_{nm} + A_{nm} + Q_{nm}]}$
- The molecules in level n then emit via spontaneous emission into 4π sterradians:

  Number of photons/(unit volume - sec) $= N_n A_{nm}$; and the emitted power/unit volume is then: $N_n A_{nm} h\nu$
- In these expressions the N_n we have been using is number of molecules n per unit volume. To get the total number of photons we have to multiply by the sample volume V:

  Emitted power is then: $N_n V A_{nm} h\nu$.

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Laser induced fluorescence

Basic equations

- When we do LIF measurements we collect light from a fairly small solid angle ($\Omega =$ lens diameter/distance^2), so the fluorescence signal collected is given by:

  $S_F = N_n V A_{nm} h\nu \frac{\Omega}{4\pi}$

  using $\Omega/4\pi$ as the fraction of the total emission that is collected by our optics.
- In the weak to moderate excitation limit, assume the rate of stimulated emission is low compared to the other terms:

$$S_F = \underbrace{\eta}_{\text{syst. efficiency}} \underbrace{(N_m W_{mn} V)}_{\text{photons abs./sec}} \underbrace{\left[\frac{A_{nm}}{A_{nm}+Q_{nm}}\right] h\nu}_{\text{fluorescence yield}} \underbrace{\frac{\Omega}{2\pi}}_{\text{frac. collected}}$$

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Laser induced fluorescence

Basic equations

- It is possible to get a decent estimate of V by measuring the beam diameter and working out the overlap with the collection optics.
- The quenching rate Q_{nm}, however, can be a serious problem. It depends upon the collision rate (a function of temperature) and the collision partners (some quench much more effectively than others). In a turbulent flame it is very difficult to know all of the local quenching partner concentrations.
- When we do experiments we involve many energy levels, not just two, and we spectrally filter the LIF to avoid problems like elastic scattering of the pump laser light. Our rate equation model would then have to model all of these population/energy transfer processes to calculate how much fluorescence would end up in the band we detect. LASKIN is a code at the University of Bielefeld that models all of these processes, but mostly just for OH.

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Laser induced fluorescence

Saturated fluorescence

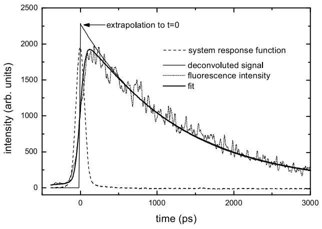
- Saturated fluorescence is an idea to escape the Q_{nm} problem (we discussed saturation in Lecture 2). Here we have such high laser intensity that W_{nm} (the stimulated rate) dominates over the spontaneous and quenching rates, and so they can be eliminated from the equations to get:

  $$S_F = (N_m V)\left(\frac{g_n}{g_n+g_m}\right) A_{nm} h\nu \frac{\Omega}{2\pi}.$$

- In practice is is not possible to saturate fluorescence fully. Saturation requires very high laser irradiance. The edges of a Gaussian cross section beam will never reach saturation irradiance, and the trailing edge of a ns pulse dies away slowly, so the tail of the pulse does not saturate either.

Picosecond LIF

- Picosecond laser pulses have bandwidth that overlaps well with absorption lines, but they are short in time (1 ps = 10^{-12} sec).
- If we excite LIF with a short pulse (much shorter than quenching times) and then time-resolve the fluorescence decay we are looking directly at the effect of quenching.
- And if we extrapolate the LIF curve back to the time of the pulse arrival, that indicates a "quench free" LIF measurement.
- Because a fast detector is required, this is usually a single point measurement.



Short-pulse techniques: Picosecond fluorescence, energy transfer and 'quench-free' measurements, A. Brockhinke, and M. Linne, chapter 4 of the book *Applied Combustion Diagnostics* edited by K. Kohse-Höinghaus and J. Jeffries, Taylor and Francis, New York, NY, ISBN 1-56032-913-0, (2002)

Laser induced fluorescence

Calibrated LIF

- Because of the difficulties quantifying LIF, it is common to calibrate the measurement.
- As one example, engine people like to use LIF of fuel tracers (e.g. keytones) to image the equivalence ratio as a function of position. To quantify the measurement requires calibration; tracers have very broad and unstructured spectra that can't be modeled cleanly like a diatomic spectrum can. The procedure is to set up the entire LIF system around an optically accessible engine and then mix known quantities of the tracer in the intake manifold. In the cylinder the mixture is uniform and at a known concentration, so the measured LIF signal can be related to a known concentration. It's necessary to stay in the linear LIF regime (stay away from saturation) but high laser energy can damage windows anyway.

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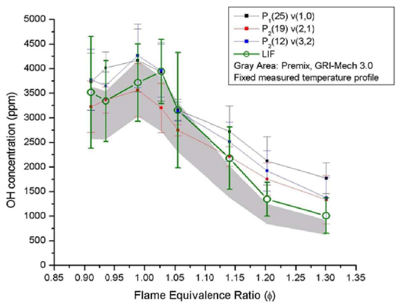
Laser induced fluorescence



Calibrated LIF

- LIF can also be calibrated with CRDS (here CRDS on three different lines), using the same laser used for LIF. Here it was calibrated at $\phi = 0.96$ and the other LIF points (other values of ϕ) are scaled for quenching (changes in T and collider mix), but not re-calibrated.

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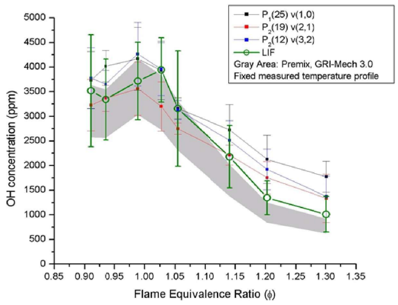
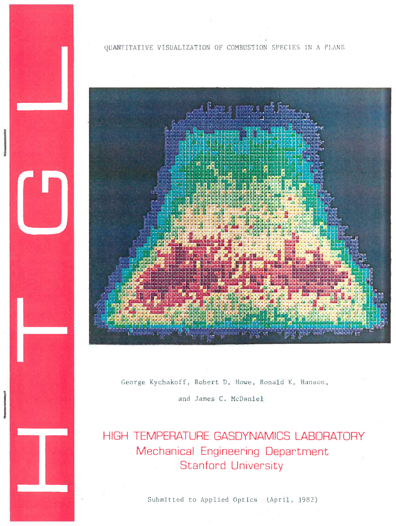
Laser induced fluorescence



Calibrated LIF

- The uncertainties are caused by flame fluctuation and temperature uncertainties.
- The calibrated LIF data agree well with PREMIX simulation using GRImech.
- CRDS has a problem at rich conditions: other absorbers interfere and it's best to calibrate lean - and look at the spectra carefully.

Planar LIF (PLIF) imaging



H T G L

QUANTITATIVE VISUALIZATION OF COMBUSTION SPECIES IN A PLANE

George Kychakoff, Robert D. Howe, Ronald K. Hanson,

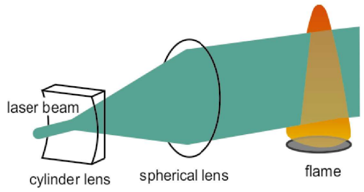
and James C. McDaniel

HIGH TEMPERATURE GASDYNAMICS LABORATORY
Mechanical Engineering Department
Stanford University

Submitted to Applied Optics (April, 1982)

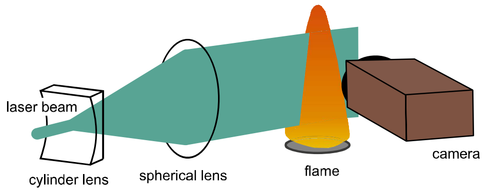
- The very first presentation on PLIF was given in 1982 by George Kychakoff at a meeting of the Western States Section of the Combustion Institute.
- The biggest advancement since then has been in lasers and cameras.

Planar LIF (PLIF) imaging



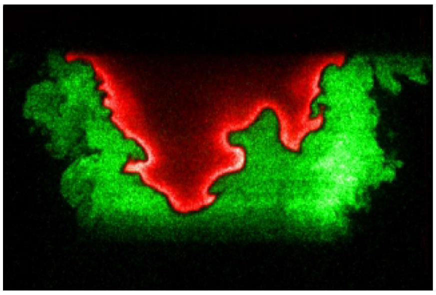
- Spread a laser beam into a sheet by first expanding it in the vertical direction only using a cylinder lens.
- Then collimate the vertical and focus the horizontal with a spherical lens.
- This is how ALL planar laser imaging techniques produce the planar laser-flame interaction.

Planar LIF (PLIF) imaging



- The camera views the laser plane at 90° to the plane.
- PLIF cameras have to be able to sense low light levels (e.g. use an image intensifier, a back-illuminated CCD, or an electron multiplying CCD).
- High-speed systems use an image intensifier.

A PLIF example



- PLIF in a low swirl burner at the University of Lund.
- Green indicates unburned acetone used as a fuel tracer.
- Red is post-flame OH.

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PLIF of fuel tracers

- We often want to see when liquid fuel has evaporated, where the vapor goes, and what is the spatial variation of equivalence ratio.
- Normal hydrocarbon fuels fluoresce quite strongly and over a very broadband region, in both liquid and vapor forms. They are not convenient markers for liquid or vapor.
- As an alternative, it is common to use several pure hydrocarbons that don't fluoresce as a surrogate fuel, and then to mix a fluorescent tracer into the surrogate fuel. Here we will discuss an example from Chalmers University†.

† M. Andersson and J. Wärnberg, "Application of laser-induced fluorescence for imaging sprays of model fuels emulating gasoline and gasoline/ethanol blends" Proceedings ICLASS 2009-189, (2009).

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PLIF of fuel tracers

- This is the gasoline surrogate used by Andersson and Wärnberg.
- And the tracers that replaced just 5% of the corresponding gasoline component with nearly the same boiling point, one at a time.

Gasoline spray studies

Component	vol. %	$T^{\circ}_{bp} C$
isopentane	15	30
cyclopentane	15	50
isooctane	45	99
cyclooctane	18	151
decalin	7	190

Component	$T^{\circ}_{bp} C$
acetone	56
3-petanone	101
methylcyclohexanone	165

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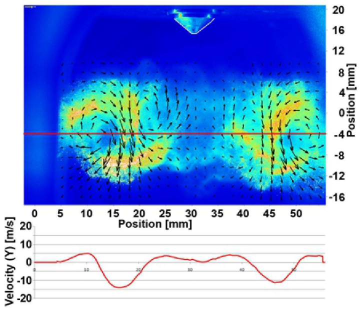
PLIF of fuel tracers

Gasoline spray studies

- The injector was a piezo-actuated hollow cone injector for gasoline direct injected engines, spraying into a high pressure and temperature spray research chamber.
- First, PIV in a plane across the center of the spray showing that two toroidal vortex structures are created.



