Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

JULY 20-25, 2014

15 Lecture Short Course at Tsinghua University

Lecturer: Ronald K. Hanson
Woodard Professor, Dept. of Mechanical Engineering
Ph.D. Stanford, Aero/Astro; at Stanford since 1972

Underlying Science:
Molecular Spectroscopy
Diagnostic Methods:
Laser Absorption, LIF
Example Applications:
Engines, Shock Tubes, Kinetics

Today: Lecture 1
Overview and Introductory Material

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Lecture 1: Overview & Introductory Material

Course Objectives and Content

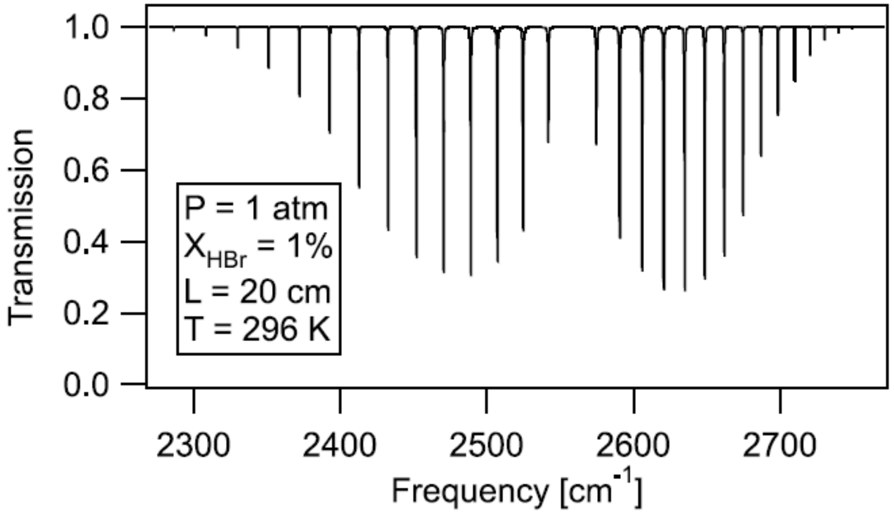
- Introduction to fundamentals of molecular spectroscopy & photo-physics
- Introduction to laser absorption and laser-induced fluorescence in gases
- Introduction to shock tubes as a primary tool for studying combustion chemistry, including recent advances and kinetics applications
- Example laser diagnostic applications including:
  - multi-parameter sensing in different types of propulsion flows and engines
  - species-specific sensing for shock tube kinetics studies
  - PLIF imaging in high-speed flows

Course Overview: Spectroscopy and Lasers

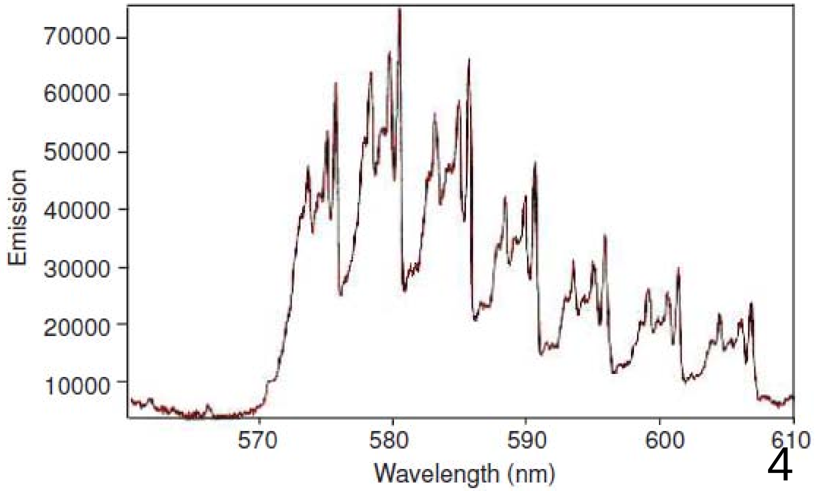
- ➢ *What is Spectroscopy?*
- Interaction of Radiation (Light) with Matter (in our case, Gases).
- Examples: IR Absorption, Emission

- ➢ *Why Lasers?*
- Enables Important Diagnostic Methods
- LIF, Raman, LII, PIV, CARS, …
- Our Emphasis: Absorption and LIF
- Why: Sensitive and Quantitative!

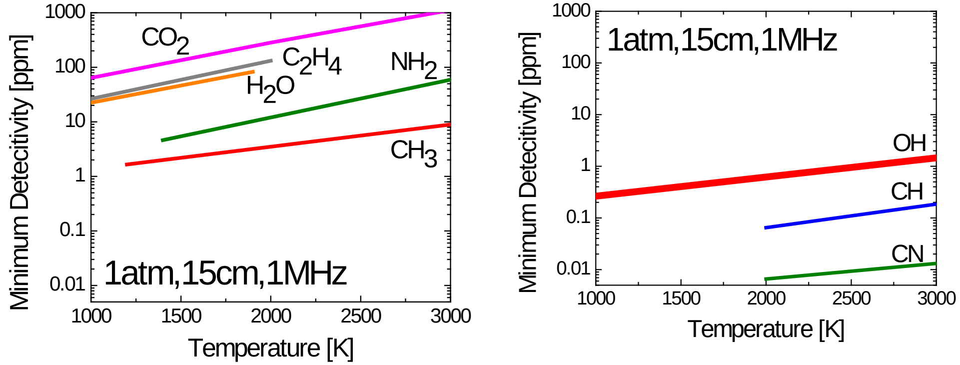
Calculated IR absorption spectra of HBr



Typical emission spectra of high-temperature air between 560-610nm.



Minimum Detectivity using Laser Absorption

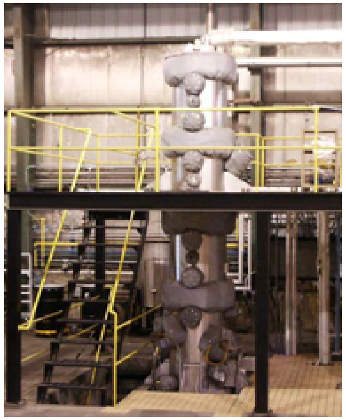


Course Overview:
Role of Lasers in Energy Sciences

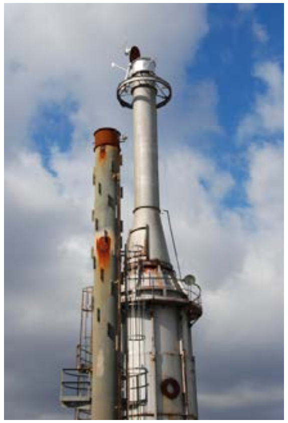
- *Example Applications:*
  Remote sensing, combustion and gasdynamic diagnostics, process control, energy systems and environmental monitoring.

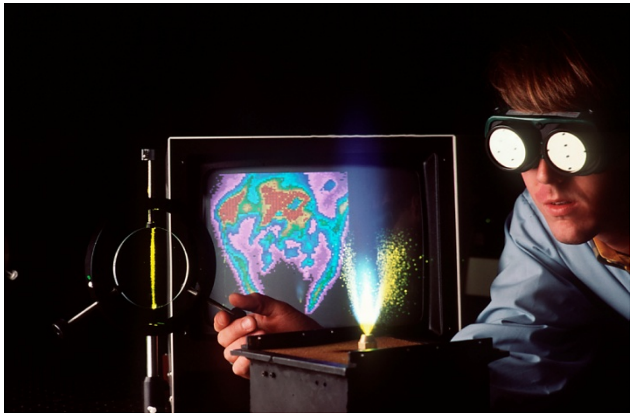
- *Common Measurements:*
  Species concentrations, temperature (T), pressure (P), density (ρ), velocity (u), mass flux (ρu).

Coal gasifiers



Swirl burners



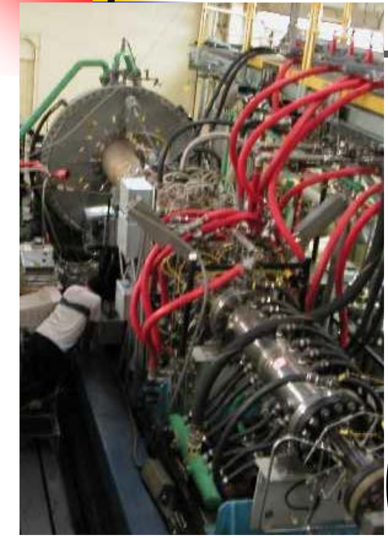


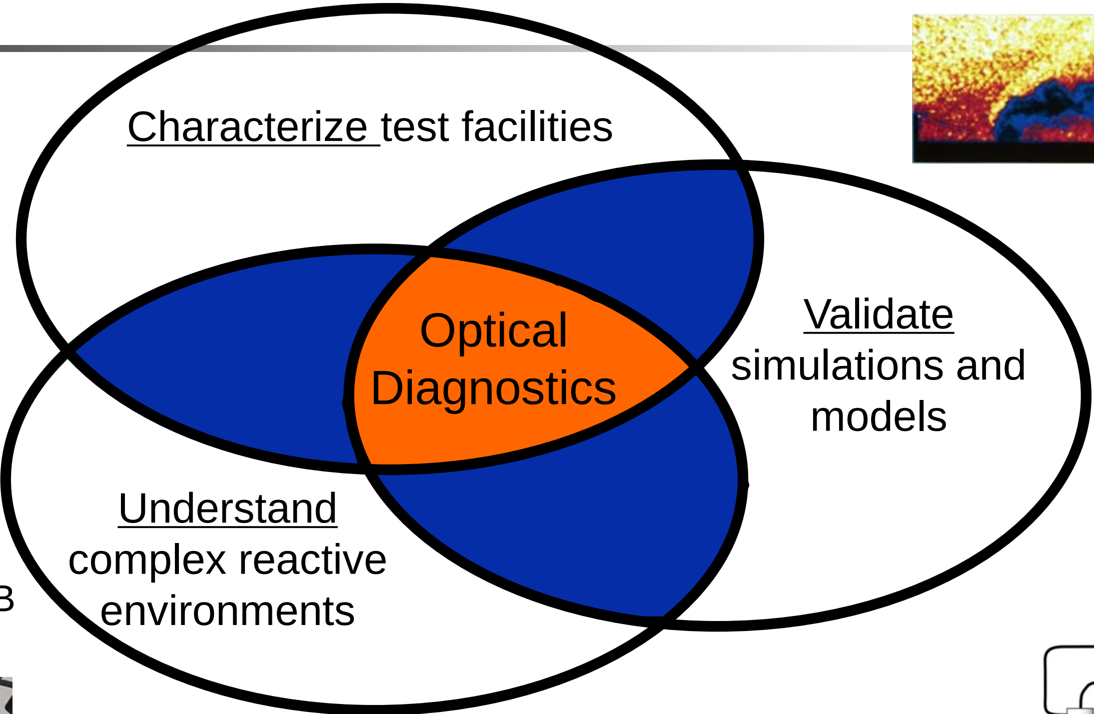
OH PLIF in spray flame

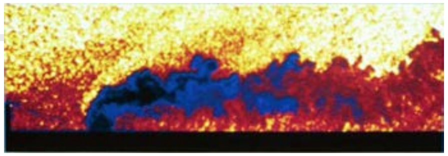
Coal-fired power plants

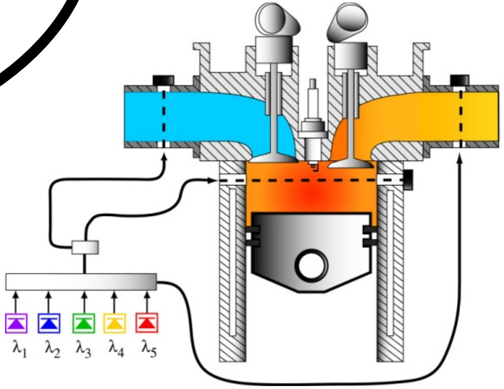
Incinerators

Course Overview:
Roles of Laser Sensing for Propulsion

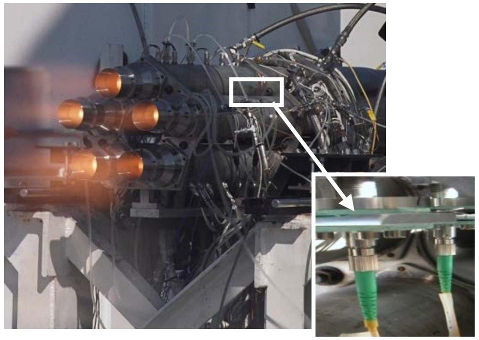

TDL Sensing in SCRAMJET @ WPAFB

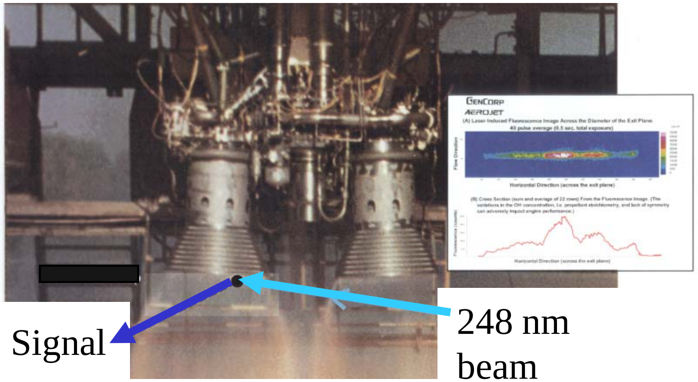



PLIF imaging of H_2 jet in model SCRAMJET @Stanford



TDL Sensing in IC-Engines @ Nissan & Sandia

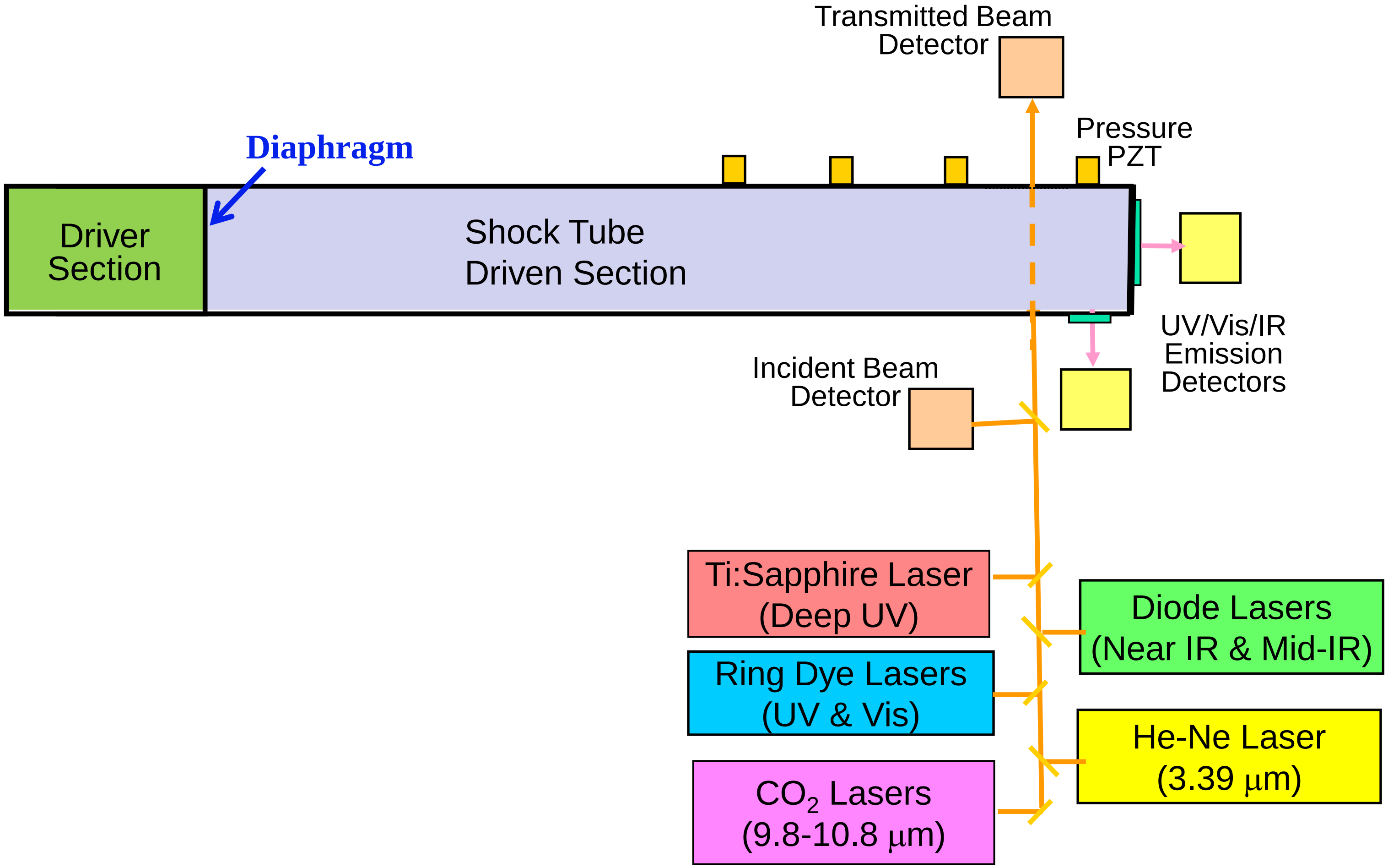

TDL Sensing in Pratt & Whitney PDE @ China Lake, CA



PLIF in plume of Titan IV @ Aerojet

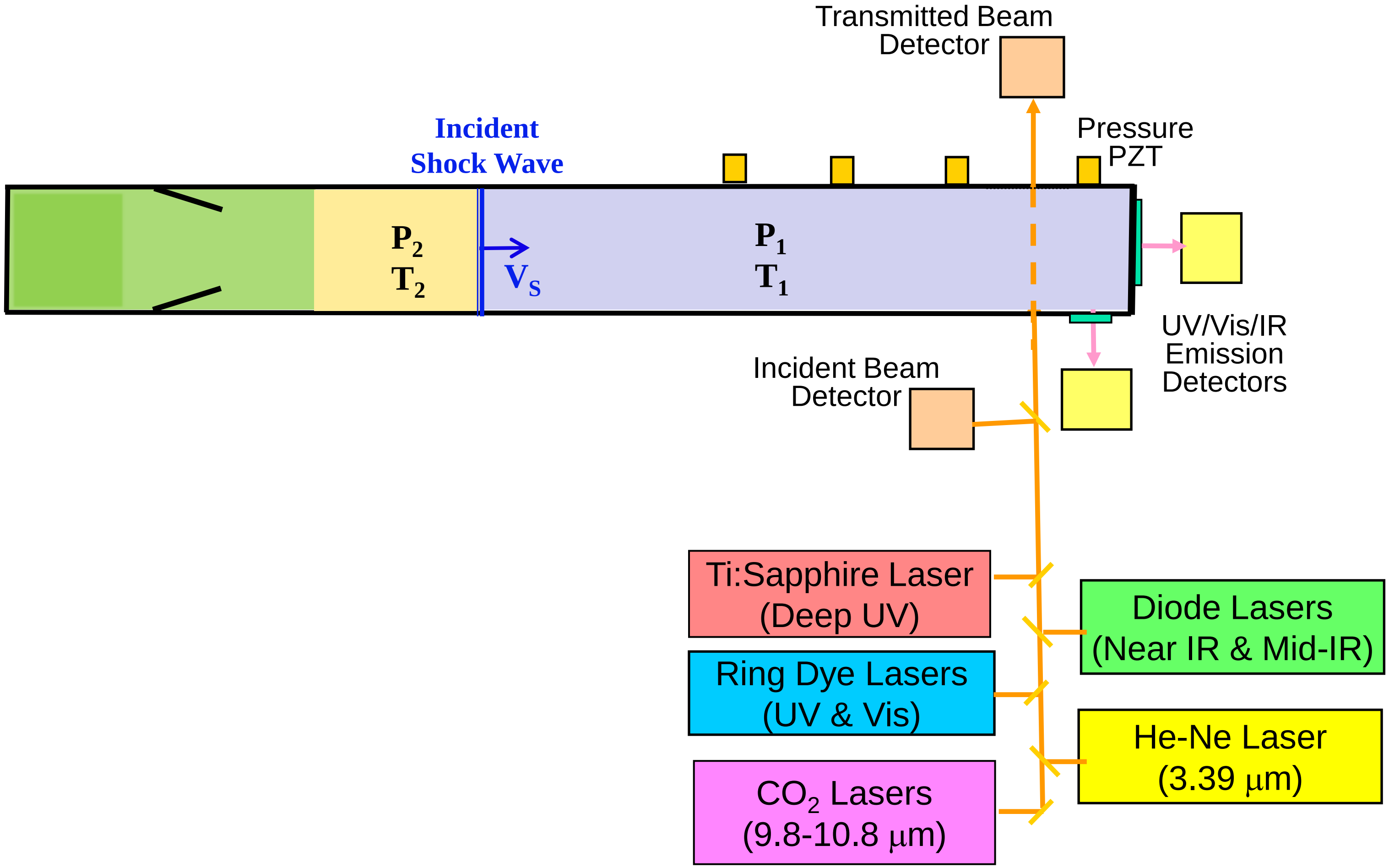
Applicable to large-scale systems as well as laboratory science

Course Overview:
Role of Lasers in Combustion Kinetics: Shock Tubes



Course Overview:

Role of Lasers in Combustion Kinetics: Shock Tubes



Course Overview:
Role of Lasers in Combustion Kinetics: Shock Tubes

Advantages of Shock Tubes

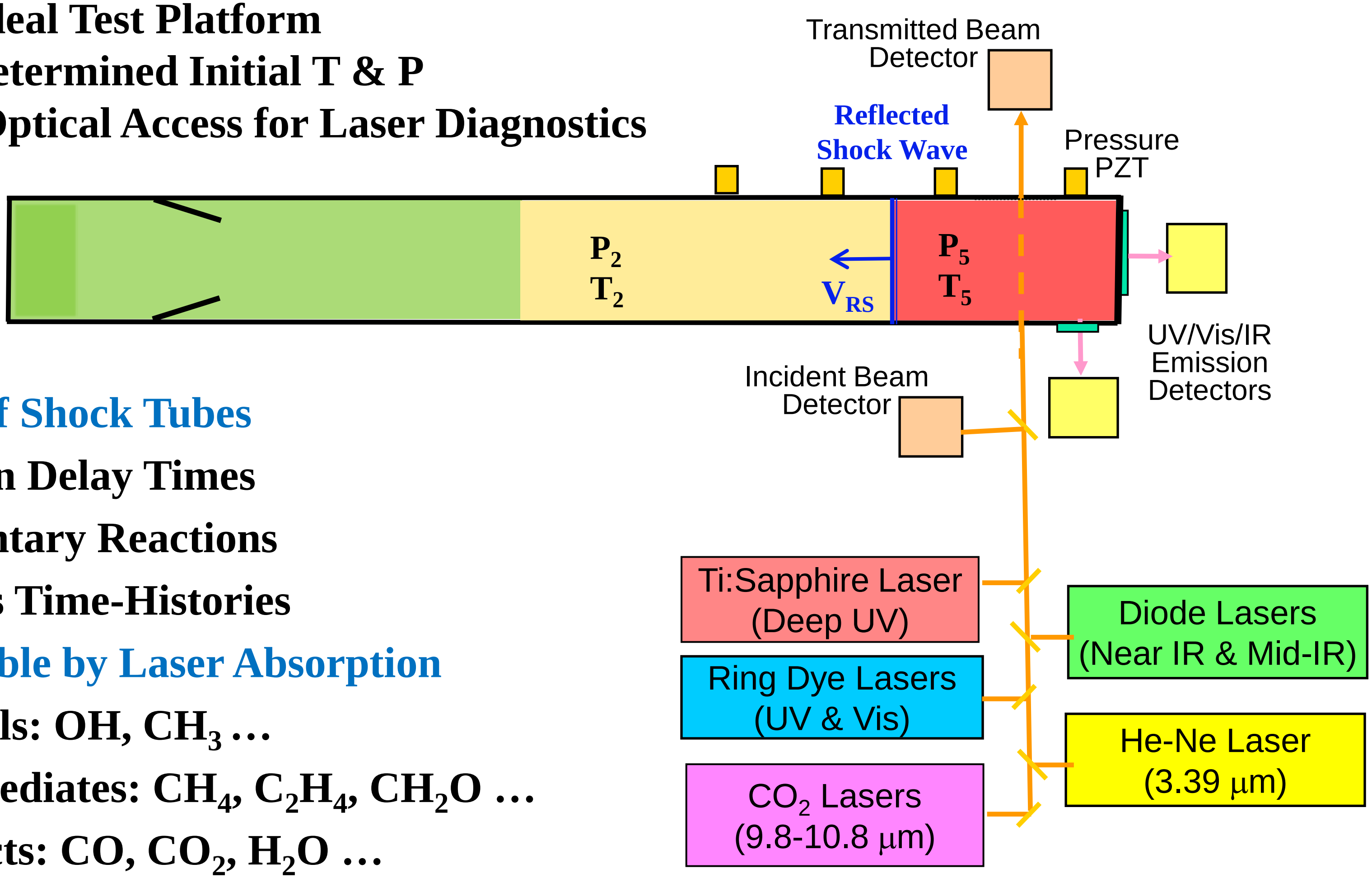
- **Near-Ideal Test Platform**
- **Well-Determined Initial T & P**
- **Clear Optical Access for Laser Diagnostics**

Applications of Shock Tubes

- **Ignition Delay Times**
- **Elementary Reactions**
- **Species Time-Histories**

Species Accessible by Laser Absorption

- **Radicals: OH, CH_3 …**
- **Intermediates: CH_4, C_2H_4, CH_2O …**
- **Products: CO, CO_2, H_2O …**



Ti:Sapphire Laser (Deep UV)

Diode Lasers (Near IR & Mid-IR)

Ring Dye Lasers (UV & Vis)

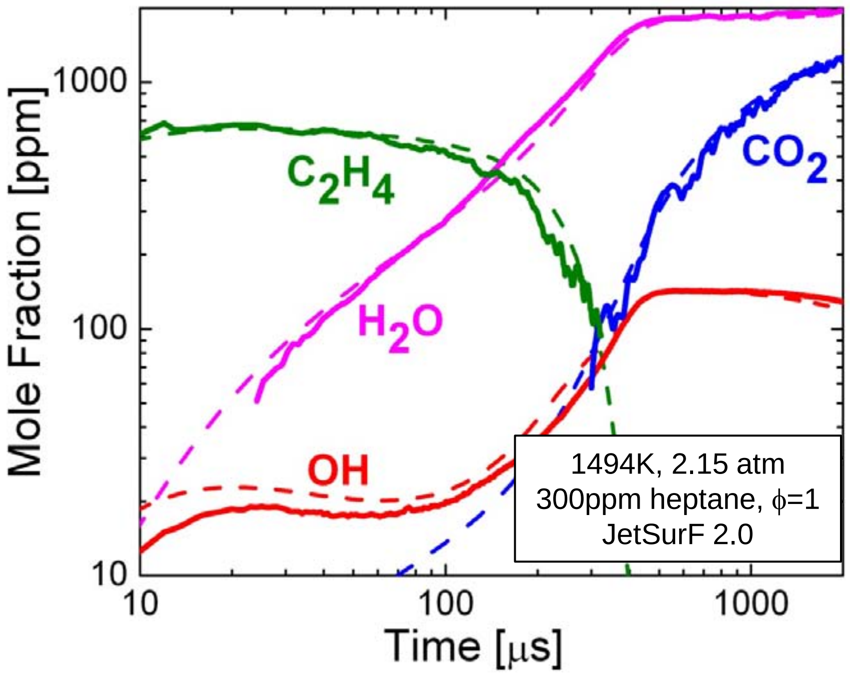
He-Ne Laser (3.39 μm)

CO_2 Lasers (9.8-10.8 μm)

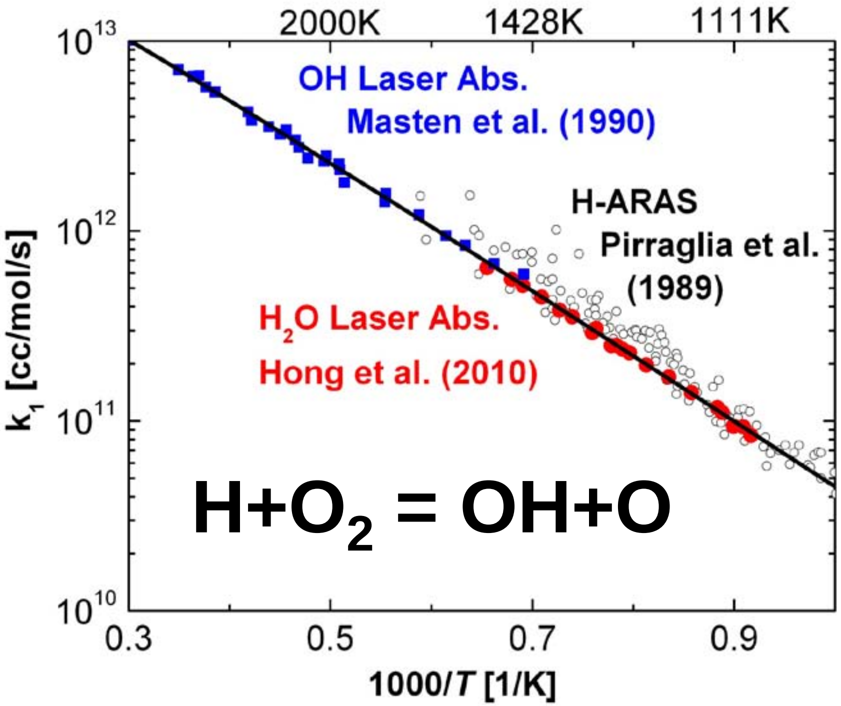
Course Overview:

Lasers and Shock Tube: Time-Histories & Kinetics

Time-Histories



Rate Constant



$$H+O_2 = OH+O$$

- Multi-wavelength laser absorption species time-histories provide quantitative targets for model refinement and validation

- Laser absorption provides high-accuracy measurements of elementary reaction rate constants

Useful Texts, Supplementary Reading

- G. Herzberg, Atomic spectra and atomic structure, 1944.
- G. Herzberg, Spectra of diatomic molecules, 1950.
- G. Herzberg, Molecular spectra and molecular structure, volume II, Infrared and Raman Spectra of Polyatomic Molecules, 1945.
- G. Herzberg, Molecular spectra and molecular structure, volume III, Electronic spectra and electronic structure of polyatomic molecules, 1966.
- C.N. Banwell and E.M. McCash, Fundamentals of molecular spectroscopy, 1994.
- S.S. Penner, Quantitative molecular spectroscopy and gas emissivities, 1959.
- A.C.G. Mitchell and M.W.Zemansky, Resonance radiation and excited atoms, 1971.
- C.H. Townes and A.L. Schawlow, Microwave spectroscopy, 1975.
- M. Diem, Introduction to modern vibrational spectroscopy, 1993.

- W.G. Vincenti and C.H. Kruger, Physical gas dynamics, 1965.
- A.G. Gaydon and I.R. Hurle, The shock tube in high-temperature chemical physics, 1963.

- J.B. Jeffries and K. Kohse-Hoinghaus, Applied combustion diagnostics, 2002.
- A.C. Eckbreth, Laser diagnostics for combustion temperature and species, 1988.
- W. Demtroder, Laser spectroscopy: basic concepts and instrumentation, 1996.
- R.W. Waynant and M.N. Ediger, Electro-optics handbook, 2000.
- J.T. Luxon and D.E.Parker, Industrial lasers and their applications, 1992.
- J.Hecht, Understanding lasers: An entry level guide, 1994.
- K.J.Kuhn, Laser engineering, 1998.

Lecture Schedule

Monday

1. Overview & Introduction
Course Organization, Role of Quantum Mechanics,
Planck's Law, Beer's Law, Boltzmann distribution
2. Diatomic Molecular Spectra
Rotational Spectra (Microwaves)
Vibration-Rotation (Rovibrational) Spectra (Infrared)
3. Diatomic Molecular Spectra
Electronic (Rovibronic) Spectra (UV, Visible)

Tuesday

4. Polyatomic Molecular Spectra
Rotational Spectra (Microwaves)
Vibrational Bands, Rovibrational Spectra
5. Quantitative Emission / Absorption
Spectral absorptivity, Eqn. of Radiative Transfer
Einstein Coefficients/Theory, Line Strength
6. Spectral Lineshapes
Doppler, Natural, Collisional and Stark broadening,
Voigt profiles

Wednesday

7. Electronic Spectra of Diatomics
Term Symbols, Molecular Models: Rigid Rotor,
Symmetric Top, Hund's Cases, Quantitative Absorption
8. Case Studies of Molecular Spectra
Ultraviolet: OH
9. TDLAS, Lasers and Fibers
Fundamentals and Applications in Aeropropulsion

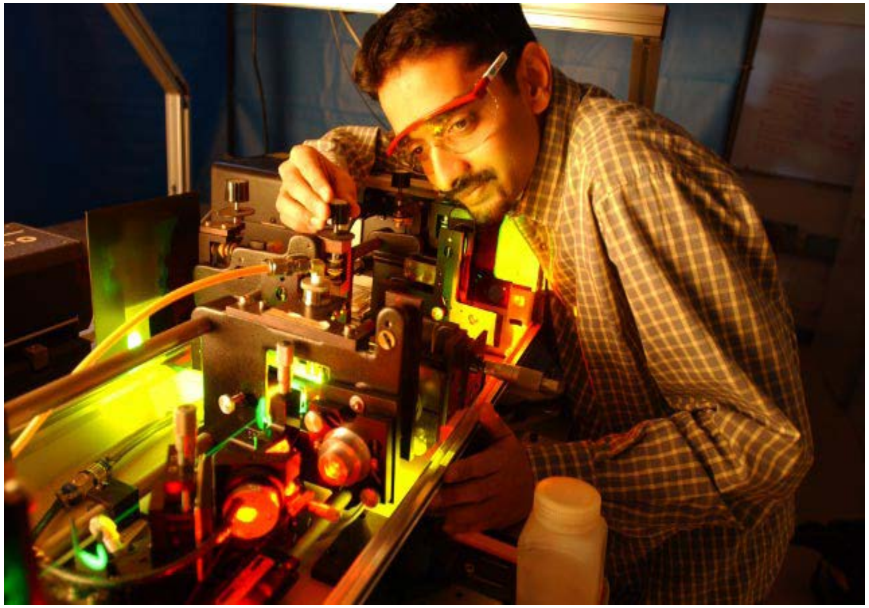
Thursday

10. TDLAS Applications in Energy Conversion
Tunable Diode Laser Applications in IC Engines
Coal-Fired Combustion
11. Shock Tube Techniques
What is a Shock Tube?
Recent Advances, ignition Delay Times
12. Shock Tube Applications
Multi-Species Time Histories
Elementary Reactions

Friday

13. Laser-Induced Fluorescence (LIF)
Two-Level Model
More Complex Models
14. Laser-Induced Fluorescence: Applications 1
Diagnostic Applications (T, V, Species)
PLIF for small molecules
15. Laser-Induced Fluorescence: Applications 2
Diagnostic Applications & PLIF for large molecules
The Future

Lecture 1: Introductory Material



1. Role of Quantum Mechanics
   - Planck's Law
2. Absorption and Emission
3. Boltzmann Distribution
4. Working Examples

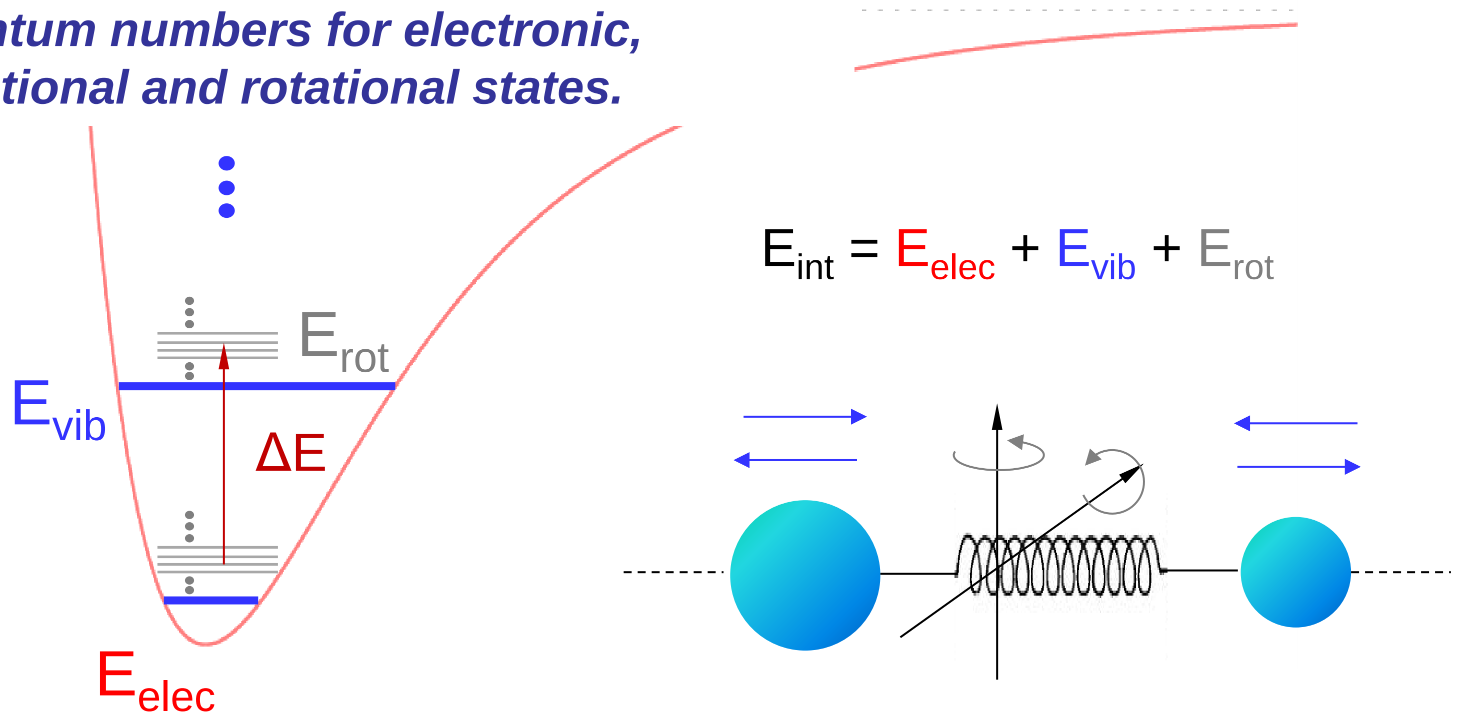
1. Role of QM - Planck's Law

- Quantum Mechanics:
  - Quantized Energy levels
  - "Allowed" transitions

} We will simply accept these rules from QM.

How are energy levels specified?

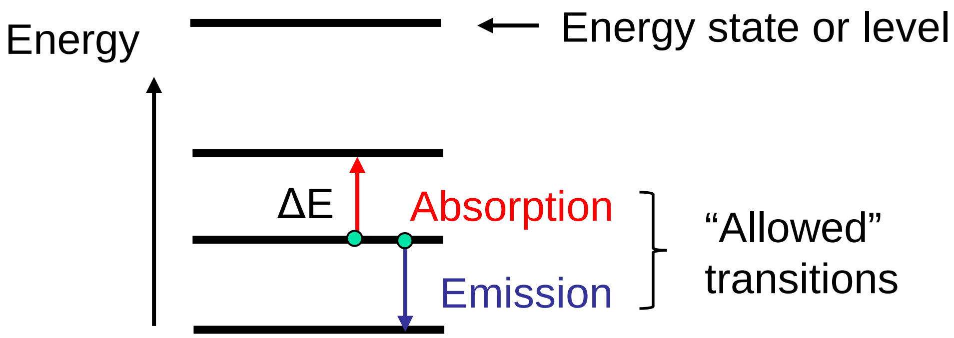
Quantum numbers for electronic, vibrational and rotational states.



$$E_{int} = E_{elec} + E_{vib} + E_{rot}$$

1. Role of QM - Planck's Law

- Quantum Mechanics


Energy

Energy state or level

ΔE

Absorption

Emission

"Allowed" transitions

Quantized Energy States (discrete energy levels)

Discrete spectra

- Small species, (e.g., NO, CO, CO_2, and H_2O), have **discrete** rovibrational transitions
- Large molecules (e.g., HCs) have **blended** features

Planck's Law:

$$\Delta E = E_{upper}\ (E') - E_{lower}\ (E'')$$
$$= h\nu$$
$$= hc/\lambda$$
$$= hc\bar{\nu}$$

← Energy in wavenumbers

Frequency [s^{-1}]

$$c = \lambda\ \nu$$

~ 3 x 10^{10} cm/s

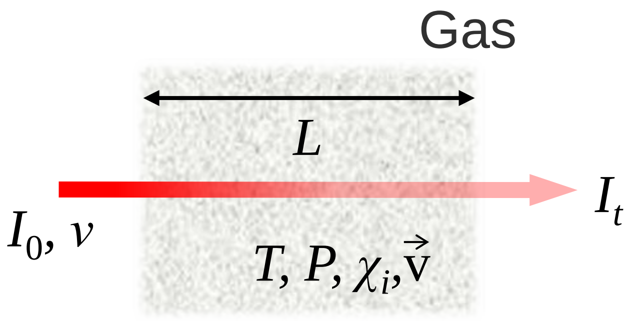
Wavelength [cm]

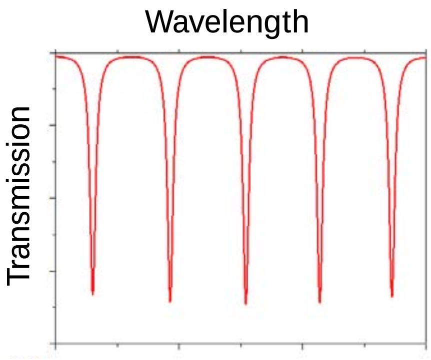
Note interchangability of **λ** & **ν**

2. Absorption and Emission

- Types of spectra:
  - Absorption; Emission; Fluorescence; Scattering (Rayleigh, Raman)

- Absorption: Governed by Beer's Law





Absorbance

Beer-Lambert Law $$\left(\frac{I_t}{I_0}\right)_\lambda = T_\lambda = \exp(-\alpha) = \exp(-n_j \sigma L) = \exp(-S P \chi_i \varphi L)$$

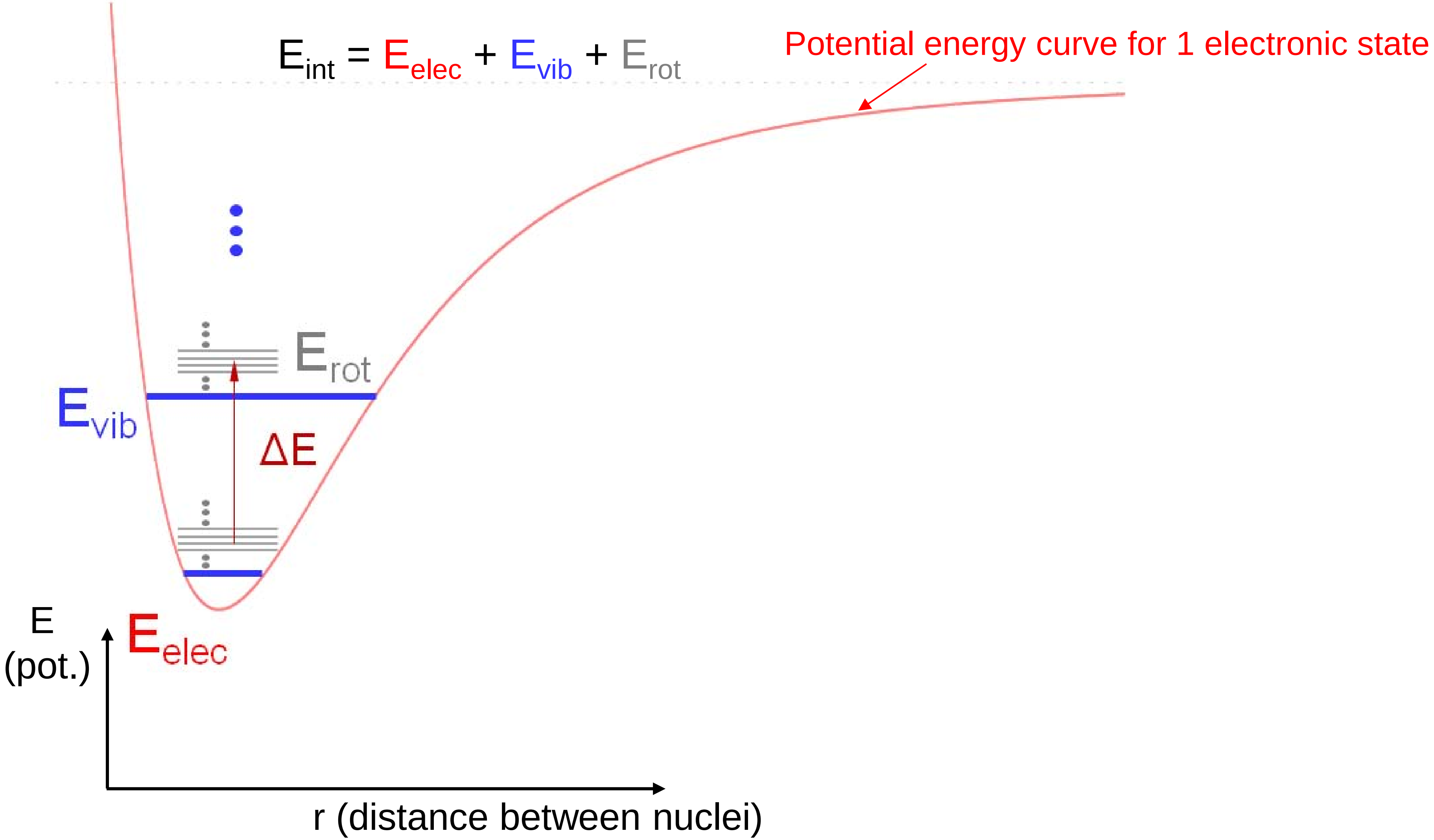
Number density of species j in absorbing state [molecule/cm^3]

Cross section for absorption [cm^2/molecule]

Path length [cm]

2. Absorption and Emission

- Components of spectra: Lines, Bands, System.



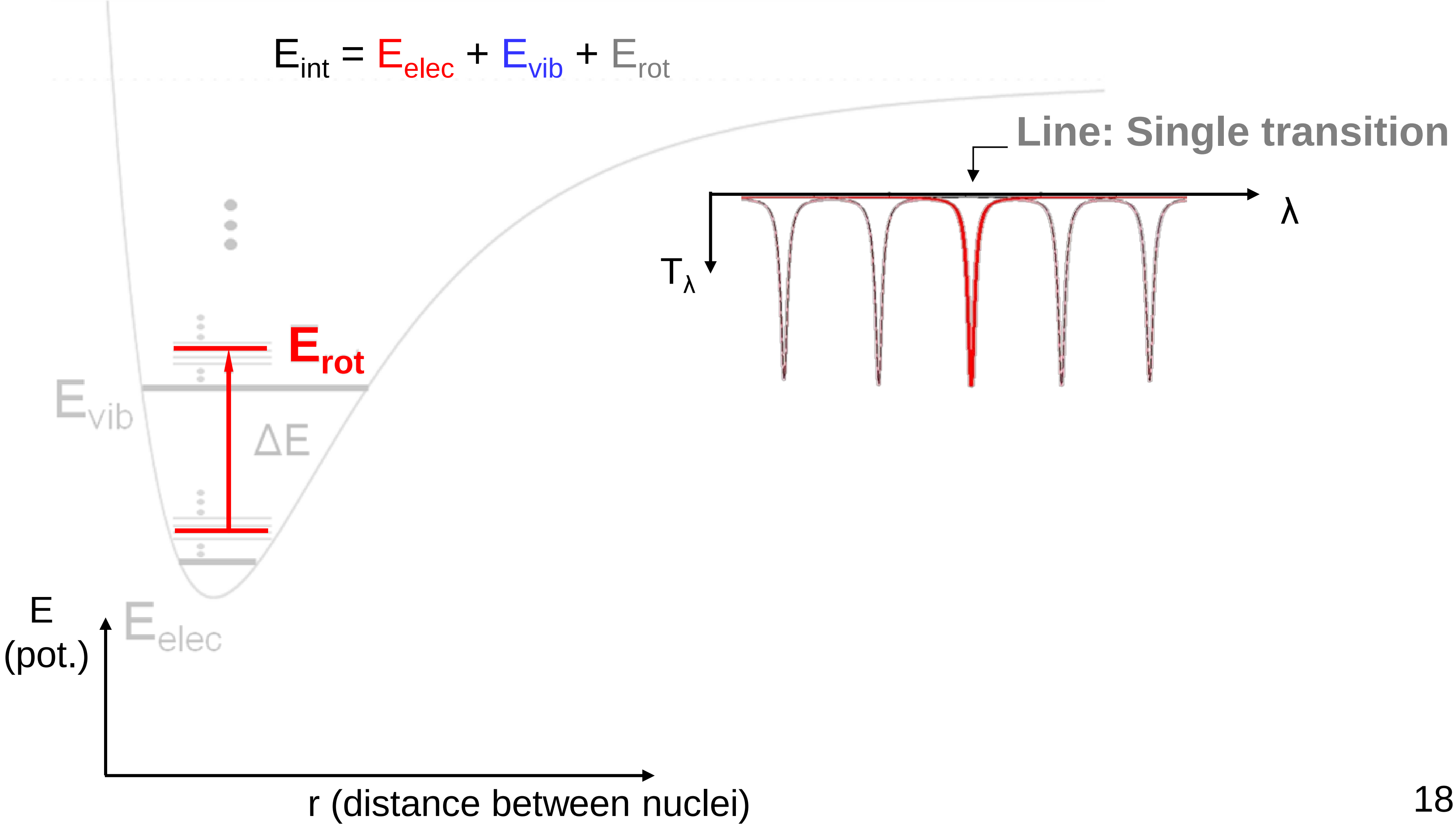
$E_{int} = E_{elec} + E_{vib} + E_{rot}$

Potential energy curve for 1 electronic state

2. Absorption and Emission

- Components of spectra: Lines, Bands, System.

$$E_{int} = E_{elec} + E_{vib} + E_{rot}$$



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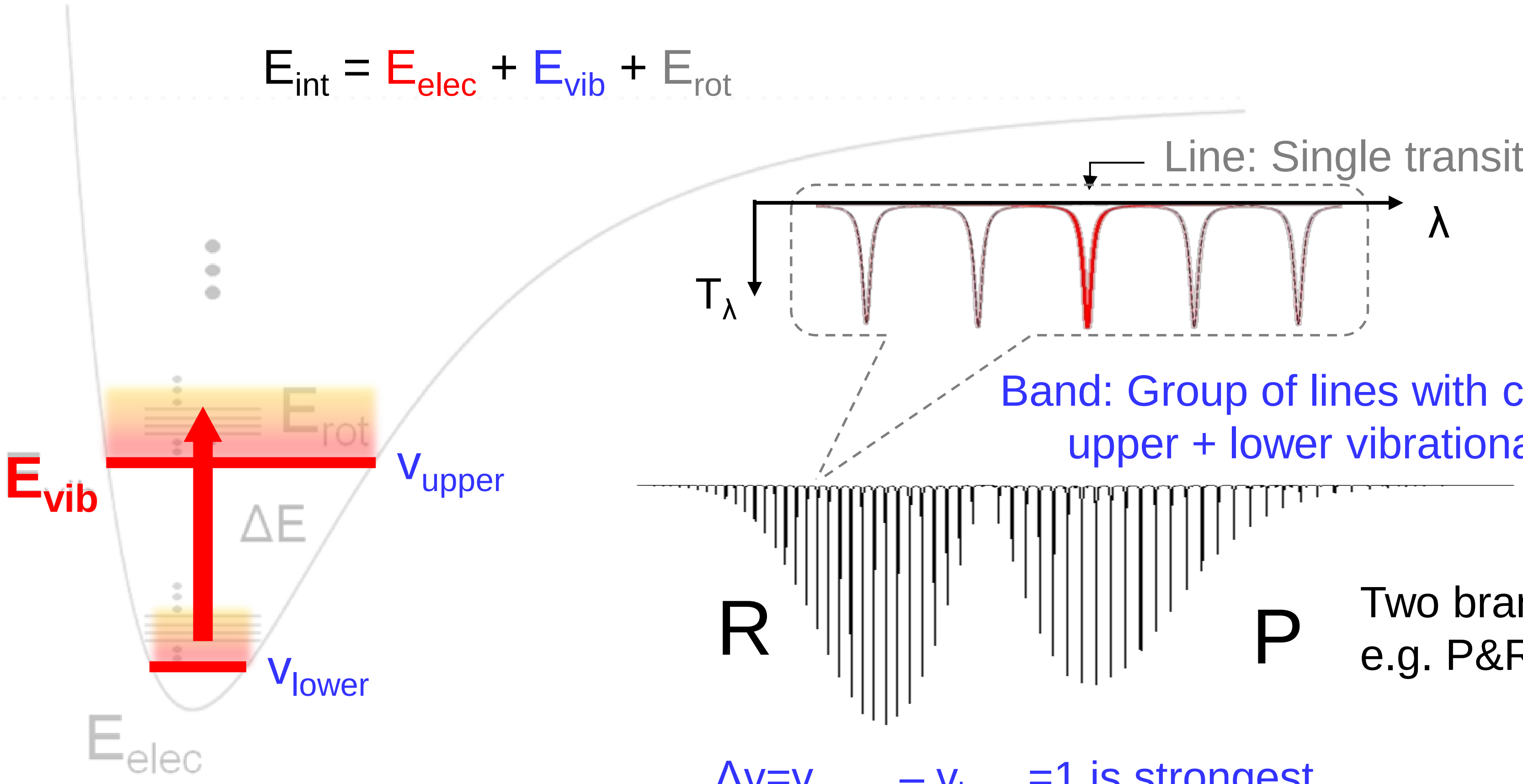


Line: Single transition

Band: Group of lines with common upper + lower vibrational levels

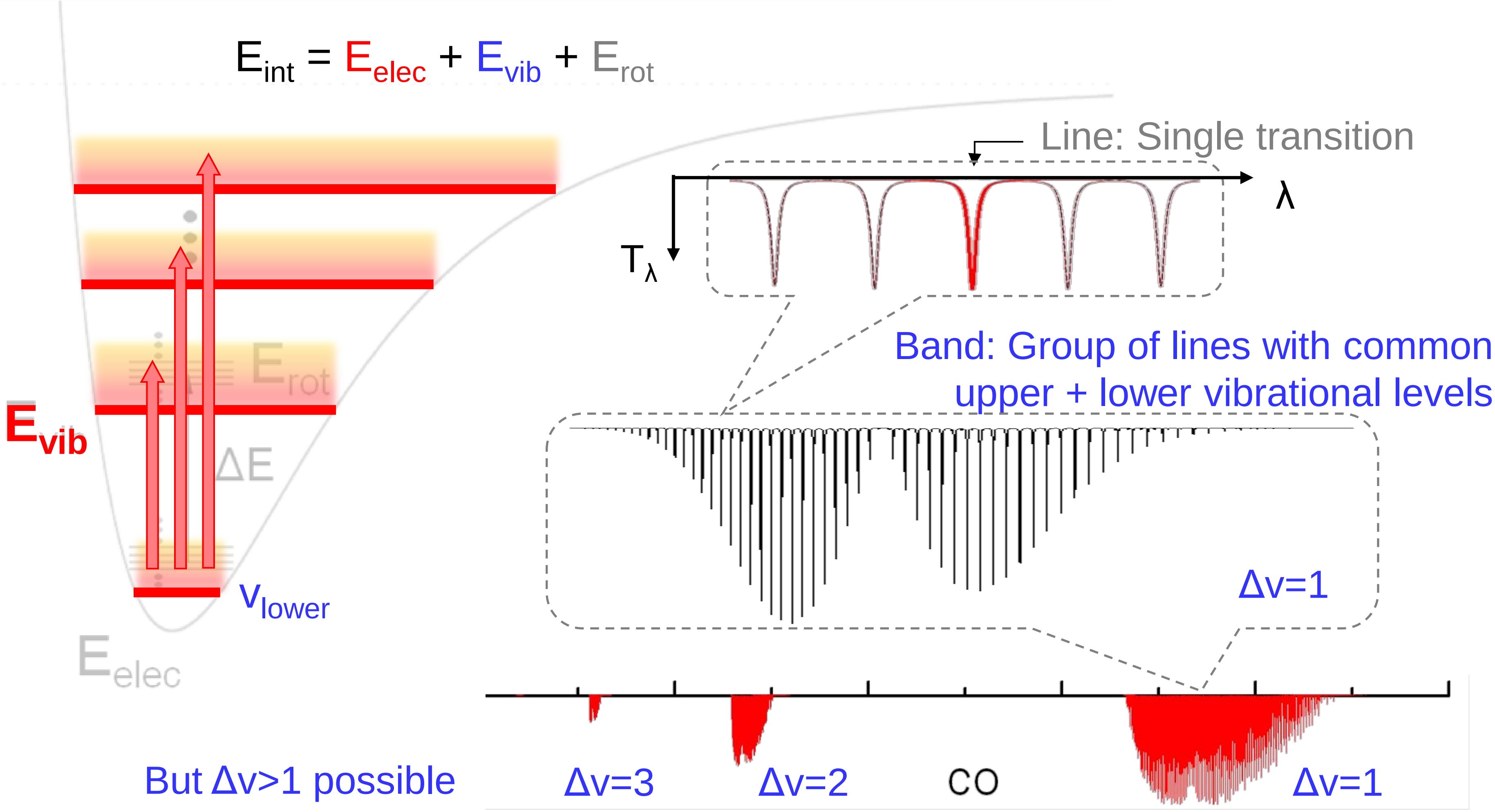
Two branches, e.g. P&R

$\Delta v = v_{upper} - v_{lower} = 1$ is strongest for rovibrational IR spectra, but $\Delta v = 2, 3, \ldots$ allowed

2. Absorption and Emission

- Components of spectra: Lines, Bands, System.

$E_{int} = E_{elec} + E_{vib} + E_{rot}$



Line: Single transition

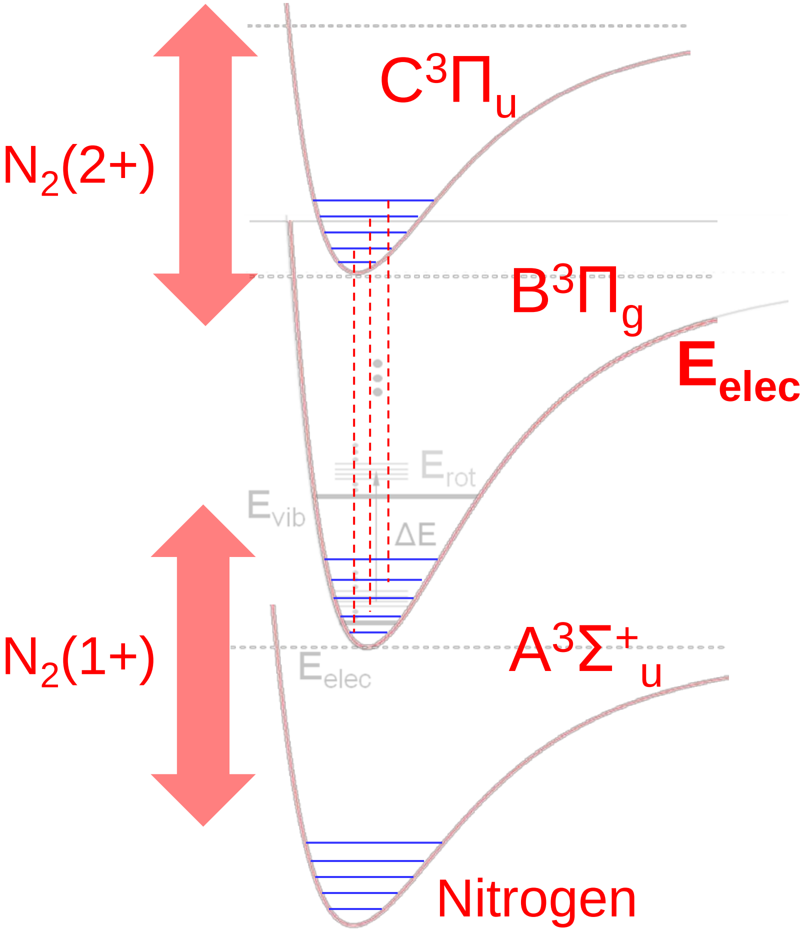
Band: Group of lines with common upper + lower vibrational levels

But Δv>1 possible

2. Absorption and Emission

- Components of spectra: Lines, Bands, System.

$E_{int} = E_{elec} + E_{vib} + E_{rot}$



System:

- Transitions between different electronic states
- Comprised of multiple bands between two electronic states
- Different combinations of v_{upper} and v_{lower} such that “bands” with $v_{upper}-v_{lower}$=const. appear

Example: N_2

- First positive SYSTEM:
  $B^3\Pi_g \rightarrow A^3\Sigma^+_u$

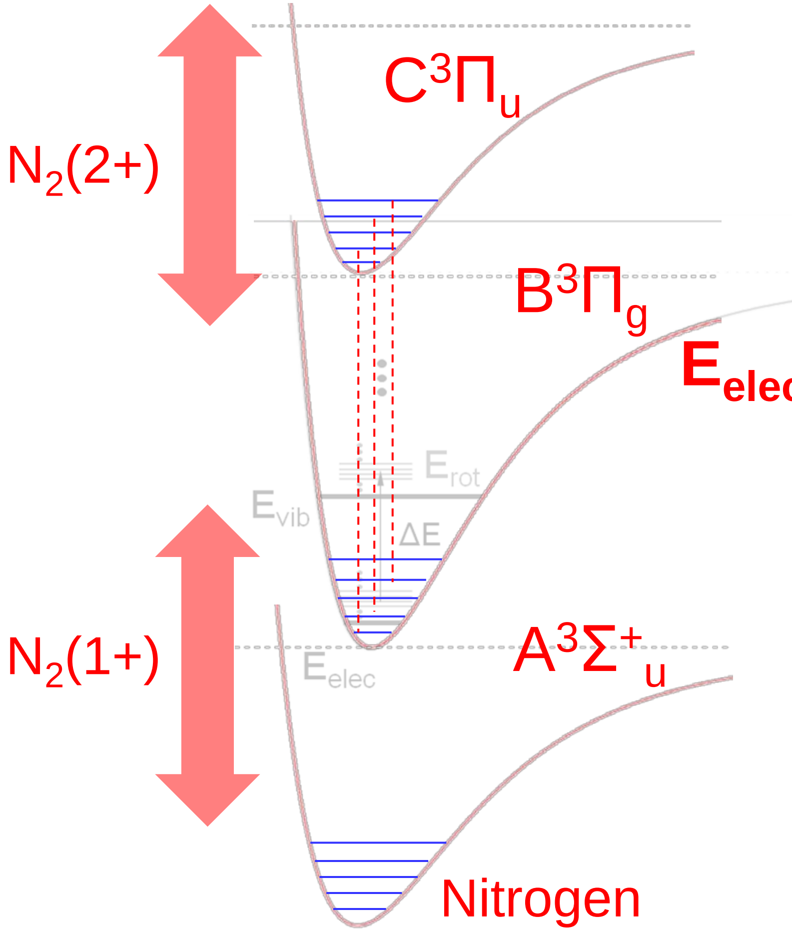
2. Absorption and Emission

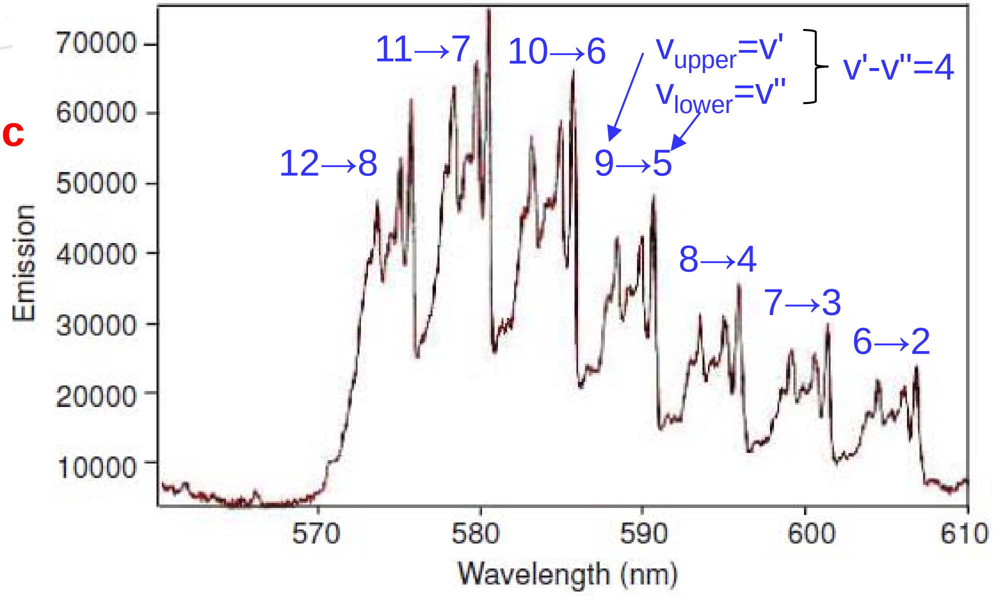
- Components of spectra: Lines, Bands, System.

$E_{int} = E_{elec} + E_{vib} + E_{rot}$

System

Example: High-temperature air emission spectra (560-610nm)



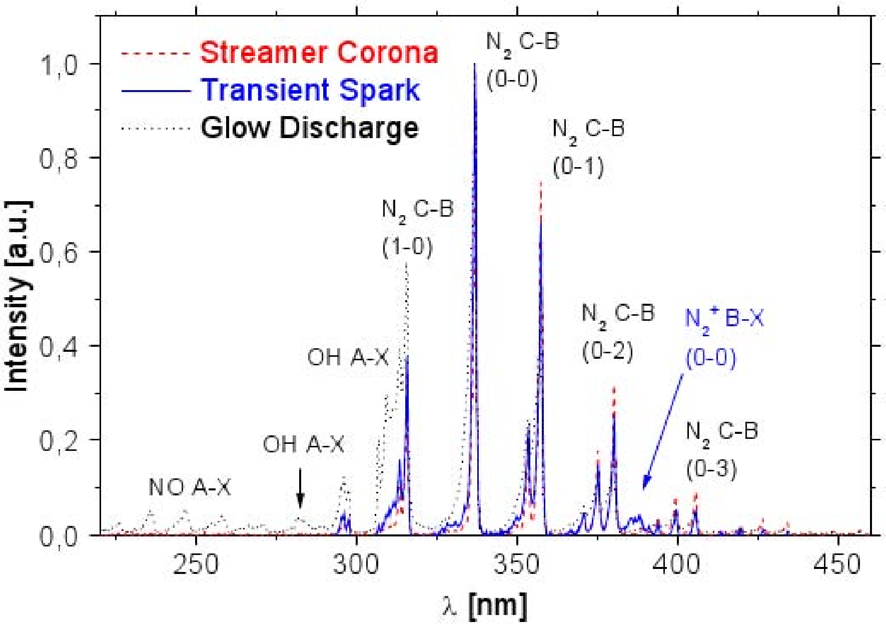


2. Absorption and Emission

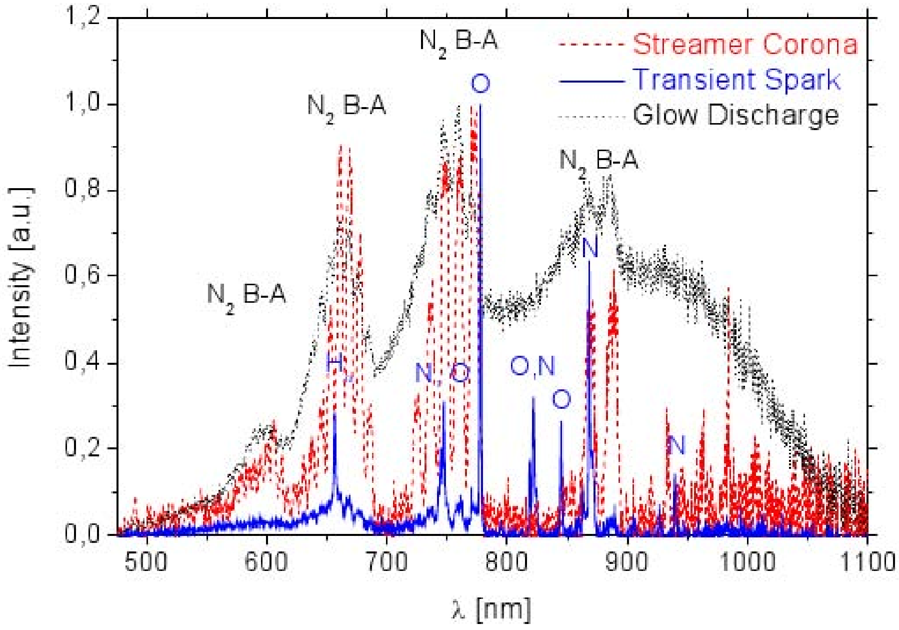
- Components of spectra: Lines, Bands, System.

System

Example: Typical emission spectra of DC discharges



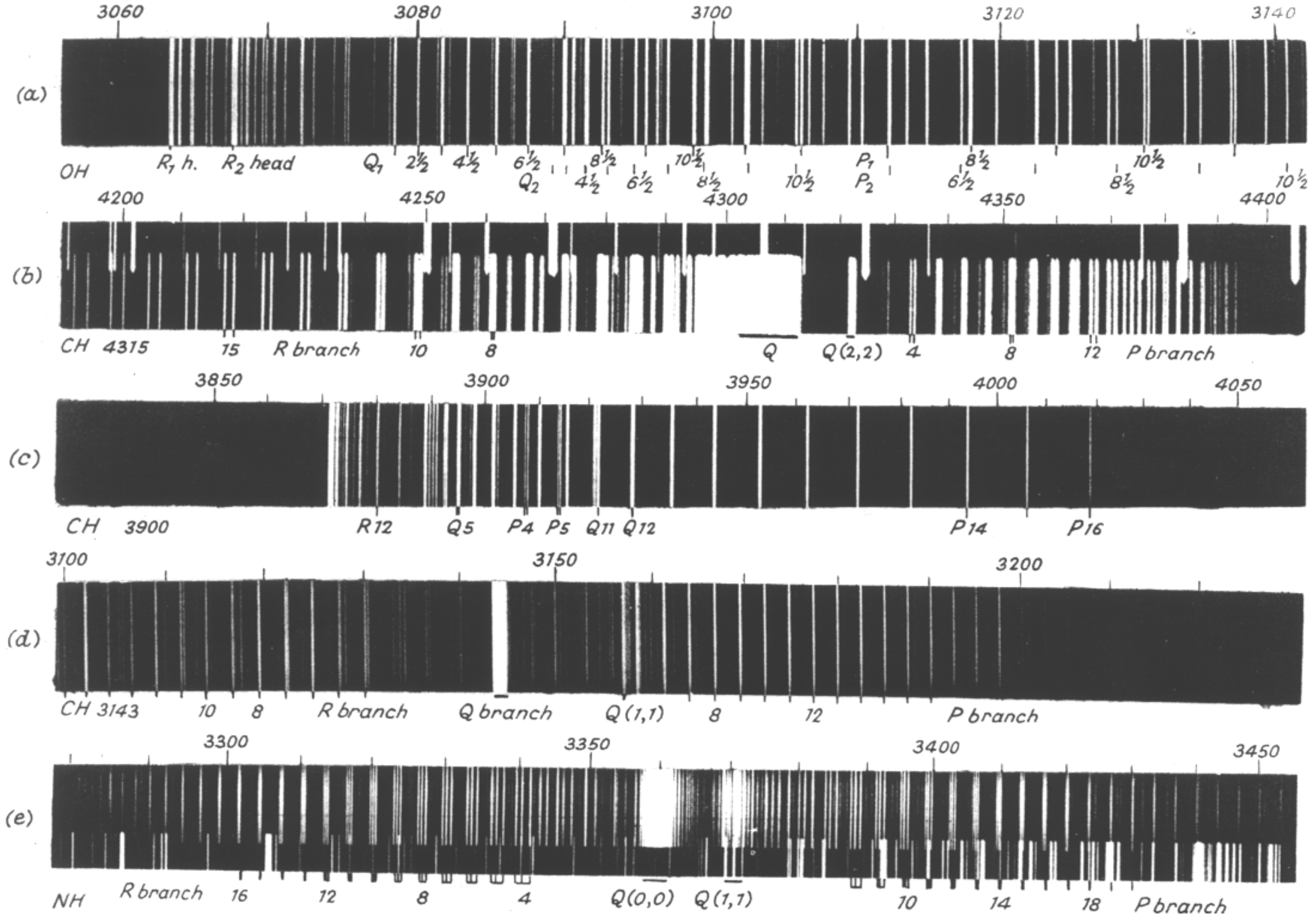
UV



Visible-NIR

2. Absorption and Emission

- Components of spectra: Lines, Bands, System.



OH $^2\Sigma-^2\Pi$ (0,0)

CH $^2\Delta-^2\Pi$

CH $^2\Sigma-^2\Pi$

CH $^2\Sigma-^2\Pi$

NH $^3\Pi-^3\Sigma$

- In early days, spectra were recorded on film!
  But now we have lasers.

2. Absorption and Emission

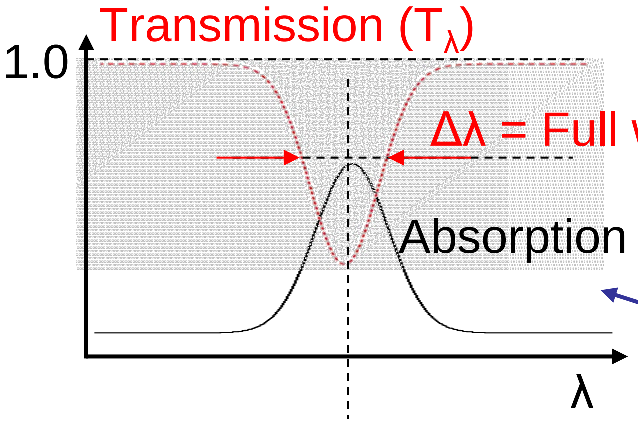
- How is T_λ (fractional transmission) measured?

Tunable Laser

Test media; Flame

I_λ; Detector

- Do lines have finite width/shape? Yes!



λ_0 = Line center

Δλ = Full width at half maximum

Δλ = f(P,T)

A resolved line has shape!

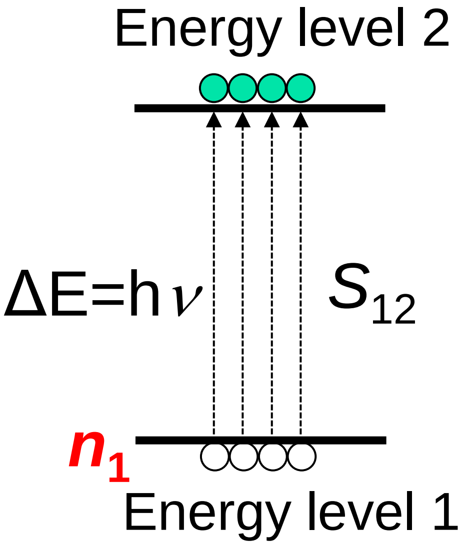
And shape is a f(T,P) → an opportunity for diagnostics!

2. Absorption and Emission

- 3 key elements of spectra
  - Line positions
  - Line strengths
  - Line shapes

3. Boltzmann Distribution

- **How strong is a transition?** ➡ Proportional to particle population in initial energy level n_1



Boltzmann fraction of absorber species *i* in level 1

$$F_i = \frac{n_i}{n} = \frac{g_i \exp\left(-\frac{\varepsilon_i}{kT}\right)}{Q}$$

- Equilibrium distribution of molecules of a single species over its allowed quantum states.

defines T

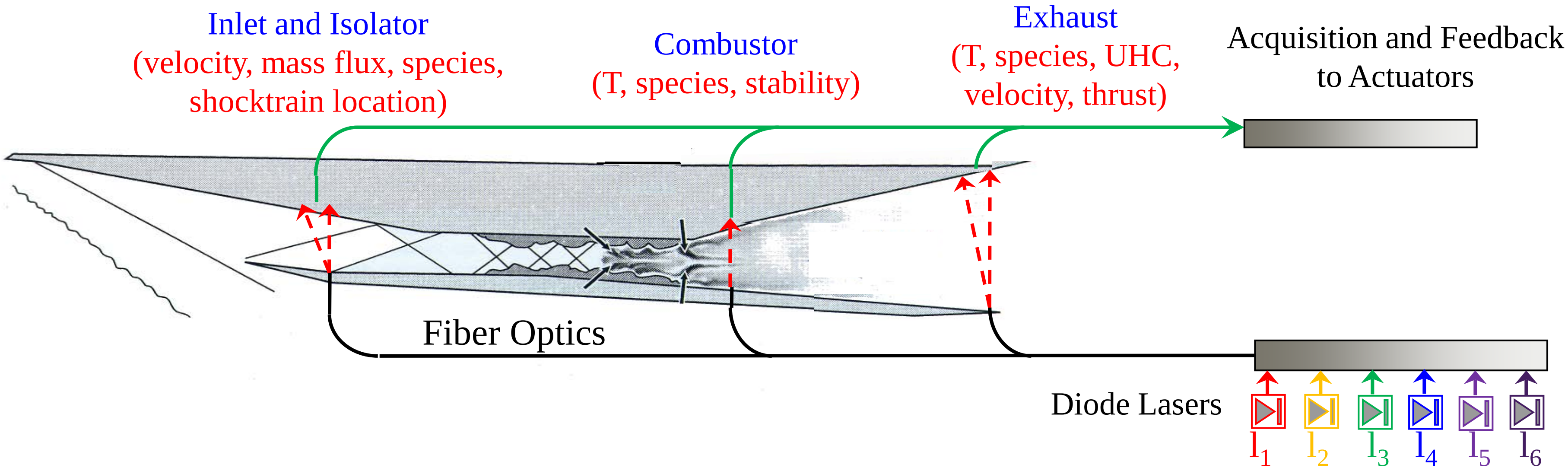
Partition function $Q = \sum_i g_i \exp\left(-\frac{\varepsilon_i}{kT}\right) = Q_{rot} Q_{vib} Q_{elec}$

Hence measurement of two densities, n_i and n_j → T

since $n_i/n_j = g_i/g_j \exp(-(\varepsilon_i-\varepsilon_j)/kT)$

4. Working Example – 1

- TDL sensing for aero-propulsion
  - Diode laser absorption sensors offer prospects for time-resolved, multi-parameter, multi-location sensing for performance testing, model validation, feedback control



Inlet and Isolator
(velocity, mass flux, species, shocktrain location)

Combustor
(T, species, stability)

Exhaust
(T, species, UHC, velocity, thrust)

Acquisition and Feedback to Actuators

Fiber Optics

Diode Lasers

- ➢ Sensors developed for T, V, H_2O, CO_2, O_2, & other species
- ➢ Prototypes tested and validated at Stanford
- ➢ Several applications successful in ground test facilities
- ➢ Now being utilized in flight

4. Working Example – 2

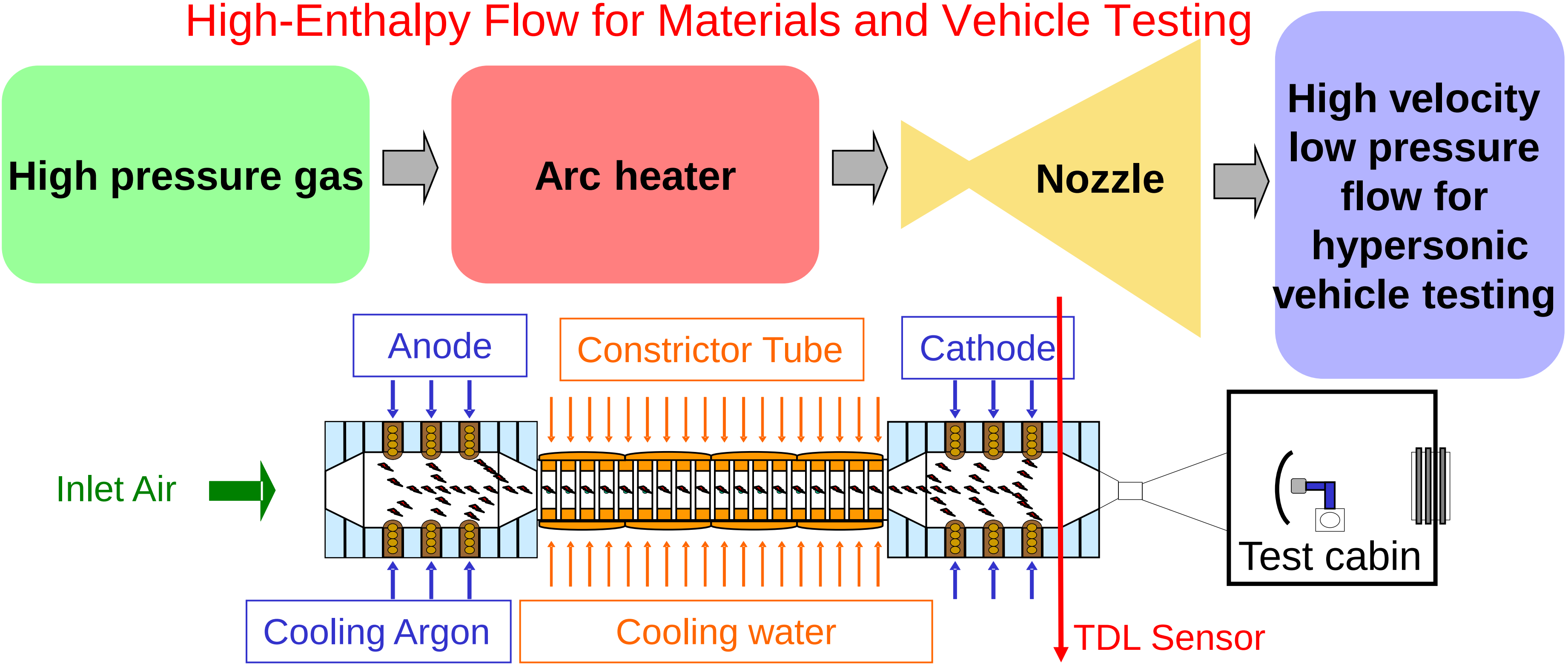
- TDL Sensing to Characterize NASA Ames ArcJet Facilities
  High-Enthalpy Flow for Materials and Vehicle Testing

High pressure gas → **Arc heater** → **Nozzle** → **High velocity low pressure flow for hypersonic vehicle testing**

4. Working Example – 2

- TDL Sensing to Characterize NASA Ames ArcJet Facilities

High-Enthalpy Flow for Materials and Vehicle Testing



High pressure gas → Arc heater → Nozzle → High velocity low pressure flow for hypersonic vehicle testing

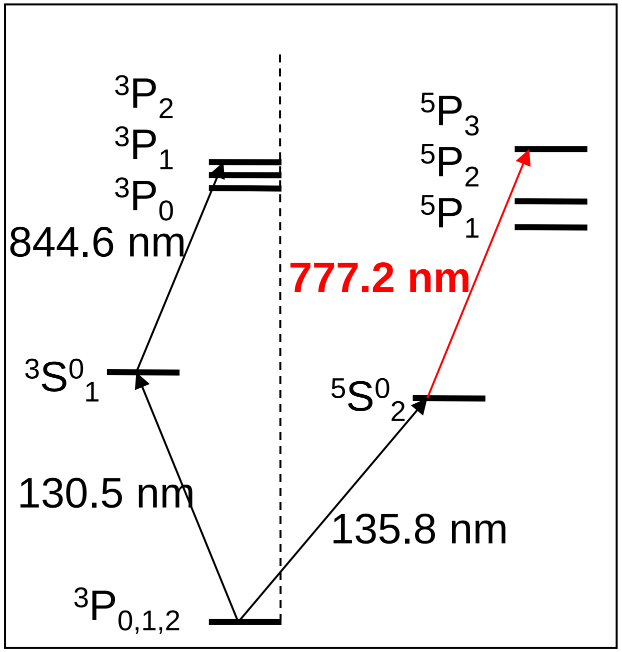
- **Goals:** (1) Time-resolved temperature sensing in the arc heater: O to infer T
  (2) Investigate spatial uniformity within heater (multi-path absorption)

Challenges: Extreme Conditions T=6000-8000K, P= 2-9 bar, I~2000A, 20 & 60 MW
Difficult access (mechanical, optical, and electrical)

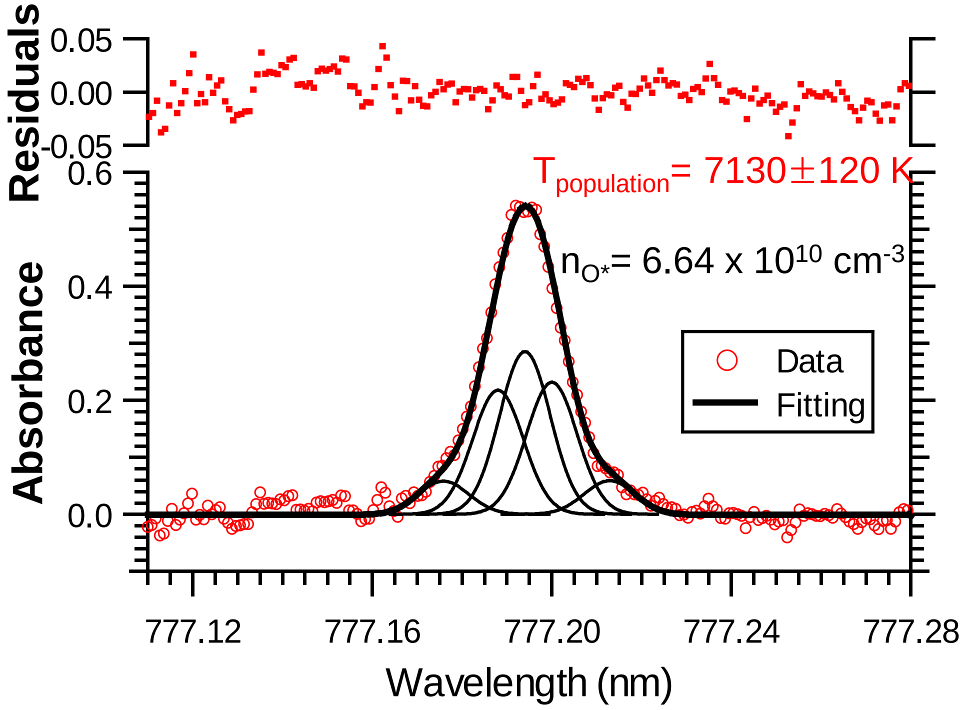
4. Working Example – 2

- Temperature from Atomic O Absorption Measurement

Atomic oxygen energy diagram



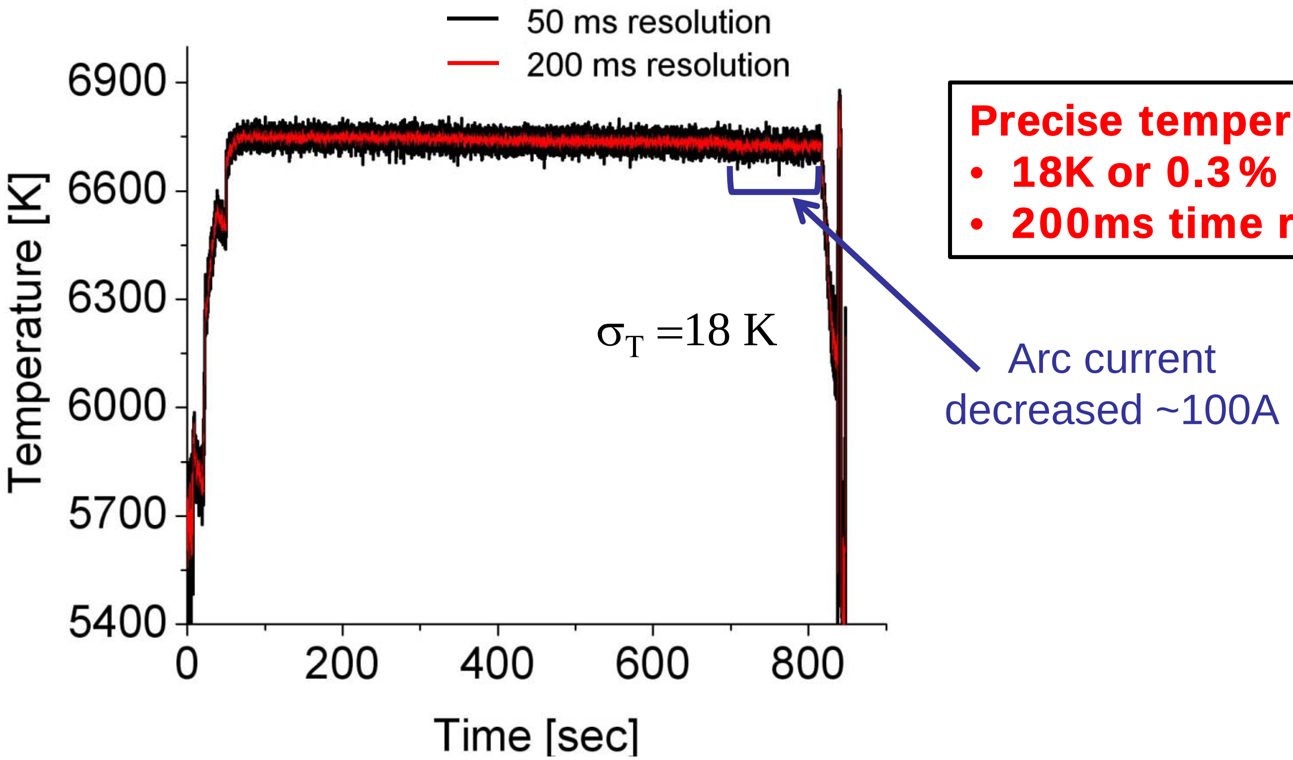
Atomic oxygen absorption measured in the arc heater



- Fundamental absorption transitions from O are VUV but excited O in NIR
- Equilibrium population of O-atom in $^5S^0_2$ extremely temperature sensitive

4. Working Example – 2

- Arc current at 2000A, power 20MW
- Last 200 seconds of run arc current decreased 100A
- Measured temperature captures change in arc conditions



Arc current decreased ~100A

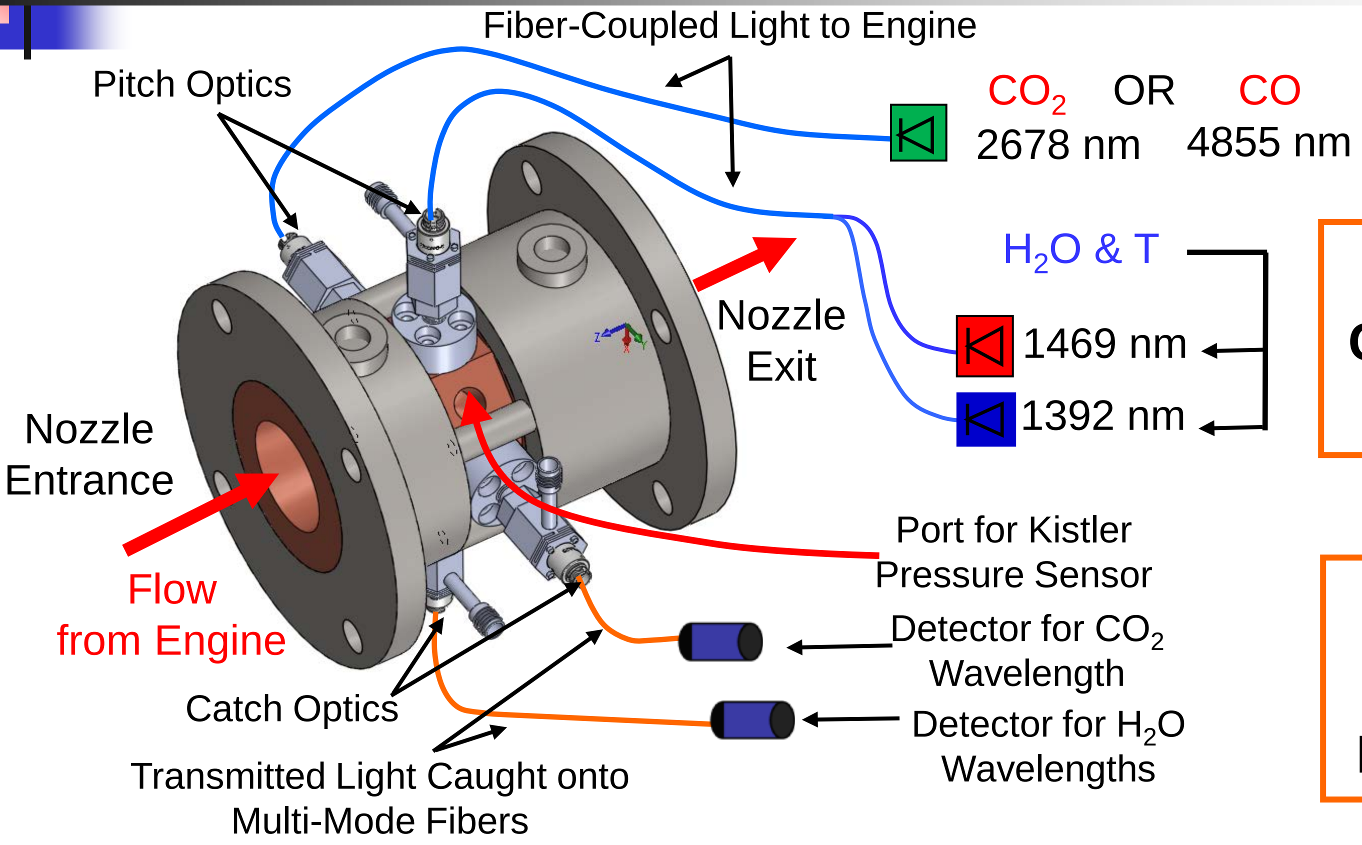
Precise temperature measurements

- **18K or 0.3% standard deviation**
- **200ms time resolution**

TDL sensor provides new tool for routine monitoring of arcjet performance

4. Working Example – 3

Time-Resolved High-P Sensing in PDC at NPS



Assumption: Choked flow T gives velocity

T, P, V & X_i yields Enthalpy Flux

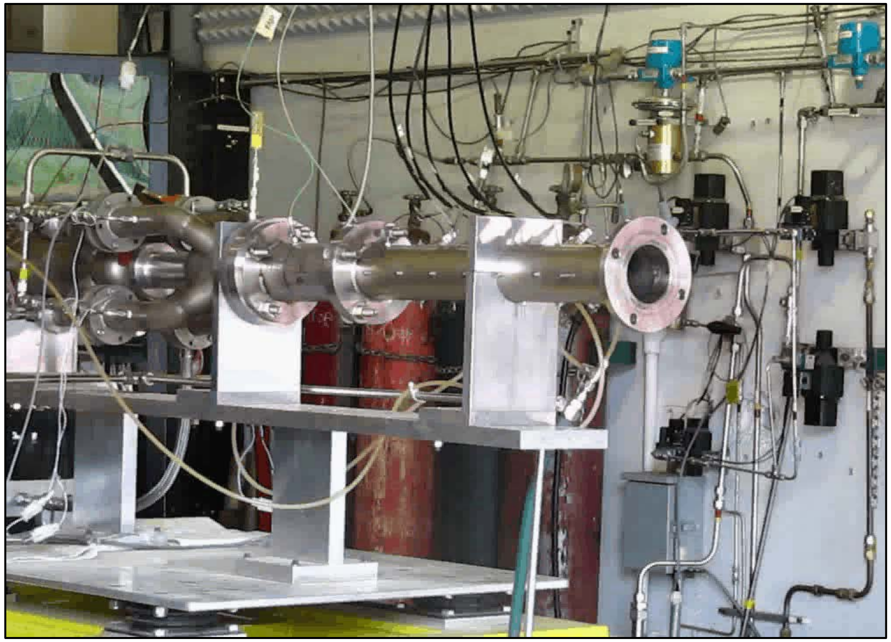
- Pulse-detonation combustor gives time-variable P/T
- Time-resolved measurements monitor performance & test CFD