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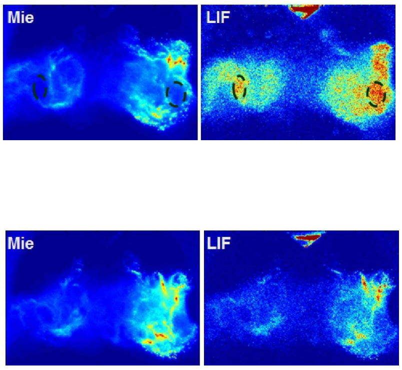
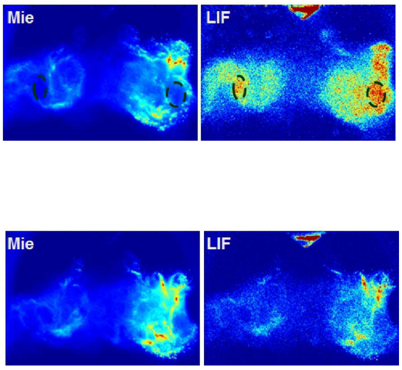
PLIF of fuel tracers



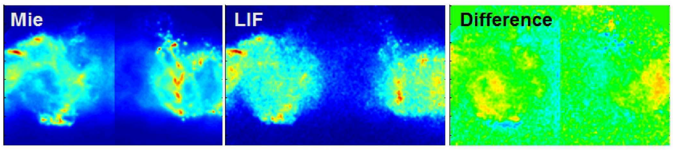
- An example with acetone tracer (the light end), at 90 C and 6 bar in the chamber. The spray is actually symmetric. The laser plane entered from the right and was scattered away from the left had side.
- Only the liquid scatters ('Mie') while both liquid and vapor fluoresce (LIF), so one must subtract the Mie image from the PLIF image to get vapor.
- The corresponding image for the heavy end tracer.

PLIF of fuel tracers



- One can see that the light end vaporized and the vapor was pulled into the core of the vortex.
- Under the same conditions the heavy end did not vaporize appreciably.
- The placement of vapor relative to the spark plug location has a big effect on cycle-to-cycle variability.

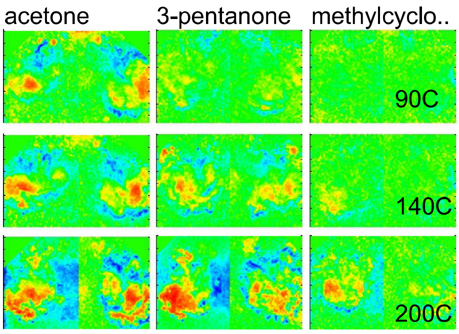
PLIF of fuel tracers



Green – zero difference
Orange – LIF stronger
Blue – Mie stronger

- Here the Mie image is scaled and subtracted from the LIF image.
- By looking at the colors one can detect where vapor is dominant.

PLIF of fuel tracers



- Results for all 3 tracers at 3 different temperatures.
- Under the same conditions the heavy end did not vaporize appreciably until 200C was reached.

Next topic

Rayleigh/Raman

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Advanced Laser Diagnostics for Combustion Research

Lecture 13: Applications of Rayleigh and Raman scattering

Mark Linne

University of Edinburgh

Tsinghua-Princeton-CI Summer School on Combustion
July 11 - 17, 2021

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Topics

Rayleigh and Raman scattering

- Rayleigh scattering measurements
- More about Raman scattering
- Raman scattering in turbulent flames
- Raman used in IC engines

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Molecular scattering

- To recap from lecture 7, the characteristic molecular times are:
  - ▷ electronic motion 10^{-16} sec
  - ▷ vibration 10^{-13} sec
  - ▷ collision interaction 10^{-12} sec
  - ▷ rotation 10^{-10} sec
  - ▷ radiative lifetime $10^{-6} - 10^{-8}$ sec
- Electronic motion is incredibly fast relative to the other time scales.
- Molecular scattering happens when the incoming electromagnetic wave is non-resonant with a spectroscopic transition, but it injects energy into the electron alone, setting it in motion (establishing a "virtual energy level"). That's the "excitation" part of scattering.
- Once excited, the electron very rapidly "re-radiates" energy, which is the scattered light.

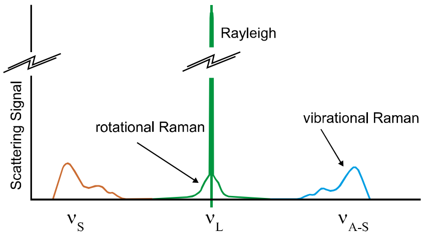
Rayleigh scattering is:

- A non-resonant, elastic ($\nu_{\text{Raman}} = \nu_{\text{laser}}$) scattering technique.
- Spatially resolved (not line-of-sight), and strong enough for imaging.
- Normally a pulsed technique for the gas phase.
- A linear technique (the signal scales with I).
- It is background-free if the laser does not excite fluorescence from some molecule, if Mie scattering from drops or particles is avoided, and if scattering from surfaces is removed.
- A way to detect density and hence temperature if pressure is constant.

Raman scattering is:

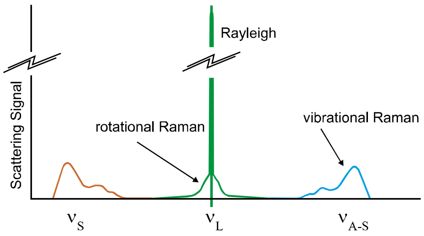
- A non-resonant, inelastic ($\nu_{\text{Raman}} \neq \nu_{\text{laser}}$) scattering technique. It is a spectroscopic technique that does not involve *direct* absorption of a photon to change state (see below for an explanation).
- Spatially resolved (not line-of-sight) - but too weak to allow imaging in most cases.
- Normally a pulsed technique for the gas phase.
- A linear technique (the signal scales with I).
- It is not background-free because the Rayleigh signature is very close in wavelength and therefore challenging to suppress. Moreover, fluorescence and laser induced incandescence of particles can interfere.
- A way to detect multiple major species and temperature in a single shot.

Rayleigh and Raman scattering



- The elastically scattered Rayleigh light is intense, while the Raman scattering process is much weaker.
- If you think like an electrical engineer, Raman scattering is analogous to an RF mixer; the interaction puts sum and difference frequency sidebands on the carrier (the carrier is the Rayleigh response here).
- The carrier mixes with ro-vibrational modes of a molecule to make sidebands.

Rayleigh and Raman scattering



- The Raman signature comes from all of the rotational-vibrational transitions in all of the 'Raman active' molecules, so it is possible to detect a number of species simultaneously.
- The Raman response is very weak so it is possible to detect only major species, and those only at a single point or along a line (not in a plane).
- If one spectrally resolves an entire vibrational manifold, one can infer temperature.

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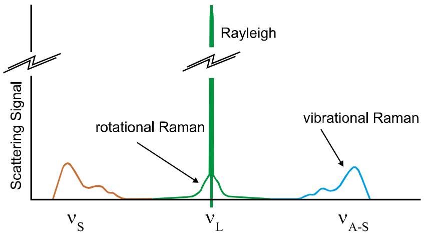
Rayleigh and Raman scattering



- When frequencies are shifted lower (more red) the Raman bands are called 'Stokes', and when higher the bands are called 'Anti-Stokes'.
- One can calibrate the system using known species (e.g. N_2) signatures that are built into the same spectrum.
- When combined with LIF of a minor species, Raman can provide LIF quencher species information.

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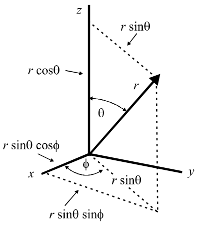
Rayleigh scattering

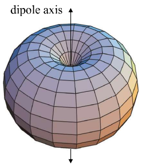
- Recall that for Rayleigh scattering we wrote the radiant intensity as (in Lecture 4):

  $$\frac{\mathrm{d}P}{\mathrm{d}\Omega} = \frac{4\pi^2\nu^4(n-1)^2}{N^2}\sin^2\theta\ I$$

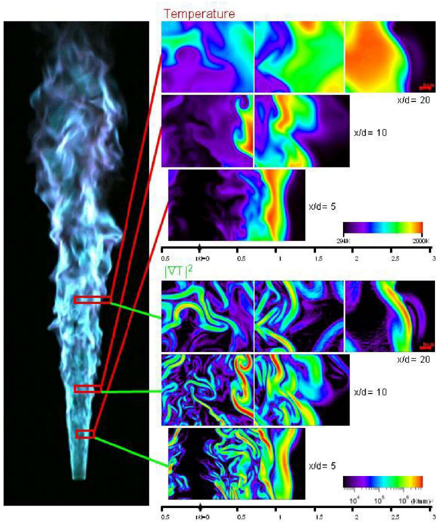
  where:

  ν is frequency expressed in wavenumbers in this case,
  n is the real index of refraction,
  N is the number density of scatterers, and
  I is the irradiance of incoming light.





Rayleigh scattering



- You have already seen this example Rayleigh scattering image of temperature in a turbulent flame, with highly resolved turbulent structures (by Jonathan Frank at Sandia).
- These images are used to extract a form of scalar dissipation from this jet.

Rayleigh scattering

- Here is a Rayleigh scattering image by Stina Hemdal at Chalmers University.
- This is an image through a piston crown looking at a SGDI head. The spray is to the right (via Mie scattering from the laser), and Rayleigh scattering from fuel vapor is to the left (hydrocarbons have a much stronger Rayleigh cross section than does air).
- The fuel Rayleigh image is representative of equivalence ratio.

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Raman scattering

- When we solved the Lorentz atom problem in Lecture 3, we discussed how an electric field can induce a dipole via the polarizability α (equation 17):

  $$\vec{\mu} = \alpha \vec{E}_m(\vec{r})$$

  where $\vec{\mu}$ is the induced dipole moment.
- The macroscopic polarization is then made up of an ensemble of these polarizations states, and they give rise to the scattered light.
- A classical way to look at Raman scattering is to consider a problem similar to the Rayleigh treatment, including the notion that scattering = excitation (via the polarizability) + reradiation (recall the torus radiation pattern from the oscillating dipole).

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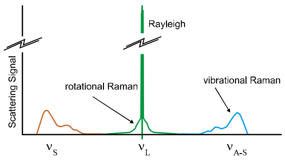
Raman scattering

- The scattering process is very fast, and so the optical interaction is with the electron cloud.
- Rayleigh scattering is related to an electron cloud that is fairly static, while Raman scattering is associated with disturbances to the electron cloud induced by nuclear motion.
- We therefore write the polarizability in an expanded form:

  $$\alpha = \alpha_\circ + \left(\frac{\partial \alpha}{\partial Q}\right)_\circ Q$$

  where Q is the normal coordinate of a vibrational mode.
- Then $\alpha_\circ$ is the Rayleigh polarizability and $\left(\frac{\partial \alpha}{\partial Q}\right)_\circ Q$ gives rise to the Raman signal.

Raman scattering



- A very simple minded way of looking at it would go as follows - assume a diatomic molecule with the nuclei that vibrate in simple harmonic motion, so that $Q = Q_\circ \cos \omega_v t$.
- Assume the electric field is $\vec{E}_\circ \cos \omega_\circ t$.
- Then:

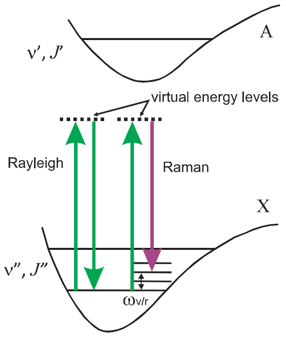
  $$\vec{\mu} = \left[\alpha_\circ + \left(\frac{\partial \alpha}{\partial Q}\right)_\circ Q_\circ \cos \omega_v t\right] \vec{E}_\circ \cos \omega_\circ t,$$

  or

  $$\vec{\mu} = \underbrace{\alpha_\circ \vec{E}_\circ \cos \omega_\circ t}_{\text{Rayleigh}} + \underbrace{\frac{Q_\circ \vec{E}_\circ}{2} \left(\frac{\partial \alpha}{\partial Q}\right)_\circ \left[\cos \overbrace{(\omega_\circ - \omega_v)}^{\text{Stokes}} t + \cos \overbrace{(\omega_\circ + \omega_v)}^{\text{Anti}-\text{Stokes}} t\right]}_{\text{Raman}}$$

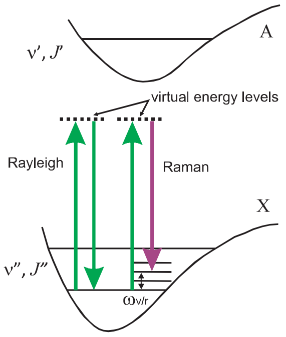
Raman scattering

- For Rayleigh scattering, the energy of the incoming photon is the same as that of the redirected outgoing photon.
- In the case of Raman there is energy exchange. The laser is not resonant with a transition (here the photon has too little energy for an electronic transition, but too much for a ro-vibrational transition). The laser therefore does not cause a population shift to an upper level before light is scattered, but the incident photons take energy (anti-Stokes) and lose energy (Stokes).



Raman scattering

- The fact that the photon can add energy to the fast-responding electron cloud during the excitation step explains the "virtual energy levels".
- When a photon with shifted frequency (Stokes shifted in this image) is re-radiated, some energy is left behind in the electron and ultimately it gets deposited into the ro-vibrational level shown.
- Anti-Stokes shifting requires additional energy for the re-radiated photon, and ultimately it comes from the molecular ro/vibrational motion.



Raman scattering

- The scattering amplitudes are not so simple as our discussion has implied; the polarizability is actually a tensor and we have to think about various polarization orientations:

  $\vec{\mu} = \vec{\alpha} \cdot \vec{E}_m(\vec{r})$,

  but the Raman shifts are simply the sum and difference frequencies.
- The quantum mechanical picture ("'Placzek polarizability theory") includes a classical electromagnetic wave and a quantum mechanical molecule.
- The outcome includes selection rules, $\Delta v = +1$ and $\Delta J = \pm 2$.
- Not all vibrational modes are "Raman active", the cross section depends on a quantum mechanical inner product and if it goes to zero the mode is not Raman active.

Raman scattering

- The final, space averaged form that is used is fairly simple, assuming we collect the signal at 90° to the laser beam:

  $P_R = P_i \, N \left(\frac{\partial\sigma}{\partial\Omega}\right) \Omega \ell \epsilon$, where

  ▷ P_R is the scattered Raman power,
  ▷ P_i is the incident power,
  ▷ N is the number density of scattering species,
  ▷ $(\partial\sigma/\partial\Omega)$ is the Raman cross section (which is a function of laser wavelength; this term includes all of the serious physics),
  ▷ Ω is the optics collection sold angle,
  ▷ ℓ is the length of the sample volume, and
  ▷ ϵ is an efficiency that takes into account all losses and conversions.

Raman scattering

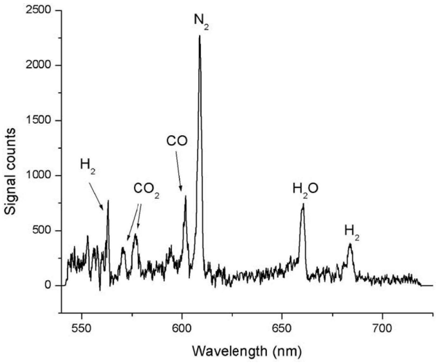
Table: Typical Raman cross sections (units of 10^{-30} cm^2/sr)

Species	**Vibrational frequency** (cm^{-1})	**Vibrational cross sections** at wavelengths of:		
		337 nm	488 nm	532 nm
N_2	2330.7	3.5	0.68	0.46
H_2	4160.2	8.7	1.32	0.94
O_2	1556	4.6	0.72	0.65
CO	2145	3.6	0.71	0.48

from Laser Diagnostics for Combustion Temperature and Species,
A.C. Eckbreth, Gordon and Breach, 1996

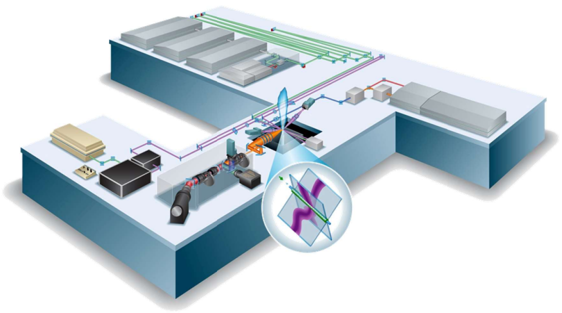
- Often the Raman signal is just calibrated.

Raman scattering



Single-shot Stokes Raman spectrum from a spray flame excited by a $532\,nm$ pulse with $\sim 300\,mJ/$pulse energy, from a project evaluating the effects of droplets and high hydrocarbon concentrations on the diagnostic.

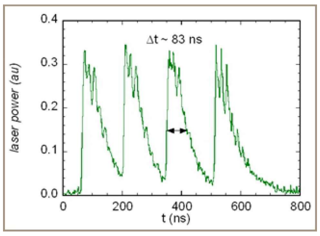
Raman scattering



- Raman can be used in applications where one wants to know many major species all at once, and this can be done along a line so there is some spatial information.
- We can use Rob Barlow's system at Sandia Labs as an example.

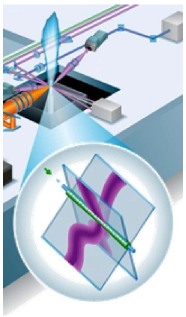
Raman scattering

- Four pulsed lasers are used because the Raman signal is small and it scales with total irradiance; so higher irradiance produces stronger signals. By combining pulses they get high irradiance without using a single pulse that has too much energy.
- In their flames, Raman provides access to temperature, N_2, O_2, CH_4, CO_2, H_2O, H_2, and CO.
- They achieve spatial resolution smaller than 100μm along a 6 mm segment in the flame.



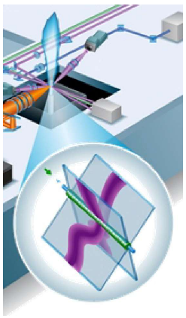
Raman scattering

- Raman is excited along a line through their flame, and it is collected and dispersed in an imaging spectrometer. On one axis of the spectrometer they get distance along the Raman line and on the other axis they acquire the spectrum.
- To know where they are with respect to the flame front (e.g. for conditional statistics) they use 2 crossed OH PLIF sheets that intersect along the Raman line.
- Then they even know the flame normal with respect to the Raman line.

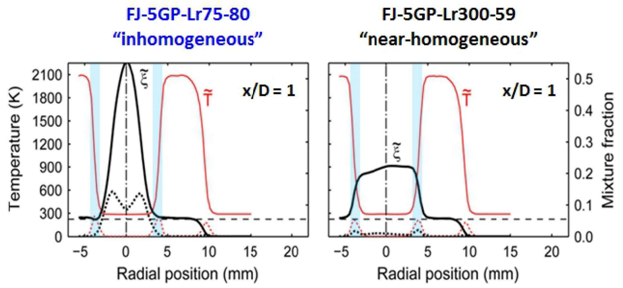


Raman scattering

- To remove background light like flame emission they use a very fast mechanical shutter.
- They then bin the spectral signals in blocks that integrate across specific Raman features to maximize signal.
- The binned signals are then related to species concentration and temperature using a combination of modeling and calibration.
- This measurement is often combined with LIF and the Raman data can be used to correct (scale) the LIF for collisional quenching.

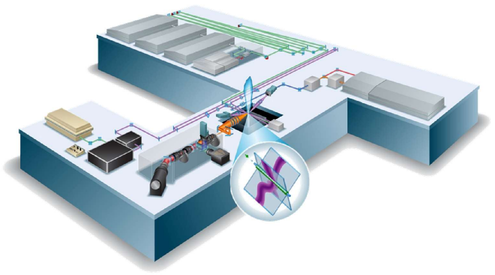


Raman scattering



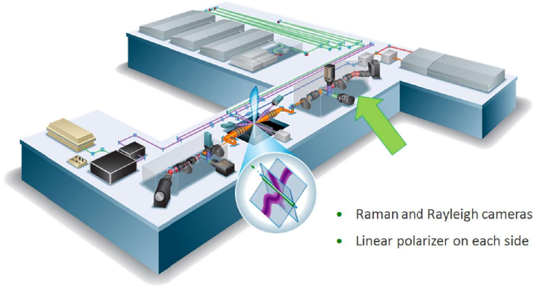
- Here are some typical example results for a piloted jet flame, where ξ is the mixture fraction and T is temperature.

Raman scattering



- Because Raman signals are weak, interferences can be a big problem. LIF (e.g. from the C_2 Swan bands) is a good example.
- In addition, this binning system is not spectrally resolved, and for hydrocarbon detection one needs better spectral resolution.

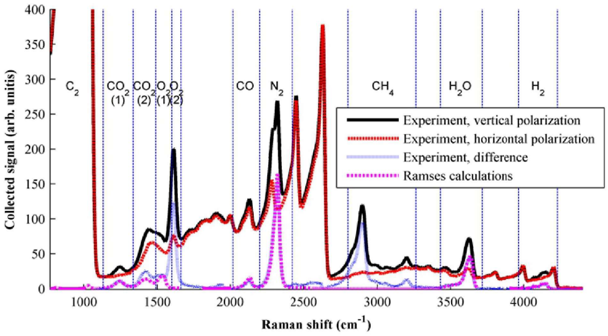
Raman scattering



- Raman and Rayleigh cameras
- Linear polarizer on each side

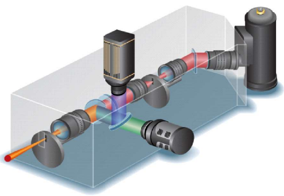
- Raman signals are strongly polarized while fluorescence interference and flame luminosity are unpolarized.
- They use simultaneous detection of orthogonal polarization components to remove interference by subtraction.

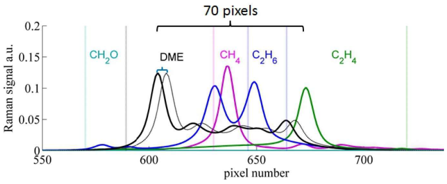
Raman scattering



- Averaged spectra show effective suppression of interferences.
- The vertical lines indicate regions of binning when using the single-shot system.