4. Working Example – 3

Time-Resolved High-P Sensing in PDC at NPS

Pulse Detonation Combustor

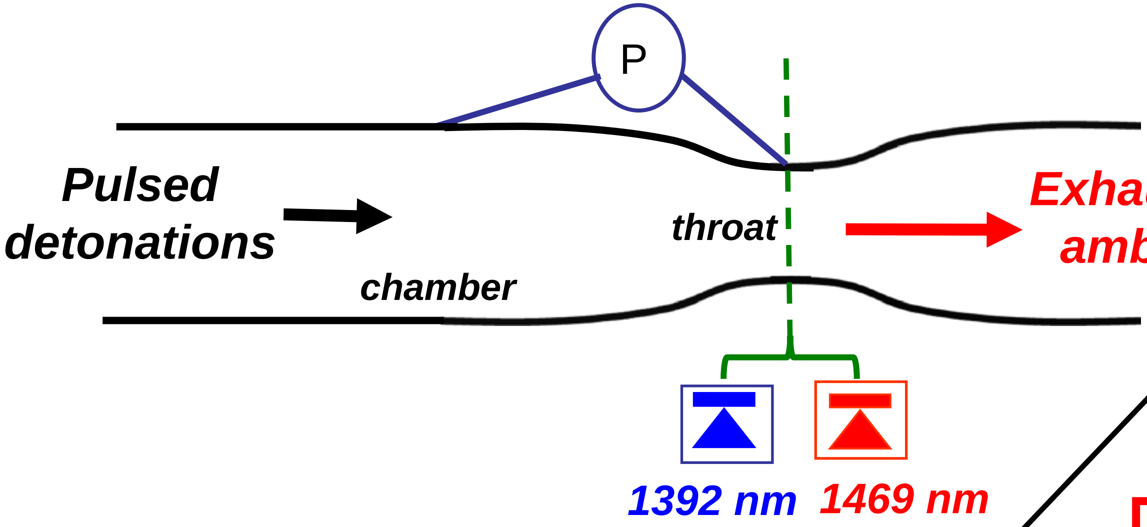
At Naval Post-graduate School in Monterey, CA



Optical sensors feasible in harsh, high pressure engine environment

4. Working Example – 3

Time-Resolved High-P Sensing in PDC at NPS



Throat Sensors

T & X_{H2O}

(CO@4.6μm; CO_2@2.7μm)

Assumption: Choked flow

↳ T gives velocity

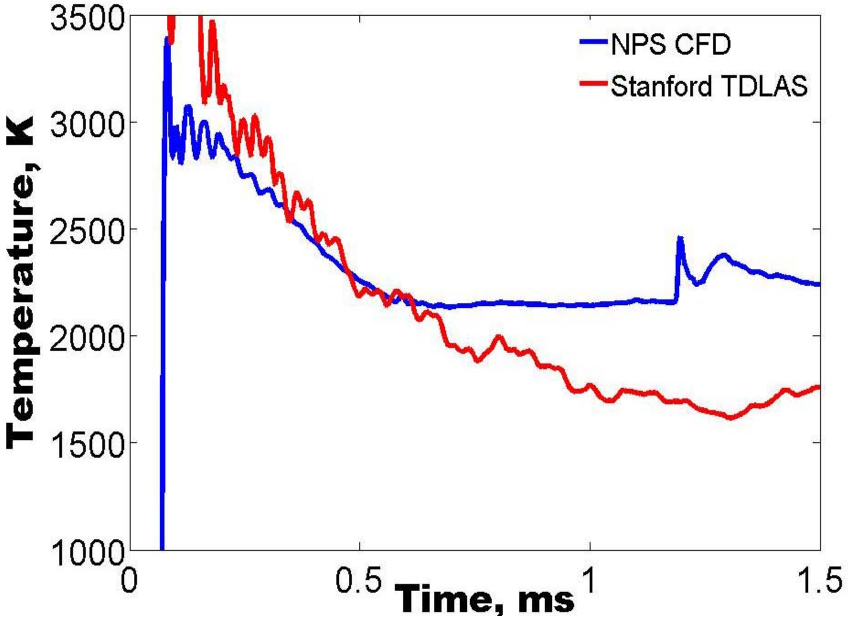
T, P, V & X_i ⟶ Enthalpy Flux

- Pulse-detonation combustor gives time-variable P/T
- Time-resolved measurements monitor performance & test CFD

4. Working Example – 3

Time-Resolved High-P Sensing in PDC at NPS

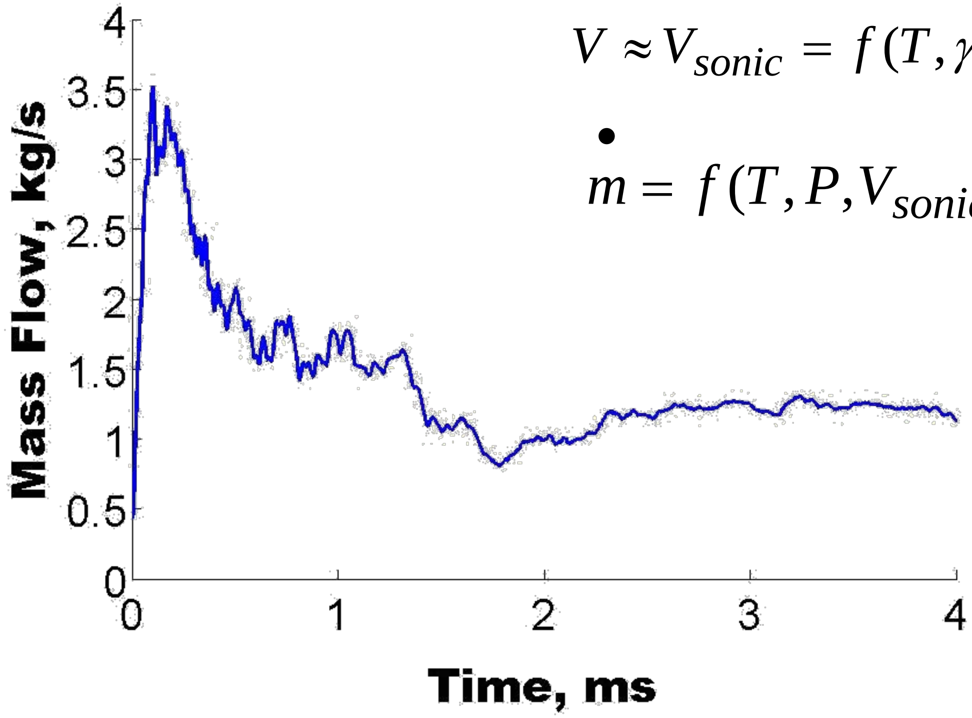
T- Data Collected in Nozzle Throat vs CFD



- T sensor performs well to >3500K, 30 atm!
- Data agrees well with CFD during primary blow down

4. Working Example – 3

Time-Resolved TDL Yields Mass Flow



$$V \approx V_{sonic} = f(T, \gamma_{mix})$$

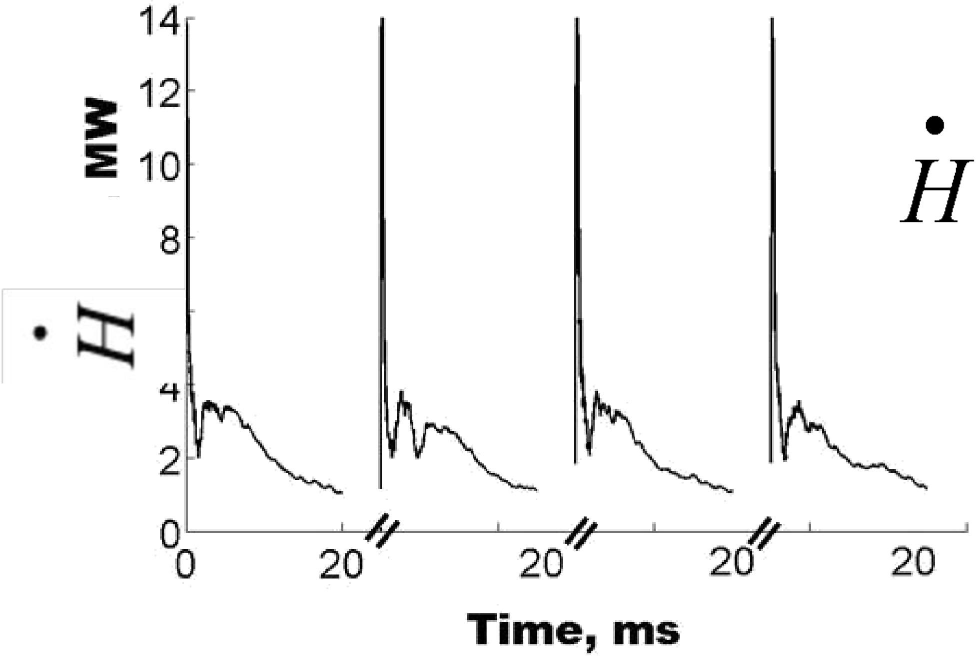
$$\dot{m} = f(T, P, V_{sonic})$$

- T and P give V and mass flow in choked throat as f(t)
- T, X, $\dot{m}$ and ideal gas can give enthalpy flow rate

4. Working Example – 3

Time-Resolved TDL Yields Enthalpy Flow Rate

4 Consecutive Cycles



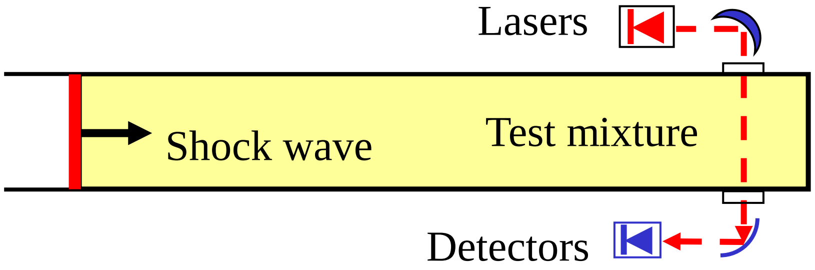
$$\dot{H} = \dot{m}\,\Delta h_{stag}(T)$$

T_{ref} = 298 K

- Time-resolved data provide key measures of engine performance
  - Power
  - Mass flow dynamics
  - H integrated over complete cycle for η_{th}

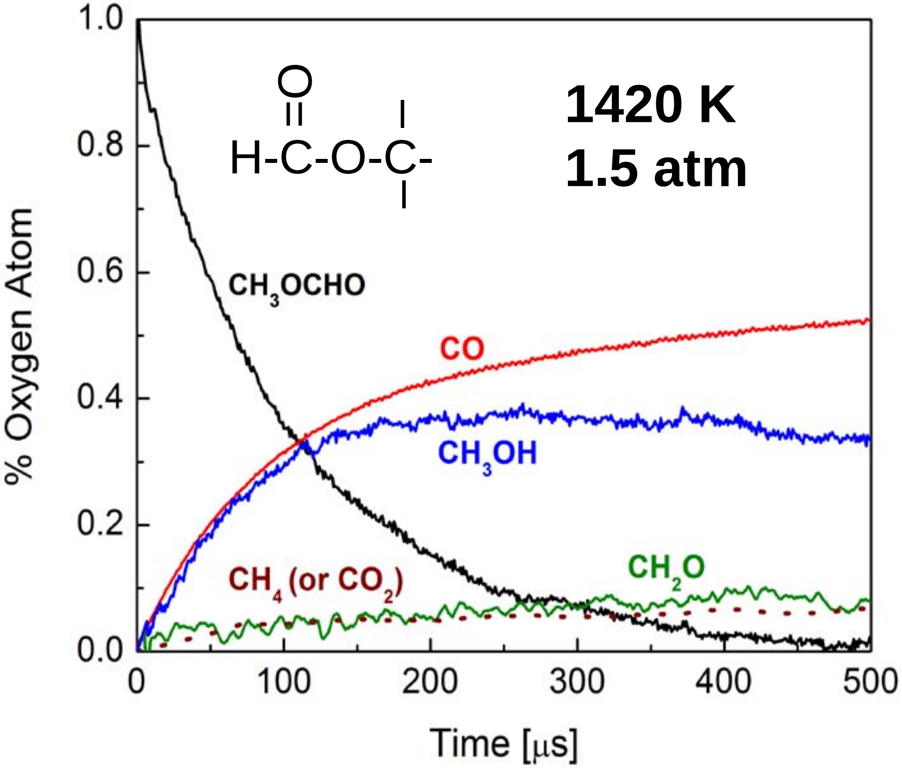
4. Working Example – 4

First Multi-Species Sensing for Shock Tube Kinetics



- Chemistry progress monitored by quantitative IR laser absorption
- Multi-species time histories provide step-changing advantage for mechanism validation
- Method accounts for nearly 100% of O-atoms

Oxygen Balance:
Methyl Formate Decomposition



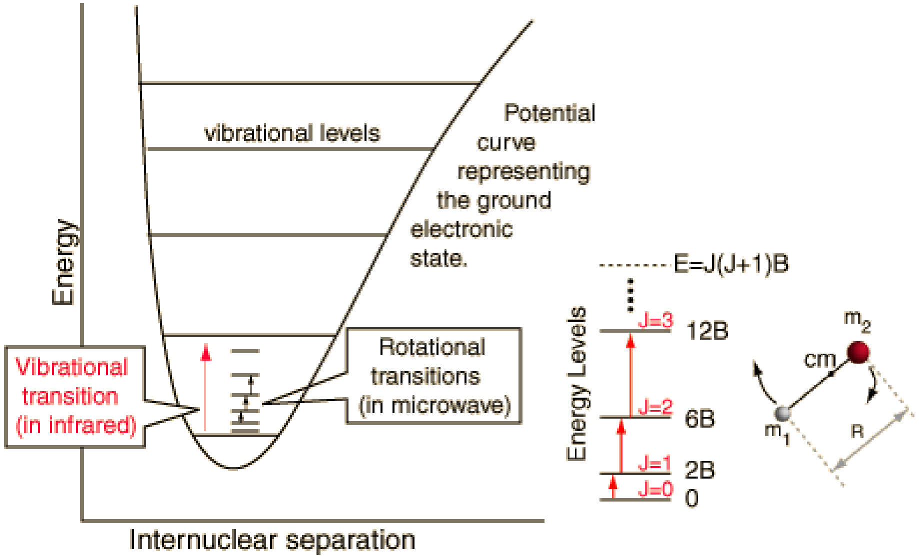
Next: Diatomic Molecular Spectra

- Rotational and Vibrational Spectra

Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

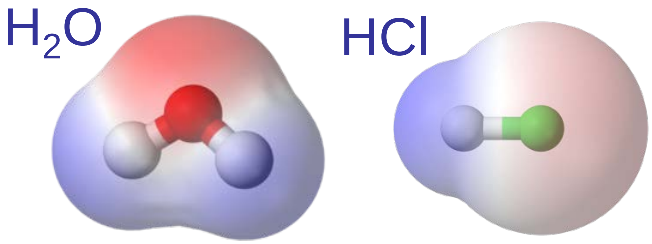
Lecture 2: Rotational and Vibrational Spectra

1. Light-matter interaction
2. Rigid-rotor model for diatomic molecule
3. Non-rigid rotation
4. Vibration-rotation for diatomics



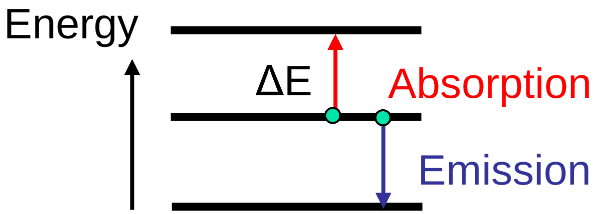
1. Light-matter interaction

- Possibilities of interaction
  - Permanent electric dipole moment
  - Rotation and vibration produce oscillating dipole (Emission/Absorption)

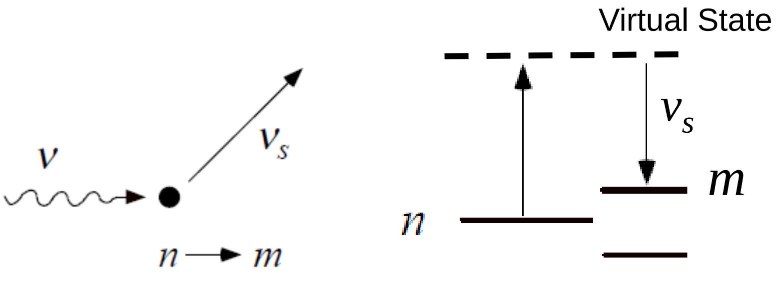


$\mu = qd$

What if Homonuclear?

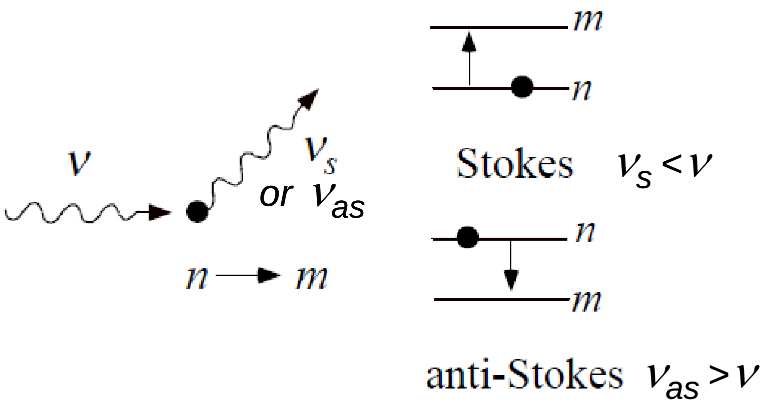


- Induced polarization (Raman scattering)



Inelastic scattering

- Elastic scattering (Rayleigh scattering)



1. Light-matter interaction

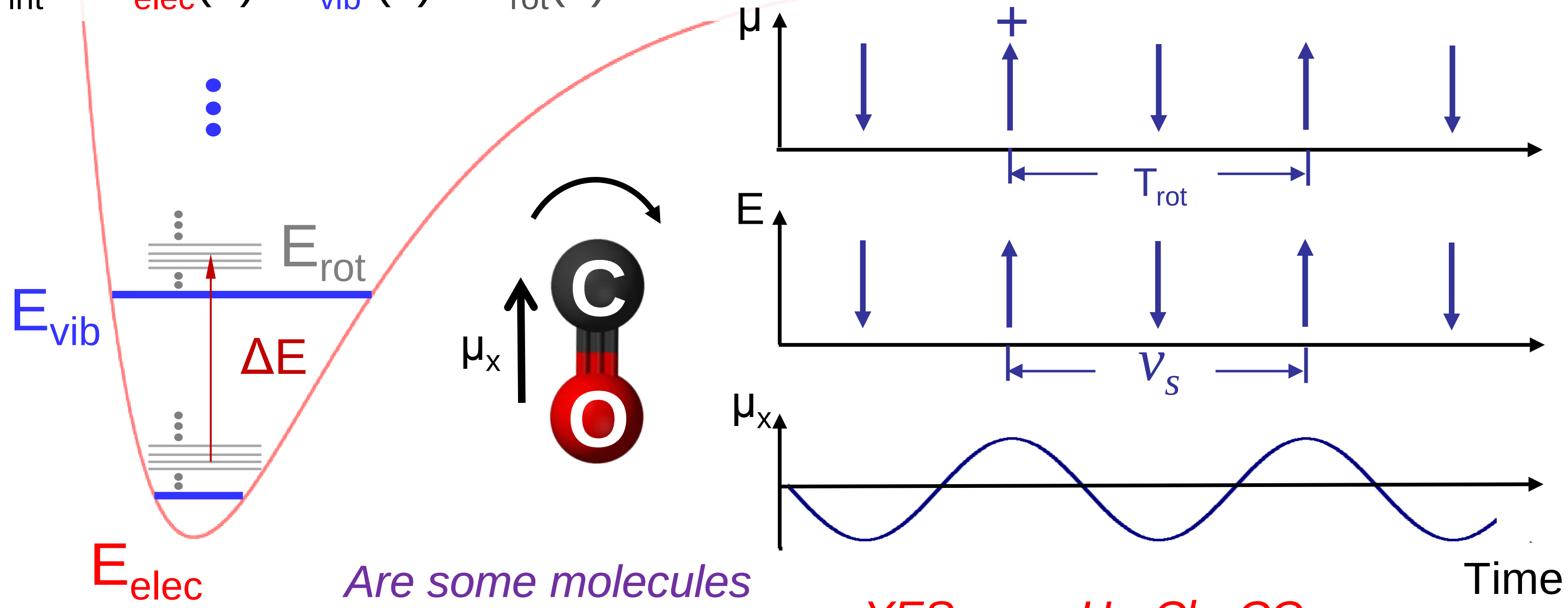
- Elements of spectra:
  - Line position
  - Line strength
  - Line shapes
- Internal Energy:

- **Line position (λ) is determined by difference between energy levels**
- **What determines the energy levels?**
- **Quantum Mechanics!**

Rotation: Microwave Region (ΔJ)

Electric dipole moment: $\vec{\mu} = \sum_i q_i \vec{r}_i$

$E_{int} = E_{elec}(n) + E_{vib}(\nu) + E_{rot}(J)$



Are some molecules "Microwave inactive"?

YES, e.g., H_2, Cl_2, CO_2

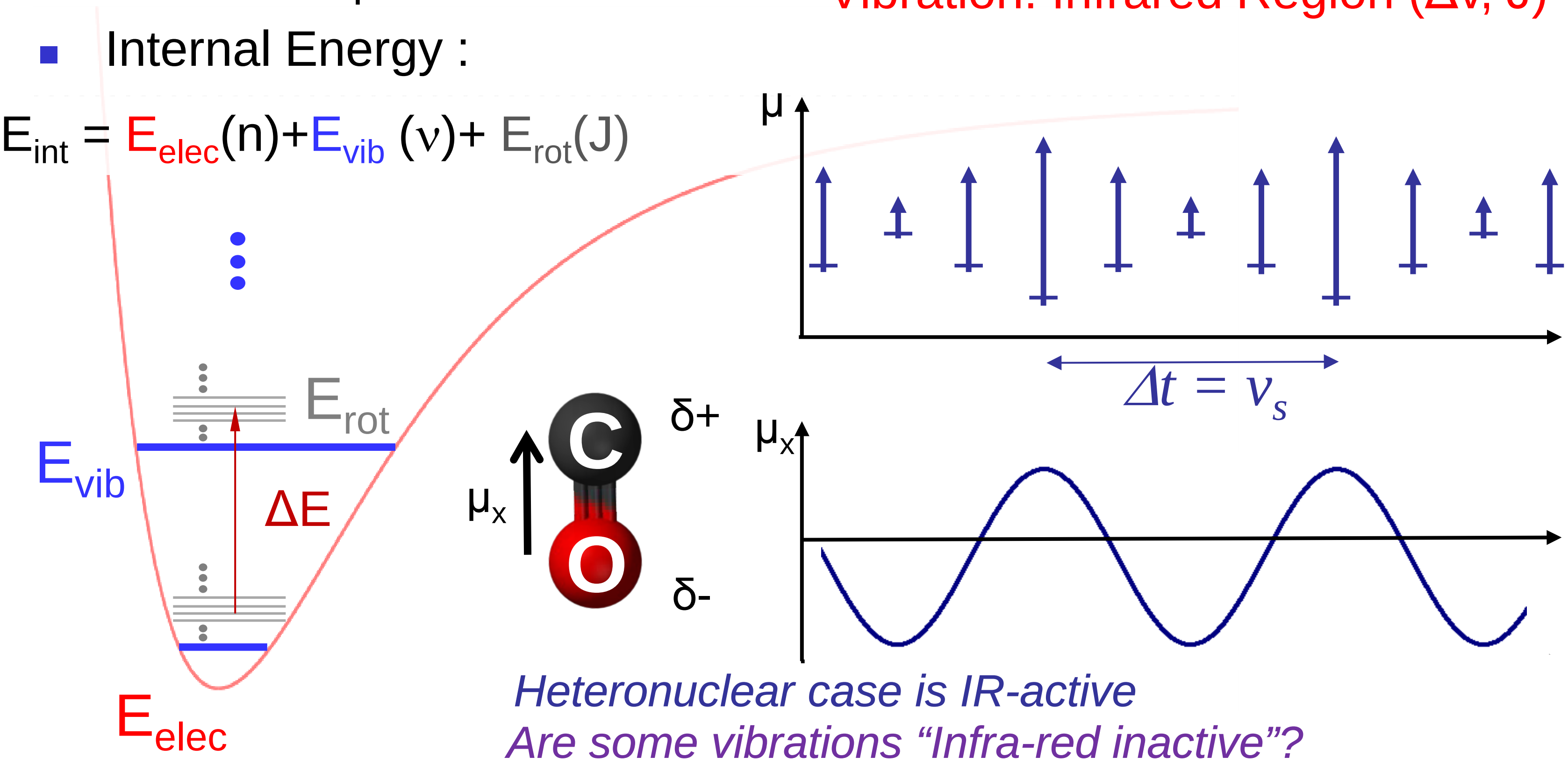
1. Light-matter interaction

- Elements of spectra:
  - Line position
  - Line strength
  - Line shapes
- Internal Energy :

Rotation: Microwave Region (ΔJ)

Vibration: Infrared Region (Δv, J)

$$E_{int} = E_{elec}(n)+E_{vib}(\nu)+E_{rot}(J)$$



Heteronuclear case is IR-active

Are some vibrations “Infra-red inactive”?

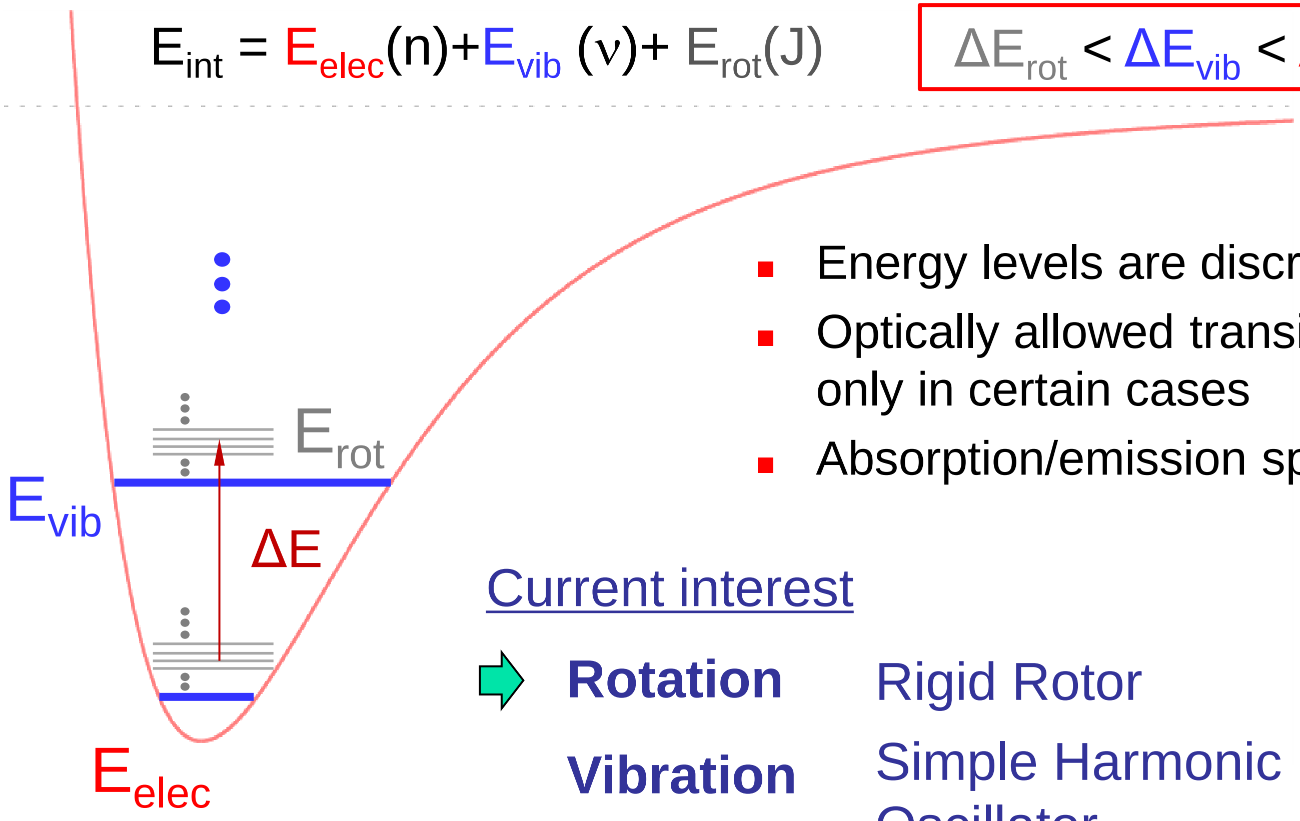
Yes, e.g., symmetric stretch of CO_2

1. Light-matter interaction

- Summary

$E_{int} = E_{elec}(n) + E_{vib}(\nu) + E_{rot}(J)$

$\boxed{\Delta E_{rot} < \Delta E_{vib} < \Delta E_{elec}}$



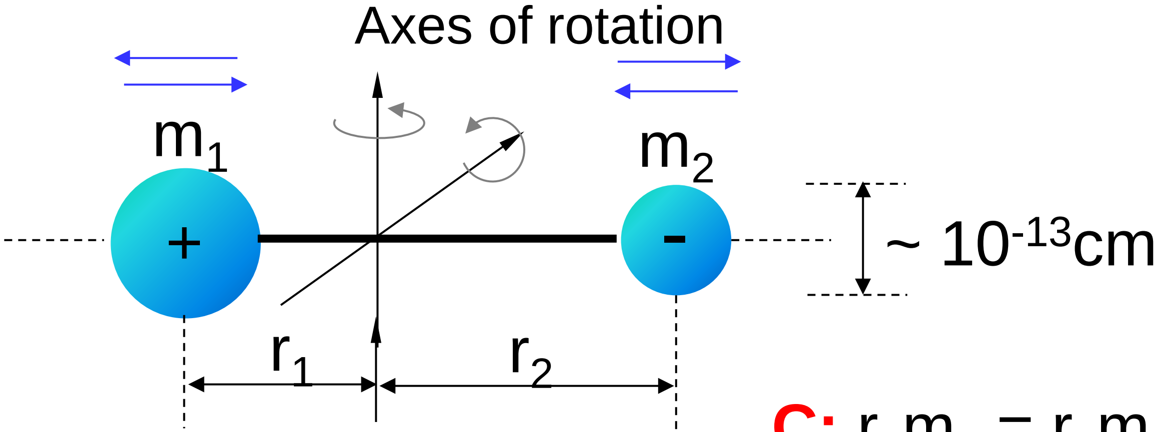
- Energy levels are discrete
- Optically allowed transitions may occur only in certain cases
- Absorption/emission spectra are discrete

Current interest

➡ **Rotation**	Rigid Rotor	Non-rigid Rotor
Vibration	Simple Harmonic Oscillator	Anharmonic Oscillator

2. Rigid-Rotor model of diatomic molecule

- Rigid Rotor



Center of mass **C**

C: $r_1 m_1 = r_2 m_2$

$r_1 + r_2 = r_e \sim 10^{-8}$cm

<u>Assume</u>:

- Point masses ($d_{nucleus} \sim 10^{-13}$cm, $r_e \sim 10^{-8}$cm)
- r_e = const. (“rigid rotor”)

➡ Relax this later

2. Rigid-Rotor model of diatomic molecule

- Classical Mechanics
  - Moment of Inertia

$$I = \sum m_i r_i^2 = \mu r_e^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \text{reduced mass}$$

2-body problem changed to single point mass

- Quantum Mechanics

Value of ω_{rot} is quantized

$$I\omega_{rot} = \sqrt{J(J+1)}\left(\hbar = h/2\pi\right)$$

$$\downarrow$$

Rot. quantum number = 0,1,2,…
∴ E_{rot} is quantized!

- Rotational Energy

$$E_{rot} = \frac{1}{2} I\omega_{rot}^2 = \frac{1}{2I}\left(I\omega_{rot}\right)^2 = \frac{1}{2I}J(J+1)\hbar^2 = J(J+1)\frac{h^2}{8\pi^2 I}$$

Convention to denote rot. energy

$$F(J), cm^{-1} = \varepsilon_J = \frac{E_{rot}}{hc} = \boxed{\left[\frac{h}{8\pi^2 Ic}\right]} J(J+1) = BJ(J+1)$$

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu} \qquad \therefore \varepsilon_J = \frac{E_{rot}}{hc}$$

2. Rigid-Rotor model of diatomic molecule

- Absorption spectrum

Schrödinger's Equation: $\frac{d^2\psi}{dx^2}+\frac{2m}{\hbar^2}\left[E-U(x)\right]\psi(x)=0$

Transition probability $\propto \int \psi_m \mu \psi_n^* d\tau \rightarrow \underline{\Delta J=\pm 1}$

ψ Wave function

ψ^* Complex conjugate

μ Dipole moment

Selection Rules for rotational transitions

$$\Delta J = \underset{\overset{\downarrow}{\text{' (upper)}}}{J'} - \underset{\overset{\downarrow}{\text{'' (lower)}}}{J''} = +1$$

Recall: $F(J)=BJ(J+1)$

e.g., $\bar{\nu}_{J=1\leftarrow J=0}=F(J=1)-F(J=0)=2B-0=2B$

2. Rigid-Rotor model of diatomic molecule

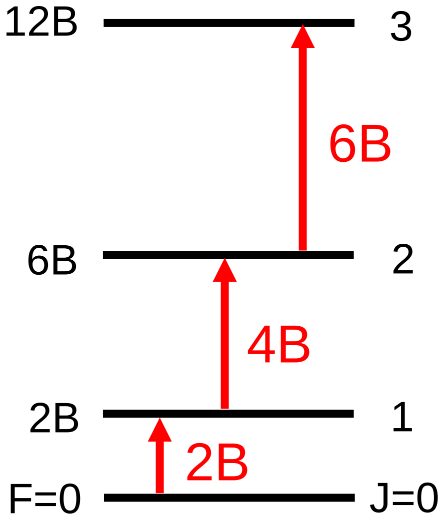
- Absorption spectrum

Remember that: $F(J) = BJ(J+1)$

E.g., $\bar{\nu}_{J=1\leftarrow J=0} = F(J=1) - F(J=0) = 2B - 0 = 2B$

J	**F**	**1st diff = $\bar{\nu}$**	**2nd diff = spacing**
0	0		
		2B	
1	2B		2B
		4B	
2	6B		2B
		6B	
3	12B		2B
		8B	
4	20B		

Lines every 2B!



In general: $\bar{\nu}_{J+1\leftarrow J} = \bar{\nu}_{J'\leftarrow J''} = B(J''+1)(J''+2) - BJ''(J''+1)$

$$\boxed{\bar{\nu}_{J'\leftarrow J''}, cm^{-1} = 2B(J''+1)}$$

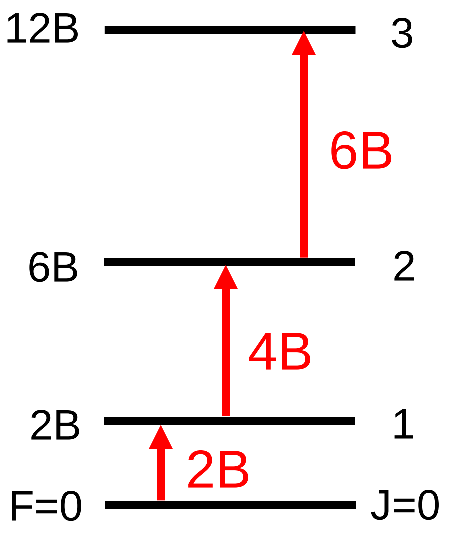
Let's look at absorption spectrum

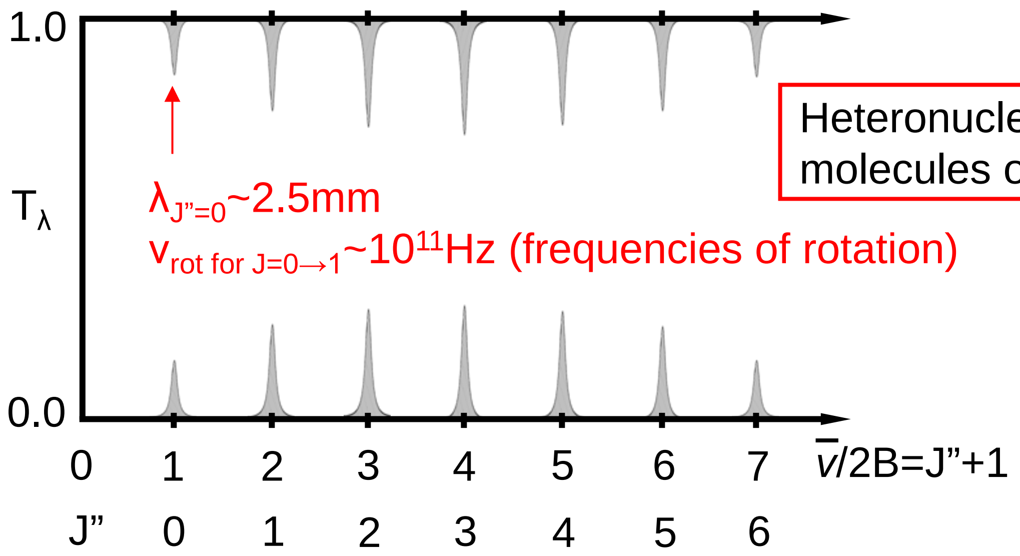
2. Rigid-Rotor model of diatomic molecule

- Absorption spectrum

Recall: $F(J) = BJ(J+1)$

E.g., $\bar{\nu}_{J=1 \leftarrow J=0} = F(J=1) - F(J=0) = 2B - 0 = 2B$





$\lambda_{J''=0}$~2.5mm

$\nu_{\text{rot for } J=0\rightarrow 1}$~$10^{11}$Hz (frequencies of rotation)

Heteronuclear molecules only!

Note:

1. Uniform spacing (easy to identify/interpret)
2. B_{CO}~2cm^{-1} ➡ $\lambda_{J''=0} = 1/\bar{\nu} = 1/4\text{cm} = 2.5\text{mm}$ (microwave/mm waves)
3. $\nu_{rot,J=1} = c/\lambda = 3\text{x}10^{10}/.25$ Hz = $1.2\text{x}10^{11}$Hz (microwave)

2. Rigid-Rotor model of diatomic molecule

- Usefulness of rotational spectra

Measured spectra ⇨ Physical characteristics of molecule

Line spacing =2B ⇨ $B = \frac{h}{8\pi^2 Ic}$ ⇨ $I = \mu r_e^2$ ⇨ r_e Accurately!

Example: CO

$B = 1.92118\ \mathrm{cm}^{-1} \rightarrow r_{CO} = 1.128227$ Å

↑

10^{-6} Å = 10^{-16} m

2. Rigid-Rotor model of diatomic molecule

- Intensities of spectral lines

Equal probability assumption (crude but useful)

✓ Abs. (or emiss.) probability per molecule, is (crudely) independent of J

✓ Abs. (or emiss.) spectrum varies w/ J like Boltzmann distribution

Degeneracy is a QM result associated w/ possible directions of Angular Momentum vector

Recall: $$\frac{N_J}{N} = \frac{(2J+1)\exp(-E_J/kT)}{Q_{rot}} = \frac{(2J+1)\exp[-\theta_r J(J+1)/T]}{T/\theta_r}$$

$$\frac{E_J}{k} = \frac{hcF(J)}{k} = \left(\frac{hc}{k}\right)BJ(J+1) = \theta_r J(J+1)$$

Partition function: $$Q_{rot} = \frac{1}{\sigma}\frac{kT}{hcB} = \frac{1}{\sigma}\frac{T}{\theta_r}$$

Symmetric no. (ways of rotating to achieve same orientation) **<u>= 1 for microwave active</u>**

Define rotational T: $$\theta_r[K] = \left(\frac{hc}{k}\right)B$$

CO: σ=1 → microwave active!

N_2: σ=2 → microwave inactive!

2. Rigid-Rotor model of diatomic molecule

- Intensities of spectral lines

Rotational Characteristic Temperature: $\theta_r[K] = \left(\frac{hc}{k}\right)B$

$$\boxed{\frac{hc}{k} = 1.44K/cm^{-1}}$$

Species	**θ_{rot} [K]**
O_2	2.1
N_2	2.9
NO	2.5
Cl_2	0.351

$$\frac{N_J}{N} = \frac{(2J+1)\exp\left[-\theta_r J(J+1)/T\right]}{T/\theta_r}$$

Strongest peak: occur where the population is at a local maximum

$$\frac{d(N_J/N)}{dJ} = 0 \quad \Rightarrow \quad \boxed{J_{\max} = (T/2\theta_{rot})^{1/2} - 1/2 = f(T/\theta_{rot})}$$

2. Rigid-Rotor model of diatomic molecule

- Effect of isotopic substitution

Recall: $B = \dfrac{h}{8\pi^2 Ic}$

Changes in nuclear mass (neutrons) do not change r_0

→ r depends on binding forces, associated w/ charged particles

→ Can determine mass from B

Therefore, for example:

$$\frac{B\left({}^{12}C^{16}O\right)}{B\left({}^{13}C^{16}O\right)} = \frac{1.92118}{1.83669} \Rightarrow m_{{}^{13}C} = 13.0007$$

$$\left(m_{{}^{12}C} = 12.00\right)$$

⇨ Agrees to 0.02% of other determinations

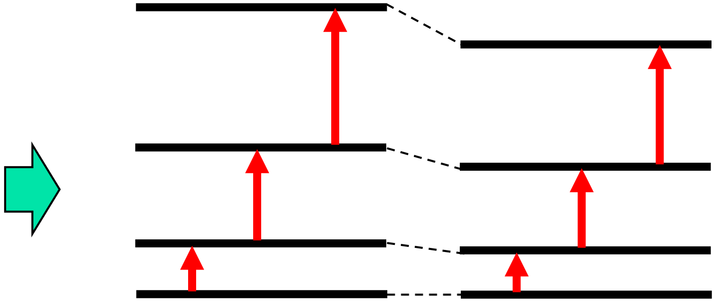
3. Non-Rigid Rotation

- Two effects; follows from $B \propto 1/r^2$
  - Vibrational stretching **r(v)**

    v↑ r↑ B↓
  - Centrifugal distortion **r(J)**

    J↑ r↑ B↓

Effects shrink line spacings/energies



Result: $F_v(J) = B_v J(J+1) - D_v J^2 (J+1)^2$

Centrifugal distribution constant

➡ $\bar{\nu}_{J'\leftarrow J'',v} = 2B_v(J''+1) - 4D_v(J''+1)^3$

Notes: 1. D_v is small; $D = \dfrac{4B^3}{\omega_e^2} << B$

e.g., $\left(\dfrac{D}{B}\right)_{NO} = 4\left(\dfrac{B}{\omega_e}\right)^2 \approx 4\left(\dfrac{1.7}{1900}\right)^2 \approx 3\times10^{-6}$

→ D/B smaller for “stiff/hi-freq” bonds

3. Non-Rigid Rotation

- Notes: 1. D_v is small; $D = \dfrac{4B^3}{\omega_e^2} << B$

  e.g., $\left(\dfrac{D}{B}\right)_{NO} = 4\left(\dfrac{B}{\omega_e}\right)^2 \approx 4\left(\dfrac{1.7}{1900}\right)^2 \approx 3\times10^{-6}$

  → D/B smaller for "stiff/hi-freq" bonds

  2. v dependence is given by $B_v = B_e - \alpha_e(v+1/2)$

  $D_v = D_e - \beta_e(v+1/2)$

E.g., NO

$B_e = 1.7046 cm^{-1}$ $\qquad \alpha_e / B_e \sim 0.01$

$\alpha_e = 0.0178$ $\qquad \beta_e / D_e \sim 0.001$

$D_e \cong 5.8\times10^{-6}\left({}^2\Pi_{1/2}\right)$

$\beta_e \cong 0.0014 D_e \sim 8\times10^{-9} cm^{-1}$

$\omega_e = 1904.03\left({}^2\Pi_{1/2}\right);1903.68\left({}^2\Pi_{3/2}\right)$

$\omega_e x_e = 13.97 cm^{-1}$

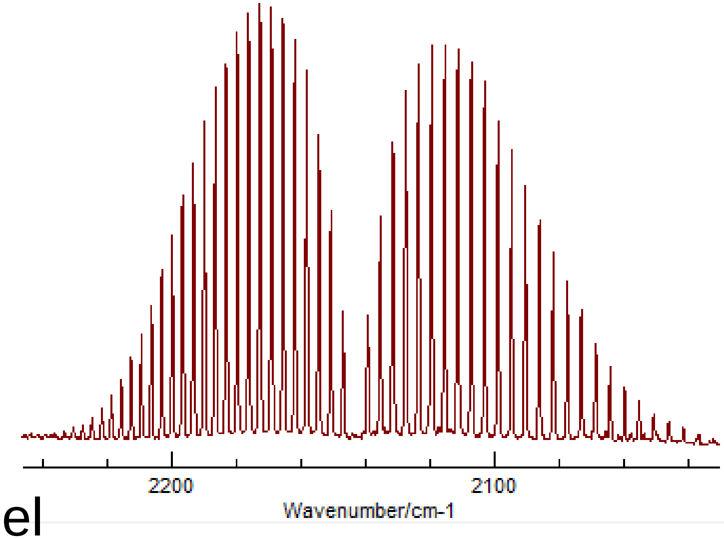
Aside:

- $\beta_e / D_e = \dfrac{8\omega_e x_e}{\omega_e} - \dfrac{5\alpha_e}{B_e} - \dfrac{\alpha_e^2\omega_e}{24B_e^3} << 1$
- Herzberg, Vol. I

e denotes "evaluated at equilibrium inter-nuclear separation" r_e

4. Vibration-Rotation Spectra (IR)

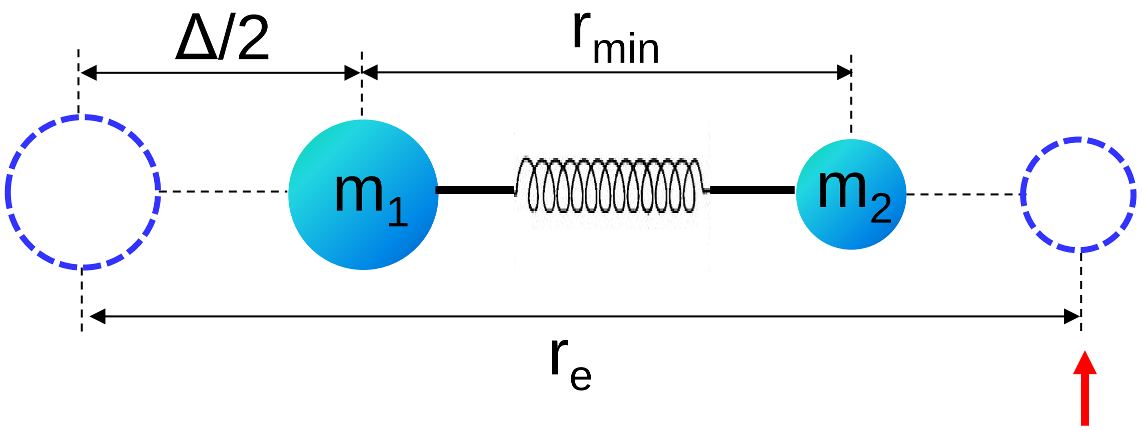
1. Diatomic Molecules
   - Simple Harmonic Oscillator (SHO)
   - Anharmonic Oscillator (AHO)
2. Vibration-Rotation spectra – Simple model
   - R-branch / P-branch
   - Absorption spectrum
3. Vibration-Rotation spectra – Improved model
4. Combustion Gas Spectra



Vibration-Rotation spectrum of CO (from FTIR)

4.1. Diatomic Molecules

- Simple Harmonic Oscillator (SHO)



Molecule at instance of greatest compression

Equilibrium position (balance between attractive + repulsive forces – min energy position

As usual, we begin w. classical mechanics + incorporate QM only as needed

4.1. Diatomic Molecules

- Simple Harmonic Oscillator (SHO)

Classical mechanics

- Force $= k_s(r - r_e)$ - Linear force law / Hooke's law
- Fundamental Freq. $\nu_{vib} = \frac{1}{2\pi}\sqrt{k_s/\mu}$ $\omega_e, cm^{-1} = \nu / c$
- Potential Energy $U = \frac{1}{2}k(r - r_e)^2$

Quantum mechanics

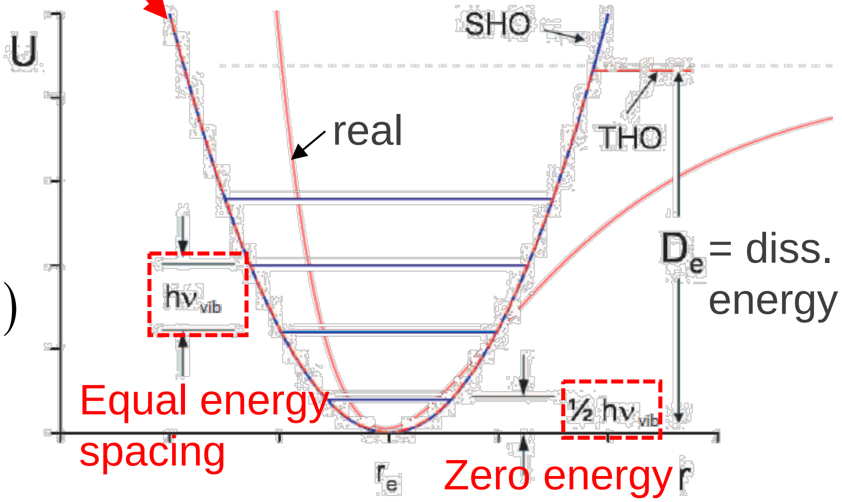
- v = vib. quantum no.