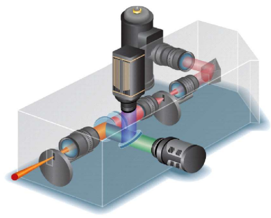
Raman scattering

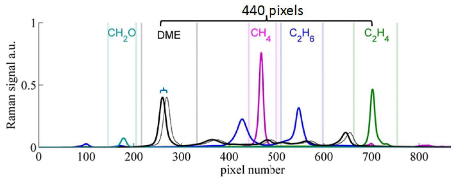




- The normal imaging spectrometer has low spectral resolution because it is very broad-band; it samples a very wide spectrum to get many species.
- Here just the hydrocarbon spectral section is shown, and there are not many pixels to capture a complex set of spectra.

Raman scattering





- In response, they use both a low resolution and high resolution system at the same time, to capture more details.
- The high resolution system detects differences between the various hydrocarbons of interest.

Next topic

Four-wave mixing and CARS

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Advanced Laser Diagnostics for Combustion Research

Lecture 14: Coherent anti-Stokes Raman spectroscopy

Mark Linne

University of Edinburgh

Tsinghua-Princeton-CI Summer School on Combustion
July 11 - 17, 2021

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Topics

Coherent anti-Stokes Raman spectroscopy (CARS)

- Introduction to the underlying theory
- Classical vibrational CARS and various broadband techniques
- Short pulse CARS
- Short pulse CARS line imaging

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Coherent anti-Stokes Raman spectroscopy (CARS)

CARS is -

- A non-resonant spectroscopic technique - sort of - it detects spectroscopic signatures but does not cause a change of quantum level.
- Spatially resolved (when used as a crossed-beam technique).
- Normally a pulsed technique for the gas phase.
- A non-linear technique (the signal scales with I^3).
- It is background-free.
- A way to detect temperature and some species concentrations.
- A parametric process - meaning that energy is conserved automatically by the way the four waves mix (more on this point later).

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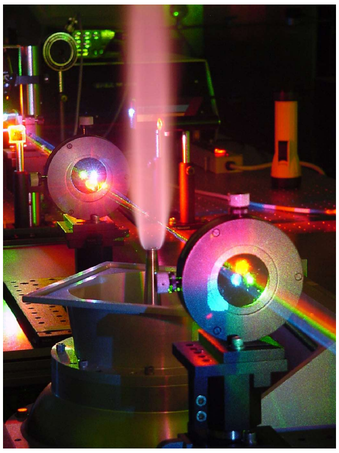
Coherent anti-Stokes Raman spectroscopy (CARS)



- Here, beams at several wavelengths (sometimes several lasers) are crossed in the flame to define a sample point.
- The beams excite 'Raman coherences' in a nonlinear fashion and a probe beam reads them out.
- A fourth signal beam exits the flame, carrying an entire nonlinear Raman spectrum.
- This technique produces a strong signal because it excites resonant Raman coherences and the entire signal propagates in one direction.

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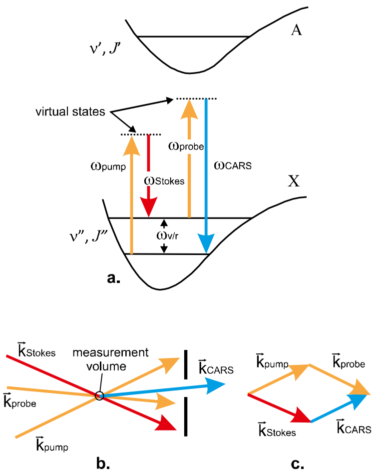
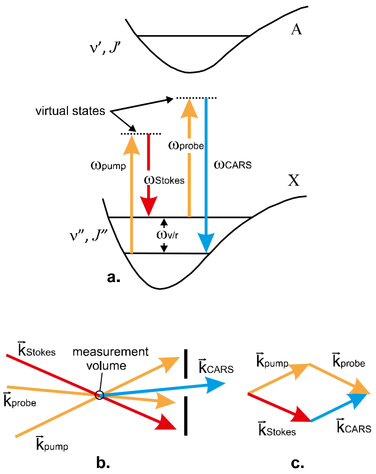
CARS



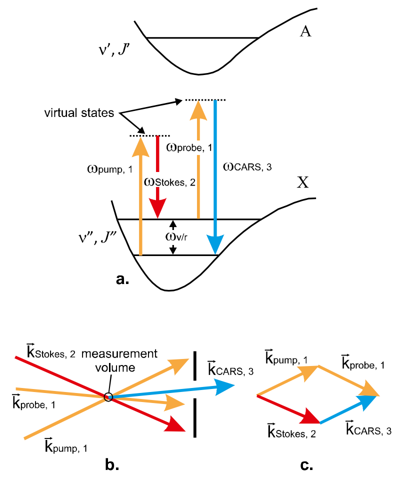
- Beam names: 'Pump' because it helps drive dipoles, 'Stokes' because it is red-shifted relative to the pump, and 'Probe' because it reads out the Raman coherences.
- The difference between the Pump and Stokes beams (generating a beat) is matched in energy to one or more ro-vibrational transitions in the molecule.
- It's two-photon excitation of a Raman coherence.

CARS



- The frequencies of the Pump and Stokes beams do not excite the molecule to an actual quantum level $(\nu_{\mathrm{ro-vib}} < \nu_{\mathrm{laser}} < \nu_{\mathrm{A}\leftarrow\mathrm{X}})$, hence the label "virtual state" again.
- An additional point - the three input beams have to be arranged at specific angles relative to each other ('phase matching') and then the signal beam comes out at a known location and angle.

CARS



- In the first part of this presentation we will label the Pump beam with ’1’, the Stokes beam with ’2’ and the Probe beam with ’1’ (in this implementation both Pump and Probe beams have the same frequency; in many cases one beam is split into two and used for both).
- We will change designations when we get to rotational CARS.

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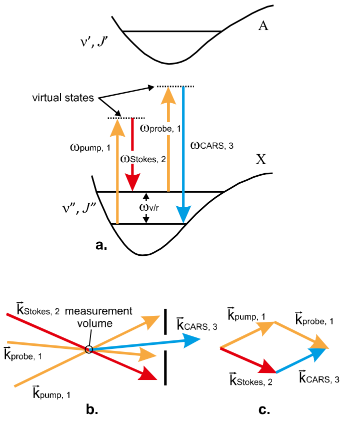
CARS

- One way to think about this:
  - ▷ As we have already discussed, scattering is a very fast process; it happens much faster than population changes (changes in quantum levels).
  - ▷ We rely on the Born Oppenheimer assumption again; that the electron cloud responds quickly but the nuclei do not.
  - ▷ This is a dipole interaction; meaning the electromagnetic waves interact with an electron cloud and here the electron cloud responds instantly.



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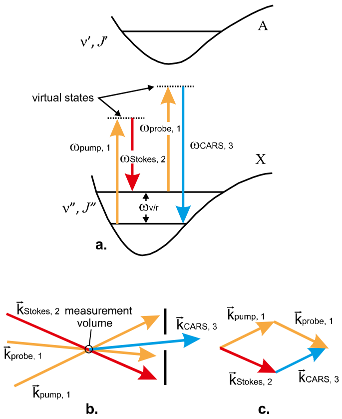
CARS

- One way to think about this:
  - ▷ We can think of a relatively stationary part of the electron cloud that gives rise to Rayleigh scattering (it is a steady oscillation driven at the laser frequency), and a component of the electron cloud that is affected by the rotational and vibrational motion of the nuclei that gives rise to Raman scattering (that part oscillates at sum and difference frequencies). Here we focus on an electron cloud that has the harmonics of the nuclear motion embedded in it, an oscillatory signature imposed on the electrons.



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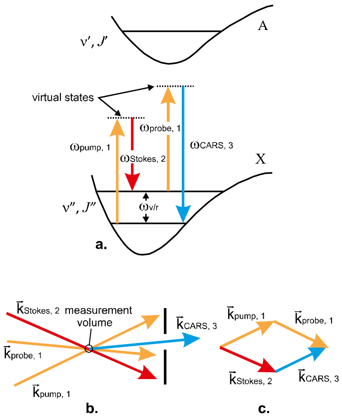
CARS

- One way to think about this:
  - ▷ The incoming Pump and Stokes beams generate a beat at their frequency difference ($\omega_1 - \omega_2$), and that beat coincides exactly with a ro-vibrational transition in the molecule ($\omega_{\mathrm{v/r}}$) the signature of which has been embedded in the oscillatory portion of the electron cloud. These two signatures oscillate in phase (the beat is coherent with the $\mathrm{v/r}$ signature in the electron, the beat excites the Raman coherences).
  - ▷ The Probe beam now interacts with this driven oscillation.



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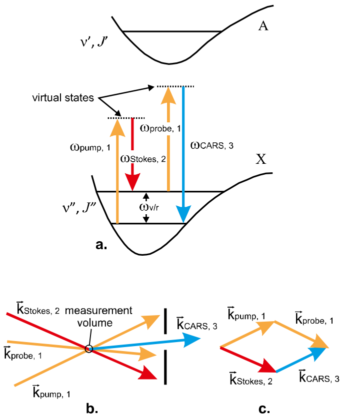
CARS

- One way to think about this:

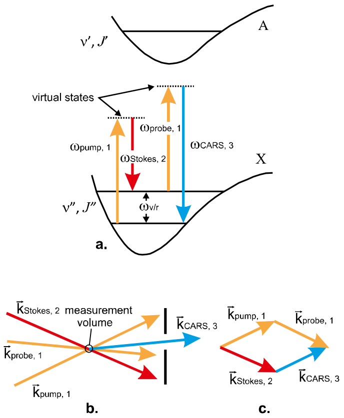
  ▷ One way to describe the interaction is to say that the Probe beam scatters off of a spatial array of these Raman excited, oscillating dipoles at a specific scattering angle (like Bragg scattering off of a grating) with a shifted frequency (similar to the Doppler shift from acoustic fields in an acousto-optic device). That's one explanation for the generation of a CARS beam.



CARS

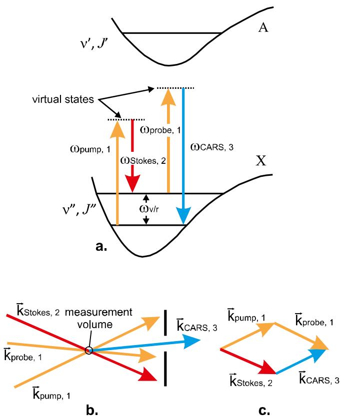
- One way to think about this:

  ▷ Alternatively, we can say that the Probe beam interacts with the excited Raman coherence (the stimulated electronic signature), also driving the electron cloud. The dipole interaction in the electron cloud then develops side-bands on the Probe frequency (Stokes and Anti-Stokes shifts). The dipole oscillation generates electromagnetic waves, albeit a complex collection of them.