  = 0,1,2,3,…
- Vibration energy G=U/hc

  $G(\mathrm{v}), cm^{-1} = (\omega_e = \mathrm{v}_{vib}/c)(\mathrm{v} + 1/2)$
- Selection Rules:

  $\Delta\mathrm{v} = \mathrm{v}' - \mathrm{v}'' = 1$ only!

Parabola centered at distance of min. potential energy



Equal energy spacing

Zero energy

4.1. Diatomic Molecules

- Anharmonic Oscillator (AHO)

SHO

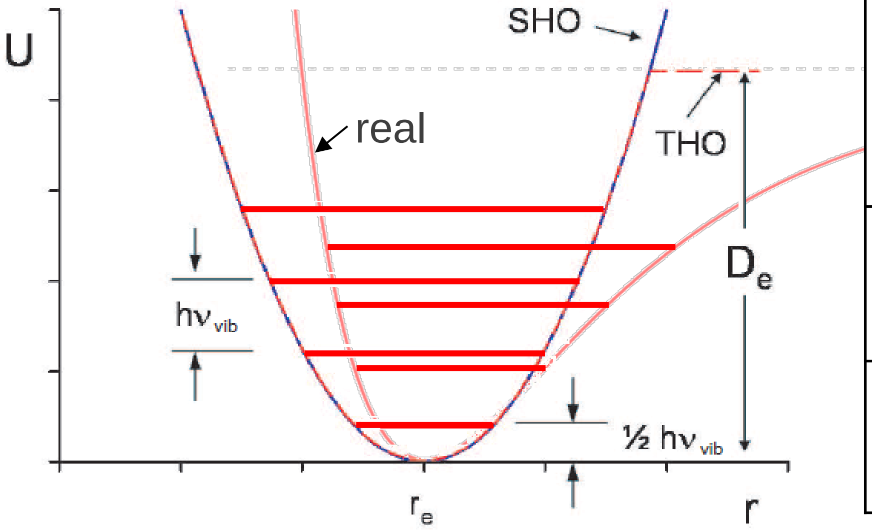
$$G(\mathrm{v}), cm^{-1} = \omega_e(\mathrm{v}+1/2)$$

AHO

$$G(\mathrm{v}), cm^{-1} = \omega_e(\mathrm{v}+1/2) - \underbrace{\omega_e x_e(\mathrm{v}+1/2)^2} + \ldots + H.O.T.$$

Decreases energy spacing

1^{st} anharmonic correction



Δv=+1	"Fundamental" Band (e.g., 1←0,2←1)	$\bar{\nu}_{1\leftarrow 0} = G(1) - G(0)$ $= \omega_e(1-2x_e)$ $\bar{\nu}_{2\leftarrow 1} = \omega_e(1-4x_e)$
Δv=+2	1^{st} Overtone (e.g., 2←0,3←1)	$\bar{\nu}_{2\leftarrow 0} = 2\omega_e(1-3x_e)$
Δv=+3	2^{nd} Overtone (e.g., 3←0,4←1)	$\bar{\nu}_{3\leftarrow 0} = 3\omega_e(1-4x_e)$

In addition, breakdown in selection rules

4.1. Diatomic Molecules

- Vibrational Partition Function

$$Q_{vib} = \left[1 - \exp\left(\frac{-hc\omega_e}{kT}\right)\right]^{-1} \exp\left(\frac{-hc\omega_e}{2kT}\right)$$

Choose reference (zero) energy at v=0, so $G(\mathrm{v}) = \omega_e \mathrm{v}$

➡ $$Q_{vib} = \left[1 - \exp\left(\frac{-hc\omega_e}{kT}\right)\right]^{-1}$$

The same zero energy must be used in specifying molecular energies E_i for level i and in evaluating the associated partition function

- Vibrational Temperature

$$\theta_{vib}[K] = \left(\frac{hc}{k}\right)\omega_e$$

$$\frac{N_{vib}}{N} = \frac{g_{vib}\exp(-\mathrm{v}\theta_{vib}/T)}{Q_{vib}}$$

$$= \exp\left(-\frac{\mathrm{v}\theta_{vib}}{T}\right)\left[1 - \exp\left(-\frac{\theta_{vib}}{T}\right)\right]$$

where $g_{vib} = 1$

Species	**θ_{vib} [K]**	**θ_{rot} [K]**
O_2	2270	2.1
N_2	3390	2.9
NO	2740	2.5
Cl_2	808	0.351

4.1. Diatomic Molecules

- Some typical values (Banwell, p.63, Table 3.1)

Gas	Molecular Weight	Vibration ω_e [cm^{-1}]	Anharmonicity constant x_e	Force constant k_s [dynes/cm]	Internuclear distance r_e [Å]	Dissociation energy D_{eq} [eV]
CO	28	2170	0.006	19×10^5	1.13	11.6
NO	30	1904	0.007	16×10^5	1.15	6.5
H_2†	2	4395	0.027	16×10^5	1.15	6.5
Br_2†	160	320	0.003	2.5×10^5	2.28	1.8

  - † Not IR-active, use Raman spectroscopy!
  - $\omega_e \propto \sqrt{k/\mu} \leftarrow \mu = m/2$ for homonuclear molecules
  - $D_e \approx \omega_e / 4x_e \leftarrow$ large k, large D
  - Weak, long bond → loose spring constant → low frequency

4.1. Diatomic Molecules

- Some useful conversions
  - Energy $1\,\text{cal} = 4.1868\,\text{J}$

    $1\,\text{cm}^{-1} = 2.8575\,\text{cal/mole}$

    $1\,\text{eV} = 8065.54\,\text{cm}^{-1} = 23.0605\,\text{kcal/mole} = 1.60219 \times 10^{-19}\ \text{J}$
  - Force $1\,\text{N} = 10^5\ \text{dynes}$
  - Length $1\,\overset{\text{o}}{\text{A}} = 0.1\,\text{nm}$

How many HO levels? (Consider CO)

$$D_o = 256\ \text{kcal}$$

$$\text{N} = \text{no. of HO levels}$$

$$= \frac{256\ \text{kcal/mole}}{\left(2.86\ \text{cal/mole cm}^{-1}\right)\left(2170\ \text{cm}^{-1}\right)} \cong \underline{41}$$

➡ Actual number is GREATER

as AHO shrinks level spacing

4.2. Vib-Rot spectra – simple model

- Born-Oppenheimer Approximation
  - Vibration and Rotation are regarded as independent

→ Vibrating rigid rotor

Energy: $$T(\mathrm{v},J) = RR + SHO = F(J) + G(\mathrm{v})$$
$$= BJ(J+1) + \omega_e(\mathrm{v}+1/2)$$

ΔJ = J' - J"

Selection Rules: $\Delta\mathrm{v} = +1$

$\Delta J = \pm 1$

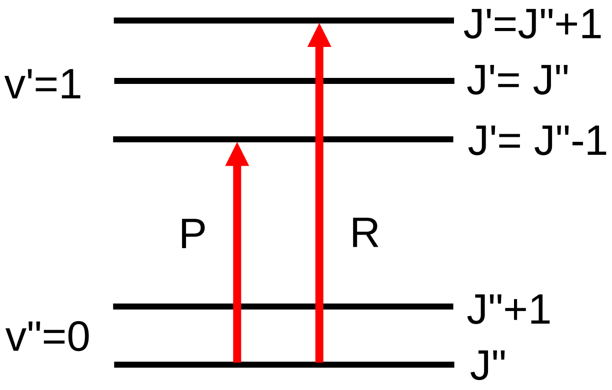
⇨ Two Branches: P (ΔJ = -1)

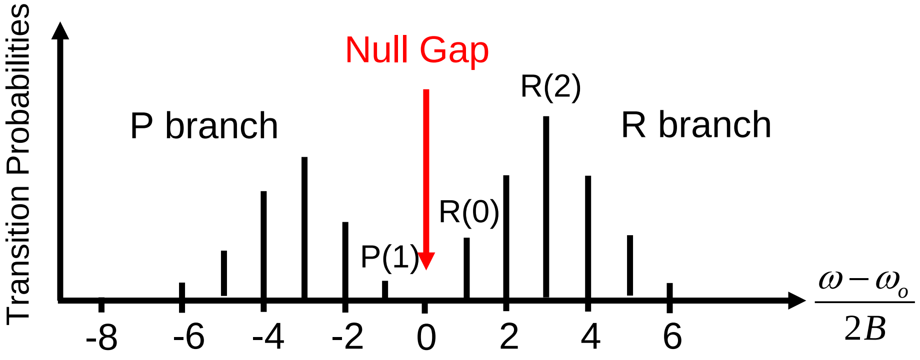
R (ΔJ = +1)

Line Positions: $$\bar{\nu} = T' - T'' = T(\mathrm{v}', J') - T(\mathrm{v}'', J'')$$

Aside: Nomenclature for "branches"

	Branch	O	P	Q	R	S
▪	Branch	O	P	Q	R	S
▪	ΔJ	-2	-1	0	+1	+2





4.2. Vib-Rot spectra – simple model

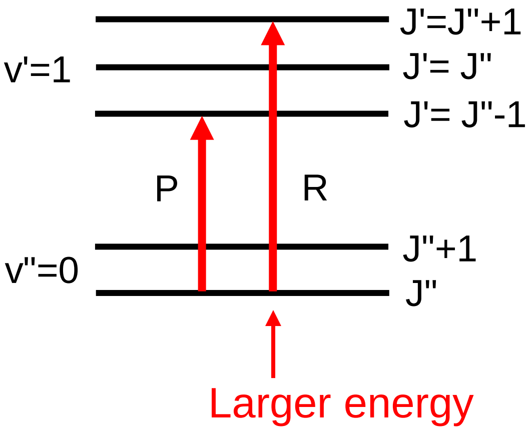
- R-branch
  - $R(J''), cm^{-1} = \underbrace{\left[G(v') - G(v'')\right]} + B(J''+1)(J''+2) - BJ''(J''+1)$

$$\begin{aligned}\omega_o = \bar{\nu}_o &= \text{Rotationless transition wavenumber} \\ &= \omega_e \text{ (SHO)} \\ &= \omega_e(1-2x_e)(\text{AHO}, 1 \leftarrow 0) \\ &= \omega_e(1-4x_e)(\text{AHO}, 2 \leftarrow 1) \\ &= \ldots\end{aligned}$$

$$\boxed{R(J'') = \omega_0 + 2B(J''+1)}$$ ⇨ Note: spacing = 2B, same as RR spectra

- P-branch
  - $\boxed{P(J'') = \omega_0 - 2BJ''}$ ⇨ Note: ω_o = f(v'') for AHO

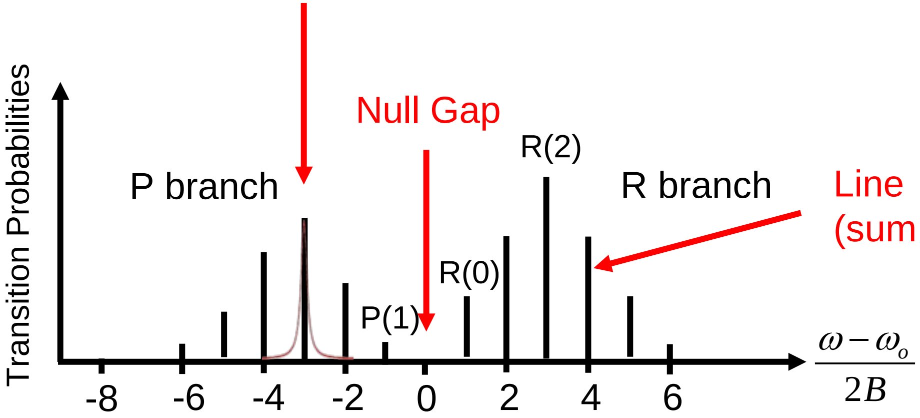
- P-R Branch peak separation $\Delta\bar{\nu} = \sqrt{\frac{8BkT}{hc}}$



Larger energy

4.2. Vib-Rot spectra – simple model

- Absorption spectrum (for molecule in v" = 0)



Width, shape depends on instrument, experimental conditions

Null Gap

Line
(sum of all lines is a “band”)

  - Height of line ∝ amount of absorption ∝ N_J/N
  - “Equal probability” approximation – independent of J (as with RR)

What if we remove RR limit? → Improved treatment

4.3. Vib-Rot spectra – improved model

- Breakdown of Born-Oppenheimer Approximation
  - Allows non-rigid rotation, anharmonic vibration, vib-rot interaction

$$T(\mathrm{v},J)=G(\mathrm{v})+F(\mathrm{v},J)$$

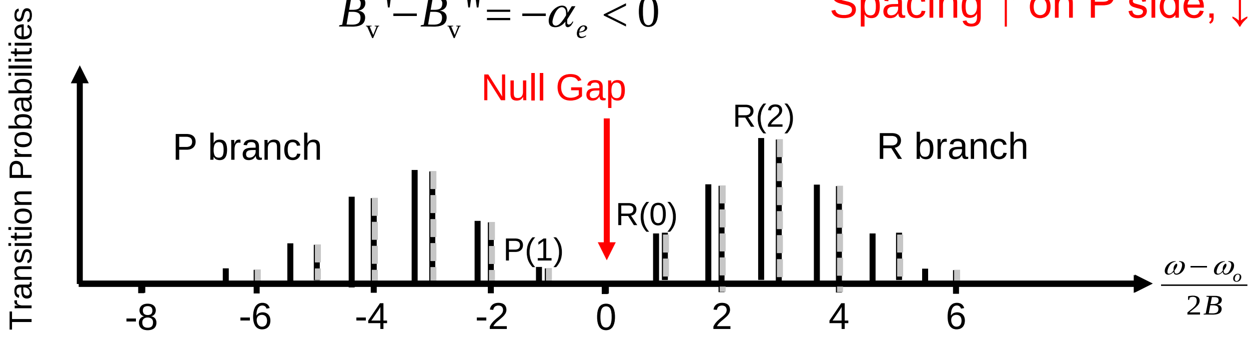
$$=\underbrace{\omega_e(\mathrm{v}+1/2)}_{\text{SHO}}-\underbrace{\omega_e x_e(\mathrm{v}+1/2)^2}_{\text{Anharm. corr.}}+\overset{\text{B(v)}}{\boxed{\underbrace{B_\mathrm{v}J(J+1)}_{\text{RR(v)}}}}-\underbrace{D_\mathrm{v}J^2(J+1)^2}_{\text{Cent. dist. term}}$$

- R-branch $R(\mathrm{v}'',J'')=\omega_o(\mathrm{v}'')+2B_\mathrm{v}'+(3B_\mathrm{v}'-B_\mathrm{v}'')J''+(B_\mathrm{v}'-B_\mathrm{v}'')J''^2$
- P-branch $P(\mathrm{v}'',J'')=\omega_o(\mathrm{v}'')-(B_\mathrm{v}'+B_\mathrm{v}'')J''+(B_\mathrm{v}'-B_\mathrm{v}'')J''^2$

$$B_\mathrm{v}=B_e-\alpha_e(\mathrm{v}+1/2)\qquad\left\{\begin{array}{l}B_\mathrm{v}'=B_e'-\alpha_e(\mathrm{v}'+1/2)\\ B_\mathrm{v}''=B_e''-\alpha_e(\mathrm{v}''+1/2)\end{array}\right.\qquad\Rightarrow\quad B_\mathrm{v}'<B_\mathrm{v}''$$

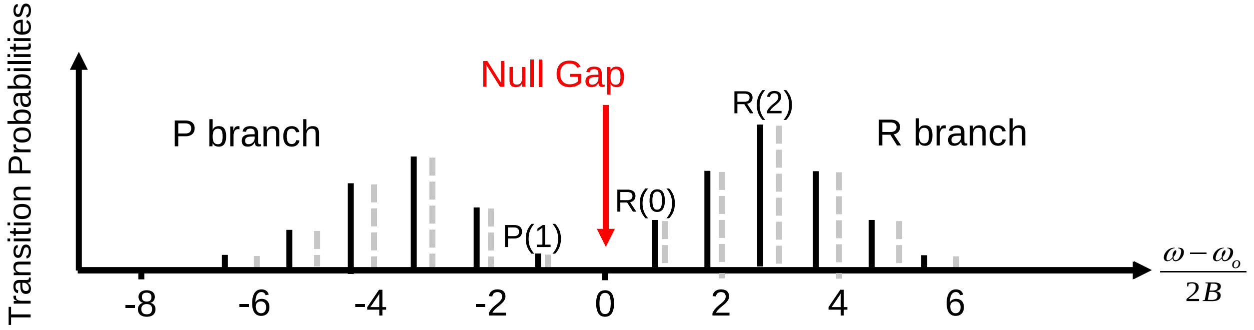
$$B_\mathrm{v}'-B_\mathrm{v}''=-\alpha_e<0$$

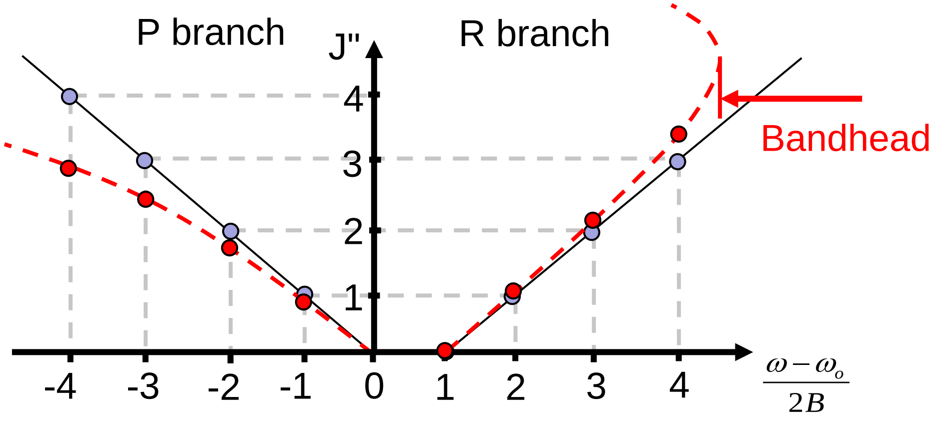
Spacing ↑ on P side, ↓ on R side

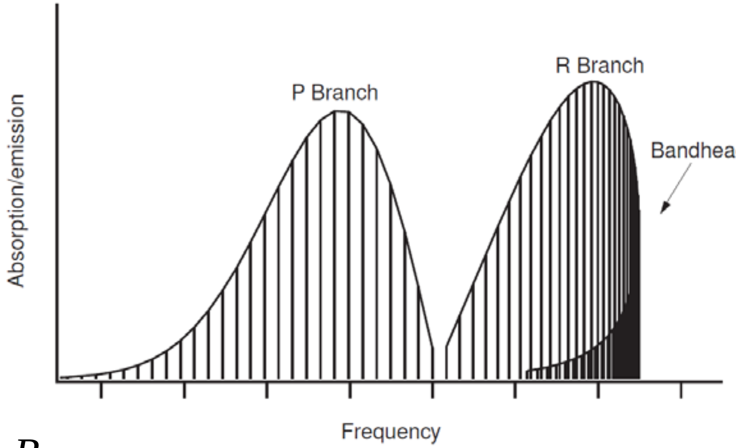


4.3. Vib-Rot spectra – improved model

- Bandhead







Increasing spacing ← → Decreasing spacing

$$\frac{dR(J)}{dJ} = \underbrace{(3B'-B'')}_{2B'-\alpha_e} + 2\underbrace{(B'-B'')}_{-\alpha_e} J'' = 0 \Rightarrow J''_{bandhead} \approx \frac{2B'-\alpha_e}{2\alpha_e} \approx \frac{B}{\alpha_e}$$

E.g., CO $\frac{B}{\alpha_e} \approx \frac{1.9}{0.018} \approx 106$ → not often observed

4.3. Vib-Rot spectra – improved model

- Finding key parameters: B_e, α_e, ω_e, x_e
  - 1st Approach:

    Use measured band origin data for the fundamental and first overtone, i.e., $\Delta G_{1\leftarrow 0}$, $\Delta G_{2\leftarrow 0}$, to get ω_e, x_e

$$\begin{aligned}\Delta G_{1\leftarrow 0} &= G(1)-G(0)=\omega_e(1-2x_e)\\ \Delta G_{2\leftarrow 0} &= G(2)-G(0)=2\omega_e(1-3x_e)\end{aligned} \quad \Rightarrow \quad \omega_e, x_e$$

  - 2nd Approach:

    Fit rotational transitions to the line spacing equation to get B_e and α

$$\omega=\omega_o+(B'+B'')m+(B'-B'')m^2$$

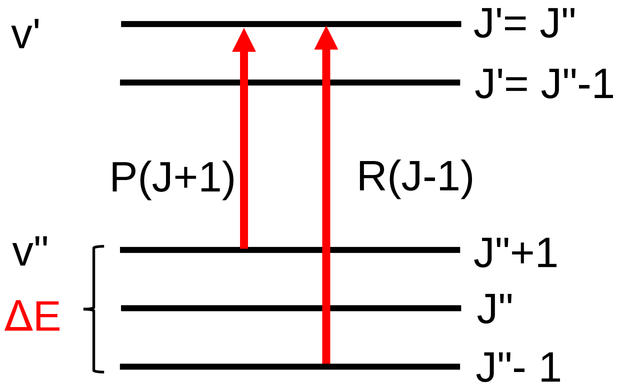
$$m=J+1 \text{ in R-branch}$$

$$m=-J \text{ in P-branch}$$

$$\boxed{\begin{aligned}B' &= B_e-\alpha_e(\mathrm{v}'+1/2)\\ B'' &= B_e-\alpha_e(\mathrm{v}''+1/2)\end{aligned}} \quad \Rightarrow \quad B', B'' \quad \Rightarrow \quad B_e, \alpha$$

4.3. Vib-Rot spectra – improved model

- Finding key parameters: B_e, α_e, ω_e, x_e
  - 3^{rd} Approach: Use the “method of common states”

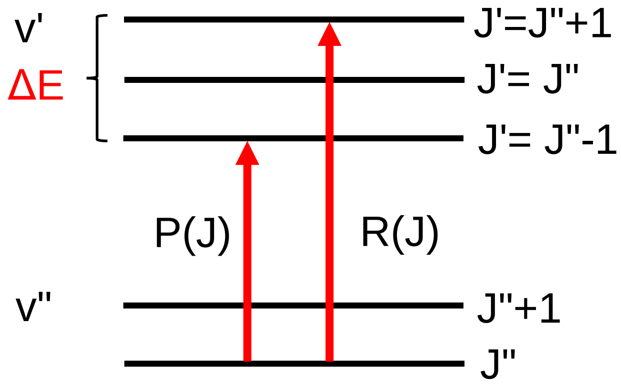


← Common upper-state

In general $F(J) = BJ(J+1)$

$$\begin{aligned}\Delta E &= F(J+1) - F(J-1)\\ &= R(J-1) - P(J-1)\\ &= B''(J+1)(J+2) - B''(J-1)J\end{aligned}$$

$$\boxed{\therefore \Delta E = B''(4J+2) \Rightarrow B''}$$



$$\begin{aligned}\Delta E &= F(J+1) - F(J-1)\\ &= B'(J+1)(J+2) - B'(J-1)J\end{aligned}$$

$$\boxed{\therefore \Delta E = B'(4J+2) \Rightarrow B'}$$

← Common lower-state

B'', B' → B_e, α

4.3. Vib-Rot spectra – improved model

- Isotopic effects

$$B \propto \frac{1}{I} \propto \frac{1}{\mu}$$ → Line spacing changes as μ changes

$$\omega_e \propto \sqrt{\frac{k_s}{\mu}} \propto \sqrt{\frac{1}{\mu}}$$ → Band origin changes as μ changes

1st Example: CO Isotope $^{13}C^{16}O$

$$\frac{\mu_{^{13}C^{16}O}}{\mu_{^{12}C^{16}O}} = 1.046$$

- $$B_{^{13}C^{16}O} = \frac{B_{^{13}C^{16}O}}{1.046}$$

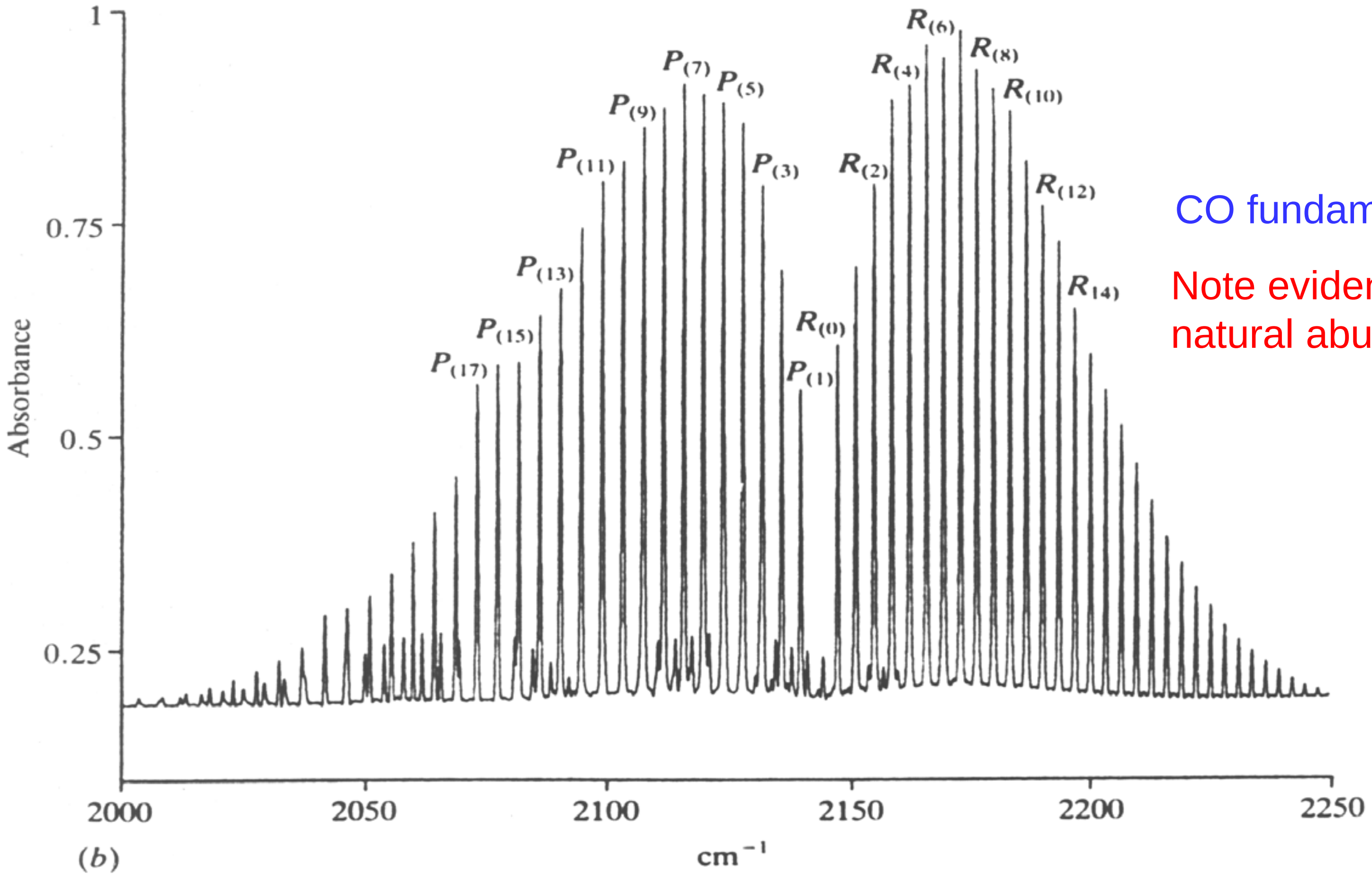
⇨ $$\Delta(2B) = -0.046 \times 3.88 \approx -0.17 cm^{-1}$$

- $$\omega_{e\,^{13}C^{16}O} = \frac{\omega_{e\,^{13}C^{16}O}}{\sqrt{1.046}}$$

⇨ $$\Delta\omega_e = 0.046 \times 2200/2 \approx 50 cm^{-1}$$

4.3. Vib-Rot spectra – improved model

- Isotopic effects



CO fundamental band

Note evidence of 1.1% natural abundance of ^{13}C

4.3. Vib-Rot spectra – improved model

- Isotopic effects

$$B \propto \frac{1}{I} \propto \frac{1}{\mu}$$ → Line spacing changes as μ changes

$$\omega_e \propto \sqrt{\frac{k_s}{\mu}} \propto \sqrt{\frac{1}{\mu}}$$ → Band origin changes as μ changes

2nd Example: HCl Isotope $H^{35}Cl$ and $H^{37}Cl$

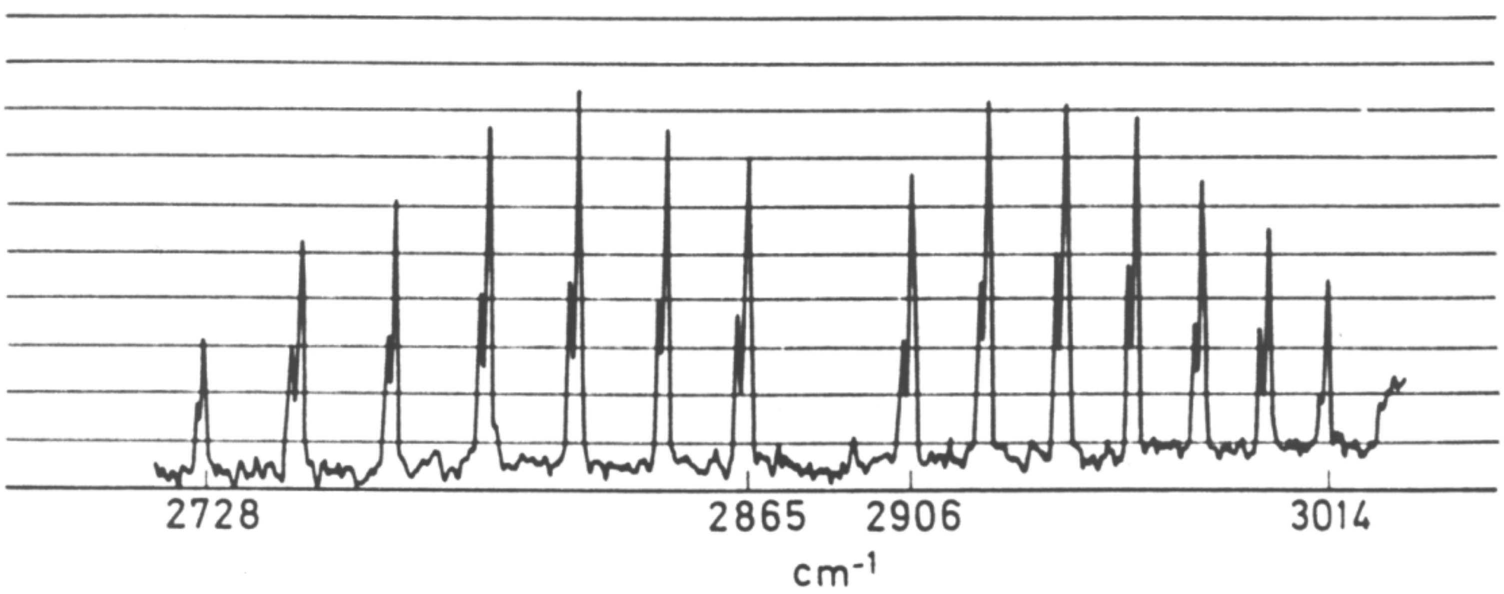
- $\left[H^{35}Cl\right] \cong 3\left[H^{37}Cl\right]$
- $\mu_{37} / \mu_{35} = \dfrac{37.1/38}{35.1/36} \cong 1.0015$

⇨ Shift in ω_e is $.00075\omega_e = 2.2 cm^{-1}$ → Small!

4.3. Vib-Rot spectra – improved model

- Isotopic effects

HCl fundamental band



Note isotropic splitting due to H^{35}Cl and H^{37}Cl

4.3. Vib-Rot spectra – improved model

- Hot bands

When are hot bands (bands involving excited states) important?

$$\frac{N_v}{N}=\frac{g\exp\left(-\frac{v\theta_v}{T}\right)}{Q_{vib}}=\exp\left(-\frac{v\theta_v}{T}\right)\left[1-\exp\left(-\frac{\theta_v}{T}\right)\right]$$

E.g. $\theta_{v,CO}=3000K$ $$\frac{N_1}{N}=\begin{cases} e^{-10}\approx 0 & @300K \\ e^{-1}\left(1-e^{-1}\right)\approx 0.23 & @3000K \end{cases}$$

⇨ “Hot bands” become important when temperature is comparable to the characteristic vibrational temperature

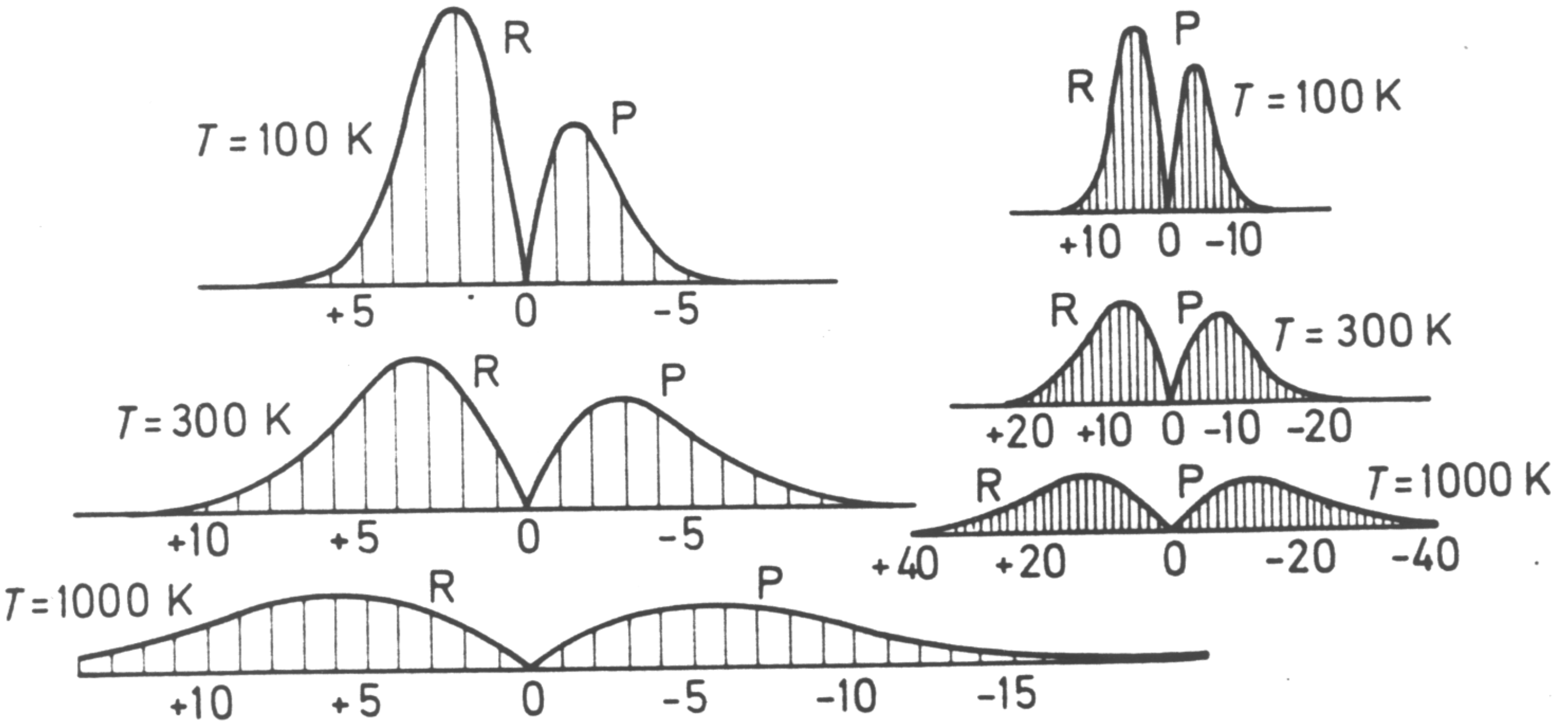
Gas	$\bar{\nu}_{0\to 1}\left(cm^{-1}\right)$	$N_1/N_0=e^{-hc\bar{\nu}/kT}$	
		300K	1000K
H_2	4160.2	2.16×10^{-9}	2.51×10^{-3}
HCl	2885.9	9.77×10^{-7}	1.57×10^{-2}
N_2	2330.7	1.40×10^{-5}	3.50×10^{-2}
CO	2143.2	3.43×10^{-4}	4.58×10^{-2}
O_2	1556.4	5.74×10^{-4}	1.07×10^{-1}
S_2	721.6	3.14×10^{-2}	3.54×10^{-1}
Cl_2	566.9	6.92×10^{-2}	4.49×10^{-1}
I_2	213.1	2.60×10^{-1}	7.36×10^{-1}

4.3. Vib-Rot spectra – improved model

- Examples of intensity distribution within the rotation-vibration band

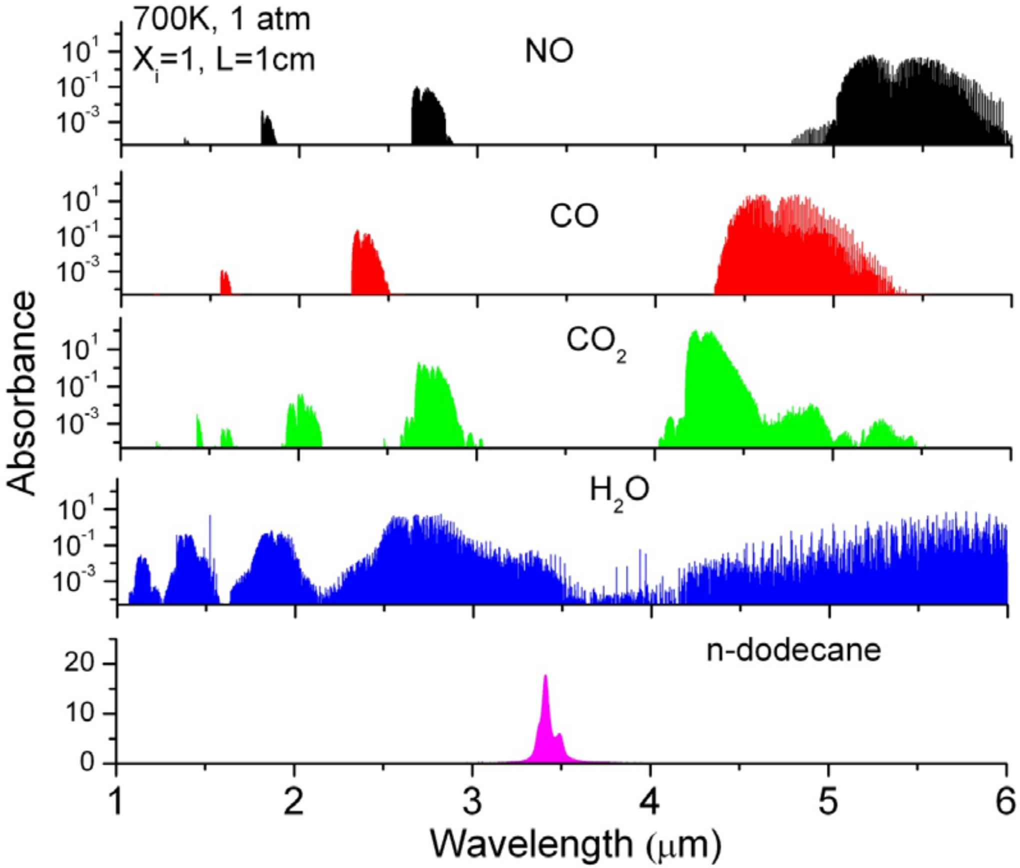
B = 10.44cm^{-1} (HCl)

B = 2cm^{-1} (CO)



4.4. Absorption Spectra for Combustion Gases

- TDL Sensors Provide Access to a Wide Range of Combustion Species/Applications



- Small species such as NO, CO, CO_2, and H_2O have discrete rotational transitions in the vibrational bands

- Larger molecules, e.g., hydrocarbon fuels, have blended spectral features

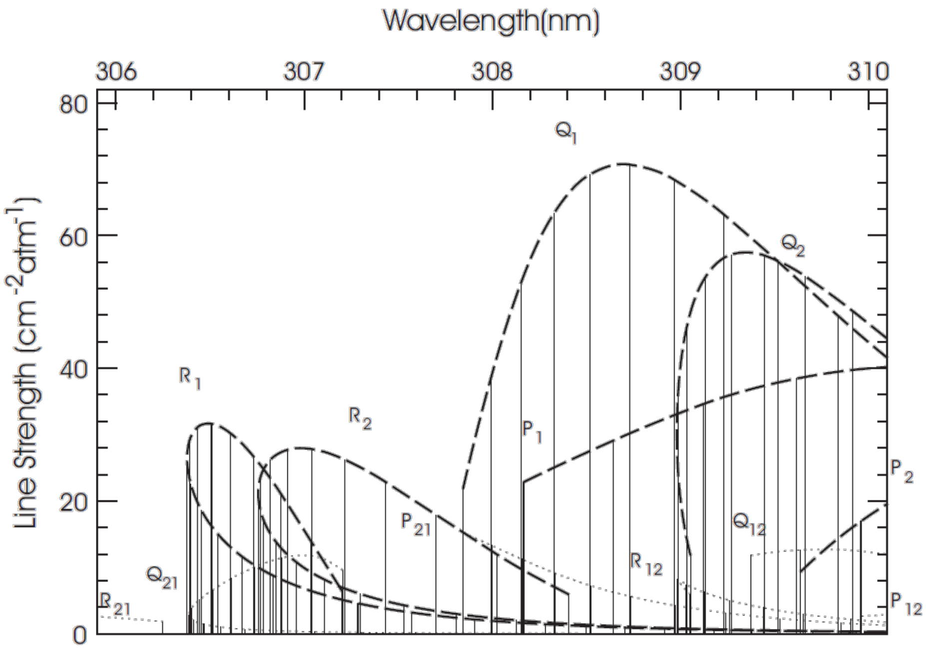
Next: Diatomic Molecular Spectra

- Electronic (Rovibronic) Spectra (UV, Visible)

Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

Lecture 3: Electronic Spectra, Bond Diss. Energy

1. Potential energy wells
2. Types of spectra
3. Rotational analysis
4. Vibrational analysis
5. Analysis summary
6. Dissociation Energies



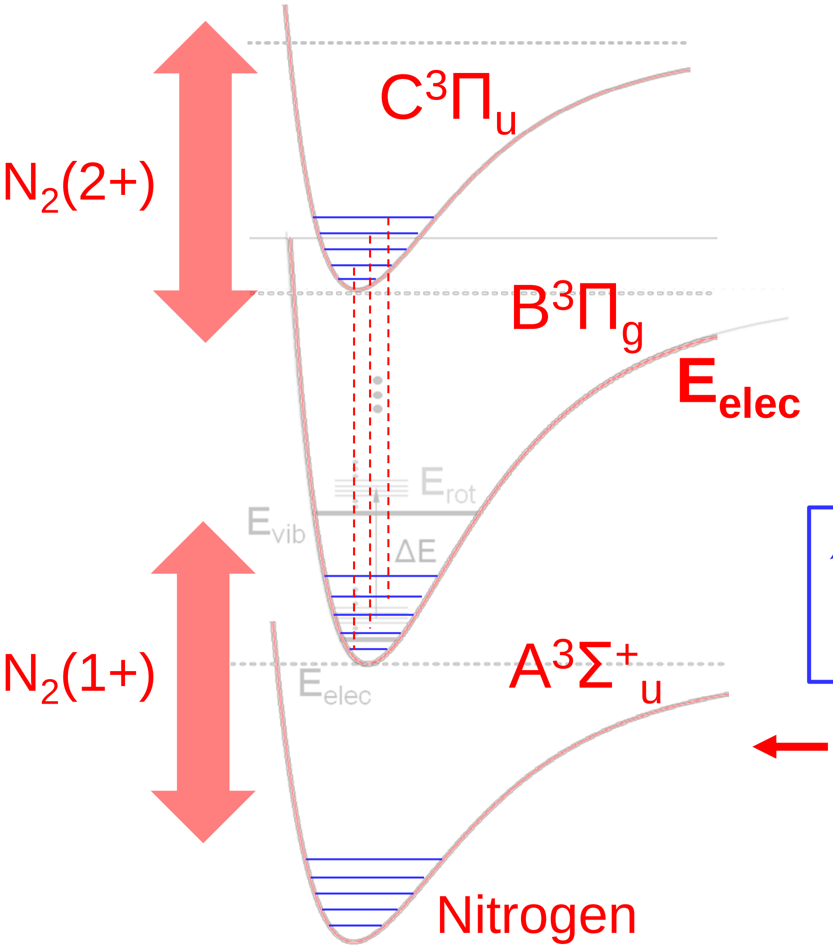
OH line strengths for a selected region of the $A^2\Sigma^+ \leftarrow X^2\Pi(0,0)$ band at 2000K

An example of what we need to calculate

1. Potential energy wells

- Electronic transitions

Recall: Lecture 1 – Line, Band, System



System:

- Transitions between different potential energy well

⬇

Depends on electronic configuration

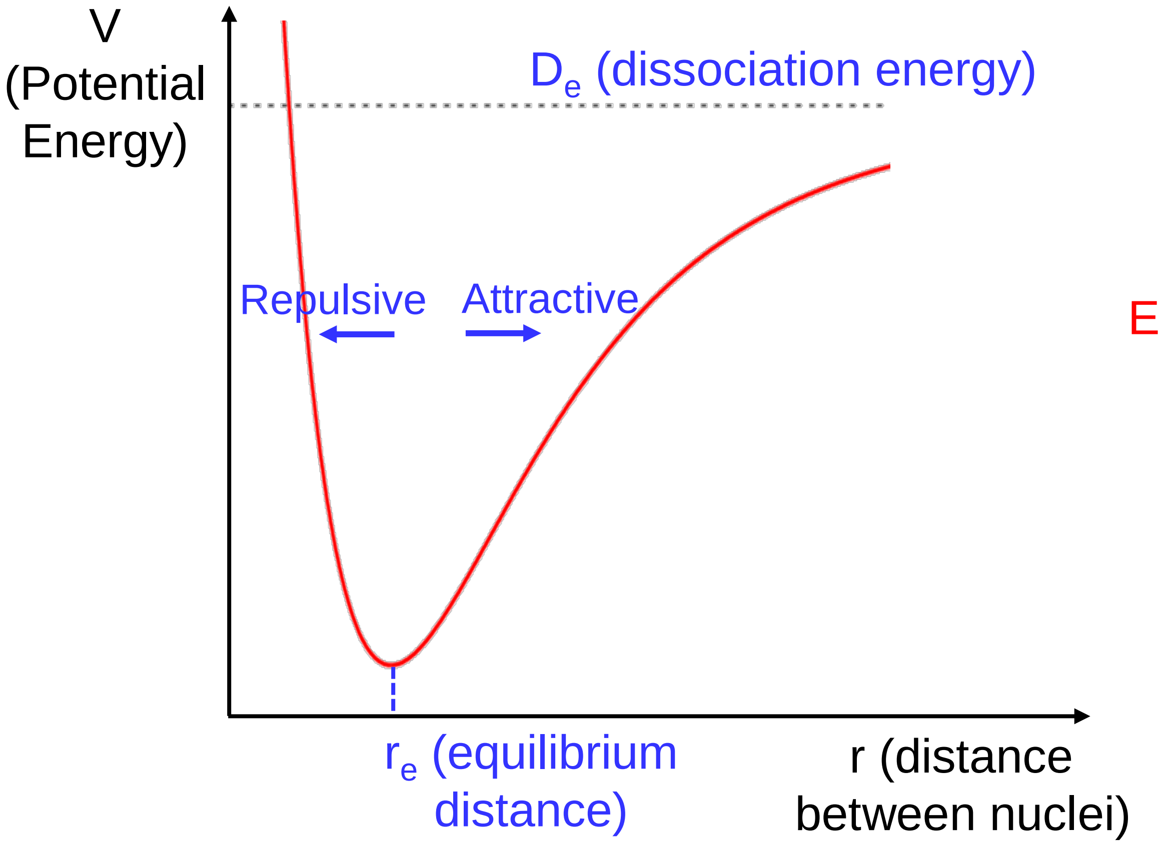
✎ Note: Both homonuclear and heteronuclear can have electronic spectra, in contrast w/ rotational and rovibrational spectra

Example: N_2

- First positive SYSTEM:
  $B^3\Pi_g \rightarrow A^3\Sigma^+_u$

1. Potential energy wells

- Electronic force and potential energy



Force $F = -\frac{dV}{dr}$

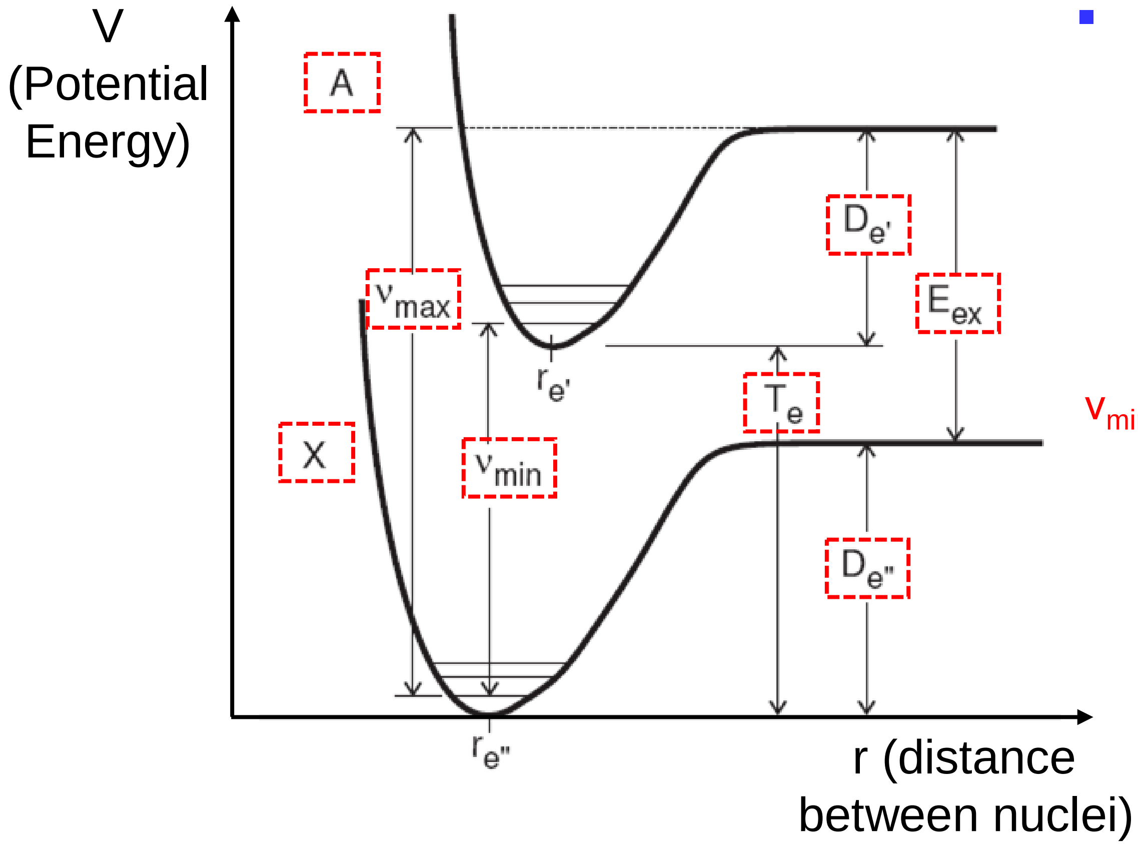
Electronic configurations change

↓

Potential well changes shape

1. Potential energy wells

- Electronic force and potential energy



Example:

- Potential energy wells for N_2

A	First excited state
X	Ground electronic state
T_e	Energy of A-state w/ respect to ground state
ν_{min}, ν_{max}	Extremes of photon energies for discrete absorption from v"=0
E_{ex}	Difference in electronic energy of atomic fragments
D_e	Dissociation energy

✎ Note: not to be confused with the rotational distortion const.

1. Potential energy wells

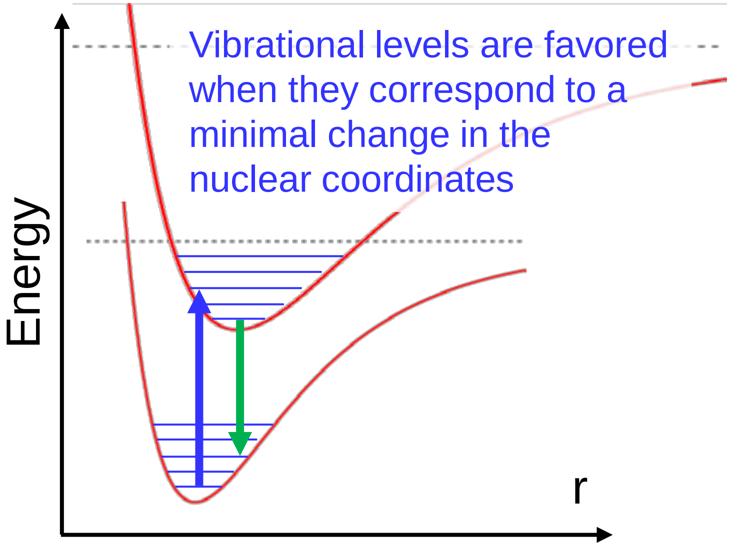
- Characteristic event times

$\tau_{elec} \approx 10^{-16} s$	time to move/excite electrons
$\tau_{vib} \approx 10^{-13} s$	characteristic time for vibration
$\tau_{coll} \approx 10^{-12} s$	duration of collision
$\tau_{rot} \approx 10^{-10} s$	characteristic time for rotation
$\tau_{emiss} \approx 10^{-6} - 10^{-8} s$	"radiative lifetime" – average time a molecule (or atom) spends in an excited state before radiative emission

- Frank-Condon Principle

As $\tau_{elec} << \tau_{others}$, the molecule's vibration and rotation appear "frozen" during electronic transition

Vertical lines between potential wells to represent an electronic transition at constant r



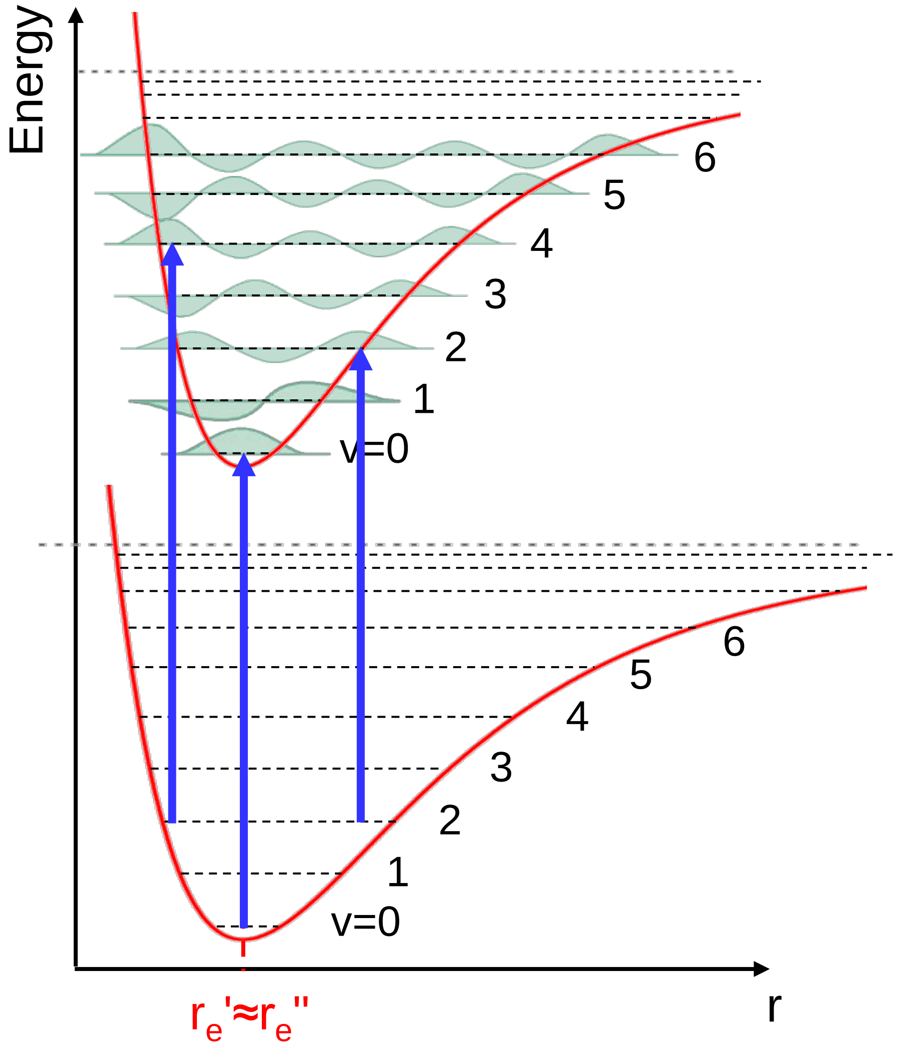
Vibrational levels are favored when they correspond to a minimal change in the nuclear coordinates

When $\tau_{coll} \approx \tau_{vib}$ → Increased probability of V-T energy transfer

2. Types of spectra

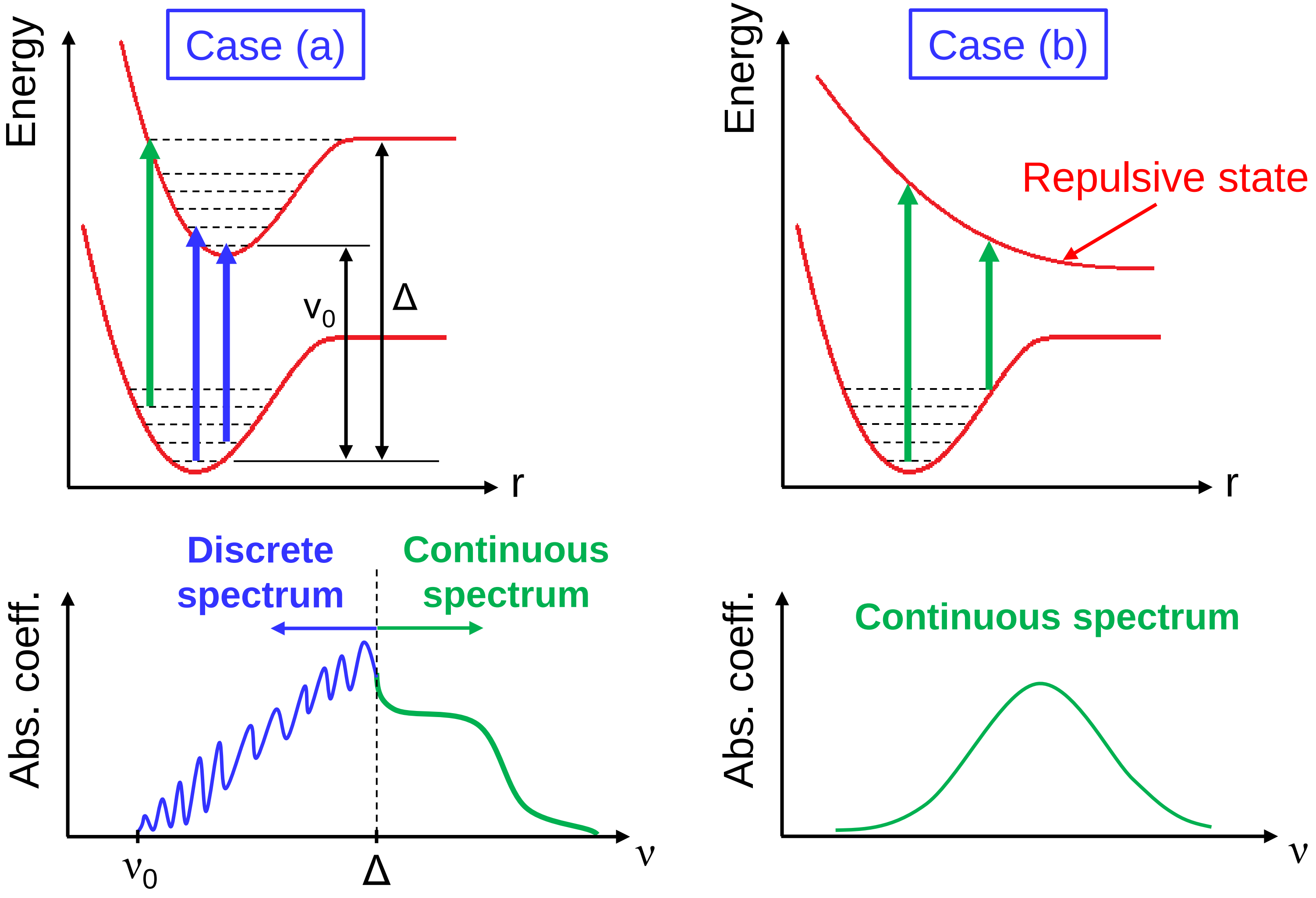
- Discrete
  - $r_e' \approx r_e''$
  - Franck-Condon Principle:

    r ≈ const. in absorption and emission
  - Vibrationally excited molecules (v≠0) spend more time near the edges of the potential well, so that transitions to and from these locations will be favored
  - Lowest v'' levels are most populated



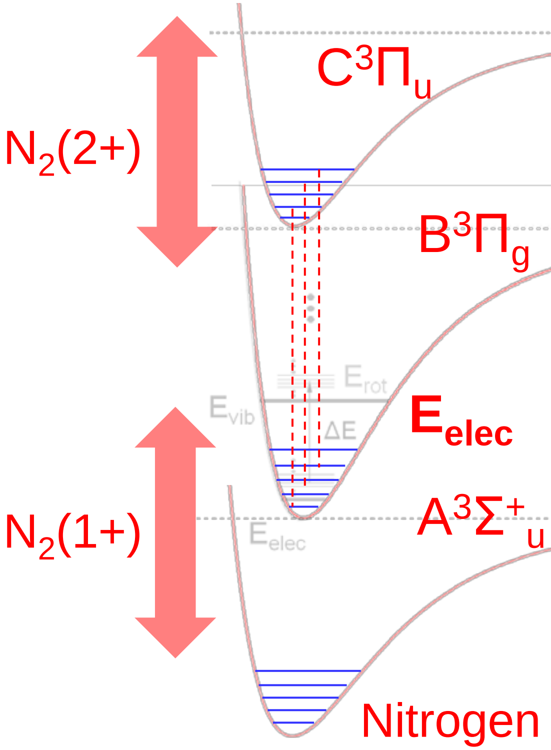
2. Types of spectra

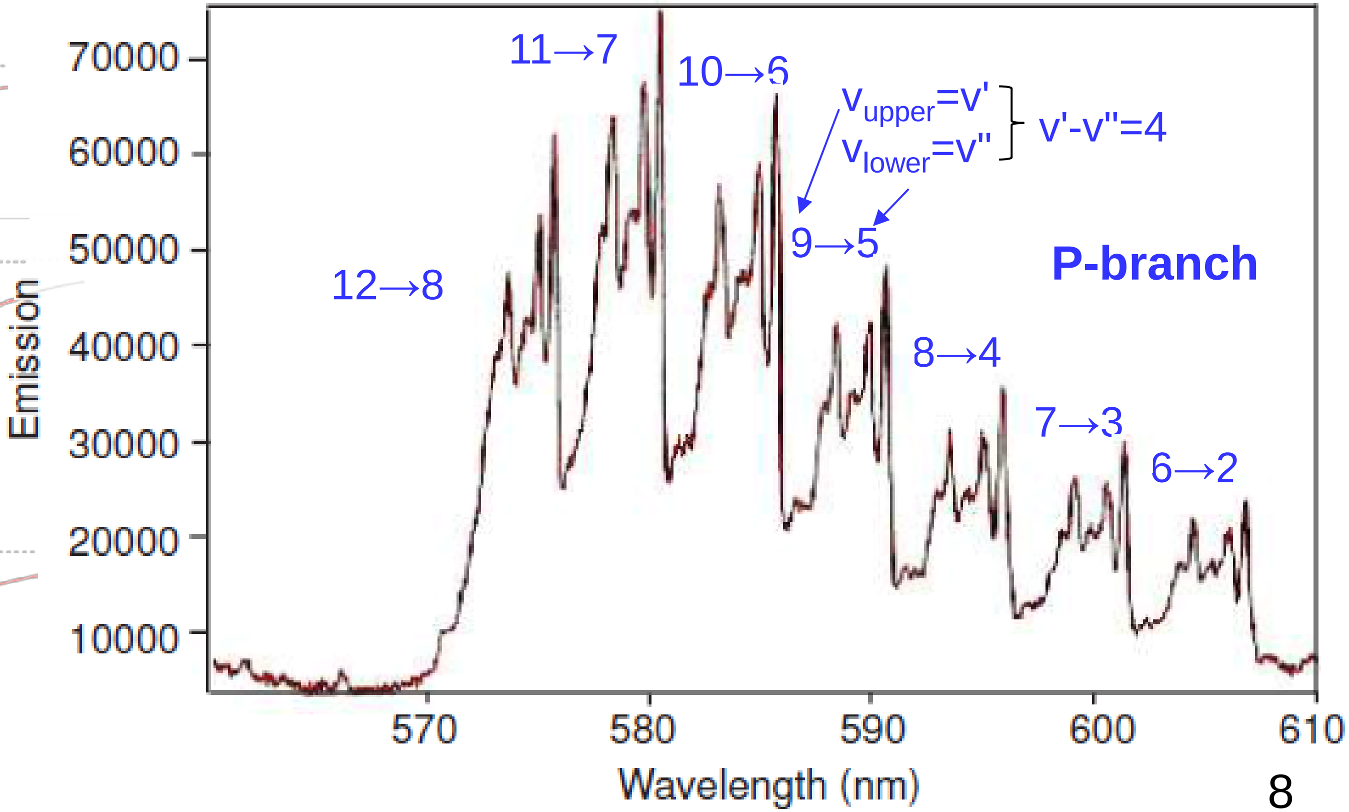
- Continuum



2. Types of spectra

- High-temperature air emission spectra (560-610nm) (part of the N_2(1+) system $B^3\Pi_g \rightarrow A^3\Sigma^+_u$)
  - Review multiband structure and apparent bandhead structure
  - Can we make use of rotational analysis to understand the band structure?





3. Rotational analysis

- Fortrat Parabola

Upper: $$T' = T_{rot} + T_{vib} + T_{elec} = F(J') + G(v') + T'_{elec} = BJ'(J'+1) + \underbrace{\omega_e(v'+1/2) - \omega_e x'_e (v'+1/2)^2 + T'_{elec}}_{C'}$$

Lower: $$T'' = T_{rot} + T_{vib} + T_{elec} = F(J'') + \underbrace{G(v'') + T''_{elec}}_{C''}$$

C=C'-C''

C' (const. for rot. analysis in a single band)

➡ $$T' - T'' = BJ'(J'+1) - BJ''(J''+1) + C$$ ➡ $$T = T' - T'' = am^2 + bm + C$$

$$where\ \ m = \begin{cases} -J & \text{for P branch} \\ J+1 & \text{for R branch} \end{cases} \qquad \begin{aligned} a &= B' - B'' \\ b &= B' + B'' \end{aligned}$$

Bandhead $$\frac{dT}{dm} = 2am + b = 0$$

➡ $$m_{bandhead} = -\frac{b}{2a} = \frac{B' + B''}{2(B'' - B')}$$

✎ Note:

1. $r_e' > r_e''$, B' < B'', a<0, bandhead in R branch
2. $r_e' < r_e''$, B' > B'', a>0, bandhead in P branch

Example: O_2

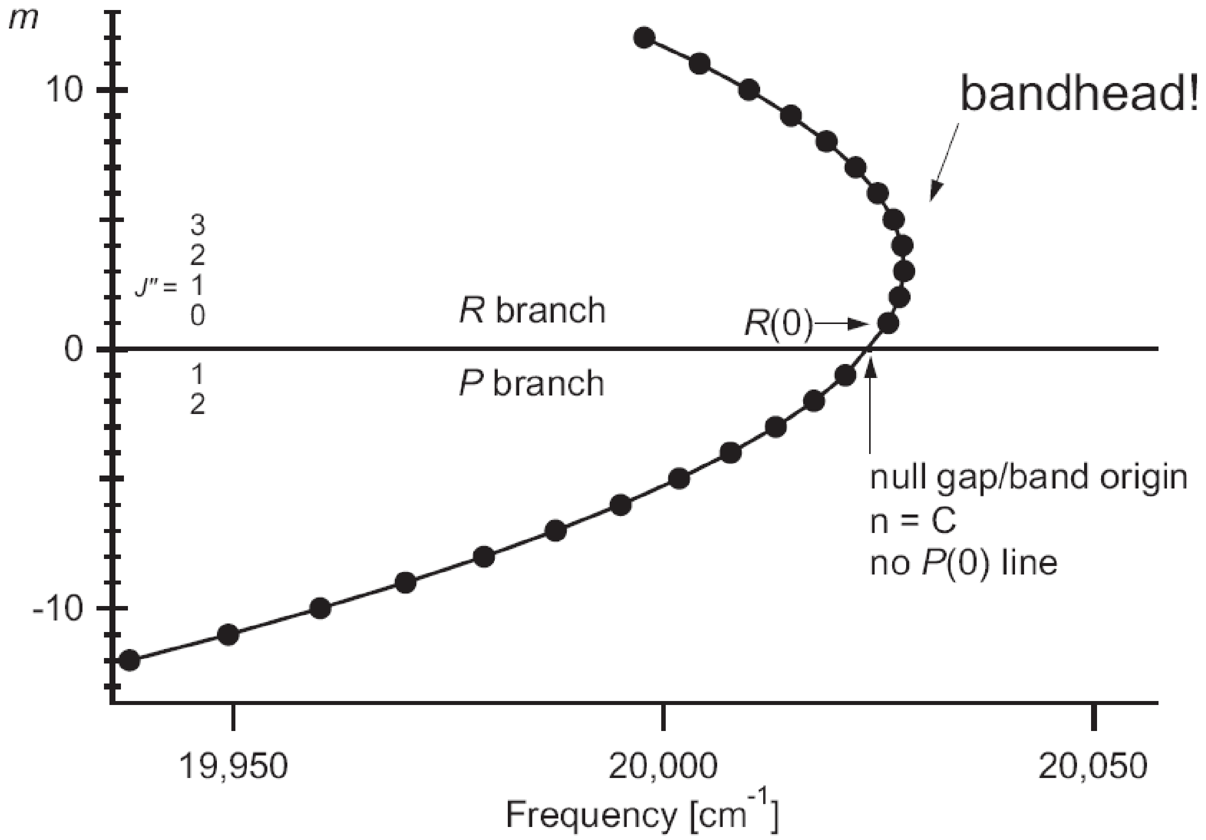
- $X^3\Sigma^-_g$ ground state: B''=1.44cm^{-1}
- $A^3\Pi^-_u$ upper state: B'=1.05cm^{-1}

➡ $$m_{bandhead} = \frac{2.49}{2 \times 0.39} \approx 3$$

3. Rotational analysis

- Fortrat Parabola

$$T = T' - T'' = am^2 + bm + C \qquad m = \begin{cases} -J & \text{for P branch} \\ J+1 & \text{for R branch} \end{cases} \qquad \begin{aligned} a &= B' - B'' \\ b &= B' + B'' \end{aligned}$$



3. Rotational analysis

- Fortrat Parabola

Steps for rotational analysis

1. Separate spectra into bands (v′, v")
2. Tabulate line positions
3. Identify null gap and label lines (not trivial)
4. Infer B' and B" from the Fortrat equation or common states

Strategy for labeling the lines:

- Bandhead → lines overlap
- No bandhead → a null gap is obvious
- Bandhead → start from the wings of the parabola and work backwards using a const second difference
    - 1st difference: $T_1 = T(m+1) – T(m)$
    - 2nd difference: $T_2 = T_1(m+1) – T_1(m) = 2(B'-B") = 2a$

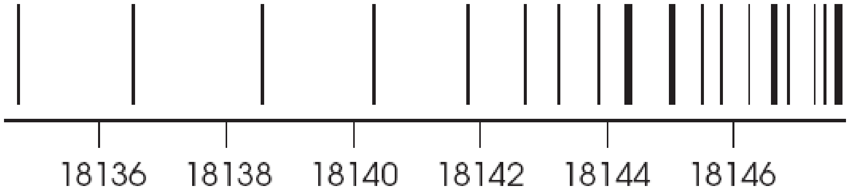
3. Rotational analysis

- Fortrat Parabola

Example:

Rotational analysis of electronic spectra

Line positions observed:



Rotational spectrum in the 0-0 band of an electronic transition ($A^3\Pi_{0+u} - X^1\Sigma^+_g$) in $^{35}Cl_2$

Find B_e', B_e'', r_e', r_e'', and the null gap frequency ν_0

ν, cm^{-1}

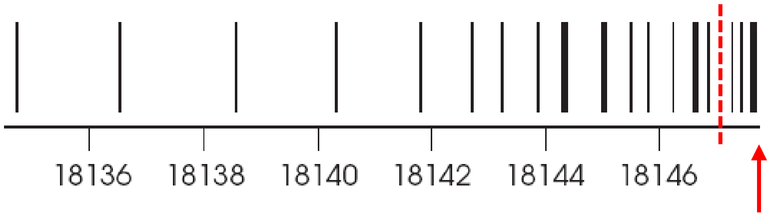
18147.85
18147.81
18147.71
18147.60
18147.22
18146.91
18146.66
18146.25
18145.93
18145.42
18145.02
18144.41
18143.94
18143.23
18142.69
18141.87
18140.34
18138.64
18136.76

3. Rotational analysis

- Fortrat Parabola

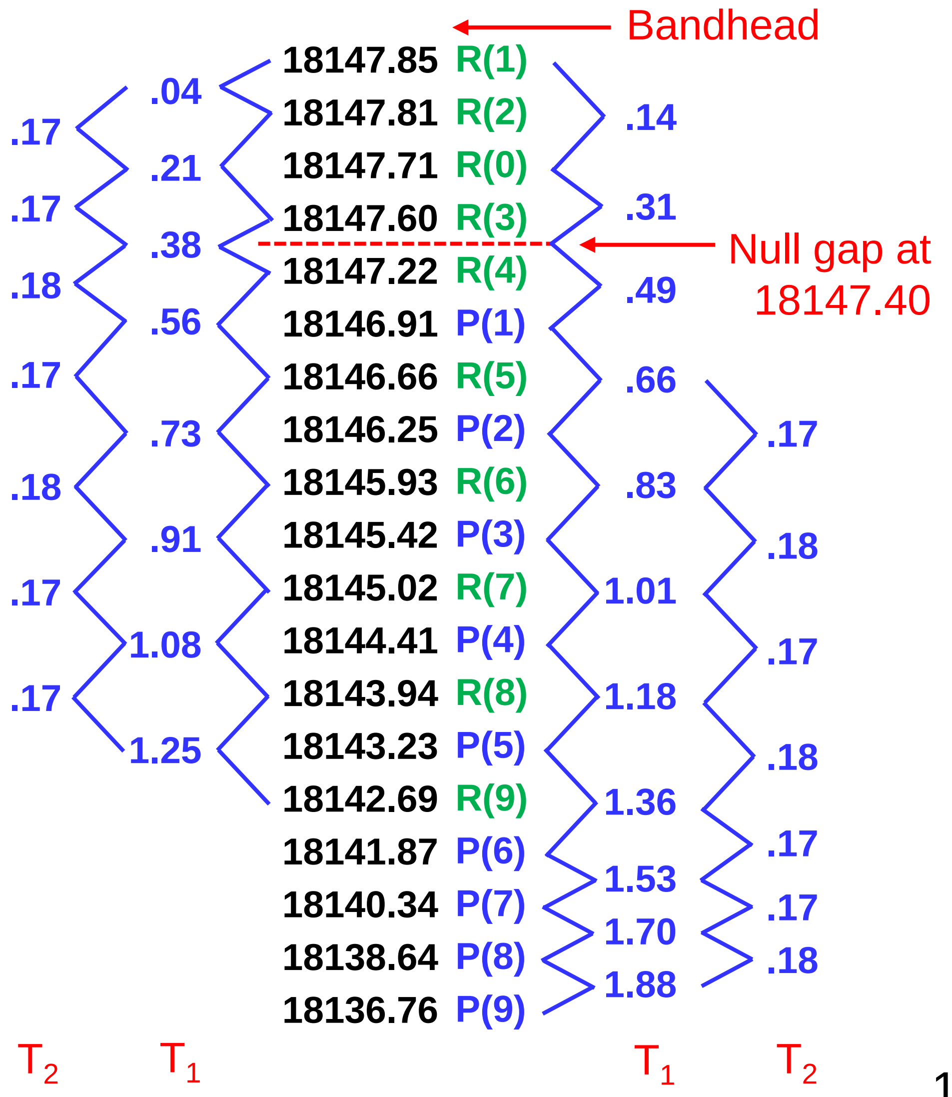
Example:
Rotational analysis of electronic spectra

Find B_e', B_e'', r_e', r_e'', and the null gap frequency ν_0



1. $\nu_0 = 18147.40\ \mathrm{cm}^{-1}$
2. $2a = T_2 = -0.173\ \mathrm{cm}^{-1}$

Note: All T_2 are negative!



Bandhead

Null gap at 18147.40

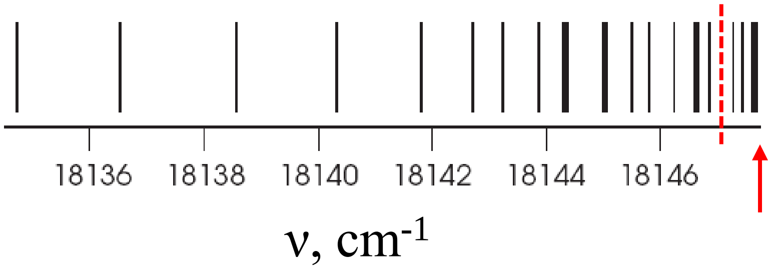
18147.85	R(1)
18147.81	R(2)
18147.71	R(0)
18147.60	R(3)
18147.22	R(4)
18146.91	P(1)
18146.66	R(5)
18146.25	P(2)
18145.93	R(6)
18145.42	P(3)
18145.02	R(7)
18144.41	P(4)
18143.94	R(8)
18143.23	P(5)
18142.69	R(9)
18141.87	P(6)
18140.34	P(7)
18138.64	P(8)
18136.76	P(9)

3. Rotational analysis

- Fortrat Parabola

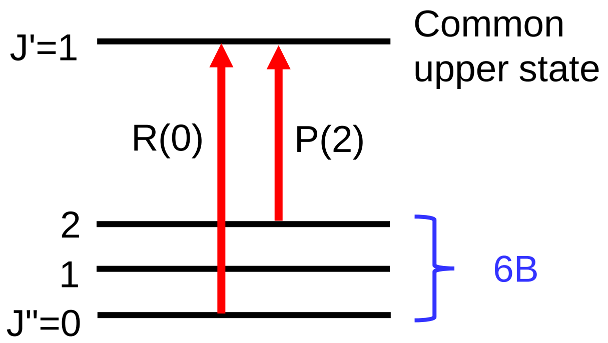
Example:
Rotational analysis of electronic spectra

Find B_e', B_e'', r_e', r_e'', and the null gap frequency ν_0



1. $\nu_0 = 18147.40\ \text{cm}^{-1}$
2. $2a = T_2 = -0.173\ \text{cm}^{-1}$
3. Use common states to get B"
4. Solve for r', r" from B' and B"

Could also have used common lower states to get B'



$$R(0) = 18147.71, P(2) = 18146.25$$

$$R(0) - P(2) = 1.46$$

$$B'' = 1.46/6 = 0.243 cm^{-1}$$

$$B' = B'' + a = 0.157 cm^{-1}$$

$$B_e'' = 0.2438, \alpha_e = 0.0017$$

$$\Rightarrow B_0'' = 0.2438 - 0.0008 = 0.243$$

$$B_e' = 0.158, \alpha_e = 0.003$$

$$\Rightarrow B_0' = 0.158 - 0.0015 \approx 0.157$$

$$T_e = 18310.5, r_e'' = 1.988\ \overset{\circ}{A}, r_e' = 2.47\ \overset{\circ}{A}$$

4. Vibrational analysis

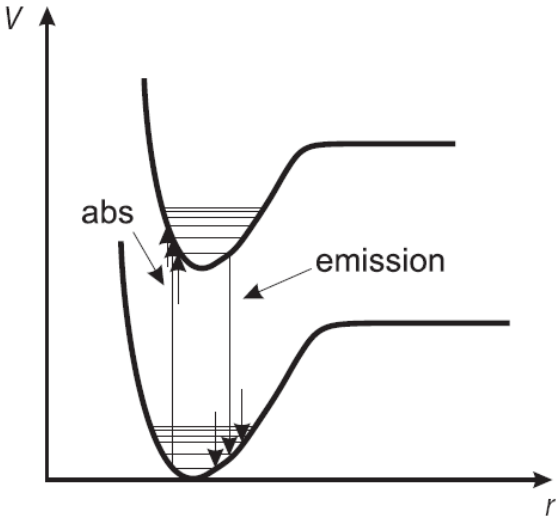
- Band origin data

Vibrational analysis can be used to determine information regarding ω_e, x_e

Absorption → information on upper states

Emission → information on lower states

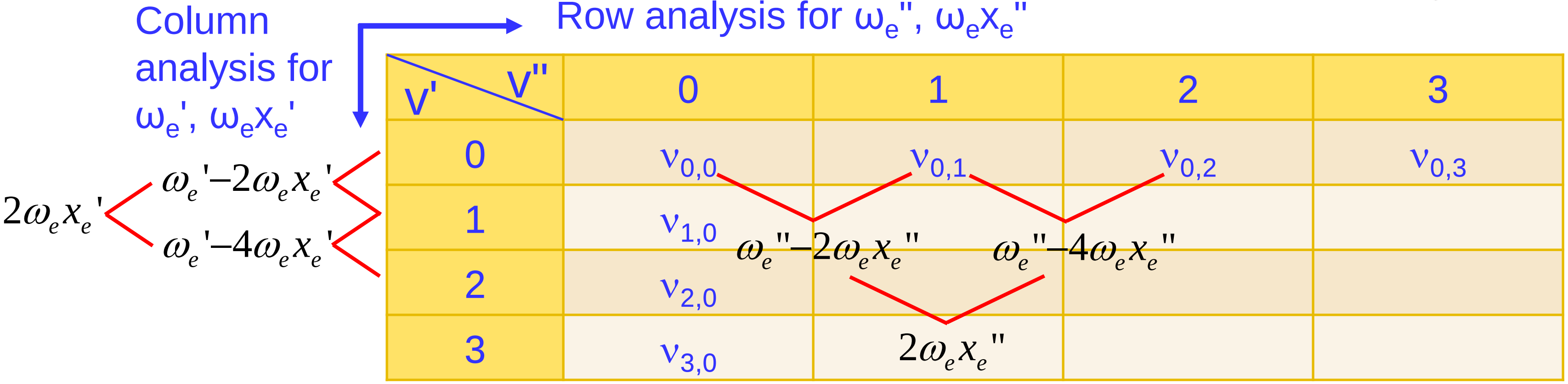
Tables of band origin values



- Deslandres Table

Recall: $G(\mathrm{v}) = \omega_e(\mathrm{v}+1/2) - \omega_e x_e(\mathrm{v}+1/2)^2$

$$\left.\begin{aligned} G(1)-G(0) &= \omega_e - 2\omega_e x_e \\ G(2)-G(1) &= \omega_e - 4\omega_e x_e \end{aligned}\right\} 2\omega_e x_e$$



Column analysis for ω_e', $\omega_e x_e'$

Row analysis for ω_e'', $\omega_e x_e''$

V' \ V''	0	1	2	3
0	$\nu_{0,0}$	$\nu_{0,1}$	$\nu_{0,2}$	$\nu_{0,3}$
1	$\nu_{1,0}$			
2	$\nu_{2,0}$			
3	$\nu_{3,0}$			

$\omega_e'' - 2\omega_e x_e''$ $\omega_e'' - 4\omega_e x_e''$

$2\omega_e x_e''$

$\omega_e' - 2\omega_e x_e'$

$\omega_e' - 4\omega_e x_e'$

$2\omega_e x_e'$

4. Vibrational analysis

- Deslandres Table

Transition v' ← v"	Energy required to observe transition	1st difference	2nd difference
0 ← 0	$T_e + 1/2\omega_e' - 1/4\omega_e x_e' - 1/2\omega_e" + 1/4\omega_e x_e"$	$\omega_e' - 2\omega_e x_e'$	
1 ← 0	$T_e + 3/2\omega_e' - 9/4\omega_e x_e' - 1/2\omega_e" + 1/4\omega_e x_e"$	$\omega_e' - 4\omega_e x_e'$	$2\omega_e x_e'$
2 ← 0	$T_e + 5/2\omega_e' - 25/4\omega_e x_e' - 1/2\omega_e" + 1/4\omega_e x_e"$	$\omega_e' - 6\omega_e x_e'$	$2\omega_e x_e'$
3 ← 0	$T_e + 7/2\omega_e' - 49/4\omega_e x_e' - 1/2\omega_e" + 1/4\omega_e x_e"$	$\omega_e' - 8\omega_e x_e'$	$2\omega_e x_e'$
4 ← 0	$T_e + 9/2\omega_e' - 81/4\omega_e x_e' - 1/2\omega_e" + 1/4\omega_e x_e"$		

v' \ v"	0	1	2	3	4
		20	20		
	1480	1460	1440		
0	29647.5	28167.5	26707.5	25267.5	
	760				
1 40	30407.5	28927.5	27467.5	26027.5	24607.5
	720				
2 40	31127.5	29647.5	28187.5	26747.5	25327.5
	680				
3 40	31807.5	30327.5	28867.5	27427.5	26007.5
	640				
4	32447.5	30967.5	29507.5		
5		31567.5	30107.5	28667.5	
6			30667.5	29227.5	27807.5
7				29747.5	28327.5

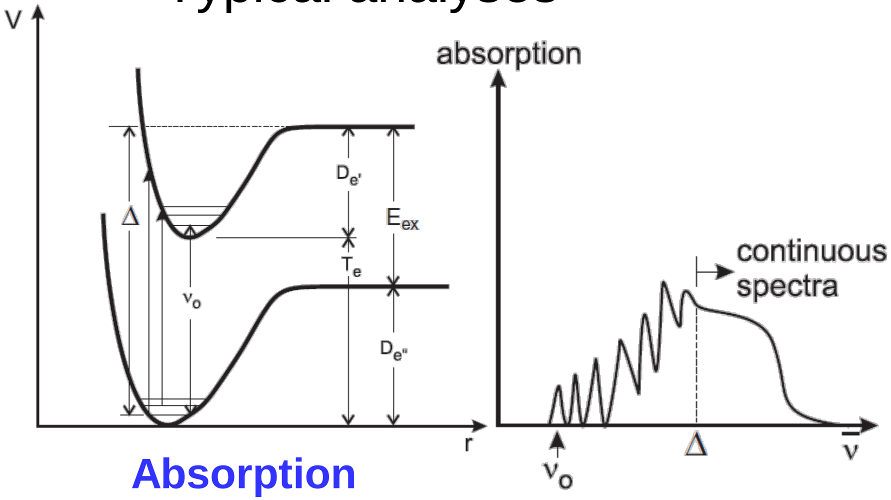
Band origin data from an emission spectrum

5. Analysis summary

- Analysis techniques and related fundamental quantities

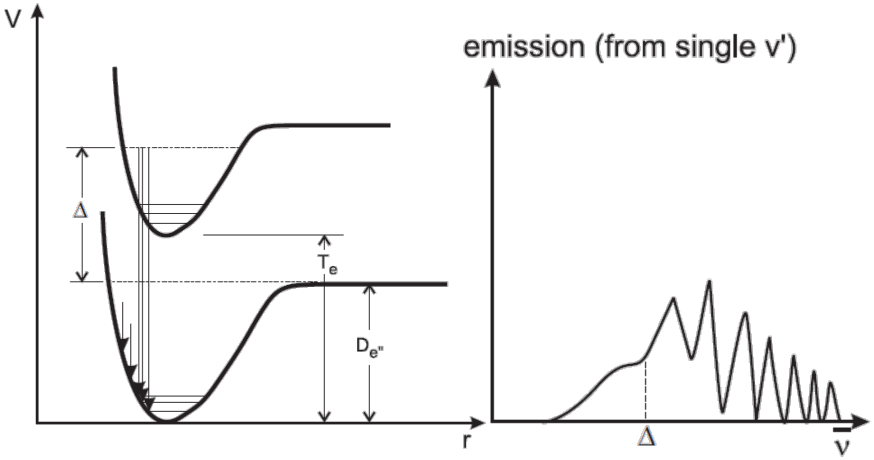
Analysis	Parameters
Rotational analysis	B_e, α_e, D_e, β_e
Vibrational analysis	ω_e, $\omega_e x_e$
Emission analysis	D_e'', $G(v'')$
Absorption analysis	D_e', T_e, $G(v')$

- Typical analyses



Absorption

1. Band origin → $G(v')$
2. $\nu_0 = T_e + G(v') - G(v'') \rightarrow T_e$
3. $\Delta + G(v'') = T_e + D'_e \rightarrow D'_e$



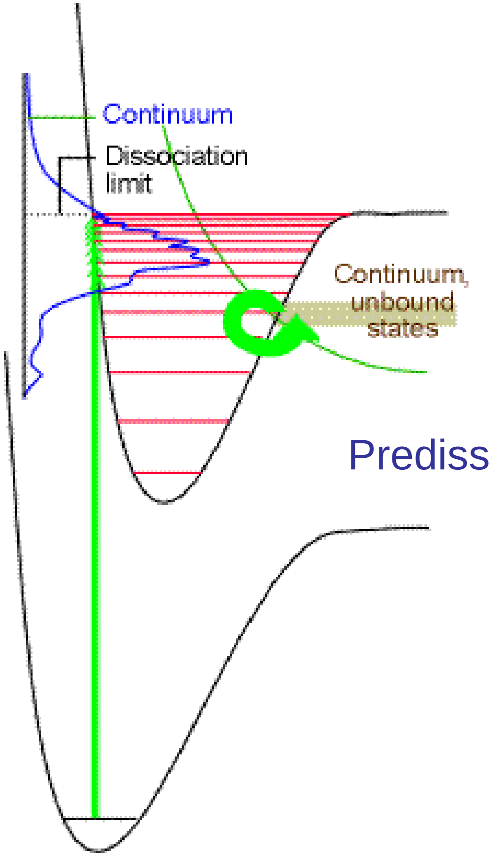
(change from continuum to band structure)

Emission

1. Band origin → $G(v'')$
2. $D''_e + \Delta = T_e + G(v') \rightarrow D''_e$

6. Bond Dissociation Energies

1. Absorption and emission analysis
2. Birge-Sponer method
3. Thermochemical approach
4. Working example

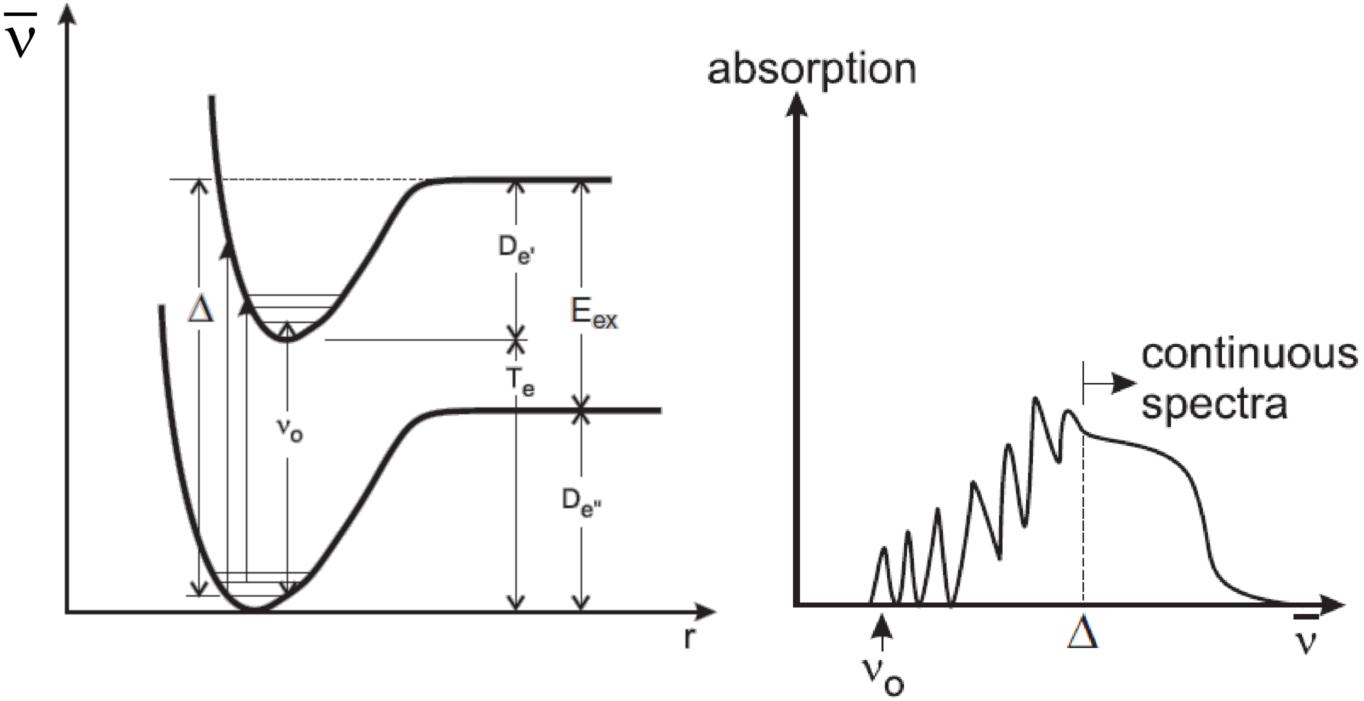


Predissociation

6. Bond dissociation energies

- Absorption

Absorption → D_e', T_e, $G(v')$

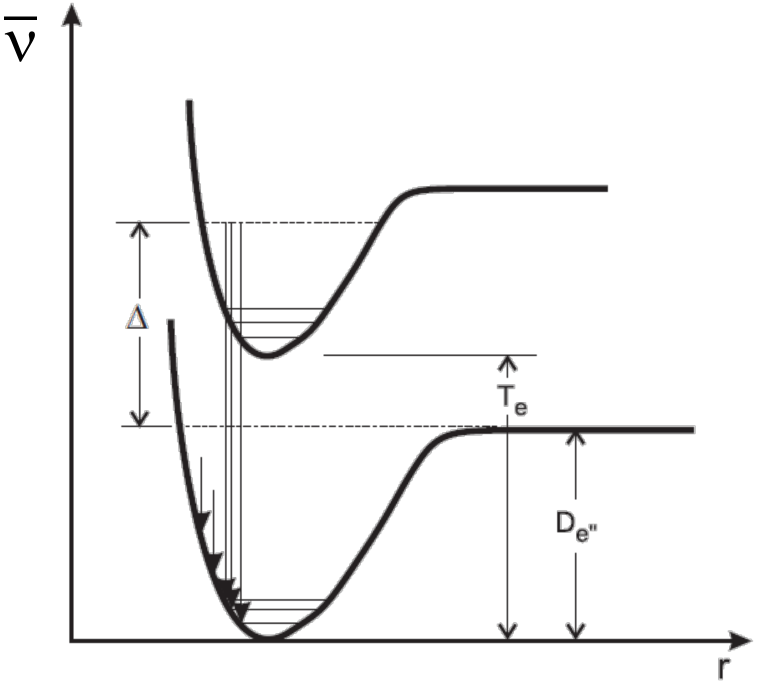


1. Band origin → $G(v')$ ← Enter in Deslandres Table
2. $\bar{\nu}_0 = T_e + G(v') - G(v'') \rightarrow T_e$
3. $\Delta + G(v'') = T_e + D'_e \rightarrow D'_e$