CARS

- One way to think about this:
  - ▷ The waves emitted by each dipole are coherent with each other and so they can add up constructively, but in restricted directions - phase matching. The coherently added Anti-Stokes waves form the CARS beam.
  - ▷ This version of the story includes excitation and then re-radiation stages of the scattering process. You will read and hear both versions of the explanation, but this second one is more correct. Unlike Rayleigh or Mie scattering, however, the emitter dipole has a complex oscillatory structure.



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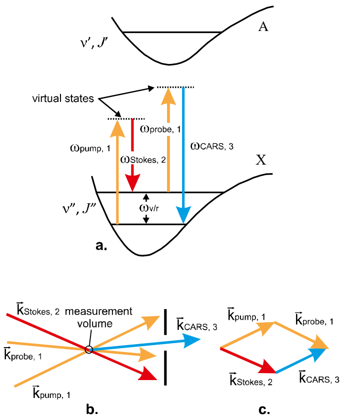
CARS

- There is no energy deposited into molecular quantum levels (at pseudo steady state), although the signal beam leaves with more energy/photon than the probe beam had.
- In this case, CARS is a "parametric process". If we do some bookkeeping on the four waves we find that $\hbar\omega_1 - \hbar\omega_2 + \hbar\omega_1 - \hbar\omega_3 = 0$. There is no net energy exchange.



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CARS

Now more detail

- What's a Raman coherence really?
- The word 'coherence' comes from the density matrix equations of quantum mechanics. These are the equations one must use to describe more exactly the dynamics (especially time dependence) of spectroscopic transitions:
  ▷ We produce a matrix of densities (ρ) where the diagonal elements (ρ_{ii}, ρ_{jj} etc.) represent probability that a molecule will be in state i or j (here we speak more generally about many levels, and label them with variables like i and j). The diagonal elements are called 'populations'.
  ▷ The off-diagonal elements are written ρ_{ij} or ρ_{ji} and they are called 'coherences' because they represent the phase relationship between the wave functions of states i and j (and hence a phase relationship between the transitions and the laser light).

CARS

Now more detail

▷ Coherences are connected to the transition dipole moment leading to, for example, the Einstein A and B coefficients. Those specific ρ_{ij} and ρ_{ji} are agents that, over a finite transition time, feed population from one level to another with the input or loss of energy.

▷ The coherences can actually go in and out of phase with the local radiation field, hence the phenomenon called 'dephasing' (and the effect on line broadening).

▷ For CARS, we have to think in terms of a classical electromagnetic field (at a beat frequency) interacting with Raman coherences (not the same as the coherences related to the A and B coefficients).

▷ It can be thought of as a two-photon interaction that directly addresses the Raman coherences in a way that does not shift population. We make that happen by specific ordering of input photons, by specific wavelength choices, by specific orientation of the input beams, and by looking for the signal in specific locations.

CARS

More detail

- Fine - but in Lecture 3 we quickly discussed nonlinear optics and we described material polarization by:

  $$\vec{P} = \epsilon_\circ \left[\chi^{(1)}\vec{E} + \chi^{(2)}\vec{E}^2 + \chi^{(3)}\vec{E}^3 ...\right]$$

  where each of the nonlinear susceptibilities (the $\chi^{(n>1)}$ terms) is a physical constant associated with various nonlinear optical interactions. And that produced a new wave equation (equation 16):

  $$\nabla^2 \vec{E} - \mu_\circ \epsilon_\circ \frac{\partial^2 \vec{E}}{\partial t^2} = \mu_\circ \frac{\partial^2 \vec{P}_{\mathrm{NL}}}{\partial t^2}$$

  so $\vec{P}_{\mathrm{NL}}$ is a source for a totally new wave (different color, different direction etc.). Absorption and fluorescence are $\chi^{(1)}$ processes, second harmonic generation (a laser 'doubling crystal') uses a $\chi^{(2)}$ process, and CARS is $\chi^{(3)}$.

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CARS

More detail

- In terms of what we have said so far:

  ▷ Equation 16 represents the idea of a classical electromagnetic wave that interacts with a quantum mechanical description, via $\chi^{(3)}$. The three beams interacting are built into $\chi^{(3)}$ and $\vec{P}_{\mathrm{NL}}$.

  ▷ In this description of CARS we talk about the creation of a volumetric distribution of nonlinear polarization states in the medium via the interaction of the three beams (Pump, Stokes, and Probe) and $\chi^{(3)}_{\mathrm{CARS}}$. This distribution of nonlinear polarization states then radiates coherently into the correct direction (the contributions of individual dipoles must add coherently) to produce the CARS beam.

  ▷ We get $\chi^{(3)}_{\mathrm{CARS}}$ from a solution to the density matrix equations, and that's how the Raman coherences come into play.

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CARS

More detail

- One fact we need to emphasize before continuing - for an isotropic medium like a gas there are no $\chi^{(2)}$ processes because they do not occur when the medium has inversion symmetry (under inversion symmetry one gets $P_{\mathrm{NL}}^{(2)} = -P_{\mathrm{NL}}^{(2)}$ and that can be true only when $P_{\mathrm{NL}}^{(2)} = 0$). By it's nature, the collection of molecules in an gas will have inversion symmetry and so $\chi^{(2)}$ processes are not supported.
- Consider the wave equation (a modified equation 16) for the CARS beam (number 3). Assume that the electric field has $\exp(-i\omega_3 t)$ time dependence and remembering that $c = 1/\mu_\circ\epsilon_\circ$:

  $$\nabla^2\vec{E}(\omega_3,\vec{r}) + \tfrac{\omega_3^2}{c^2}\vec{E}(\omega_3,\vec{r}) = -\mu_\circ\omega_3^2\vec{P}(\omega_3,\vec{r})$$

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CARS

More detail

- For this case (no $\chi^{(2)}$ and assuming any response past $\chi^{(3)}$ is avoided):

  $$\vec{P}(\omega_3,\vec{r}) = \vec{P}^{(1)}(\omega_3,\vec{r}) + \vec{P}^{(3)}(\omega_3,\vec{r}) = \epsilon_\circ\chi^{(1)}\vec{E}(\omega_3,\vec{r}) + \vec{P}^{(3)}(\omega_3,\vec{r})$$
- Rearranging the wave equation (including the fact that $\epsilon/\epsilon_\circ = 1 + \chi^{(1)}$):

  $$\nabla^2\vec{E}(\omega_3,\vec{r}) + \tfrac{\omega_3^2}{c^2}\tfrac{\epsilon}{\epsilon_\circ}\vec{E}(\omega_3,\vec{r}) = -\mu_\circ\omega_3^2\vec{P}^{(3)}(\omega_3,\vec{r})$$
- About $\vec{P}^{(3)}$; $\chi^{(3)}$ is a tensor. The situation can be simplified if we assume that all of the beams have the same polarization and that $\omega_{\mathrm{Pump}} = \omega_{\mathrm{Probe}} = \omega_1$. These are not always the case, but under those assumptions:

  $$P^{(3)}(\omega_3,\vec{r}) = P_{\mathrm{CARS}}(\omega_3,\vec{r}) = \epsilon_\circ\chi_{\mathrm{CARS}}E^2(\omega_1,\vec{r})E(\omega_2,\vec{r})$$

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CARS

More detail

- We already assumed a time dependence of the electric field given by $\exp(-i\omega_3 t)$. Now we assume a spatial dependence of:

  $$\vec{E}(\omega_3,\vec{r}) = \vec{E}(\omega_3)\exp(i\vec{k}_3\cdot\vec{r})$$

- The wave equation becomes:

  $$\nabla^2\vec{E}(\omega_3,\vec{r}) + \frac{\omega_3^2}{c^2}\frac{\epsilon}{\epsilon_\circ}\vec{E}(\omega_3,\vec{r}) =$$
  $$-\frac{\omega_3^2}{c^2}\chi_{\mathrm{CARS}}E^2(\omega_1)E^*(\omega_2)\exp[i(2\vec{k}_1-\vec{k}_2)\cdot\vec{r}]$$

  where the * denotes a complex conjugate (necessary to generate the beat).

- The CARS beam experiences maximum growth along the line where $(2\vec{k}_1-\vec{k}_2)\cdot\vec{r}=0$, or along the coordinate $z=(2\vec{k}_1-\vec{k}_2)$.

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CARS

More detail

- Along z, then, the wave equation is:

  $$\frac{\partial^2 E(\omega_3,\vec{r})}{\partial z^2} + \frac{\omega_3^2}{c^2}\frac{\epsilon}{\epsilon_\circ}E(\omega_3,\vec{r}) =$$
  $$-\frac{\omega_3^2}{c^2}\chi_{\mathrm{CARS}}E^2(\omega_1)E^*(\omega_2)\exp[i(2k_1-k_2)z]$$

- Now assume the CARS signal beam is a clean plane wave along z:

  $$E(\omega_3,\vec{r}) = E(\omega_3,z)\exp(ik_3 z)$$

- To get:

  $$\frac{\partial^2 E(\omega_3,z)}{\partial z^2} + 2ik_3\frac{\partial E(\omega_3,z)}{\partial z} = -\frac{\omega_3^2}{c^2}\chi_{\mathrm{CARS}}E^2(\omega_1)E^*(\omega_2)\exp[i\Delta k z]$$

  where $\Delta k = 2k_1 - k_2 - k_3$ is a phase mismatch term.

- If Δk is small then the variation of E over small distances (wavelengths) is small so the second derivative can be neglected.

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CARS

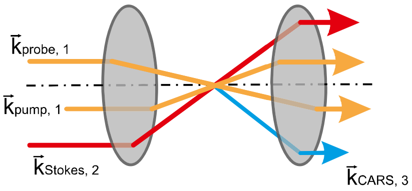
More detail

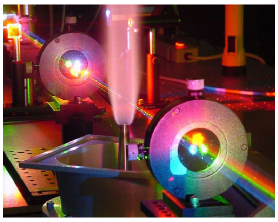
- Solving for E and writing the result as an irradiance:

$$I_3 = \frac{\omega_3^2}{n_1^2 n_2 n_3\, c^4 \epsilon_\circ^2}\, I_1^2 I_2\, |\chi_{\mathrm{CARS}}|^2\, \ell^2 \left(\frac{\sin \frac{\Delta k \ell}{2}}{\frac{\Delta k \ell}{2}} \right)^2 \tag{44}$$

- Equation 44 contains scaling arguments: the result scales with I^3 (a third order process), because it scales with the modulus of the susceptibility squared it scales with density squared, and it scales with interaction length squared.
- Note that for effective signal generation, $\Delta k = 0$, meaning $\vec{k}_3 = 2\vec{k}_1 - \vec{k}_2$, which is the phase matching requirement.

CARS





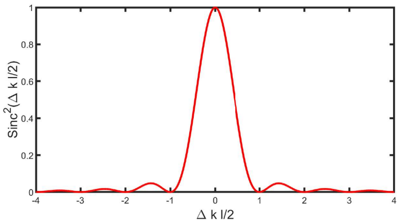
- To work out the phase matching, remember that the various wave vectors ($\vec{k}$) are vectors but the phase match involves magnitude and direction. The magnitude changes with wavelength.
- The two most common forms of phase matching are to make all beams co-linear, or to use the forward "boxCARS" geometry shown.