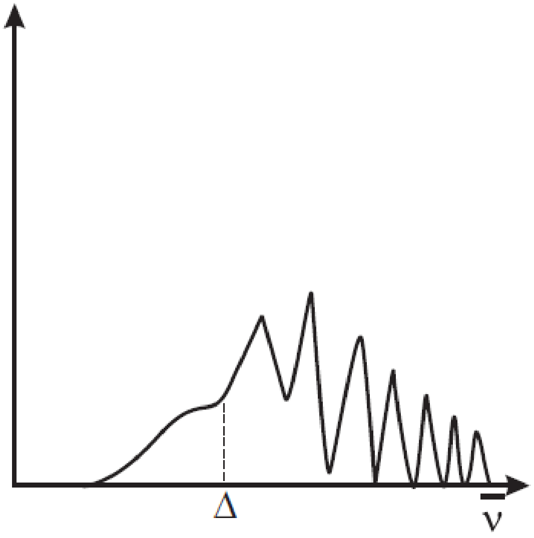
6.1. Absorption and emission

- Emission

Emission → D_e'', $G(v')$



emission (from single v')



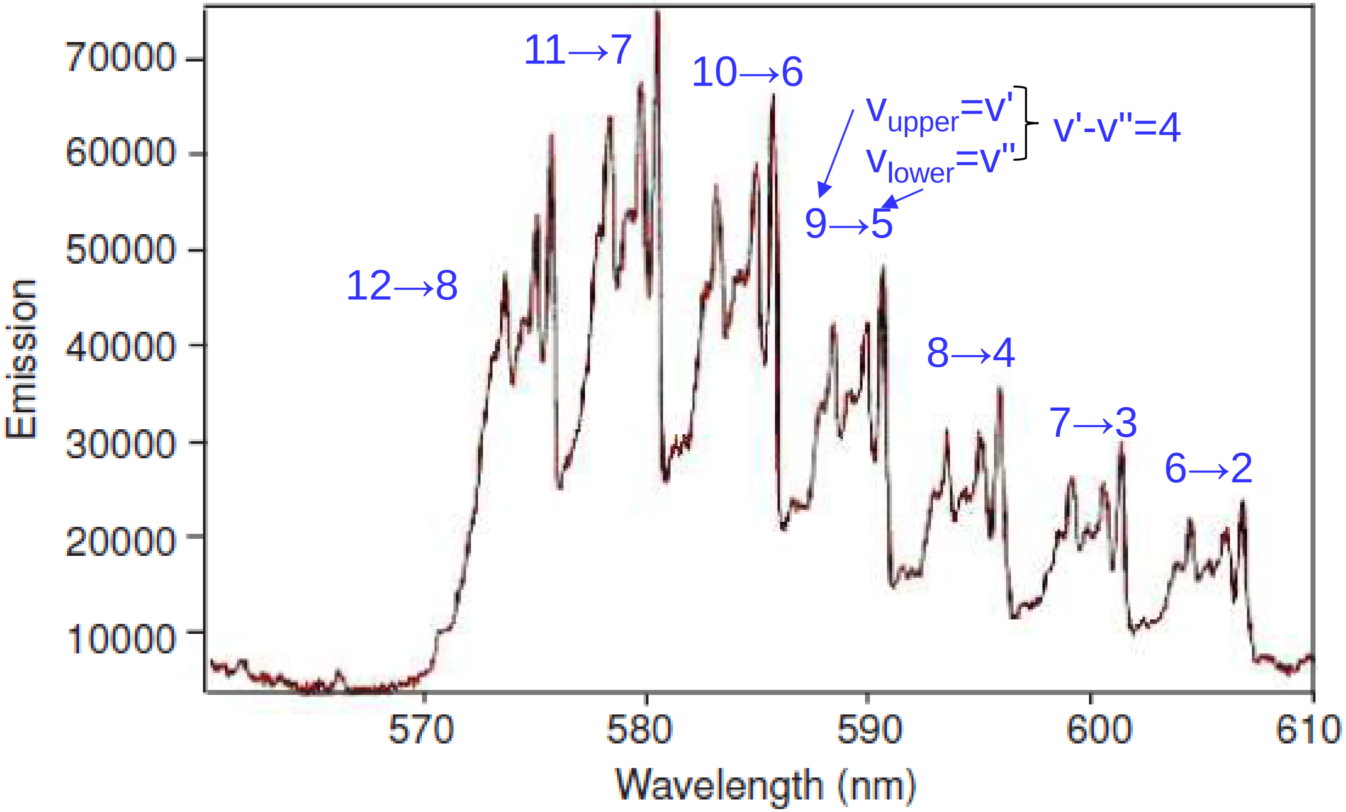
(change from continuum to band structure)

1. Band origin from fixed v'→ G(v'') ← Enter in Deslandres Table
2. $D''_e + \Delta = T_e + G(v') \rightarrow D''_e$

6.1. Absorption and emission

- Emission

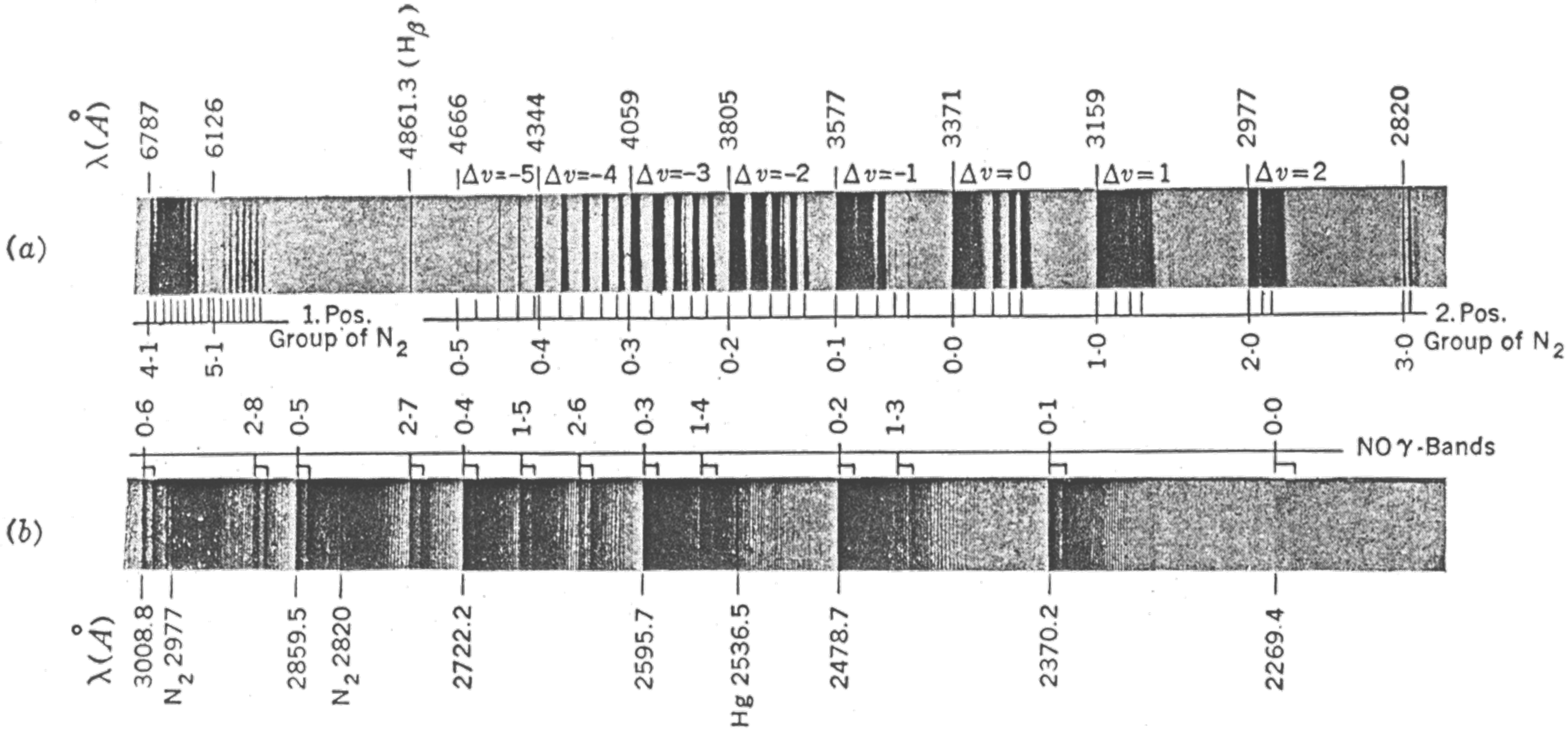
Example: High-temperature air emission spectra (560-610nm)



6.1. Absorption and emission

- Emission

Example: Band spectrum of an air-filled Geissler tube. (a) Long-wavelength part. (b) Short wavelength part



6.2. Birge-Sponer method

- Determine dissociation energies

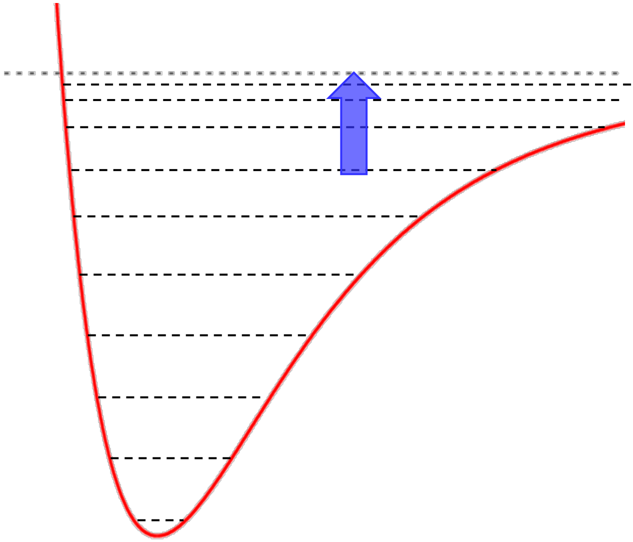
Dissociation energies

➡
- [Thermodynamics] Heats of formation and reaction
- [Kinetics] Rates of reaction

Birge-Sponer method

- Spectroscopic parameters ➡ Dissociation energies

Constant anharmonicity



Vibrational level spacing → 0 in the limit of dissociation

$$\ominus \qquad G(\mathrm{v}) = \omega_e(\mathrm{v}+1/2) - \omega_e x_e(\mathrm{v}+1/2)^2$$

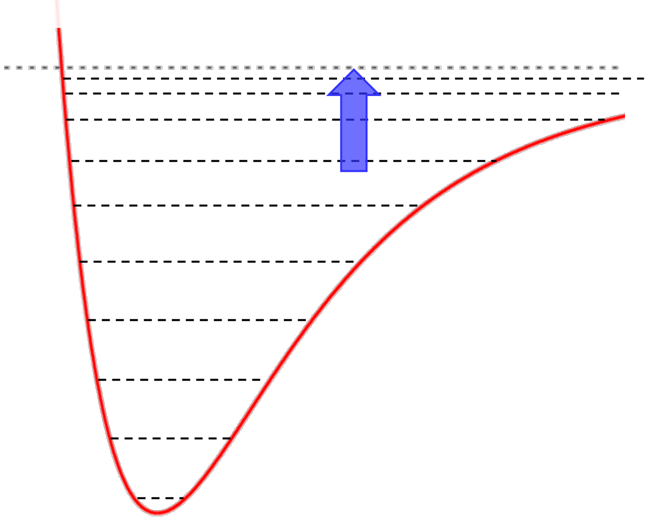
$$G(\mathrm{v}+1) = \omega_e(\mathrm{v}+3/2) - \omega_e x_e(\mathrm{v}+3/2)^2$$

$$\Delta G(\mathrm{v}) = G(\mathrm{v}+1) - G(\mathrm{v}) = \underbrace{-2\omega_e x_e}_{a}\mathrm{v} + \underbrace{(\omega_e - 2\omega_e x_e)}_{b}$$

➡ $\Delta G(\mathrm{v}) = a\mathrm{v} + b$ Linear dependence on v!

6.2. Birge-Sponer method

- Determine dissociation energies



Vibrational level spacing → 0 in the limit of dissociation

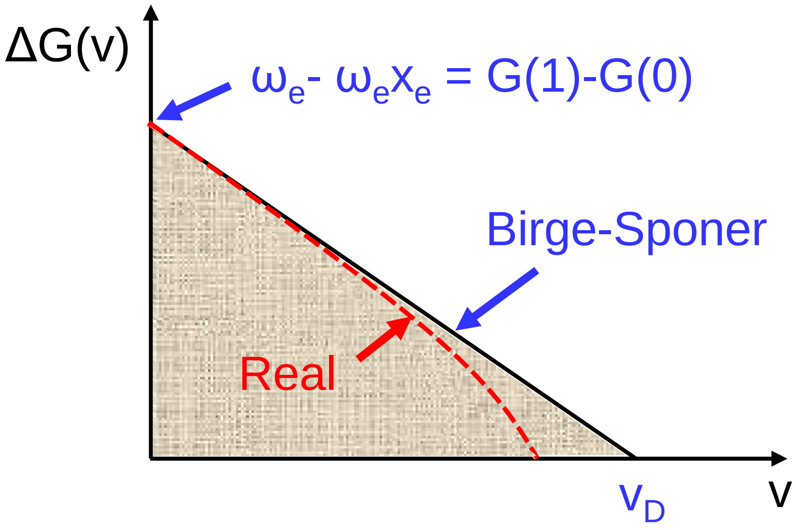
$$\Delta G(\mathrm{v}) = a\mathrm{v} + b = 0$$ @ dissociation

$$\boxed{\mathrm{v}_D = -\frac{b}{a} = \frac{\omega_e}{2\omega_e x_e} - 1}$$

$$D_e = \omega_e(\mathrm{v}_D + 1/2) - \omega_e x_e (\mathrm{v}_D + 1/2)^2$$

$$\boxed{D_e = \frac{\omega_e^2}{4\omega_e x_e} - \frac{\omega_e x_e}{4} \approx \frac{\omega_e^2}{4\omega_e x_e} = \frac{\omega_e}{4x_e}}$$

$\propto$ Area under curve

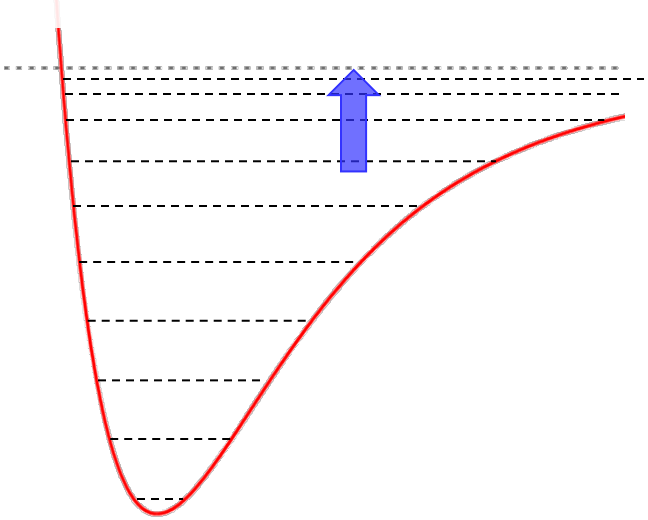


Real case: anharmonicity increases near dissociation limit

Birge-Sponer overpredicts D_e

6.2. Birge-Sponer method

- Determine dissociation energies



Vibrational level spacing → 0 in the limit of dissociation

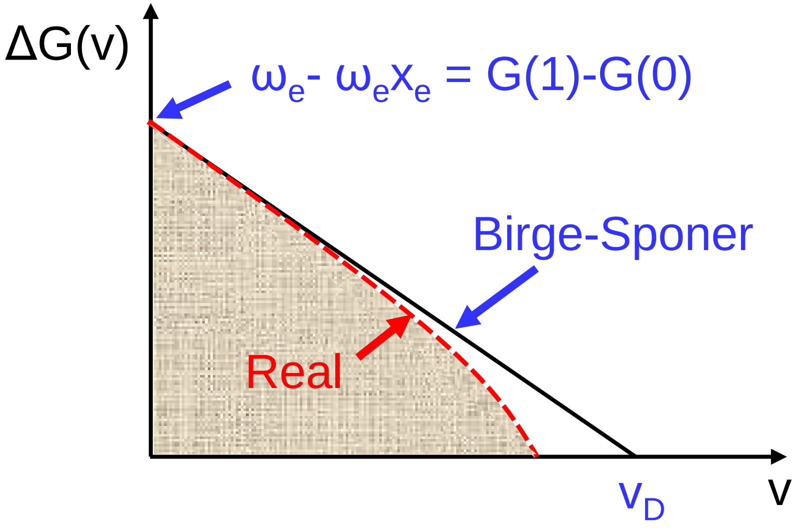
⇨ $\Delta G(\mathrm{v}) = a\mathrm{v} + b = 0$ @ dissociation

⇨ $$\boxed{\mathrm{v}_D = -\frac{b}{a} = \frac{\omega_e}{2\omega_e x_e} - 1}$$

$$D_e = \omega_e(\mathrm{v}_D + 1/2) - \omega_e x_e(\mathrm{v}_D + 1/2)^2$$

⇨ $$\boxed{D_e = \frac{\omega_e^2}{4\omega_e x_e} - \frac{\omega_e x_e}{4} \approx \frac{\omega_e^2}{4\omega_e x_e} = \frac{\omega_e}{4x_e}}$$

$\propto$ Area under curve



Example: HCl

$\omega_e = 2990\,cm^{-1}, x_e = 0.0174$

$\Rightarrow v_D = 27.7 \rightarrow 27$

$\Rightarrow D_e = 513\,kJ/mole$

Actual:

$D_e = 427\,kJ/mole$

⇨ Overpredicts by ~20%

6.3. Thermochemical approach

- Determine dissociation energies

E.g., $I_2 \rightarrow 2I$

$$K_p = \frac{P_I^2}{P_{I_2}}$$

$$\frac{d(\ln K_p)}{dT} = \frac{\Delta H}{RT^2} \quad \text{where} \quad \Delta H = \sum v_i H_i = H_{prod} - H_{react} = D_e + 2\int_I \hat{c}_p dT - \int_{I_2} \hat{c}_p dT$$

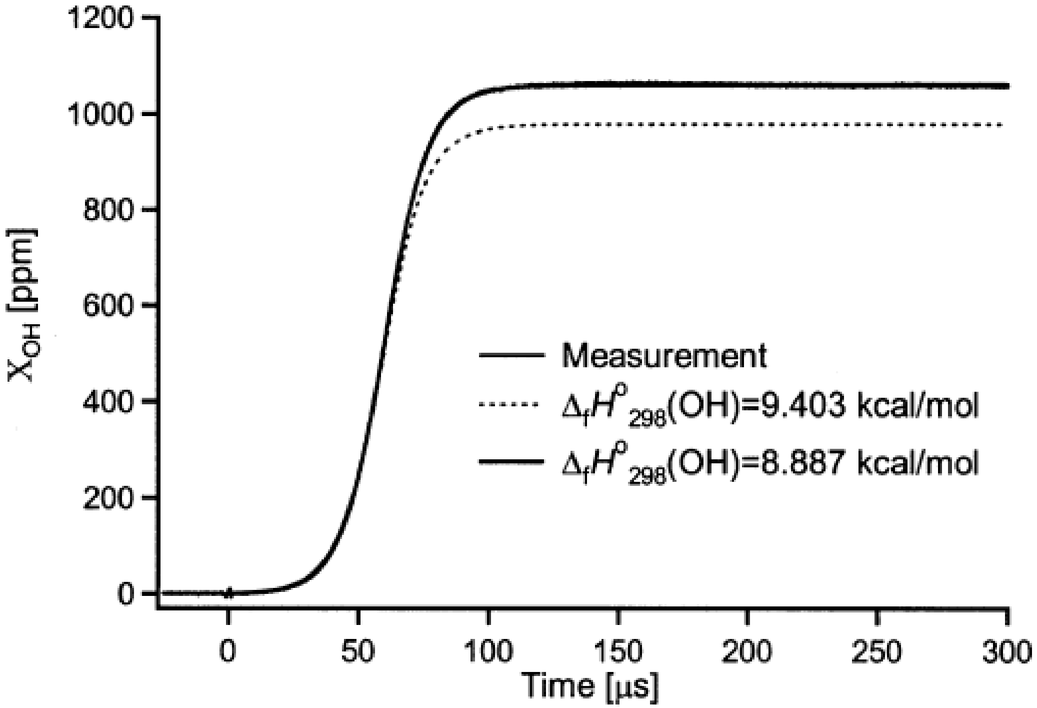
Measurements of partial pressures ⇨ $K_p(T)$ ⇨ $\Delta H, \boxed{D_e''}$

⇧

Measured spectroscopically (e.g., by laser absorption)

6.4. Working example

- A shock tube study of the enthalpy of formation of OH



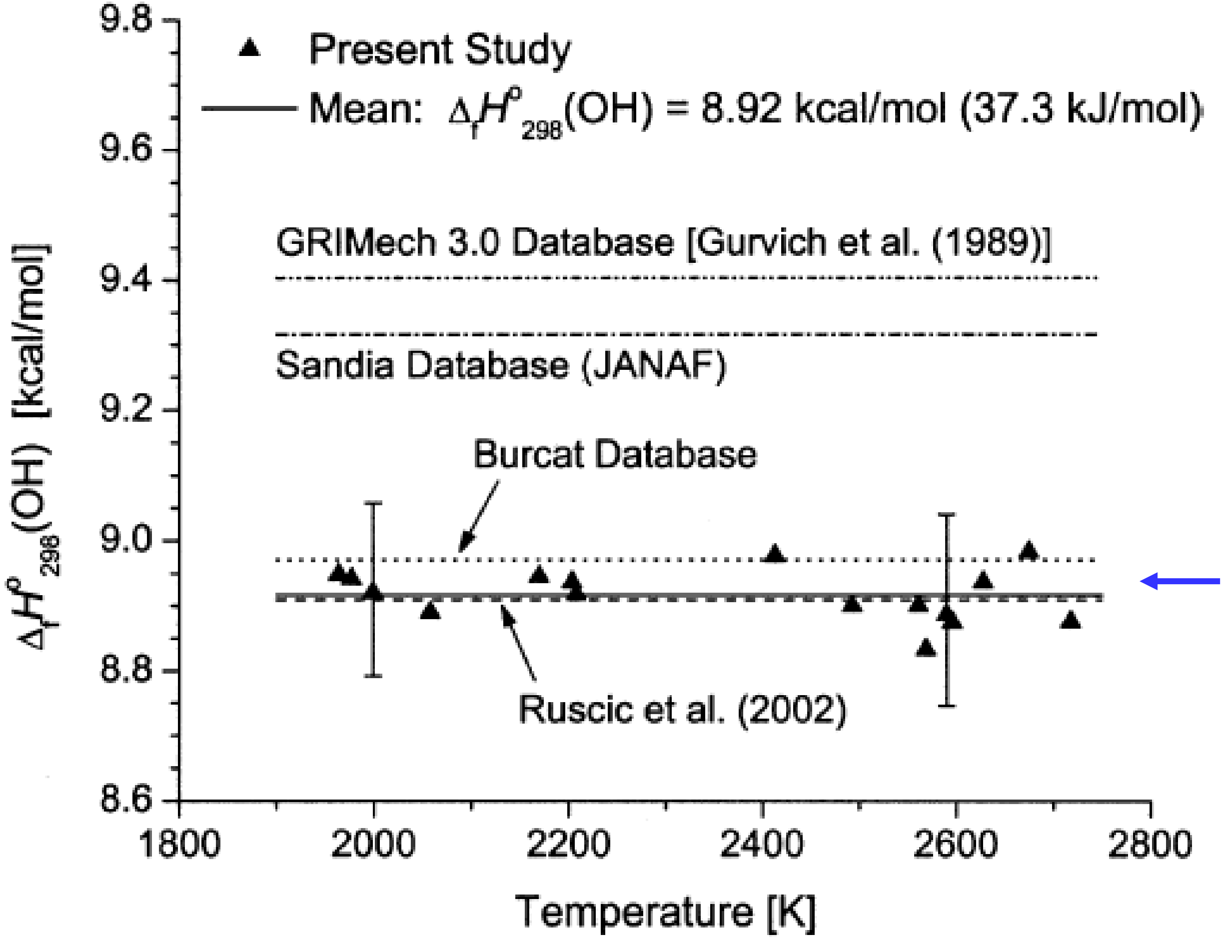
Experimentally measured and modeled OH mole fraction time histories.

- T_5=2590K, P_5=1.075atm, mixture: 4002ppm H_2/3999ppm O_2/balance Ar.
- The OH concentration is modeled using GRI-MECH 3.0 and the GRI-MECH 3.0 thermodynamics database, with 0.5ppm additional H atoms to match the induction time.
- The fit required a change in $\Delta_f H^0_{298}$(OH) from 9.403 to 8.887kcal/mol

6.4. Working example

- A shock tube study of the enthalpy of formation of OH

Experimentally derived values for $\Delta_f H^0_{298}$(OH).



← σ=0.04

Next: Polyatomic Molecular Spectra

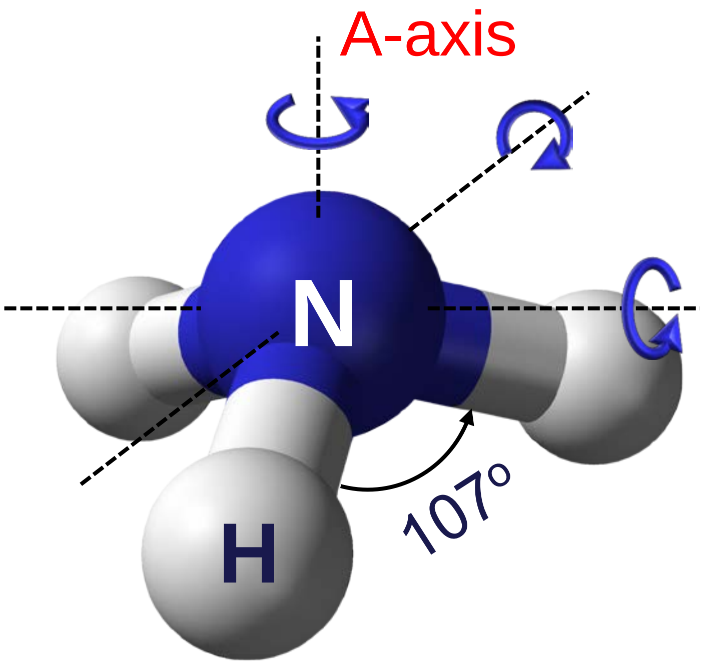
- Rotational Spectra
- Vibrational Bands, Rovibrational Spectra

Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

Lecture 4: Polyatomic Spectra

1. From diatomic to polyatomic
2. Classification of polyatomic molecules
3. Rotational spectra of polyatomic molecules
4. Vibrational bands, vibrational spectra

Ammonia molecule



1. From diatomic to polyatomic

- Rotation – Diatomics

Recall: For diatomic molecules

Energy: $F(J), cm^{-1} = \underbrace{BJ(J+1)}_{R.R.} - DJ^2(J+1)^2$

Centrifugal distortion constant

Rotational constant: $B, cm^{-1} = \frac{h}{8\pi^2 Ic}$

Selection Rule: $J' = J''+1 \rightarrow \Delta J = +1$

Line position: $\bar{\nu}_{J''+1\leftarrow J''} = 2B(J''+1) - 4D(J''+1)^3$

✐ Notes:

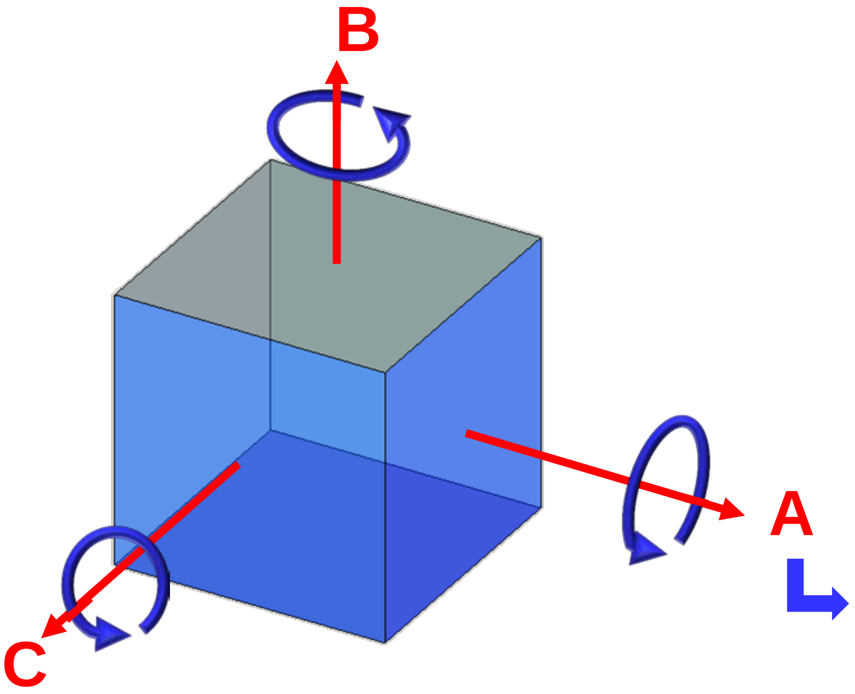
1. D is small, i.e., $D/B = 4\left(B/\bar{\nu}_{vib}\right)^2 << 1$
2. E.g., for NO, $\left(\frac{D}{B}\right)_{NO} = 4\left(\frac{B}{\omega_e}\right)^2 \approx 4\left(\frac{1.7}{1900}\right)^2 \approx 3\times10^{-6}$

→ Even @ J=60, $D/B\cdot J^2 \sim 0.01$

What about polyatomics (≥3 atoms)?

1. From diatomic to polyatomic

- 3D-body rotation

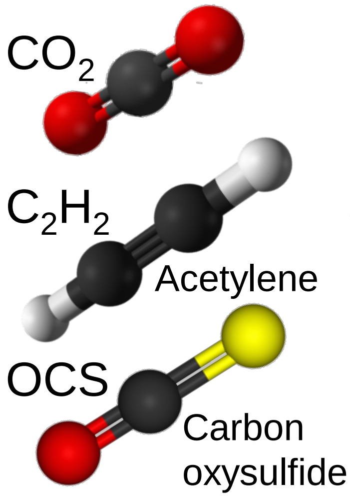
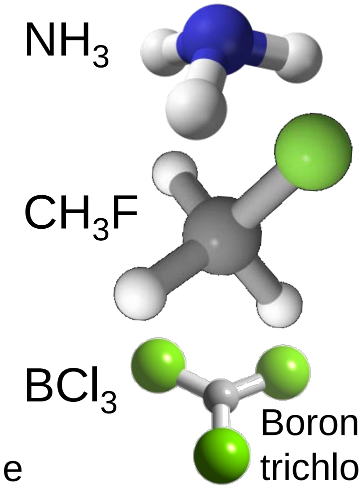
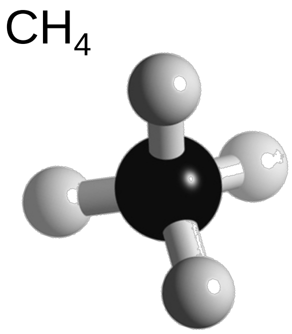
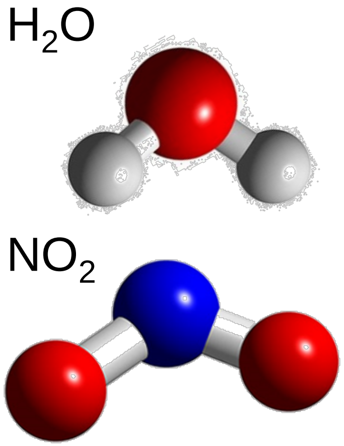


- Convention:
A-axis is the “unique” or “figure” axis, along which lies the molecule’s defining symmetry

- 3 principal axes (orthogonal): A, B, C
- 3 principal moments of inertia: I_A, I_B, I_C
- Molecules are classified in terms of the relative values of I_A, I_B, I_C

2. Classification of polyatomic molecules

- Types of molecules

Type	**Linear Molecules**	**Symmetric Tops**	**Spherical Tops**	**Asymmetric Rotors**
Relative magnitudes of $I_{A,B,C}$	$I_B=I_C$; $I_A \approx 0$*	$I_B=I_C \neq I_A$ $I_A \neq 0$	$I_A=I_B=I_C$	$I_A \neq I_B \neq I_C$
Examples				

Relatively simple

No dipole moment
Not microwave active

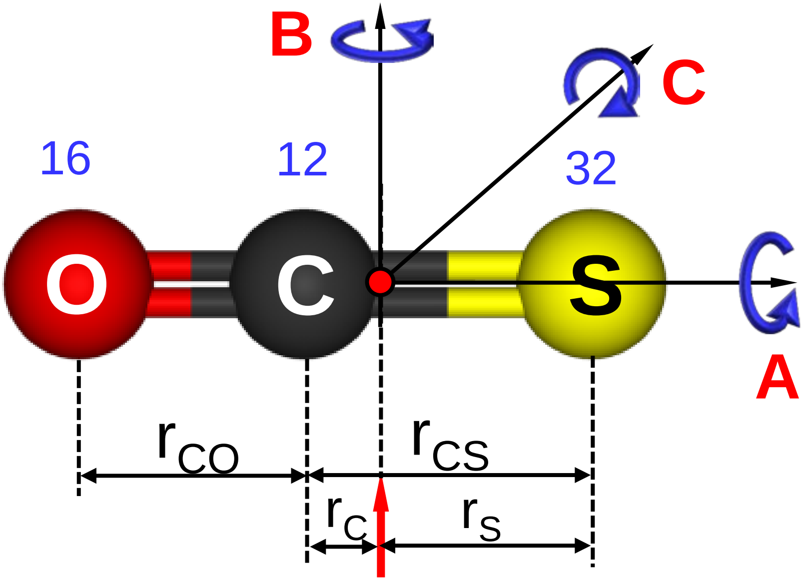
Largest category
Most complex

*Actually finite, but quantized momentum means it is in lowest state of rotation

2. Classification of polyatomic molecules

- Linear molecules

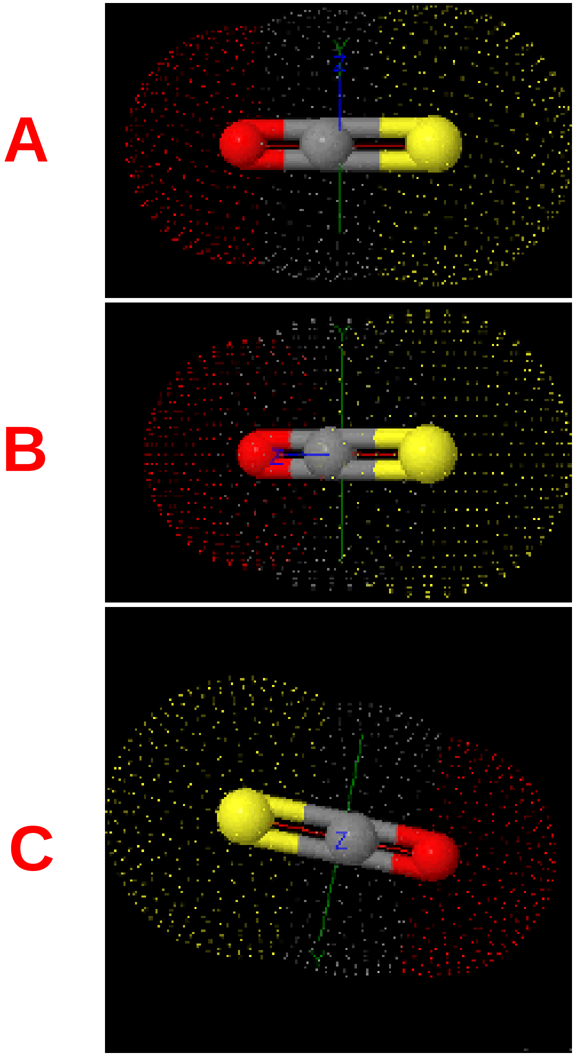
E.g., Carbon oxy-sulfide (OCS)



r_{CO} = 1.165Å
r_{CS} = 1.558Å

$$I_B=I_C;\ I_A\approx 0$$

$$B, cm^{-1} = \frac{h}{8\pi^2 I_B c}$$



2. Classification of polyatomic molecules

- Symmetric tops

Prolate

$I_A<I_B=I_C$, $A>B=C$

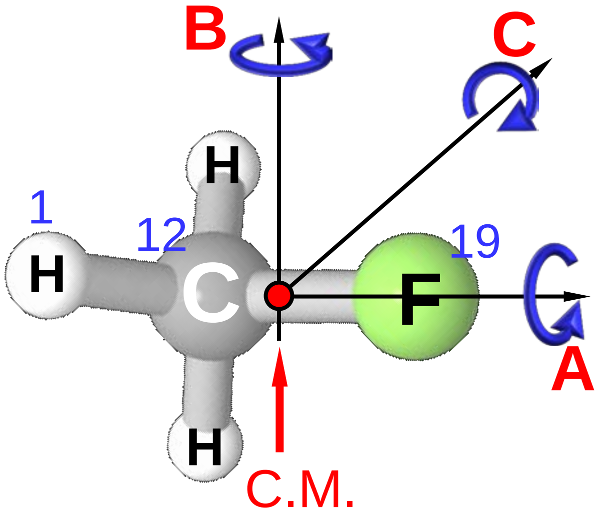
E.g., CH_3F

$$\boxed{I_B=I_C\neq I_A;\ I_A\neq 0}$$

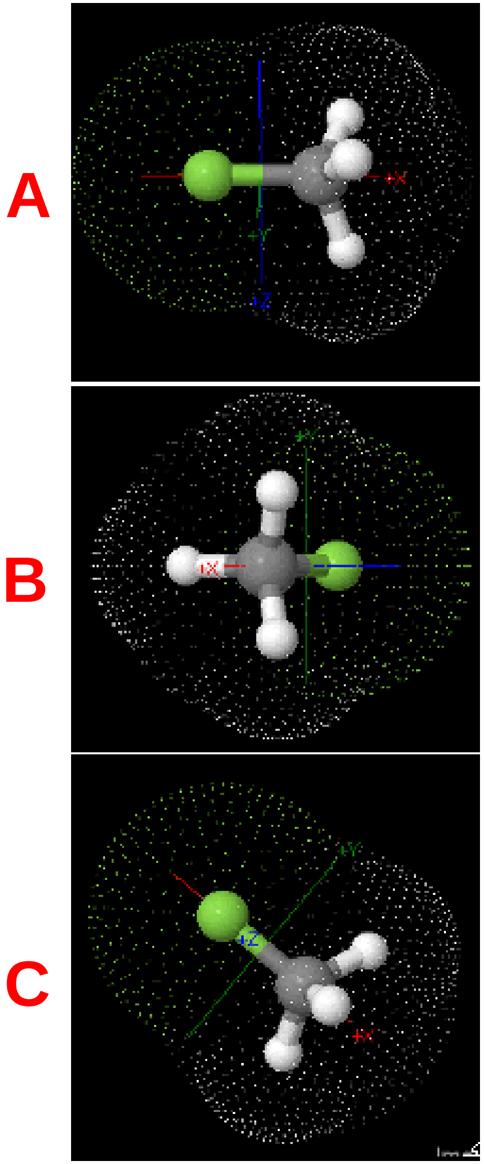
$$A, cm^{-1}=\frac{h}{8\pi^2 I_A c}$$

$$B, cm^{-1}=\frac{h}{8\pi^2 I_B c}$$

$$C, cm^{-1}=\frac{h}{8\pi^2 I_C c}$$



Tripod-like (tetrahedral bonding)



2. Classification of polyatomic molecules

- Symmetric tops

Oblate

$I_A > I_B = I_C$, A<B=C

E.g., BCl_3 (Planar)

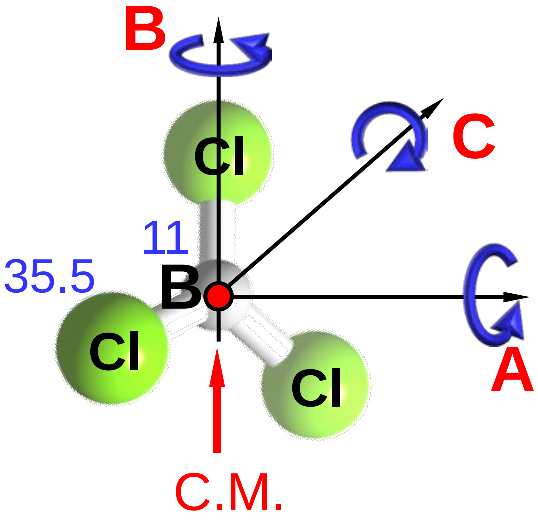
✐ No elec. dipole mom. → no QM selection rule

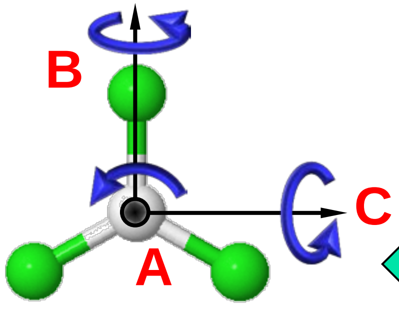
$$\boxed{I_B = I_C \neq I_A;\ I_A \neq 0}$$

$$A, cm^{-1} = \frac{h}{8\pi^2 I_A c}$$

$$B, cm^{-1} = \frac{h}{8\pi^2 I_B c}$$

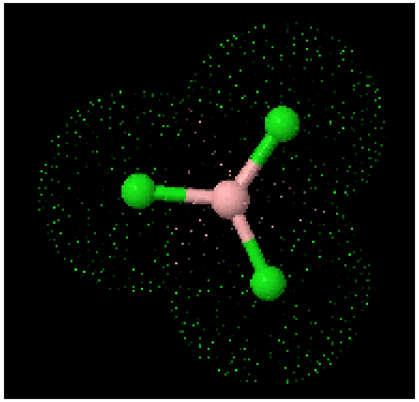
$$C, cm^{-1} = \frac{h}{8\pi^2 I_C c}$$



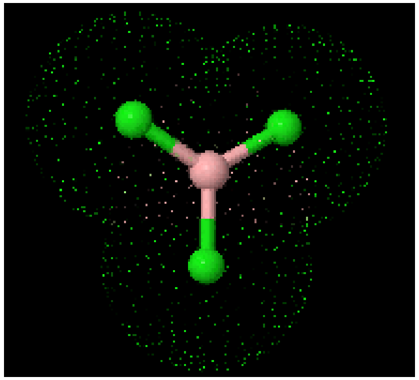


Planar view

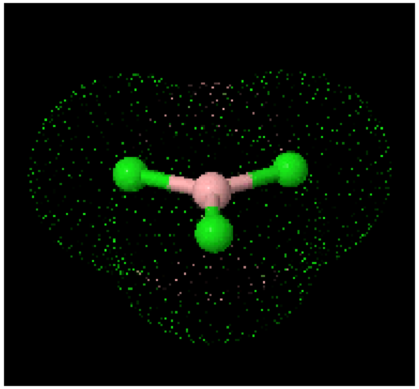
A



B



C

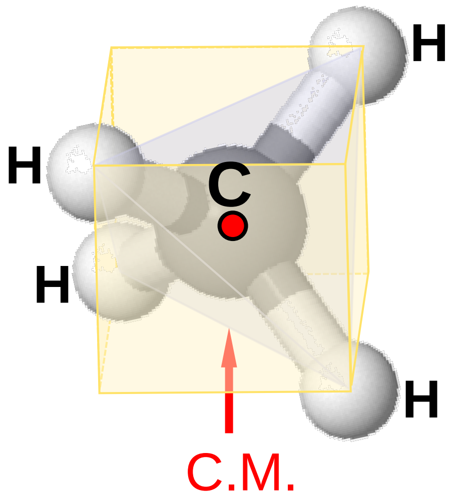


2. Classification of polyatomic molecules

- Spherical tops

$I_A=I_B=I_C$

E.g., CH_4 (methane)



Cube w/ C at center and H at diagonal corners

✎ Symmetric, but

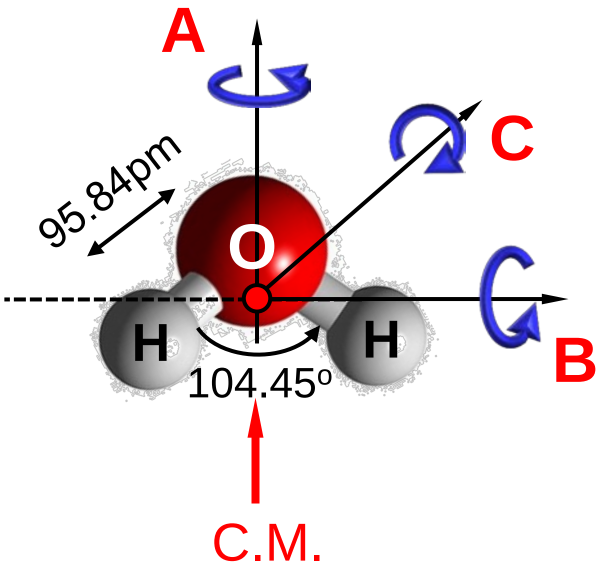
No dipole moment

No rotational spectrum

- Asymmetric rotors

$I_A \neq I_B \neq I_C$

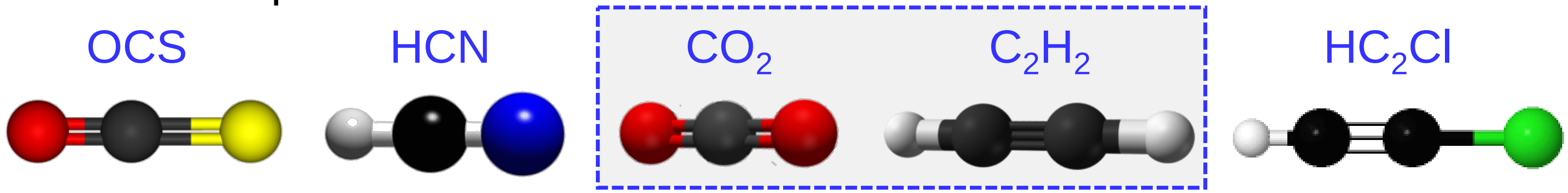
E.g., H_2O



✎ Complex and not addressed here

3. Rotational spectra of polyatomic molecules

- Linear molecules ($I_B=I_C$; $I_A\approx0$)
  - Examples



Symmetric, no dipole moment

Must be asymmetric to have electric dipole moment (isotopic substitution doesn’t change this as bond lengths remain fixed)