CARS

More detail

- The term $\left(\frac{\sin\frac{\Delta k\ell}{2}}{\frac{\Delta k\ell}{2}}\right)^2$ in Equation 44

  is actually $\mathrm{sinc}^2\left(\frac{\Delta k\ell}{2}\right)$.
- This form applies to any nonlinear phase matching (so long as Δk is properly defined).
- Anybody who has angle-tuned a frequency doubling crystal has seen this result.



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CARS

More detail

- As mentioned earlier, the physics on the Raman process are contained in χ_{CARS}, which is one of many possible $\chi^{(3)}$'s. The solution involves the density matrix equations and the outcome is a large number of possible $\chi^{(3)}$ processes. The mechanics of that development are beyond the scope of this class.
- For the situation already discussed, the outcome is the following:

  $\chi_{\mathrm{CARS}} = \sum_l (\chi' + i\chi'')_l + \chi_{\mathrm{nr}}$

  where the summation is over the possible Raman transitions l, and nr denotes 'non-resonant', meaning not associated with the Raman transitions. The nonresonant susceptibility can arise via coupling to other virtual states or other sources of interaction.
- It's interesting to note that, just like the Lorentz atom solution, we find a real and imaginary part of the susceptibility. If we plot their spectral shapes, for high concentrations of the species of interest, they look quite similar to the real and imaginary Lorentz spectra presented in Lecture 3.

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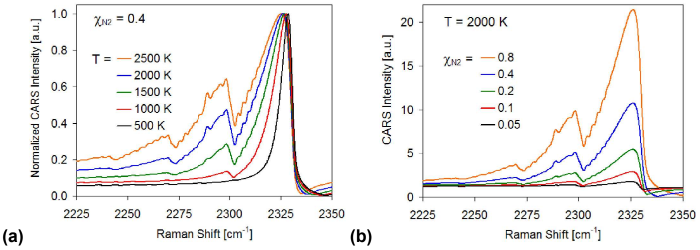
CARS

More detail

- Because I_3 depends upon $|\chi_{\mathrm{CARS}}|^2$, this nonresonant (NR) background can cause a significant interference in the CARS signal.
- For nanosecond type laser systems the main technique for reducing the NR background was to use polarization tricks to minimize that signal, but polarization can not be used in practical systems like an optical engine because the windows will become birefringent when pressurized (stress induced birefringence) and the polarization of the CARS beam will be un-knowable.
- The nonlinear polarization states of the Raman coherences have a longer lifetime than the NR component, and so if short pulses (picosecond or femtosecond) are used, and if the Probe is delayed in time a bit, the CARS signal can be generated with very little NR background. Nanosecond systems cannot do this.

CARS

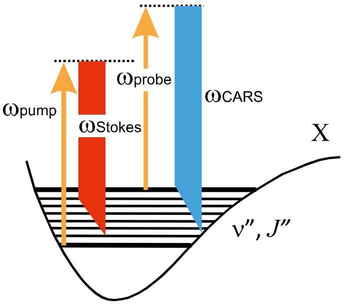


- Here are typical CARS spectra of nitrogen (synthesized in this case). There are many different ways to measure such a spectrum, but for now imagine that we take an averaged scan over time and slowly tune the Stokes beam across this spectrum.
- The vibrational spectral fit is strongly temperature dependent (good thermometer).

Example applications of CARS

Broadband CARS

- This is the simplest implementation of broadband CARS (BB-CARS).
- Here a broadband dye laser is used for the Stokes beam, and so the CARS mixing process happens simultaneously over the entire rotational manifold in the vibrational transition shown.
- This allows one to capture the entire spectrum in a single laser shot, and from that it is possible to acquire temperature via N_2 CARS, for example.
- One can also use a broadband Pump (Dual BB-CARS) to capture several molecules in one shot.



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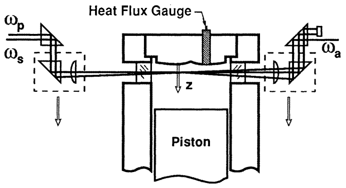
Example applications of CARS

Broadband CARS

- In 1991, Bob Lucht and co-workers used nanosecond BB-CARS to measure temperatures in the boundary layer of a motored engine (old images!).
- They used the green output (532 nm) from their pump laser as the Pump and Probe beams and then used a broadband dye output as the Stokes beam. They used the forward BoxCARS geometry for small sample volume and less disturbance from thermal index gradients.



R. P. Lucht, D. Dunn-Rankin, T. Walter, T. Dreier, S. C. Bopp, SAE Technical Paper No. 910722

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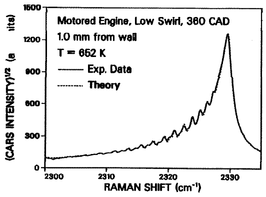
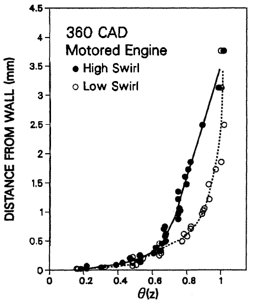
Example applications of CARS





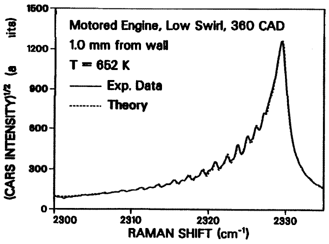
Broadband CARS

- They achieved good quality single-shot spectra and fits to the spectra.
- The results were thermal boundary layer measurements.
- Heat transfer from engines is becoming a very important topic with engine boosting and downsizing. CARS is no longer used in engines very much, but stay tuned for some interesting results.

Example applications of CARS

Broadband CARS

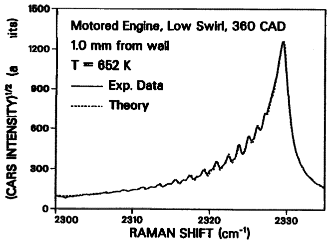
- Did you notice how indistinct the spectrum was?
- At high pressures, collision broadening is greater so lines can smear out, but there is also a narrowing of the overall feature.
- This narrowing is caused by line mixing, which occurs between closely spaced lines. At high pressure, collisions can cause population changes between states that are close to each other, and this goes on while the measurement is underway.



Example applications of CARS

Broadband CARS

- This line mixing favors lower J states, so the spectral manifold can be narrowed, especially at a band head where lines are close.
- Line mixing must be modeled by considering all of the potential rotational states and how they can be interchanged, using what is called the "G-matrix".
- Getting the lineshape models right is a major challenge for CARS, especially in the nanosecond variety when the NR background is also present (it also has a spectral structure, albeit broad).



Short pulse CARS

- There has been a recent renaissance in CARS research based on the use of short pulse [picosecond (ps, 10^{-12} s) and femtosecond (fs, 10^{-15} s)] lasers[§].
- As discussed in the Laser lecture (number 10) short pulses are based upon a Fourier transform limit; that the shortest pulse possible from a light source is given by the Fourier transform of the bandwidth. Broad bandwidth generates short pulses (and only cw single-frequency lasers have very narrow bandwidth).
- Short pulses have high irradiance (W/m^2) at the peak of the pulse because the pulse is so short. Short-pulse lasers do not need to have the same energy/pulse to perform CARS as does a ns laser.
- Short pulses generated by a mode-locked laser (and perhaps amplified past the mode-locked laser) have excellent amplitude stability, spectral stability, and timing jitter.

[§] S. Roy,J.R. Gord, A.K. Patanik, Progress in Energy and Combustion Science, 36, (2010).

Short pulse CARS

ps CARS

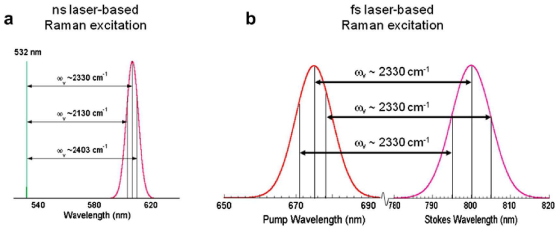
- In the picosecond regime, the bandwidth of the laser is fairly broad compared to a narrow-band (injection seeded) pulsed (10 ns) Nd:YAG laser. Typical 60 ps bandwidths are broader than an absorption line but not by much, and hundreds of fs can hit an entire manifold.
- As mentioned previously, if a ps laser is used for CARS it is possible to delay the probe pulse because the Raman coherences have a lifetime that is longer than 100 ps but the NR signal dies away almost instantly. The Probe delay will reduce the observed NR background by orders of magnitude and it will affect the measured temperature by a few percent (the spectra evolve weakly over time but that evolution can be modeled).

Short pulse CARS

Hybrid fs/ps CARS

- A short pulse version of Dual BB-CARS can be developed by using a ps and a fs laser, in so called "Hybrid fs/ps CARS".
- As one example, a broadband fs Ti:sapphire laser at a wavelength of 790 nm can be used for the Pump and Stokes beams, exciting an array of Raman coherences. The correct wavelengths can be set by using an amplified laser system and sending a portion of the output into an optical parametric amplifier (OPA). The original 790 nm radiation can form the Pump beam and the OPA beam can be used for the Stokes beam.
- The picosecond Probe pulse can be had simply by band-limiting one of the fs pulses (e.g. the original 790 nm laser pulse).
- The narrow bandwidth of the probe ensures a high resolution CARS spectrum can be acquired in a single-shot at high repetition rates (in the kHz regime).

Short pulse CARS



- One of the real advantages is that various regions of the fs spectra for the Pump and Stokes beams can excite Raman coherences at the same time. As shown, a ns system can hit the desired $\omega_v = 2330\,\mathrm{cm}^{-1}$ only at the center of the laser spectrum, whereas the fs bandwidth hits it a number of times. This also happens in Hybrid fs/ps CARS.
- So long as their beat frequency matches ω_v each combination can work.

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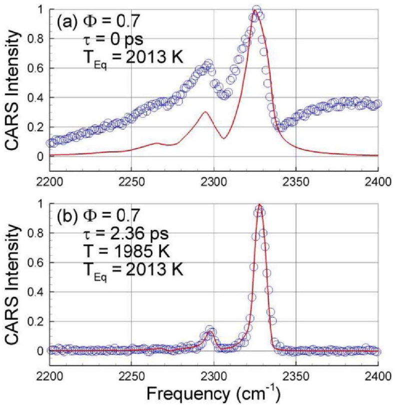
Short pulse CARS



J. D. Miller, M. N. Slipchenko, T. R. Meyer, H. U. Stauffer, and J. R. Gord, Optics Letters, Vol. 35, No. 14, 2010

Hybrid fs/ps CARS

- Example results showing normalized N_2 CARS spectra in a hydrogen/air flame for a probe delay of (a) 0 ps and (b) 2.36 ps. Solid curve is the best-fit theoretical simulation with suppressed non-resonant interference, and open symbols are experimental data.