  - Energies and line positions

Can treat like diatomic (1 value of I) → same spectrum

$$F(J)=BJ(J+1)-DJ^2(J+1)^2$$

$$\overline{\nu}(J)=2\underset{\substack{\uparrow\\ \text{Rotational}\\ \text{const.}}}{B}(J+1)-4\underset{\substack{\uparrow\\ \text{Centrifugal}\\ \text{distortion const.}}}{D}(J+1)^3$$

Note: Larger I, smaller B (& line spacing) than diatomics

(“ is suppressed, i.e. J=J”)

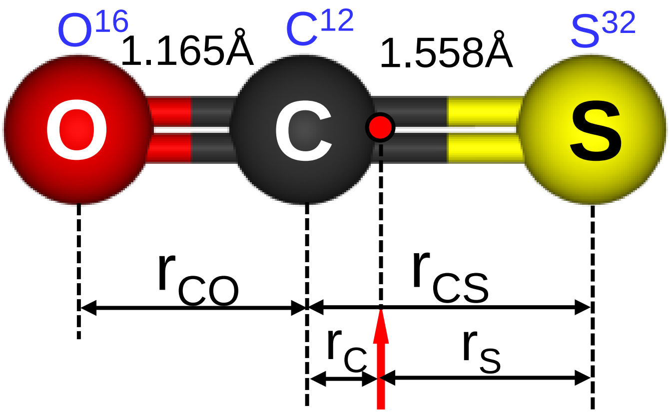
3. Rotational spectra of polyatomic molecules

- Linear molecules ($I_B=I_C$; $I_A \approx 0$)
  - Bond lengths

N atoms → N-1 bond lengths to be found

- Abs./Emis. spectra → B → 1 value of I_B
- Use N-1 isotopes → N-1 values of I_B

Example: OCS (carbon oxy-sulfide)



Center of mass

Use 2 isotopes for 2 equations:

$$I_{^{16}O^{12}C^{32}S} = \mathcal{F}\left(masses, r_{CO}, r_{CS}\right)$$

$$I_{^{18}O^{12}C^{32}S} = \mathcal{F}\left(masses, r_{CO}, r_{CS}\right)$$

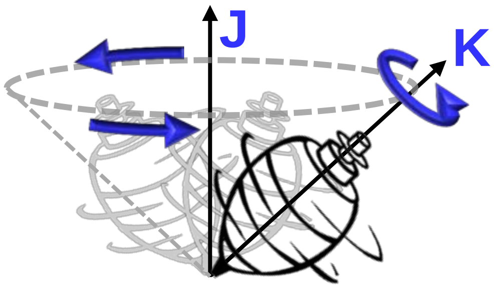
↓

Solve for r_{CO}, r_{CS}

3. Rotational spectra of polyatomic molecules

- Symmetric tops ($I_B=I_C \neq I_A$; $I_A \neq 0$)
  - 2 main directions of rotation → 2 quantum numbers
    - **J** (total angular momentum): 0, 1, 2, …
    - **K** (angular momentum about A): J, J-1, …, 1, 0, -1, … -J
    - + & - allowed, w/o change in energy

      ⇨ 2J+1 possibilities of K for each J
  - Quantized angular momentum



As before: $I_A^2\omega_A^2 + I_B^2\omega_B^2 + I_C^2\omega_C^2 = J(J+1)\hbar^2$

Plus new: $I_A^2\omega_A^2 = K^2\hbar^2$

  - Energy levels

$$E_{J,K} = \frac{1}{2}\sum_i I_i\omega_i^2 \quad \Rightarrow \quad \boxed{F(J,K) = BJ(J+1) + (A-B)K^2}$$

✎ Note degeneracy, i.e., independent of sign of K

3. Rotational spectra of polyatomic molecules

- Symmetric tops ($I_B=I_C\neq I_A$; $I_A\neq 0$)
  - Q.M. Selection rules
    - **ΔJ** = +1 Remember that ΔJ = J' – J"
    - **ΔK** = 0

      ➡ No dipole moment for rotation about A-axis
      No change in K will occur with abs./emis.
  - Line positions

$$\boxed{\bar{\nu}_{J.K} = F(J+1,K) - F(J,K) = 2BJ(J+1) \quad \left[cm^{-1}\right]}$$

✐ Note: Independent of K for a rigid rotor
Same as rigid diatomic!
K-dependence introduced for non-rigid rotation

3. Rotational spectra of polyatomic molecules

- Symmetric tops ($I_B = I_C \neq I_A$; $I_A \neq 0$)
    - Non-rigid rotation

Effect of extending bond lengths (w/ changes in K)

Change energies of rotation

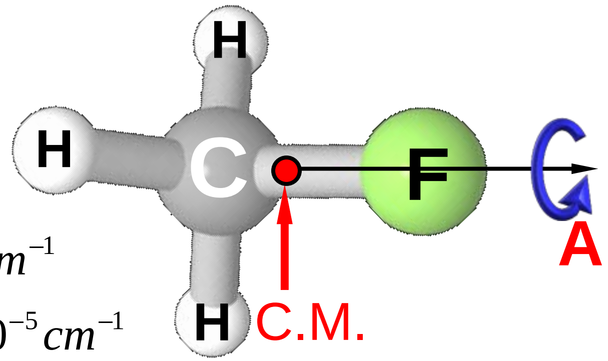
Centrifugal distortion const. D_J, D_K, D_{JK}

$$F(J,K) = BJ(J+1) + (A-B)K^2 - D_J J^2 (J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4$$

$$\bar{\nu}_{J.K} = 2(J+1)\left[B - 2D_J (J+1)^2 - D_{JK} K^2\right] \ \left[cm^{-1}\right]$$

✏ Note: Each J has 2J+1 components, but only J+1 frequencies

E.g., CH_3F, Methyl Fluoride

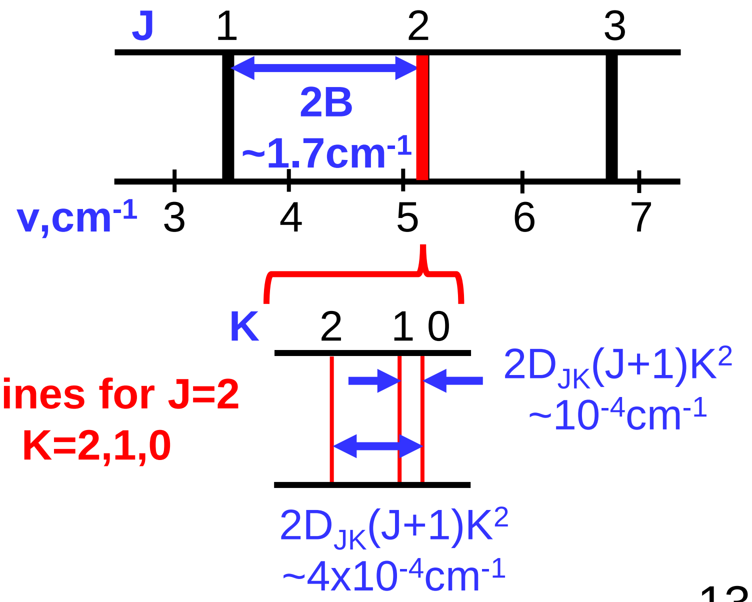


$B = 0.851 cm^{-1}$

$D_J = 2 \times 10^{-6} cm^{-1}$

$D_{JK} = 1.47 \times 10^{-5} cm^{-1}$

If $J \approx 20$, $J^2 \approx 400$, $2DJ^2 \approx 1.6 \times 10^{-3}$, $2DJ^2/B \approx .2\%$



3 lines for J=2 K=2,1,0

3. Rotational spectra of polyatomic molecules

- Symmetric tops ($I_B = I_C \neq I_A$; $I_A \neq 0$) → gets complex fast!

Prolate

$I_A < I_B = I_C$, $A > B = C$

$$F(J,K) = BJ(J+1) + (A-B)K^2$$

$$A - B = \frac{h}{8\pi^2 c}\left(\frac{1}{I_A} - \frac{1}{I_B}\right) > 0$$

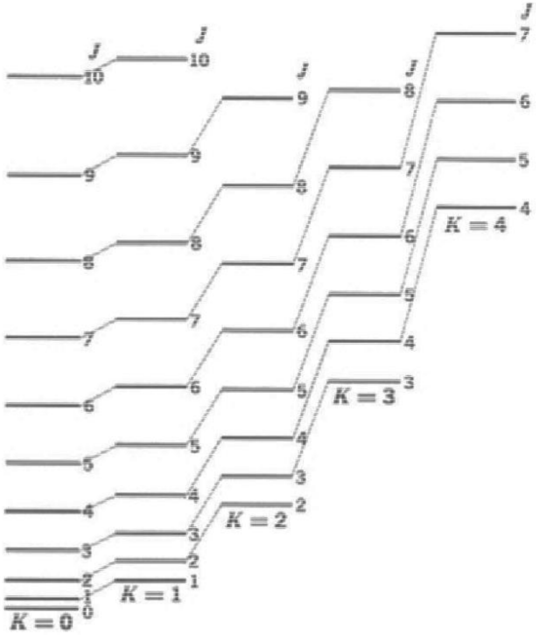
Oblate

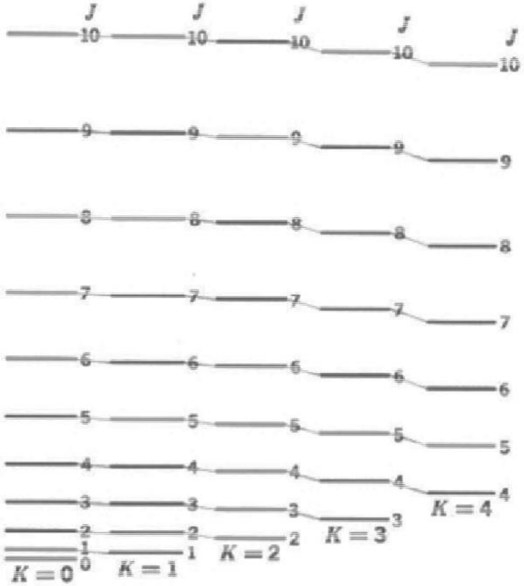
$I_A > I_B = I_C$, $A < B = C$

$$F(J,K) = BJ(J+1) + (A-B)K^2$$

$$A - B = \frac{h}{8\pi^2 c}\left(\frac{1}{I_A} - \frac{1}{I_B}\right) < 0$$

Example energy levels





3. Rotational spectra of polyatomic molecules

- Rotational partition function

Linear	Symmetric top	Spherical top	Asymmetric rotor
B=C; $I_A \approx 0$	B=C≠A; $I_A \neq 0$	A=B=C	A≠B≠C
$Q_{rot} = \dfrac{kT}{\sigma hcB}$	$Q_{rot} = \dfrac{1}{\sigma}\sqrt{\dfrac{\pi}{AB^2}\left(\dfrac{kT}{hc}\right)^3}$	$Q_{rot} = \dfrac{1}{\sigma}\sqrt{\dfrac{\pi}{B^3}\left(\dfrac{kT}{hc}\right)^3}$	$Q_{rot} = \dfrac{1}{\sigma}\sqrt{\dfrac{\pi}{ABC}\left(\dfrac{kT}{hc}\right)^3}$

$$A, cm^{-1} = \frac{h}{8\pi^2 I_A c}$$

$$B, cm^{-1} = \frac{h}{8\pi^2 I_B c}$$

$$C, cm^{-1} = \frac{h}{8\pi^2 I_C c}$$

σ – molecule-dependent symmetry factor

Molecule	σ	Molecule Type
CO_2	2	Linear
NH_3	3	Symmetric Top
CH_4	12	Spherical Top
H_2O	2	Asymmetric Rotor

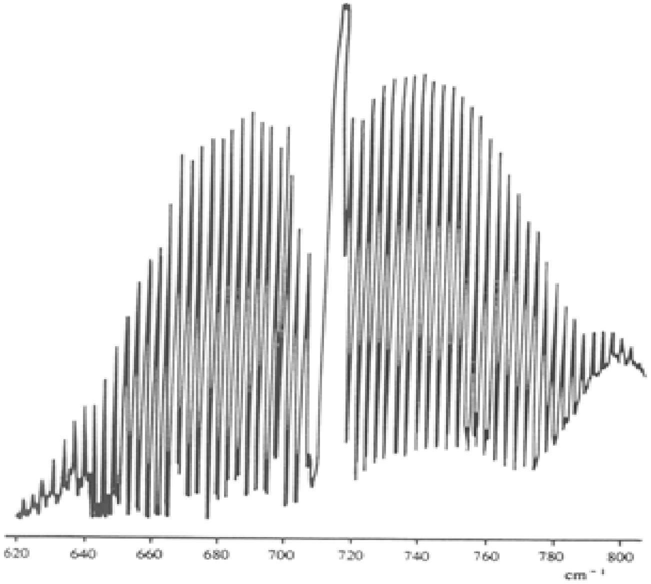
3. Rotational spectra of polyatomic molecules: Summary

- Linear (diatomic & polyatomic) and symmetric top molecules give similar (equal spacing) spectra at rigid rotor level
- High resolution needed to detect corrections / splittings
- Spectra → microscopic parameters (r_e, angles)
- Isotopes useful for spectral studies

4. Vibrational Bands, Rovibrational Spectra

1. Number of vibrational modes
2. Types of bands
   - Parallel and perpendicular
   - Fundamental, overtones, combination and difference bands
3. Relative strengths
4. Rovibrational spectra of polyatomic molecules
   - Linear molecules
   - Symmetric tops

Spectrum of bending mode of HCN



1. Number of vibrational modes

- N-atom molecule

  3N dynamical coordinates needed to specify instantaneous location and orientation

Total: **3N**

Center of Mass:	**3** coordinates (3 translational modes)	
Rotation:	Linear molecules **2** angular coordinates (rot. modes)	Nonlinear molecules **3** angular coordinates (rot. modes)
Vibration:	Linear molecules **3N-5** vibrational coordinates (vib. modes)	Nonlinear molecules **3N-6** vibrational coordinates (vib. modes)

4.2. Types of bands

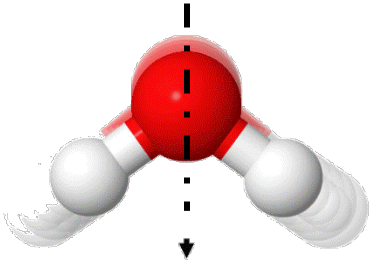
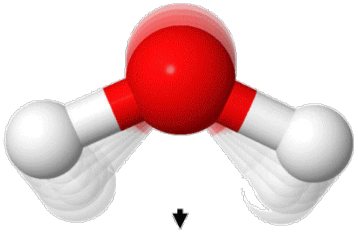
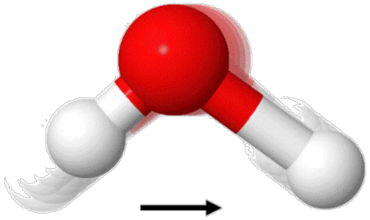
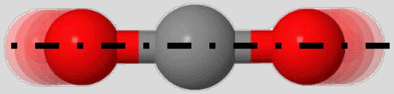
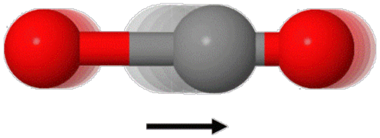
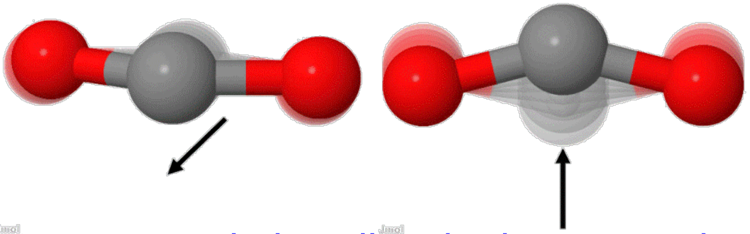
- Numbering (identification) convention of vibrational modes
  - Symmetry
  - Decreasing energy

	[cm^{-1}]	
Symmetric Declining frequency	ν_1	Highest-frequency <u>symmetric</u> vibrational mode
	ν_2	2nd highest symmetric mode
	…	…
	ν_i	Lowest-frequency <u>symmetric</u> mode
Asymmetric Declining frequency	ν_{i+1}	Highest-frequency <u>asymmetric</u> vibrational mode
	ν_{i+2}	2nd highest symmetric mode
	…	…

✎ <u>Exception</u>: the perpendicular vibration for linear XY_2 and XYZ molecules is always called $\boldsymbol{\nu_2}$

4.2. Types of bands

- Parallel and perpendicular modes

Examples:	**Parallel (||)** Dipole changes are || to the main axis of symmetry		**Perpendicular (⊥)** Dipole changes are ⊥ to the main axis of symmetry
H_2O (3x3-6=3 vib. modes)	 Symmetric stretch ν_1=3652cm^{-1}	 Symmetric bending ν_2=1595cm^{-1}	 Asymmetric stretch ν_3=3756cm^{-1}
CO_2 (3x3-5=4 vib. modes)	 No dipole moment Not IR-active! Symmetric stretch ν_1=1330cm^{-1}	 Asymmetric stretch ν_3=2349cm^{-1}	 Symmetric bending (2 degenerate) ν_2=667cm^{-1}

4.2. Types of bands

- Parallel and perpendicular modes

Symmetric molecules: vibrational modes are <u>either</u> IR-active <u>or</u> Raman-active (Chapter 6)

Vibrational modes of CO_2

Mode	Frequency [cm^{-1}]	Type	Description	IR	Raman
ν_1	1388	--	Symmetric stretch	Not active	Active
ν_2	667	⊥	Symmetric bend (Degenerate)	Strong	Not active
ν_3	2349	||	Asymmetric stretch	Very strong	Not active

Vibrational modes of HCN

Mode	Frequency [cm^{-1}]	Type	Description	IR	Raman
ν_1	3310	||	Symmetric stretch	Strong	Weak
ν_2	715	⊥	Symmetric bend (Degenerate)	Very strong	Weak
ν_3	2097	||	Asymmetric stretch	Weak	Strong

4.2. Types of bands

- Terminology for different types of vibrational bands

Fundamental Bands:	ν_i, the i^{th} vibrational mode; $\Delta\upsilon=\upsilon'-\upsilon''=1$ for the i^{th} mode
1^{st} Overtone:	$2\nu_i$; $\Delta\upsilon=\upsilon'-\upsilon''=2$ for the i^{th} mode
2^{nd} Overtone:	$3\nu_i$; $\Delta\upsilon=\upsilon'-\upsilon''=3$ for the i^{th} mode
Combination bands:	Changes in multiple quantum numbers, e.g., $\nu_1+\nu_2$; $\Delta\upsilon_1=\Delta\upsilon_2=1$, i.e., υ_1 and υ_2 both increase by 1 for absorption or decrease by 1 for emission $2\nu_1+\nu_2$; $\Delta\upsilon_1=2$ and $\Delta\upsilon_2=1$
Difference bands:	Quantum number changes with mixed sign $\nu_1-\nu_2$; $\upsilon_{1,\mathrm{final}}-\upsilon_{1,\mathrm{initial}}=\pm1$ and $\upsilon_{2,\mathrm{final}}-\upsilon_{2,\mathrm{initial}}=\mp1$, i.e., a unit increase in υ_1 is accompanied by a unit decrease in υ_2, and vice-versa.

4.2. Types of bands

- Vibrational partition function

$$\boxed{Q_{vib} = \prod_{i}^{\text{modes}} \left[1 - \exp\left(-\frac{hc\omega_{e,i}}{kT}\right)\right]^{-g_i}}$$

E.g., NH$_3$: 3N-6 = 6 vib. modes

Degenerate

$$Q_{vib} = \left[1 - \exp\left(-\frac{hc\omega_{e,1}}{kT}\right)\right]^{-1} \left[1 - \exp\left(-\frac{hc\omega_{e,2}}{kT}\right)\right]^{-1} \left[1 - \exp\left(-\frac{hc\omega_{e,3}}{kT}\right)\right]^{-2} \left[1 - \exp\left(-\frac{hc\omega_{e,4}}{kT}\right)\right]^{-2}$$

Vibration	**Frequency [cm^{-1}]**	**Type**	**Description**
ν_1	3337	$\parallel$	Symmetric stretch
ν_2	950	$\parallel$	Symmetric bend
ν_3	3444	$\perp$	Asymmetric stretch (Degenerate)
ν_4	1627	$\perp$	Asymmetric bend (Degenerate)

4.3. Relative strength

- In general
  - Fundamental bands are much stronger than combination, difference, and overtone bands
- Fairly harmonic molecules
  - E.g., CO
  - Relative strength between fundamental and overtones ~ 10^2
  - Closely SHO, overtone bands are *nearly* forbidden (low transition probabilities)
- Highly anharmonic molecules
  - E.g., NH_3
  - Relative strength between fundamental and overtones ≤ 10
  - Overtone bands are less forbidden

Exception – Fermi resonance:

Accidental degeneracies (i.e., near resonances) can strengthen weak processes.
Two vib. Modes strongly coupled by radiative and collisional exchanges.
E.g., $2\boldsymbol{\nu}_\mathbf{2}$ CO_2 (@ 1334cm^{-1}) $\approx \boldsymbol{\nu}_{\mathbf{1,\ CO2}}$

4.4. Rovibrational spectra of polyatomic molecules

- Linear polyatomic molecules

(limit consideration to fundamental transitions)

Energy: $T(\mathrm{v}_i, J) = G(\mathrm{v}_i) + F(J)$

  - Case I: Parallel bands (*symmetric* and *asymmetric* stretch)

Selection Rule: $\Delta \mathrm{v}_i = 1$

$\Delta J = \pm 1$

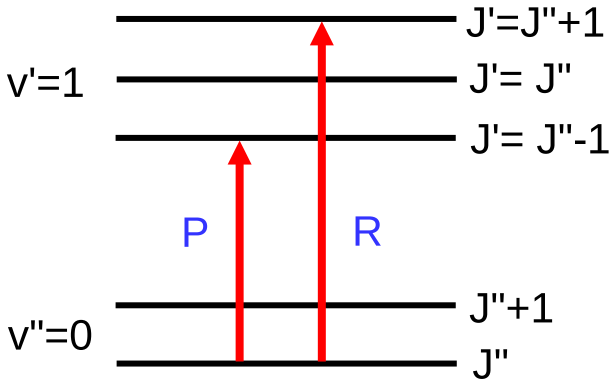
(R and P branches)

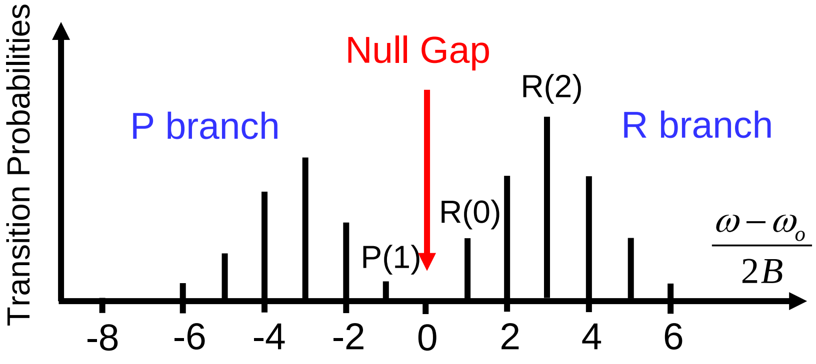
$\Delta \mathrm{v}_j = 0,\ j \neq i$

Absorption Spectrum: *P* & *R* branches only

Example: HCN($\boldsymbol{\nu_1}$, $\boldsymbol{\nu_3}$)

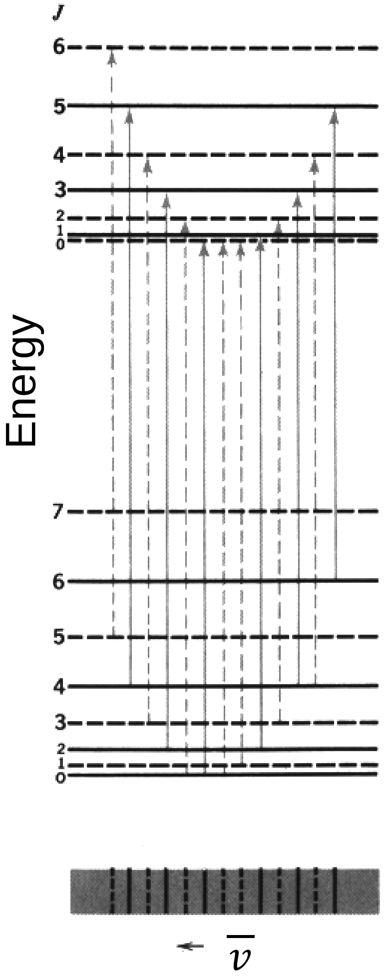
Note: No $\boldsymbol{\nu_1}$ parallel band for CO_2





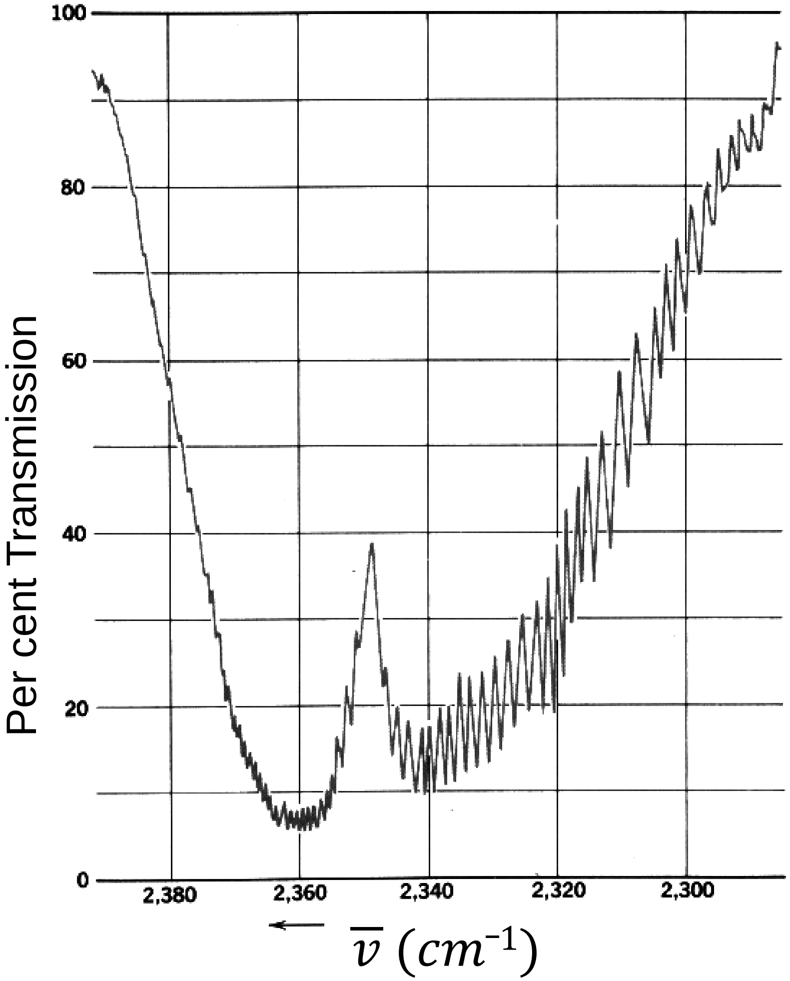
4.4. Rovibrational spectra of polyatomic molecules

- Linear polyatomic molecules
  - Case I: Parallel band



ν = 1
Anti-symmetric
Stretching
Vibration

ν = 0



Example-2: A parallel band of the linear molecule CO_2

4.4. Rovibrational spectra of polyatomic molecules

- Linear polyatomic molecules

  (limit consideration to fundamental transitions)

  Energy: $T(\mathrm{v}_i, J) = G(\mathrm{v}_i) + F(J)$

  - Case II: Perpendicular bands

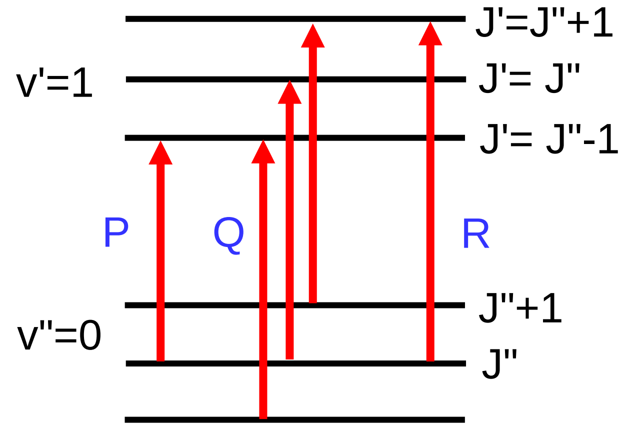
Selection Rule: $\Delta \mathrm{v}_i = 1$

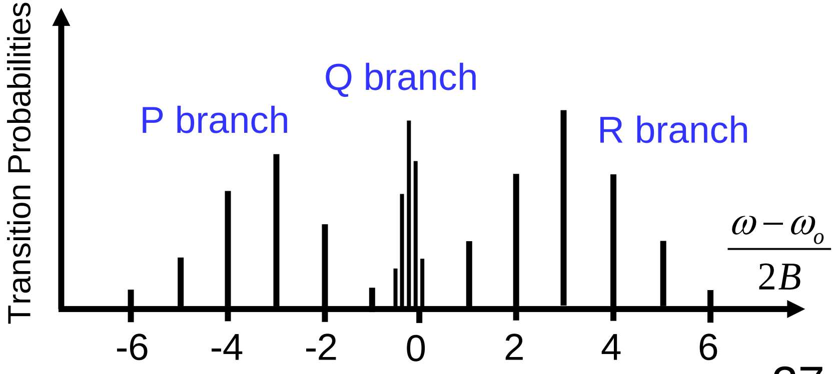
$\Delta J = \pm 1, 0$

R, P and Q branches)

$\Delta \mathrm{v}_j = 0,\ j \neq i$

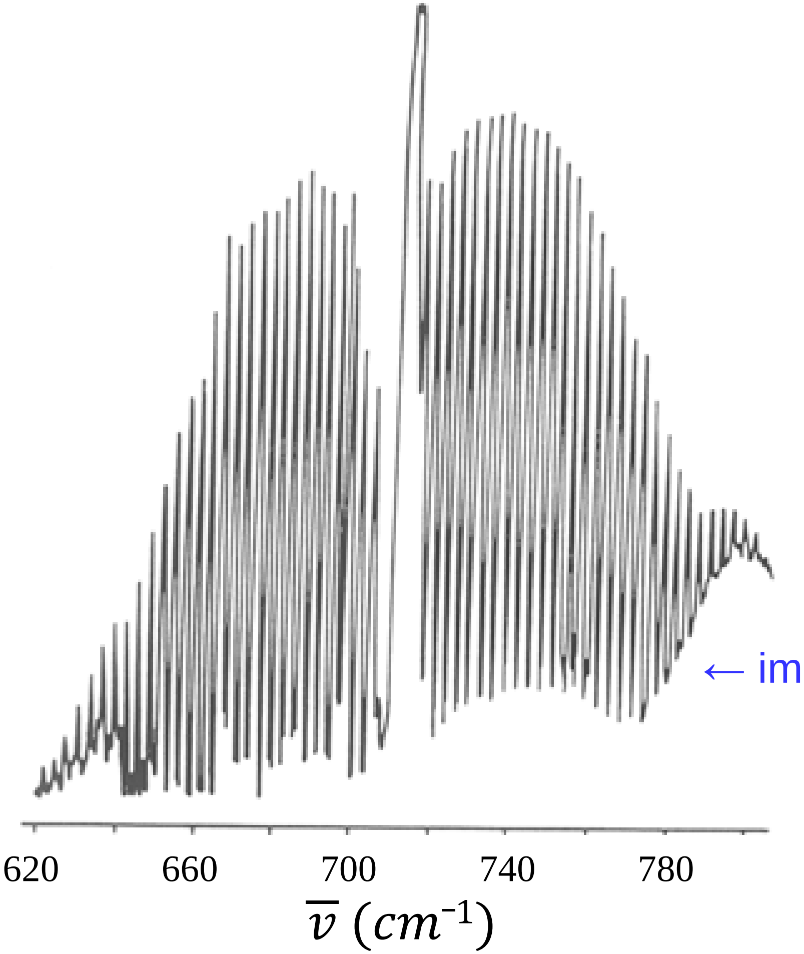
1. If B'=B", all Q branch lines occur at the same frequency
2. If B'≠B", $Q(J'') = \omega_0 + \overbrace{(B' - B'')}^{-\alpha<0} J''(J''+1)$
   Q branch “degrades” to lower frequencies (i.e., to the “red” in wavelength)





4.4. Rovibrational spectra of polyatomic molecules

- Linear polyatomic molecules
  - Case II: Perpendicular bands



← impurity

Example:
Spectrum of the bending mode of HCN, showing the PQR structure

4.4. Rovibrational spectra of polyatomic molecules

- Symmetric top molecules (e.g., CH_3F, BCl_3)

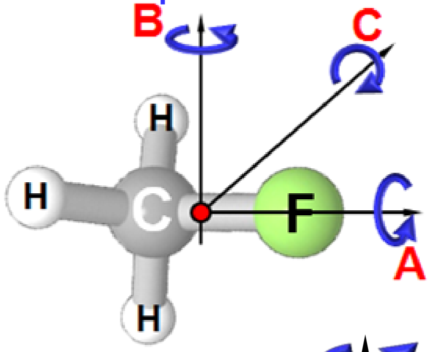
  Recall: K – quantum number for angular momentum around axis A

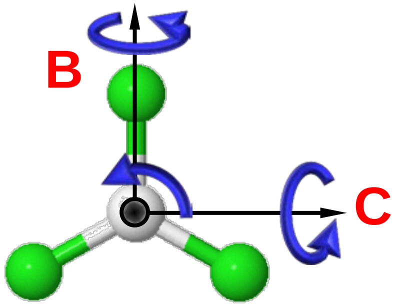
  Energy: $T(\mathrm{v}_i, J, K) = G(\mathrm{v}_i) + F(J, K)$

  $$= (\mathrm{v}_i + 1/2)\omega_e^i - \omega_e^i x_e^i (\mathrm{v}_i + 1/2)^2 + BJ(J+1) + (A-B)K^2$$

  - Case I: Parallel bands

Tripod-like





Planar

Selection Rule: $\Delta \mathrm{v}_i = 1$

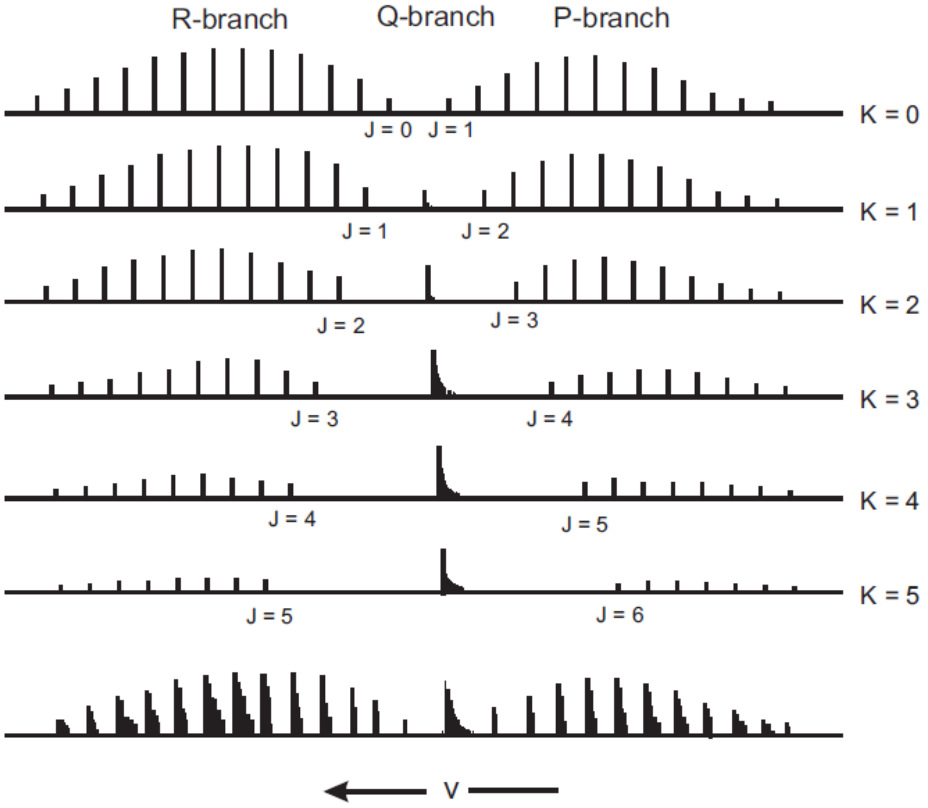
$\Delta J = \pm 1, 0$ (P, Q, R branches)

$\Delta K = 0$

1. 2J+1 values of K (K=J, J-1, …, 0, …, -J)
2. Intensity of Q branch is a function of (I_A/I_B)
3. As $(I_A/I_B) \rightarrow 0$
   symmetric top → linear molecule
   strength of Q branch → 0

4.4. Rovibrational spectra of polyatomic molecules

- Symmetric top molecules (e.g., CH_3F, BCl_3)
  - Case I: Parallel bands



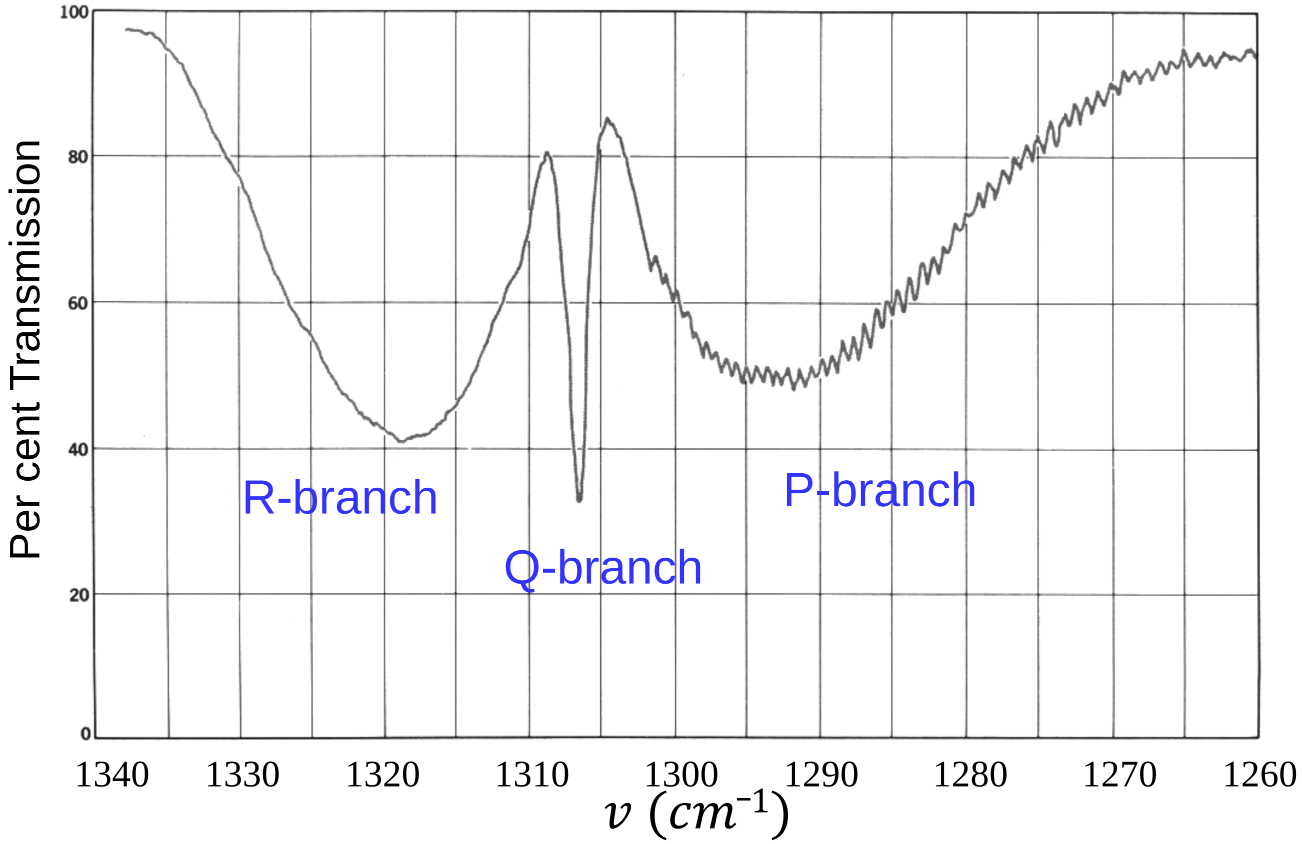
Resolved components of a parallel band showing contributions from each of the K levels of the v=0 state

Note:

1. Splitting in P and R branch due to a difference in (A-B) in upper and lower vib. levels
2. Splitting in Q branch due to difference in B in upper and lower vib. levels
3. For K=0, spectrum reduces to that of linear molecules, no Q branch
4. K cannot exceed J

4.4. Rovibrational spectra of polyatomic molecules

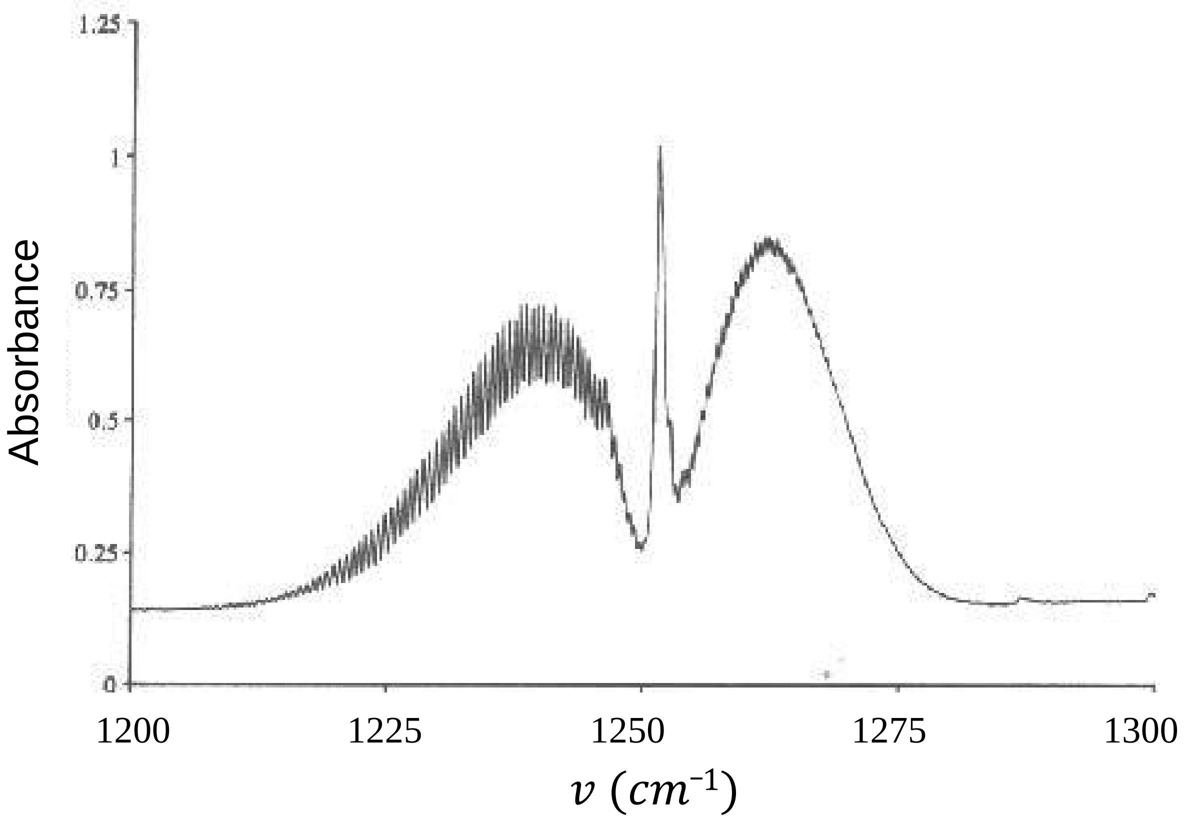
- Symmetric top molecules
    - Case I: Parallel bands



Example-1: A parallel absorption band of the symmetric top molecule CH_3Br. The P branch is partly resolved, while only the contours of the R and Q branches is obtained

4.4. Rovibrational spectra of polyatomic molecules

- Symmetric top molecules
  - Case I: Parallel bands



Example-2: The parallel stretching vibration, centered at 1251 cm^{-1}, of the symmetric top molecule CH_3I, showing the typical PQR contour.