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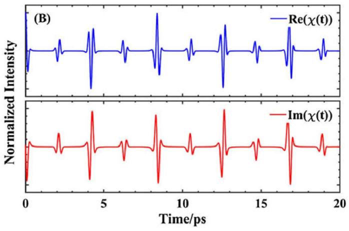
Short pulse CARS

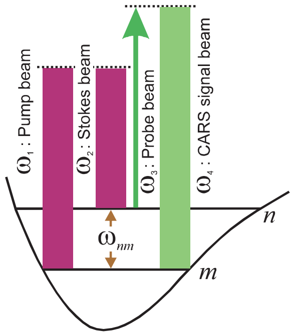
Coherence revivals

- In the discussion on free induction decay, we described the idea of a volumetric collection of coherences that go in and out of phase over a decay time.
- A similar process occurs with Raman coherences, called "coherence revivals". When Raman coherences are excited impulsively by fs pulses, and the probe is only a few ps wide, the probe can be scanned in time to reveal the effect of these revivals.
- The timing of the Probe pulse relative to the Pump/Stokes pulses thus becomes important.



C. Yang, D. Escofet-Martin, D. Dunn-Rankin, Y.-C. Chien, X. Yu, and S. Mukamel, J. Raman Spectrosocpy, DOI:10.1002/jrs.5262, (2017)

Short pulse CARS



Note the change of beam notation. Here one laser provides very broadband Pump and Stokes beams, but different parts of the two laser spectra mix, so they are called beams 1 and 2. Beam 3 is the Probe, and beam 4 is the Signal now.

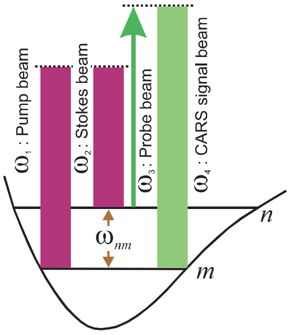
H-RCARS

- Chris Kliewer and co-workers at Sandia Labs Combustion Research Facility have been working on Hybrid fs/ps rotational CARS (H-RCARS).
- Because the rotational lines sit very close to the Rayleigh line, one fs laser (very broadband) can be used for both Pump and Stokes beams.

Short pulse CARS

H-RCARS

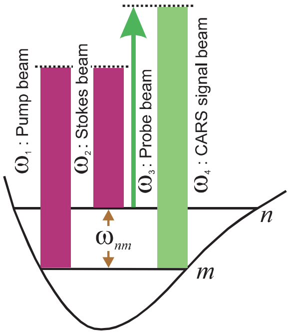
- The rotational Raman cross sections are bigger than the ro-vibrational cross sections and the lines are widely spaced, allowing us to ignore line mixing even at high pressure (e.g. 70 bar).
- One aspect of their location near the Rayleigh line is a somewhat relaxed phase match requirement. Recall that phase matching is given by $\vec{k}_3 = \vec{k}_1 - \vec{k}_2 + \vec{k}_3$, and the magnitude of $\vec{k}$ is $2\pi/\lambda$.



Short pulse CARS

H-RCARS

- This idea also includes all of the advantages of normal Hybrid fs/ps CARS, e.g. the narrow bandwidth of the probe ensures a high resolution CARS spectrum can be acquired in a single-shot at high repetition rates (in the kHz regime), the probe can be delayed to reject most of the NR background, and etc.



Short pulse CARS

Models

- Given what was just said, it becomes necessary to develop a time-dependent model for CARS.
- The nonlinear material polarization is modeled in time (ignoring positional dependence for now) by[†]:

$$\begin{aligned} P_{\mathrm{CARS}}(t) &= \left(\frac{i}{\hbar}\right)^3 \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 R_{\mathrm{CARS}}(t_3, t_2, t_1) \\ E_3(t - t_3) & \; E_2(t - t_3 - t_2) E_1(t - t_3 - t_2 - t_1) \qquad (45) \end{aligned}$$

were we have not yet explicitly included probe delay. Here $R_{\mathrm{CARS}}(t)$ describes the molecular response.

† S. Mukamel. Principles of Nonlinear Optical Spectroscopy. Oxford University Press, New York, (1995), H. U. Stauffer, J. D. Miller, M. N. Slipchenko, T. R. Meyer, B. D. Prince, S. Roy, and J. R. Gord, J. Chem. Phys., 140, 024316 (2014)

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Short pulse CARS

Models

- We assume:
  ▹ The electric fields are plane waves,
  ▹ The molecular response is fast compared to the pump and probe pulse coherence time scales, t_1 and t_3 (molecular dephasing over the t_1 and t_3 timescales is almost instantaneous),
  ▹ The pump and Stokes pulses are impulsive and short compared to the probe pulse, so that they can be replaced by delta functions.
- The third order material polarization becomes:

$$P_{\mathrm{CARS}}(t) = \left(\frac{i}{\hbar}\right)^3 E_3(t - \tau) R_{\mathrm{CARS}}(t)\, e^{-i\omega_3(t-\tau)} \qquad (46)$$

where τ is the time delay between the Pump/Stokes pulses and the Probe pulse.

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Short pulse CARS

Models

- The spectrum of the signal electric field is found by taking the Fourier transform of $P_{\mathrm{CARS}}(t)$:

$$P_{\mathrm{CARS}}(\omega, \tau) = \mathcal{F}\left[P_{\mathrm{CARS}}(t)\right] \tag{47}$$

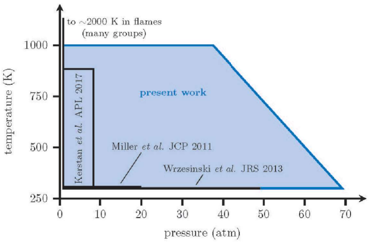
and the observed spectrum is:

$$I_{\mathrm{CARS}}(\omega, \tau) \propto \mid P_{\mathrm{CARS}}(\omega, \tau) \mid^2 \tag{48}$$

Short pulse CARS and pressure

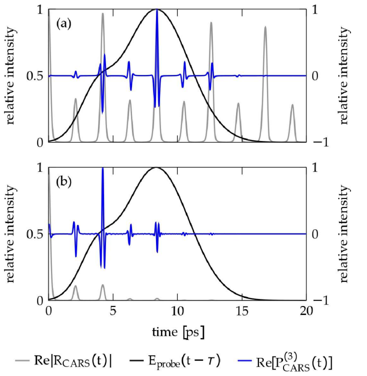
H-RCARS

- The old ns vibrational CARS data shown earlier had problems with the NR background, line-widths and line mixing.
- In short pulse CARS:
  ▷ The Probe can be delayed to minimize the NR background,
  ▷ Rotational CARS lines are well separated so they can be detected even at high pressure,
  ▷ We find no contribution from line mixing up to 70 bar.
- Because H-RCARS looks promising for pressures, we have investigated this P/T landscape.



Note: Vibrational CARS is considered more accurate above 1500 K, while rotational CARS is more accurate below 900 K.

Short pulse CARS and pressure

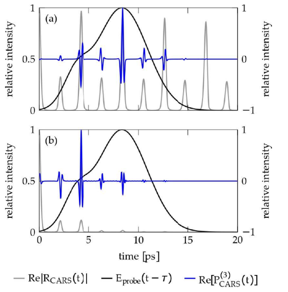


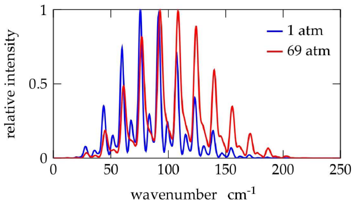
The absolute value of the real part of the molecular response (grey trace), measured probe pulse shape (black trace), and the real part of the time domain CARS signal (blue trace); (a) 1 bar and (b) 69 bar.

H-RCARS

- Here is what we expect to see in terms of the pressure effect.
- Note that ns CARS integrates over all of this activity to give a final spectrum. Here, the spectrum changes as you scan the Probe pulse in time.

Short pulse CARS and pressure





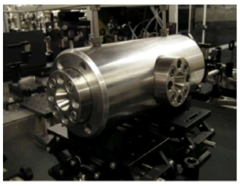
H-RCARS

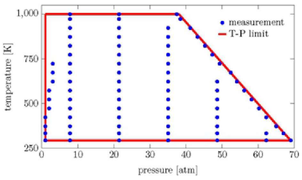
- These differences affect spectra as well.

Short pulse CARS and pressure

H-RCARS

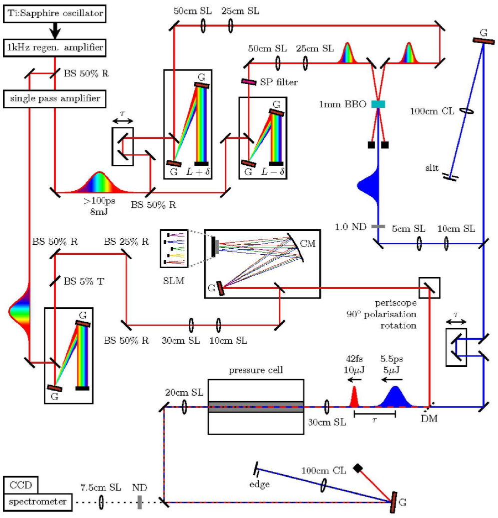
- Experiments in a high pressure and temperature chamber in the Kliewer lab at Sandia explored the applicability of H-RCARS to pressures between 7 and 70 bar, at various temperatures:
  ▷ Measurements inside a furnace with 28 mm thick windows,
  ▷ Pump/Stokes pulsewidths $\sim 40 - 55\, fs$,
  ▷ Probe pulsewidth $\sim 5ps$,
  ▷ Probe pulse delay from 5 - 12 ps,
  ▷ Temperatures measured inside using thermocouples as well.





Short pulse CARS and pressure

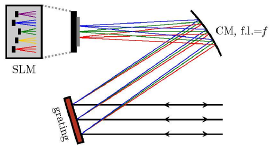
High-P H-RCARS experimental layout



Short pulse CARS and pressure

Pump/Stokes beam

- The pressure cell windows will introduce chirp into the Pump/Stokes pulses (blue slows relative to red).
- They were therefore pre-compensated so that a transform limited pulse would exist after the window.
- In the pulse shaper, a grating is used to spatially separate the pulse frequencies. A curved mirror focusses the various frequencies to different spots on the SLM.
- On the way out, the individual frequencies are recombined using the same curved mirror and grating.



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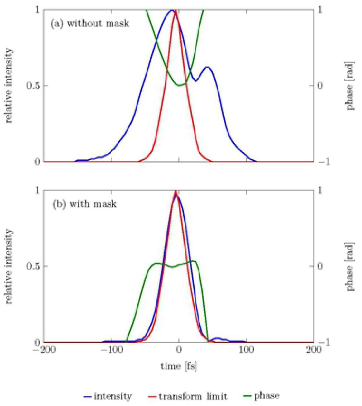
Short pulse CARS and pressure

Pump/Stokes beam

- Pulse results via FROG.
- Upper - the pulse after passing through the cell window but without pre-compensation. The pulse is far from its transform limit and the shape is asymmetric, with a width (FWHM) of 112 fs. The phase varies significantly over the length of the pulse.
- Lower - when the appropriate phase mask is used, the beam is almost symmetric and has a width of only 42 fs, which is very close to its transform limit. The phase is nearly constant over the length of the pulse.



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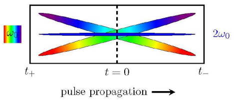
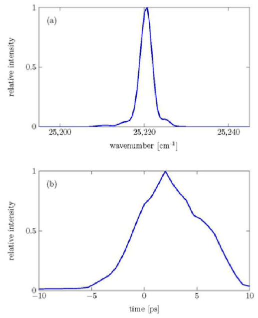
Short pulse CARS and pressure

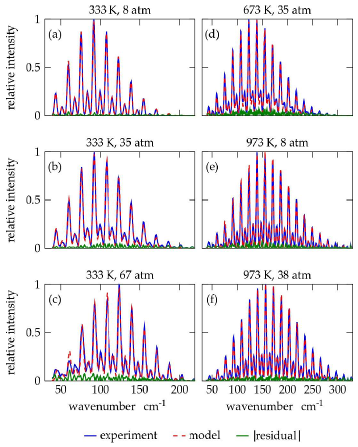
Probe beam

- The ps probe beam was generated from the same fs laser using second harmonic bandwidth compression.
- The Probe pulse spectrum was measured with a spectrometer and the temporal shape and timing relative to the Pump/Stokes pulses was measured using a NR background measurement in Argon.





Short pulse CARS and pressure



Results

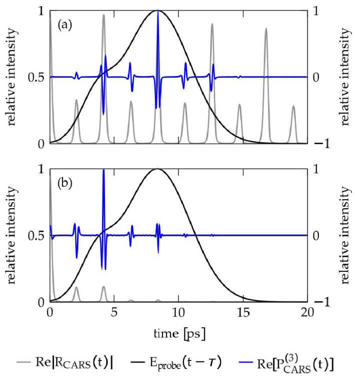
Spectra acquired with probe time delay of 8 ps (except (c) which was at 11 ps)

(a) 341 K, 2.3%
(b) 322 K, -3.2%
(c) 312 K, -6.2%
(d) 685 K, 0.4%
(e) 980 K, 1.1%
(f) 955 K, -1.8%

Short pulse CARS and pressure

Results

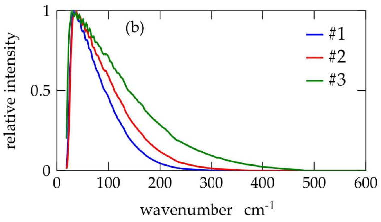
- Results get worse at high P - why?
- First - the signal decreases with pressure and so the SNR gets worse, because of this.
- Also, as pressure increased, it's certainly possible the Pump/Stokes beams developed additional chirp in the high-density gas. That needs investigation.



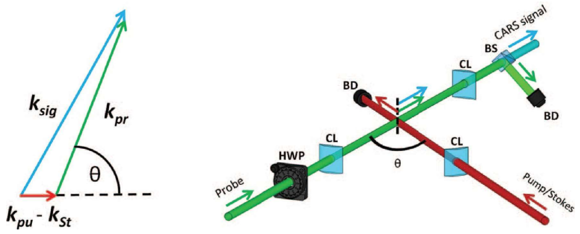
Short pulse CARS and pressure

Results

- These are NR signals (spectra) in Argon. They are used to normalize the instrument response (acquired H-RCARS spectra) for the spectral shape of the Pup/Stokes pulse.
- In general, there is a problem with drift over time in the pulse shaper caused by small changes in beam pointing. The pre-compensation degrades over time.
- One could use chirped mirrors instead, but they correct only for linear chirp.
- "This sounds like a hassle, why do it?"



Line imaging with short pulse CARS

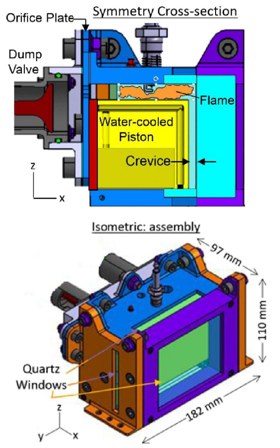


A. Bohlin, B. D. Patterson, C. J. Kliewer, J. Chem. Phys., 138, 081102 (2013)

- The Pump and Stokes beams both come from a fs laser and they are collinear (this is Dual BB-CARS). The Probe beam comes from a ps laser and it is crossed with the Pump and Stokes at nearly 90°.
- The CARS beam (labeled 'sig' here) is nearly collinear with the Probe and they are separated using polarization in this paper, but spectral separation is used most often now.
- Note that the beams have cylinder lenses in them; here CARS is performed along a line.

Example application of rotational fs/ps CARS

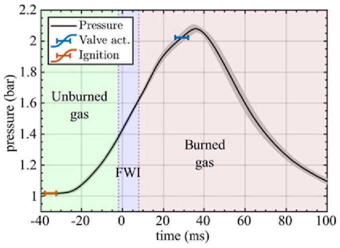
- At Edinburgh, we have constructed a specialized combustion chamber that emulates the P vs t curve of a piston engine with no moving parts but with good optical access§.
- It is used to study transient near-wall heat transfer and flame-wall interactions (FWI) during more realistic pressure transients.
- It has a "piston top" region and a "crevice" region.



§ D. Escofet-Martin, A. O. Ojo, N.T. Mecker, M.A. Linne, and B. Peterson, to be presented, 38th International Symposium on Combustion/Proceedings of the Combustion Institute, (2020)

Example application of rotational fs/ps CARS

- This pressure/time plot is slower than a real piston engine, but it was based on a fairly low-pressure fill of fuel/air, and it used methane.
- More realistic plots can be acquired using a fuel like ethane, using a higher pressure fill.
- Note the very high reproducibility.
- The three regions shown were each studied.



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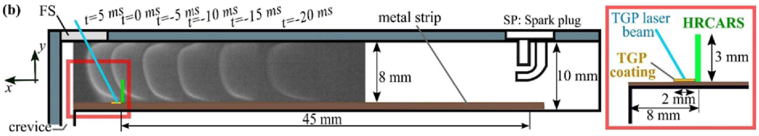
Example application of rotational fs/ps CARS



- Here we show a flame progressing across the top of the piston, imaged via high speed CH* chemiluminescence imaging.
- The red square indicates a region where 1-D H-RCARS was used (green vertical line) to detect temperature vs vertical position (the transient thermal boundary layer) with 40 μm spatial resolution.
- Note that $t = 0$ is when the flame intercepts the H-RCARS line.
- Surface temperature was also measured using thermographic phosphors.

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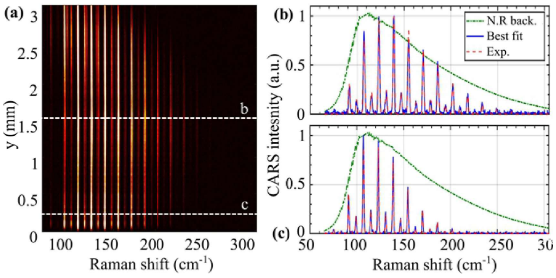
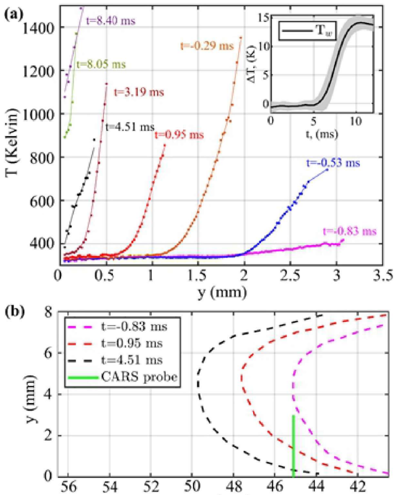
Example application of rotational fs/ps CARS



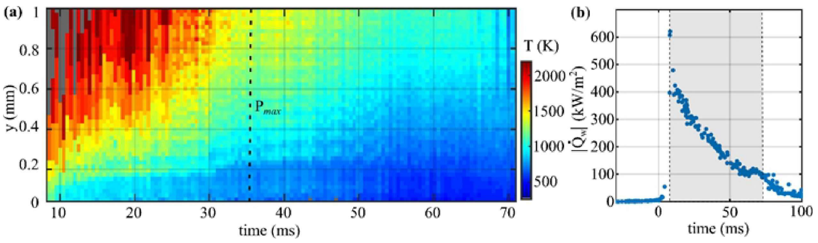
- Typical H-RCARS spectra vs position in the beginning of the FWI region.
- The two spectra indicate widely varying temperatures with position.

Example application of rotational fs/ps CARS

- Here are transient temperature profiles in the unburned gas/polytropic compression region and in the FWI period.
- Thanks to the no-slip condition at the wall, the thermal conductivity times the measured temperature gradient gives the rate of heat transfer at the wall.



Example application of rotational fs/ps CARS



- Temperature profiles and heat transfer in the burned gas region.
- I think you will agree that the effort is well worth it.

To conclude

In this short course we have discussed:

Monday	**Tuesday**
Introduction / Eqn. Rad. Transfer / Physical optics	Scattering / PIV, wOFV /SLIPI,BI
Wednesday	**Thursday**
Intro to quantum / Spectroscopy & OH / Stat. thermo, resonance,	Lasers / Absorption & lineshape / LIF
Friday	
Raman / Nonlinear optics / CARS	

To conclude

- It was a mix of theoretical ideas (i.e. an introduction to what quantum mechanics is about) and practical ideas (i.e. how to minimize PIV errors).
- There is a huge amount to know if you want to include all diagnostics.
- It's better to focus on one or two at a time. If you do that over a career, once you get older you will be familiar with a variety of techniques.
- These techniques are useful for much more than combustion, but the combustion problem is perhaps the most difficult. If you can perform combustion diagnostics you can make measurements in calmer flows.

Help is available

Especially to get started:

- For the underlying physics - M. Linne, "Spectroscopic Measurement: an Introduction to the Fundamentals", Academic Press, 2002 (I know, it's my own book, but I wrote it for engineers who need to learn some basics - a second edition is being written).
- For coverage of the latest in diagnostics -
  ▷ A. Steinberg, and S. Roy, editors, "Optical Combustion Diagnostics for Propulsion and Power Systems: Theory and Application", American Institute of Aeronautics and Astronautics, (anticipated 2022), or
  ▷ K. Kohse-Höinghaus and J.B. Jeffries, "Applied combustion diagnostics", Elsevier, 2002.
- For optics - E. Hecht, "Optics", Addison-Wesley, 2015.

Help is available

After those sources:

- Check the reading list at the start of the course.
- Go to conferences like the Gordon Conference on Laser Diagnostics in Energy and Combustion Science. I mention this one because it is a very friendly, very helpful, but no-nonsense meeting. Go and ask questions!
- You can always ask the old guard (e.g. me) for guidance.
- If history is any guide, your biggest challenge will be to find the time and resources required to make these things happen. Good luck with that!