4.4. Rovibrational spectra of polyatomic molecules

- Symmetric top molecules (e.g., CH_3F, BCl_3)
  - Case II: Perpendicular bands

Selection Rule:

$$\Delta \mathrm{v}_i = 1$$

$$\Delta J = \pm 1, 0 \ (P, Q, R \text{ branches})$$

$$\Delta K = \pm 1$$

R Branch:

$$\Delta J = +1, \Delta K = \pm 1$$

$$\bar{\nu}_R = \omega_o + 2B(J+1) + (A-B)(1 \pm 2K)$$

P Branch:

$$\Delta J = -1, \Delta K = \pm 1$$

$$\bar{\nu}_P = \omega_o - 2BJ + (A-B)(1 \pm 2K)$$

Q Branch:

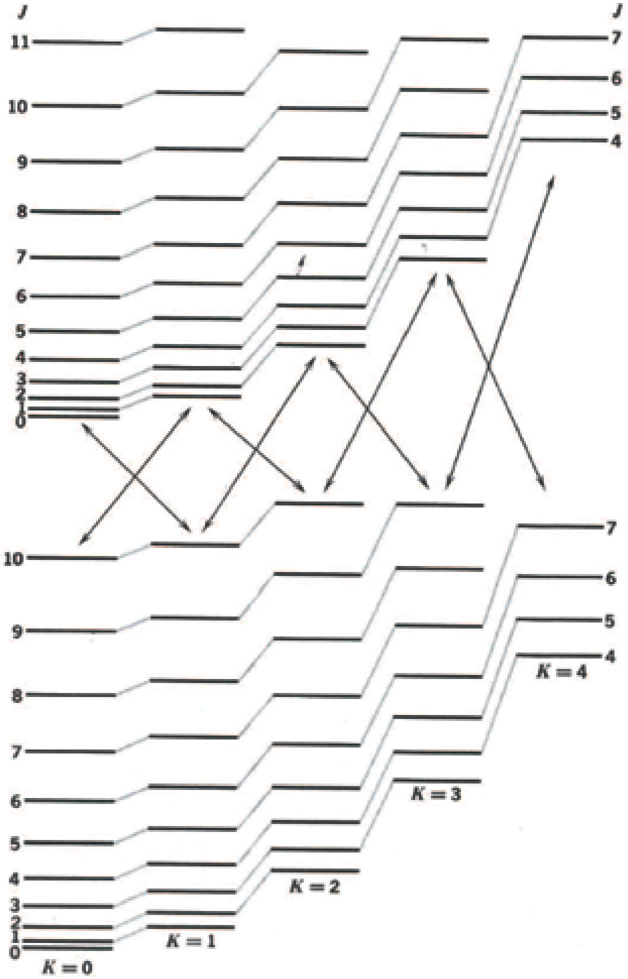
$$\Delta J = 0, \Delta K = \pm 1$$

$$\bar{\nu}_Q = \omega_o + (A-B)(1 \pm 2K)$$

✎ Note: Two sets of R, P and Q branches for each lower state value of K

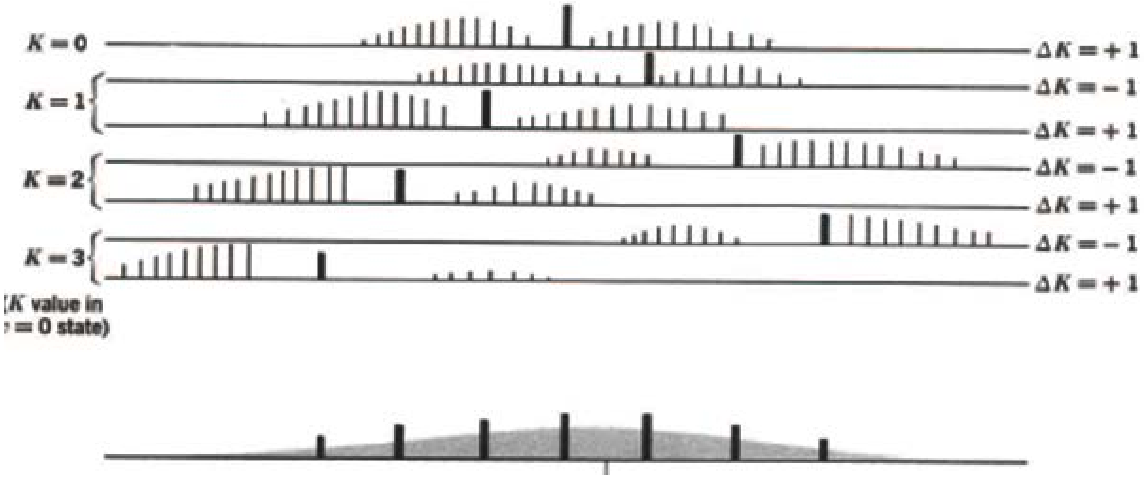
4.4. Rovibrational spectra of polyatomic molecules

- Symmetric top molecules (e.g., CH_3F, BCl_3)
  - Case II: Perpendicular bands



◀ Energy levels of a symmetric top molecule showing transitions that are allowed for a perpendicular band

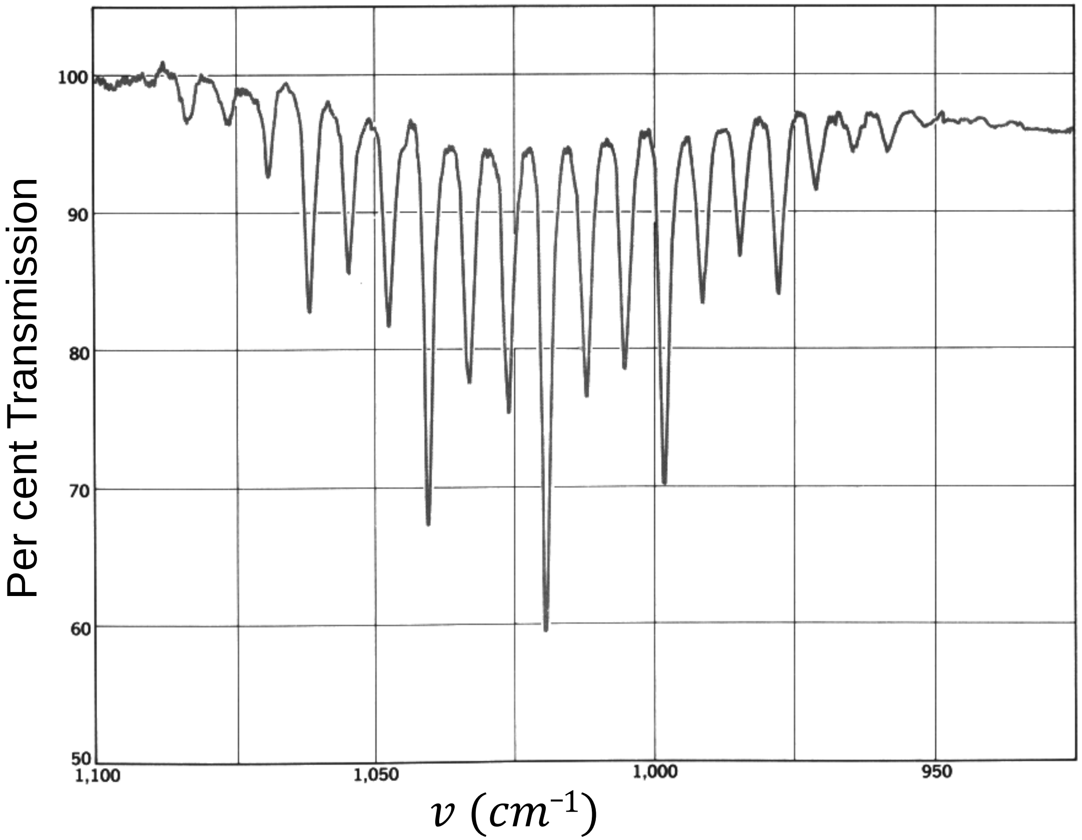
▼ Resulting spectrum, components of a perpendicular band showing the contributions from each K levels of the v=0 state



$\leftarrow v$ v_0

4.4. Rovibrational spectra of polyatomic molecules

- Symmetric top molecules
  - Case II: Perpendicular bands



✐ Note: Spacing of the Q branch lines in a perpendicular band can be identified with 2(A-B), and hence are observable if A-B is large enough

Example: The Q-branch of a perpendicular band, for the symmetric top molecule CH_3Cl

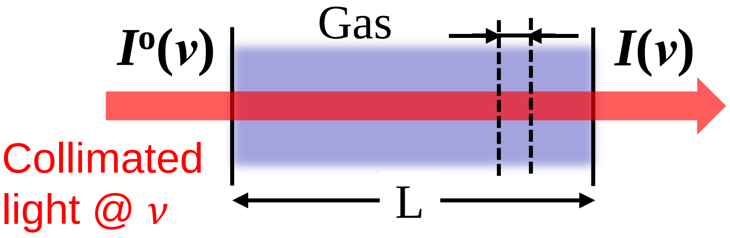
Next: Quantitative Emission/Absorption

- Spectral Absorptivity
- Eqn. of Radiative Transfer
- Einstein Coefficients/Theory
- Radiative Lifetime, Line Strength

Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

Lecture 5: Quantitative Emission/Absorption

1. Eqn. of radiative transfer / Beer's Law
2. Einstein theory of radiation
3. Spectral absorption coefficient
4. Radiative lifetime
5. Line strengths



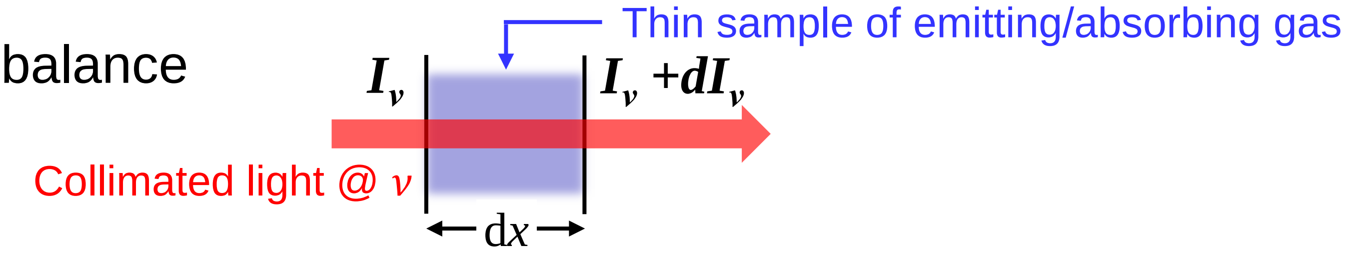
Light transmission through a slab of gas

Beer's Law

$I(\nu) = I^o(\nu) \exp(-k_\nu L)$

1. Eqn. of radiative transfer / Beer's Law

- Energy balance



$$1 = \underbrace{\text{absorption}}_{\alpha_\nu} + \underbrace{\text{reflection}}_{=0} + \underbrace{\text{scattering}}_{=0} + \underbrace{\text{transmission}}_{T_\nu}$$

$$\Rightarrow \alpha_\nu + T_\nu = 1$$

spectral absorptivity, or absorbance ↑ ↑ spectral transmissivity

$$\alpha_\nu = \boxed{k_\nu} dx = \frac{-dI_\nu}{I_\nu}\left[\text{no units}\right]$$

Spectral absorption coefficient (the fraction of incident light I_ν over frequency range $\nu \rightarrow \nu + d\nu$ which is absorbed per unit length dx

$$\boxed{k_\nu \equiv -\frac{(dI_\nu / dx)}{I_\nu}\left[\text{cm}^{-1}\right]}$$

↑ spectral intensity in $\left(\frac{\text{W/cm}^2}{\text{cm}^{-1}}\right)$ or $\left(\frac{\text{W/cm}^2}{\text{Hz}}\right)$

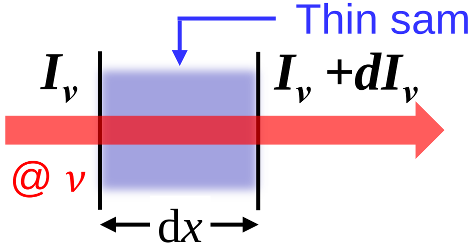
Integrate over ν for total I

$$I\left[\text{W/cm}^2\right] = \int_\nu I_\nu d\nu$$

Also applies to I @ ν

1. Eqn. of radiative transfer / Beer's Law

- Energy balance



Consider emission from the gas slab

⇨ Spectral emissivity $\varepsilon_\nu = \frac{I_\nu^{em}}{I_\nu^{bb}}[\text{no units}] = \frac{I^{em}(\nu)}{I^{bb}(\nu)}[\text{no units}]$

Blackbody spectral radiancy

Kirchhoff's Law – "emissivity equals absorptivity"

$$\varepsilon_\nu = \alpha_\nu$$

$$\text{emission} = \varepsilon_\nu I_\nu^{bb}$$

$$\text{absorption} = \alpha_\nu I_\nu$$

$$dI_\nu = \text{emission} - \text{absorption}$$

$$= \varepsilon_\nu I_\nu^{bb} - \alpha_\nu I_\nu = \alpha_\nu \left(I_\nu^{bb} - I_\nu\right)$$

⇨ Differential form of the eqn. of radiative transfer

$$\boxed{dI_\nu = k_\nu dx\left(I_\nu^{bb} - I_\nu\right)}$$

1. Eqn. of radiative transfer / Beer's Law

- Energy balance

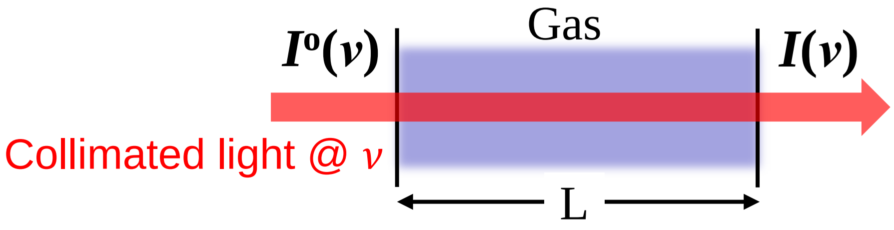
Differential form of the eqn. of radiative transfer

$$\boxed{dI_\nu = k_\nu dx\left(I_\nu^{bb} - I_\nu\right)}$$

Integrate over L

Integrated form of the eqn. of radiative transfer

$$\boxed{I_\nu = I_\nu^0 \exp\left(-\underbrace{k_\nu L}_{\text{Optical depth}}\right) + I_\nu^{bb}\left[1 - \exp\left(-k_\nu L\right)\right]}$$



Consider two interesting cases: Emission, Absorption

1. Eqn. of radiative transfer / Beer's Law

- Case I: Emission experiment $I_\nu^0 = 0$ (no external radiation source)

$$I_\nu = \cancel{I_\nu^0 \exp(-k_\nu L)} + I_\nu^{bb}\left[1-\exp(-k_\nu L)\right]$$

Spectral radiancy: $I_\nu(L) = I_\nu^{bb}\left[1-\exp(-k_\nu L)\right]$

Spectral emissivity: $\varepsilon_\nu(k_\nu, L) = \dfrac{I_\nu(L)}{I_\nu^{bb}} = 1-\exp(-k_\nu L)$

⇓ Integrate over ν

$$I(L) = \int_0^\infty I_\nu(L)\,d\nu = \int_0^\infty I_\nu^{bb}\left[1-\exp(-k_\nu L)\right]d\nu$$

$$\varepsilon\,(L) = \frac{I(L)}{I^{bb}} = \frac{1}{\sigma T^4}\int_0^\infty I_\nu^{bb}\left[1-\exp(-k_\nu L)\right]d\nu$$

Emission types: Single/multiple line
Single/multiple bands
Continuum

✎Note: $I^{bb} = \int_0^\infty I_\nu^{bb}\,d\nu = \underline{\sigma} T^4$

Stefan-Boltzmann constant

$\sigma = 5.67\times10^{-5}\left[\mathrm{erg\cdot cm^{-2}\cdot s^{-1}\cdot K^{-4}}\right]$

Optical depth: Optically thick: $k_\nu L >> 1$, $I_\nu(L) \rightarrow I_\nu^{bb}$

Optically thin: $k_\nu L << 1$, $I_\nu(L) \rightarrow (k_\nu L) I_\nu^{bb}, \varepsilon_\nu = k_\nu L$

1. Eqn. of radiative transfer / Beer's Law

- Case II: Absorption experiment $I_\nu^0 >> I_\nu^{bb}$

$$I_\nu = I_\nu^0 \exp(-k_\nu L) + \cancel{I_\nu^{bb}\left[1-\exp(-k_\nu L)\right]}$$

$$\Downarrow$$

α = absorbance

$$\boxed{I_\nu(L) = I_\nu^0 \exp(-k_\nu L)} = \mathrm{I}^0_\nu \exp(-\overset{\downarrow}{\alpha}_\nu)$$

Beer's Law / Beer-Lambert Law

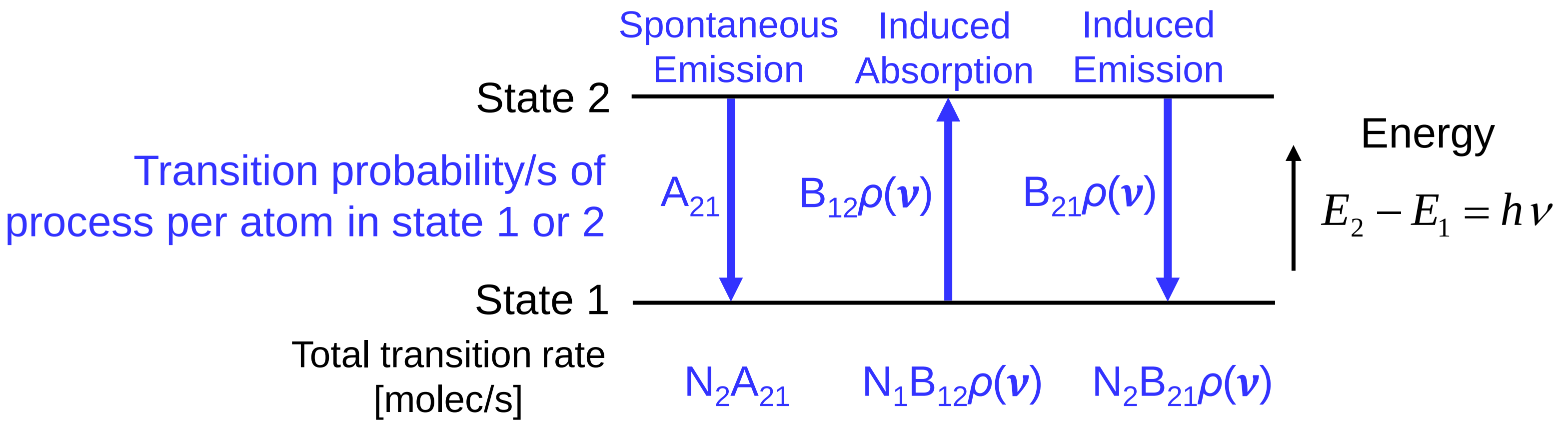
Alternate form: $T_\nu = \left(\dfrac{I}{I_0}\right) = \exp(-k_\nu L) = \dfrac{I(\nu)}{I^0(\nu)}$

- Observations:
  1. The same equation would apply to the transmission of a pulse of laser excitation, with energy E_ν [J/cm^2/cm^{-1}], i.e., $T_\nu = E_\nu / E_\nu^0$
  2. The fundamental parameter controlling absorption over length L is the spectral absorption coefficient, k_ν.

How is k_ν related to fundamental molecular parameters?

2. Einstein theory of radiation

- Simplified theory (Milne Theory)



Spontaneous Emission

Induced Absorption

Induced Emission

State 2

Transition probability/s of process per atom in state 1 or 2

A_{21}

$B_{12}\rho(\nu)$

$B_{21}\rho(\nu)$

Energy

$E_2 - E_1 = h\nu$

State 1

Total transition rate [molec/s]

N_2A_{21}

$N_1B_{12}\rho(\nu)$

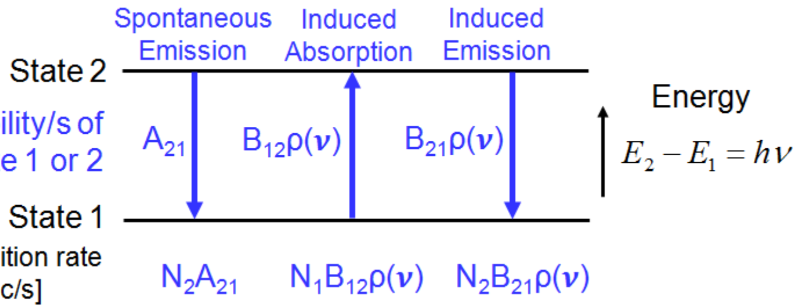
$N_2B_{21}\rho(\nu)$

- Einstein coefficients of radiation

$B_{12}\rho(\nu)$	The probability/s that a molecule in state 1 exposed to radiation of spectral density ρ(ν) [J/(cm^3Hz)] will absorb a quantum $h\nu$ and pass to state 2. The Einstein B-coefficient thus carries units of cm^3Hz(J s).
$B_{21}\rho(\nu)$	The probability/s that a molecule in state 2 exposed to radiation of spectral density ρ(ν) will emit a quantum $h\nu$ and pass to state 1.
A_{21}	The probability/s of spontaneous transfer from state 2 to 1 with release of photon of energy $h\nu$ (without regard to the presence of ρ(ν)).

2. Einstein theory of radiation

- Simplified theory (Milne Theory)



Spontaneous Emission | Induced Absorption | Induced Emission

State 2

Transition probability/s of process per atom in state 1 or 2

A_{21} | $B_{12}\rho(\nu)$ | $B_{21}\rho(\nu)$

State 1

Energy

$E_2 - E_1 = h\nu$

Total transition rate [molec/s]

N_2A_{21} | $N_1B_{12}\rho(\nu)$ | $N_2B_{21}\rho(\nu)$

- Equilibrium

Detailed balance
$$\left(\dot{N}_2\right)_{rad} = \underbrace{N_1B_{12}\rho(\nu)}_{\text{molec/s entering state 2}} - \underbrace{N_2\left(A_{21}+B_{21}\rho(\nu)\right)}_{\text{molec/s leaving state 2}} = 0$$

⇨
$$\frac{N_2}{N_1} = \underbrace{\frac{B_{12}\rho(\nu)_{eq}}{A_{21}+B_{21}\rho(\nu)_{eq}}}_{\text{rad. equil.}} = \underbrace{\frac{g_2}{g_1}\exp\left(-\frac{h\nu}{kT}\right)}_{\text{statistical equil.}}$$

Planck's blackbody distribution
$$\rho(\nu)_{eq} = \frac{\left(8\pi h\nu^3/c^3\right)}{\exp(+h\nu/kT)-1}$$

⇨
$$\rho(\nu)_{eq} = \frac{\left(A_{21}/B_{21}\right)}{\frac{g_1}{g_2}\frac{B_{12}}{B_{21}}\exp(h\nu/kT)-1} = \frac{\left(8\pi h\nu^3/c^3\right)}{\exp(h\nu/kT)-1}$$

⇨
$$\boxed{\begin{gathered} g_1B_{12} = g_2B_{21} \\ A_{21} = \left(\frac{8\pi h\nu^3}{c^3}\right)B_{21} \equiv 1/\tau_{21} \end{gathered}}$$

Radiative lifetime

✏Note: for collimated light

$$\rho(\nu)_{eq} = n_p \cdot h\nu\left[\text{J/cm}^3\text{s}^{-1}\right]$$
$$I_\nu = n_p \cdot h\nu \cdot c\left[\text{W/cm}^2\text{s}^{-1}\right]$$

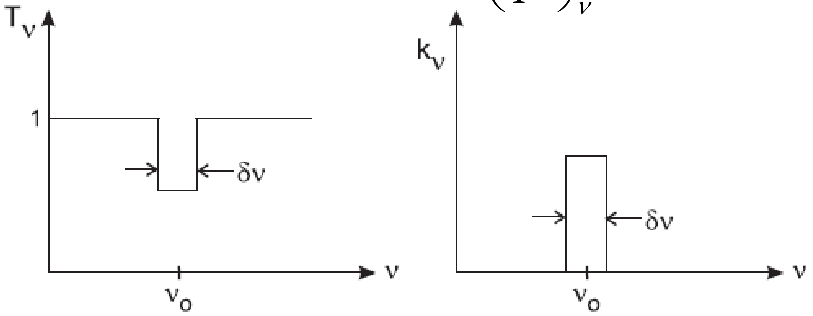
⇨ $\rho(\nu) = I_\nu / c$

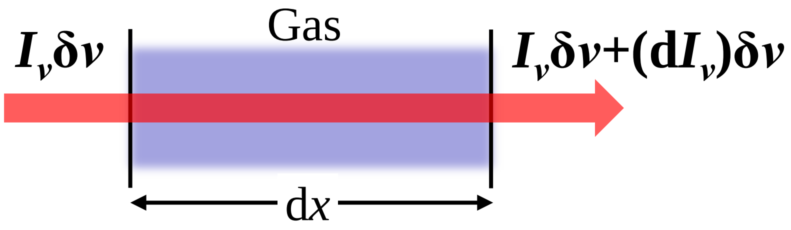
Where is the link to k_ν?

2. Einstein theory of radiation

- Find k_ν for a structureless absorption line of width $\boldsymbol{\delta\nu}$

Recall Beer's Law: $T_\nu = \left(\frac{I}{I^0}\right)_\nu = \exp(-k_\nu L)$ $\quad k_\nu \equiv -\frac{dI_\nu}{I_\nu dx}$





Absorbed power $P_{abs} = (\text{incident power over } \delta\nu) \times (\text{fraction absorbed})$ $\quad [\text{W/cm}^2]$

$$= (I_\nu^0 \delta\nu) \times (1 - T_\nu)$$

$$= (I_\nu^0 \delta\nu)(1 - \exp(-k_\nu L))$$

W/cm^{2}s^{-1} $\quad$ s^{-1}

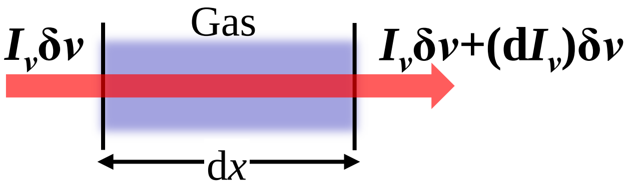
Optically thin limit $k_\nu dx << 1$ ⇨ $P_{abs} = (I_\nu^0 \delta\nu)(k_\nu dx)$

$$\frac{P_{abs}}{I_\nu^0 \delta\nu} = \text{fraction absorbed} = k_\nu dx$$

Now, let's find fraction absorbed using Einstein coefficients

2. Einstein theory of radiation

- Find k_ν for a structureless absorption line of width $\delta\nu$



Energy balance

$$(dI_\nu)\delta\nu = \left(\underline{\text{induced emission}} + \underbrace{\cancel{\text{spontaneous emission}}}_{=0}\right) - \underline{\text{induced absorption}}$$

for collimated light

Induced emission $= \underbrace{(n_2 dx)}_{\text{molec/cm}^2\text{ in state 2}} \times \underbrace{B_{21}\rho(\nu)}_{\text{prob/s of emission}} \times \underbrace{h\nu}_{\text{energy per photon}}$

Induced absorption $= \underbrace{(n_1 dx)}_{\text{molec/cm}^2\text{ in state 1}} \times \underbrace{B_{12}\rho(\nu)}_{\text{prob/s of emission}} \times \underbrace{h\nu}_{\text{energy per photon}}$

Recall:
$\rho(\nu) = I_\nu / c$

⇨ $$(dI_\nu)\delta\nu = [n_2 B_{21} - n_1 B_{12}]\frac{h\nu}{c} I_\nu dx$$

⇨ $$\frac{dI_\nu}{I_\nu dx} \equiv k_\nu = \frac{h\nu}{c}\frac{1}{\delta\nu}[n_2 B_{21} - n_1 B_{12}]$$

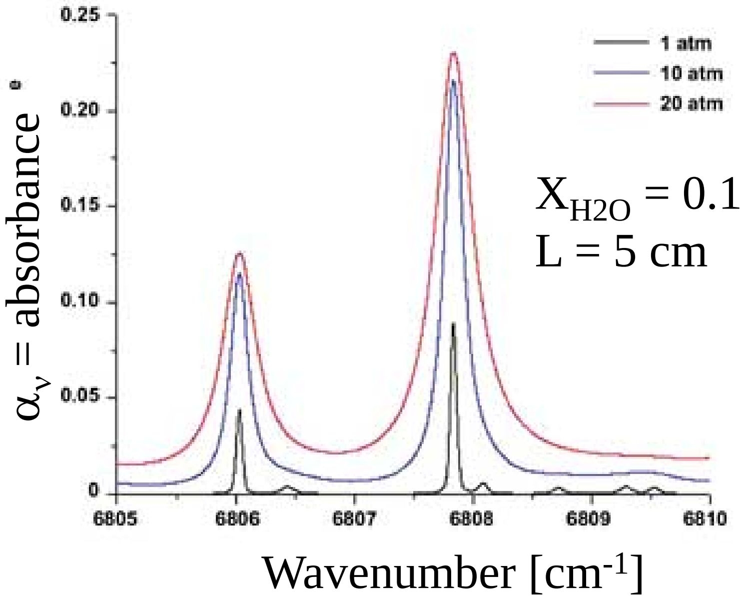
⇨ $$\boxed{k_\nu\left[\text{cm}^{-1}\right] = \frac{h\nu}{c}\frac{1}{\delta\nu} n_1 B_{12}\left(1-\exp(-h\nu/kT)\right)}$$

- Since k_ν is a function of $\delta\nu$, we conclude depends on linewidths + hence <u>shape</u>; next, repeat with realistic lineshape

Where are we headed next?

Improved Einstein Theory, Radiative Lifetime, Line Strength

3. Spectral absorption coefficient
   - with proper lineshape
4. Radiative lifetime
5. Line strengths
   - Temperature dependence
   - Band strength

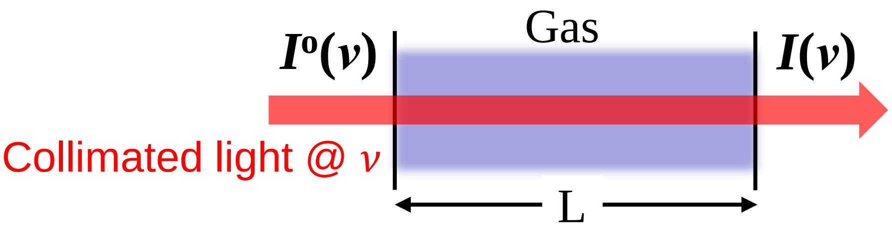


Water vapor absorption spectrum simulated from HITRAN

1. Spectral absorption coefficient

- Eqn. of radiative transfer

Recall:

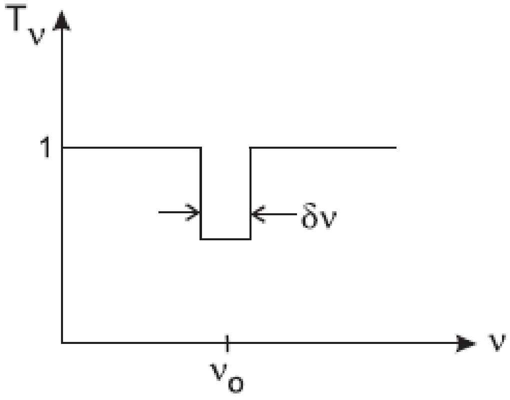


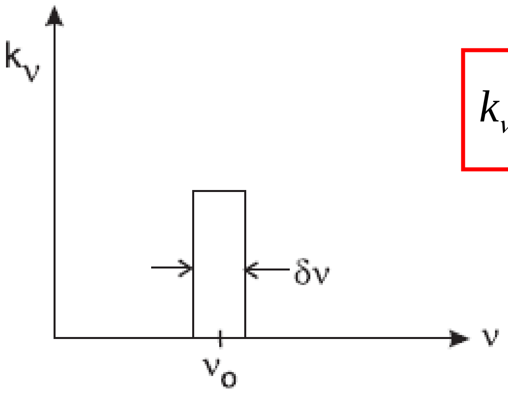
Independent of lineshape!

$$\boxed{I_\nu = I_\nu^0 \exp(-k_\nu L) + I_\nu^{bb}[1-\exp(-k_\nu L)]}$$

$$k_\nu \equiv -\frac{dI_\nu}{I_\nu dx}, cm^{-1}$$

- For <u>structureless</u> absorption line of width δν (Hz), we found





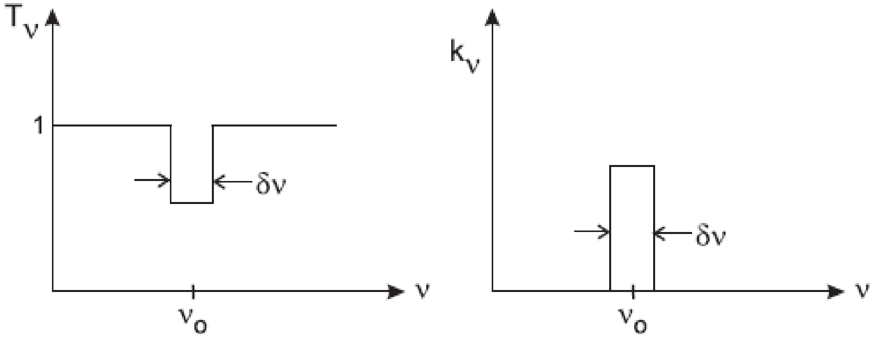
$$\boxed{k_\nu[\mathrm{cm}^{-1}] = \frac{h\nu}{c}\frac{1}{\delta\nu} n_1 B_{12}(1-\exp(-h\nu/kT))}$$

$\propto n_1$, B_{12}, and $1/\delta\nu$

Next: use realistic lineshape

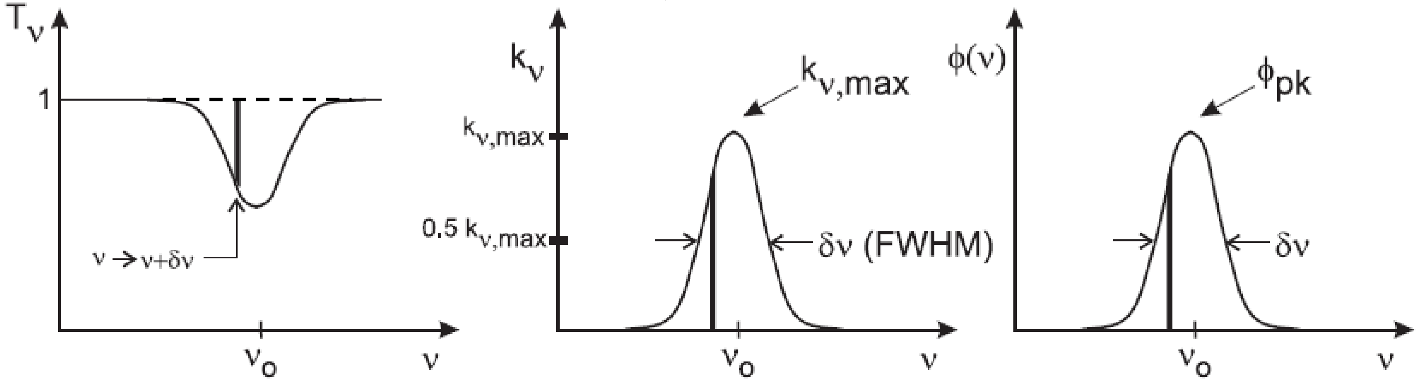
1. Spectral absorption coefficient

- Repeat derivation of k_ν using an improved lineshape model



Structureless absorption line of width δν

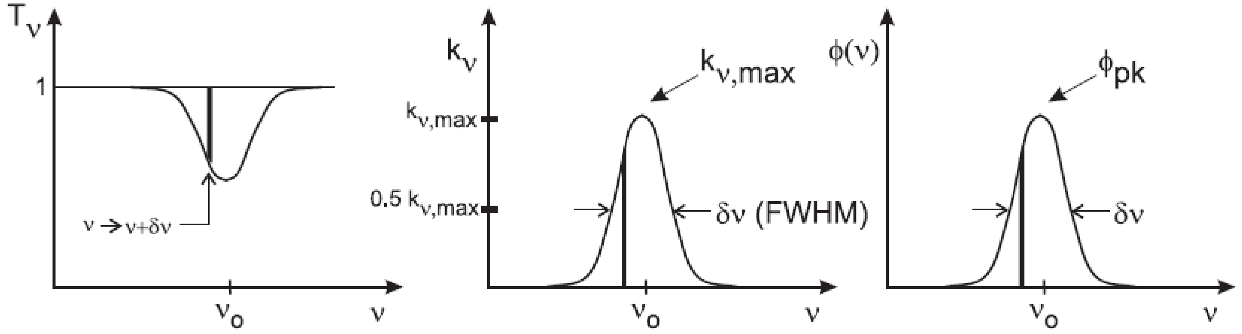
Replace with realistic lineshape



A typical absorption line with typical structure

3. Spectral absorption coefficient

- k_ν



Recall Beer's Law: $T_\nu = \left(\frac{I}{I^0}\right)_\nu = \exp(-k_\nu L)$ ➡ $k_\nu \equiv -\frac{1}{L}\ln T_\nu$

Define: Normalized lineshape function

$$\phi \equiv \frac{k_\nu}{\int_{line} k_\nu \, d\nu} \quad \underline{[\text{cm}]\ \text{or}\ [\text{s}]}, \quad \int_{line} \phi \, d\nu = 1$$

Inverse frequency

✎ Note: $\int k_\nu \, d\nu \approx k_{\nu,\max}\delta\nu$

Average width

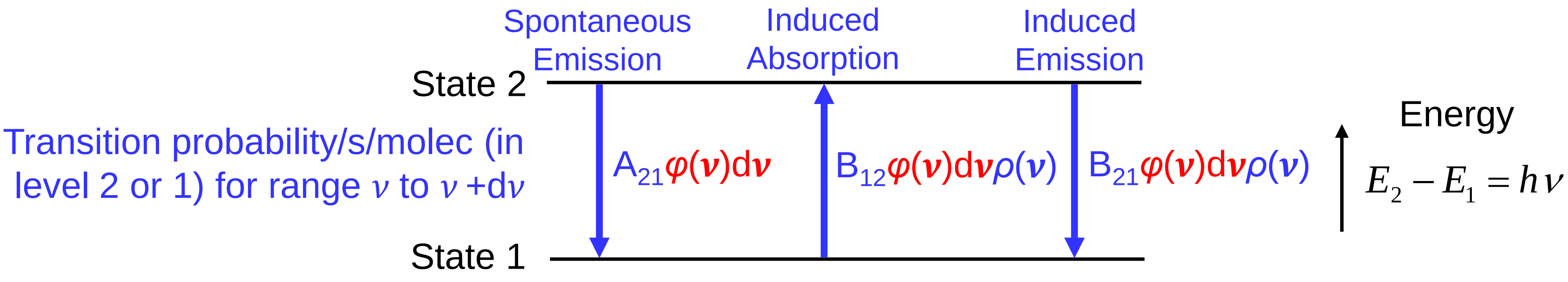
➡ $\phi_{pk} = \frac{k_{\nu,\max}}{\int k_\nu \, d\nu} \approx \frac{1}{\delta\nu}$

Relevant transition probabilities have the same spectral dependence (shape) as k_ν and φ(ν)

And we can anticipate that 1/δν will be replaced by φ in k_ν equation

3. Spectral absorption coefficient

- Modified model



Transition probability/s/molec (in level 2 or 1) for range ν to ν +dν

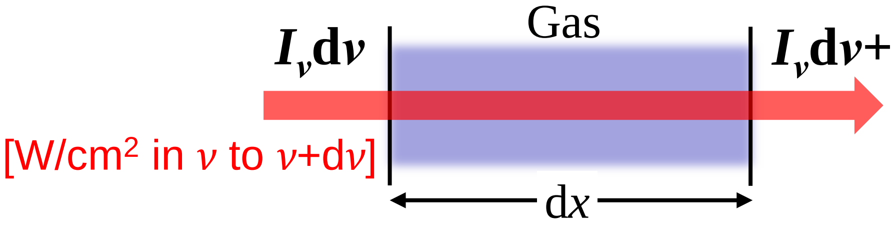
- Einstein coefficients of radiation

$A_{21}\varphi(\nu)d\nu$	The probability/s of a molecule undergoing spontaneous emission, in the range $\nu \rightarrow \nu + d\nu$. [Note that the integral of this quantity over the range of allowed is just A_{21} [s^{-1}], i.e.,$\int A_{21}\phi(\nu)d\nu = A_{21}$.]
$B_{12}\varphi(\nu)d\nu\rho(\nu)$	The probability/s of a molecule undergoing a transition from 1→2, in the range $\nu \rightarrow \nu + d\nu$.
$B_{21}\varphi(\nu)d\nu\rho(\nu)$	The probability/s of a molecule undergoing a transition from 2→1, in the range $\nu \rightarrow \nu + d\nu$.

Recall: $\rho(\nu) = I_\nu / c$

3. Spectral absorption coefficient

- Energy balance



$I_\nu d\nu$

Gas

$I_\nu d\nu+(dI_\nu)d\nu$

[W/cm² in ν to $\nu+d\nu$]

dx

$$dI_\nu d\nu = \text{emission in } d\nu - \text{absorption in } d\nu$$

$$= \underbrace{\overbrace{n_2}^{\#/\text{cc}}\, dx}_{\text{molec/cm}^2} \times \underbrace{\left[B_{21}\phi(\nu)d\nu I_\nu / c\right]}_{\text{prob/s molec for } d\nu} \times \underbrace{h\nu_0}_{\text{energy/photon}} - n_1 dx \times \left[B_{12}\phi(\nu)d\nu I_\nu / c\right] \times h\nu_0$$

⇨ $$-\frac{dI_\nu}{I_\nu dx} \equiv k_\nu = \frac{h\nu}{c}\left[n_1 B_{12} - n_2 B_{21}\right]\phi(\nu)$$

⇨ $$\boxed{k_\nu = \frac{h\nu}{c} n_1 B_{12}\left(1-\exp(-h\nu/kT)\right)\phi(\nu)}$$

Integrated absorption / Line strength $$S_{12} \equiv \int_{line} k_\nu d\nu \quad \left[\text{cm}^{-1}\text{s}^{-1}\right]$$ ⇨ $$\boxed{S_{12} = \frac{h\nu}{c} n_1 B_{12}\left(1-\exp(-h\nu/kT)\right)}$$

3. Spectral absorption coefficient

- Line strength – alternate forms

Line strength does not depend on lineshape, but is a function of n_1, T, B_{12}

$$\boxed{\begin{aligned} S_{12} &= \frac{\lambda^2}{8\pi} n_1 A_{21} \frac{g_2}{g_1}\left(1-\exp(-h\nu/kT)\right) \quad \left[\mathrm{cm^{-1}s^{-1}}\right] \\ S_{12} &= \left(\frac{\pi e^2}{m_e c}\right) n_1 f_{12}\left(1-\exp(-h\nu/kT)\right) \quad \left[\mathrm{cm^{-1}s^{-1}}\right] \end{aligned}}$$

Oscillator strength $f_{12} = \dfrac{S_{12,actual}}{S_{12,classical}\left(1-\exp(-h\nu/kT)\right)}$ $\qquad f_{21} = \left(\dfrac{g_1}{g_2}\right) f_{12}$

where $S_{12,classical} = \left(\dfrac{\pi e^2}{m_e c}\right) n_1, \left(\dfrac{\pi e^2}{m_e c}\right) = 0.0265\,\mathrm{cm^2 Hz}$

⇨ $S_{12,actual} = \left(0.0265\,\mathrm{cm^2Hz}\right) \underline{n_1} f_{12}\left(1-\exp(-h\nu/kT)\right)$ $\qquad \boxed{n_1 = \dfrac{p_1}{kT}}$

@ STP, n_1=n=2.7x10^{19}cm^{-3}, exp(–hν_{12}/kT)<<1 $\quad S_{12}\left[\mathrm{cm^{-2}/atm}\right] = 2.380\times10^{7} f_{12}$

3. Spectral absorption coefficient

- Important observations

1. From the original definition of k_ν and S_{12} we have

$$\boxed{k_\nu = S_{12}\phi(\nu)}$$

2. When

$h\nu / kT >> 1$ as is common for electronic state transitions

$$\left.\begin{aligned} S_{12}\left[\text{cm}^{-1}\text{Hz}\right] &= \left(\frac{\pi e^2}{m_e c}\right) n_1 f_{12} \\ &= \left(0.0265\,\text{cm}^2\text{Hz}\right) n_1 f_{12} \\ &= \frac{\lambda^2}{8\pi} n_1 A_{21} \frac{g_2}{g_1} \end{aligned}\right\}$$

Aside:
@λ=1440nm, $h\nu/k=10^4$K
@λ=720nm, $h\nu/k=2\text{x}10^4$K
@λ=360nm, $h\nu/k=4\text{x}10^4$K

$$1 - \exp(-h\nu/kT) \approx 1$$

⇨ $$f_{12}/A_{12} = f_{12}\tau_{21} = 1.51\frac{g_2}{g_1}\left(\lambda[\text{cm}]\right)^2$$

Radiative lifetime of the 2→1 transition $\tau_{21} = 1/A_{21}$

3. Spectral absorption coefficient

- Example: “Resonance Transition”

Resonance transition – one that couples the ground state to the first excited state

Electronic transition of a sodium atom $Na\left(\overbrace{3^2S_{1/2}}^{\text{lower (L)}} - \overbrace{3^2P_{1/2}}^{\text{upper (U)}}\right)$

$$\frac{g_2}{g_1} = 1, \qquad \lambda = 589\text{nm} = 5.89\times10^{-5}\,\text{cm}$$

Conventions:

atoms: (L-U)

molecules: (U↔L), arrow denotes absorption or emission

f_{ij}: i denotes initial state, j denotes final

$$f_{12}\tau_{589\text{nm}} = 1.51\frac{g_2}{g_1}\left(\lambda[\text{cm}]\right)^2 = 5.24\times10^{-9}\,\text{s}$$

Measured: $\tau = 16.1\times10^{-9}\,\text{s} \Leftrightarrow A = 0.62\times10^{8}\,\text{s}^{-1}$

⇨ $f \approx 0.325$ ➡Strong atomic transition: single electron

Much smaller for molecular transitions: ~ 10^{-2}-10^{-4}

3. Spectral absorption coefficient

- Oscillator strength

Transitions	**f_{21}**	**λ [nm]**
$3^2S_{1/2} - 3^2P_{1/2}$	0.33	589.6
$3^2S_{1/2} - 3^2P_{3/2}$	0.67	589.0
$3^2S - 4^2P$	0.04	330.2

Oscillator strengths of selected sodium transitions

Molecule	**v'←v"**	**Electronic Transition**	**Band center [cm^{-1}]**	**f_{12}**
CO	1←0	-	2143	1.09×10^{-5}
	2←0	-	4260	7.5×10^{-8}
OH	1←0	-	3568	4.0×10^{-6}
	0←0	$^2\Sigma \leftarrow {}^2\Pi$	32600	1.2×10^{-3}
CN	0←0	$^2\Pi \leftarrow {}^2\Sigma$	9117	2.0×10^{-2}

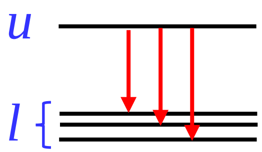
Absorption oscillator strengths of selected vibrational and vibronic bands of a few molecules

4. Radiative lifetime

- Radiative and non-radiative lifetimes
  - Rate equation for radiative decay

$$\frac{dn_u}{dt} = -n_u \sum_l A_{u\to l} \quad (\text{spontaneous emission only}) \Rightarrow n_u(t) = n_u(0)\exp\left[-t\sum_l A_{u\to l}\right]$$

Upper level *u* Lower level *l* Initial number density



⇨ Radiative lifetime (zero-pressure lifetime)

$$\boxed{\tau_r = \frac{1}{\sum_l A_{u\to l}}}$$

  - Rate equation for non-radiative decay

$$\left(\frac{dn_u}{dt}\right)_{nr} = -k_{nr} n_u = -\frac{n_u}{\tau_{nr}}$$

Rate parameter [s^{-1}]

Non-radiative decay time, depends on the transition considered and on the surrounding molecules

  - Simultaneous presence of radiative and non-radiative transitions

$$\frac{dn_u}{dt} = -\frac{n_u}{\tau_r} - \frac{n_u}{\tau_{nr}} = -\frac{n_u}{\tau}, \qquad \tau^{-1} = \tau_r^{-1} + \tau_{nr}^{-1}$$

←Life time of level u

5. Line strengths

- Alternate forms – Line strengths

1. $k_\omega\left[\text{cm}^{-1}\right] = S_{12}\left[\text{cm}^{-2}\right]\phi_\omega\left[\text{cm}\right]$

$$\phi_\omega\left[\text{cm}\right] = c\left[\text{cm/s}\right]\cdot\phi_\nu\left[\text{s}\right]$$

$$\omega\left[\text{cm}^{-1}\right] \equiv 1/\lambda\left[\text{cm}\right]$$

$$d\omega\left[\text{cm}^{-1}\right] \equiv \left(1/c\right)d\nu\left[\text{s}^{-1}\right]$$

2. $S_{12}\left[\text{cm}^{-2}\right] = \left(1/c\right)S_{12}\left[\text{cm}^{-1}/\text{s}\right]$

Number density of absorbing species i in state 1

3. $S_{12}\left[\text{cm}^{-2}/\text{atm}\right] = S_{12}\left[\text{cm}^{-2}\right]/P_i\left[\text{atm}\right] = \left(\dfrac{n_1}{P_i\left[\text{atm}\right]}\right)\left(\dfrac{c}{8\pi\nu^2}\right)A_{12}\dfrac{g_2}{g_1}\left(1-\exp\left(-h\nu/kT\right)\right)$

HITRAN unit

4. $S_{12}\left[\text{cm}^{-2}/\text{atm}\right] = \dfrac{S^*\left[\text{cm}^{-1}/\left(\text{molec}\cdot\text{cm}^{-2}\right)\right]\times n\left[\text{molec}/\text{cc}\right]}{P\left[\text{atm}\right]}$

Ideal gas law

$$S_{12}\left[\text{cm}^{-2}/\text{atm}\right] = \frac{S^*\left[\text{cm}^{-1}/\left(\text{molec}\cdot\text{cm}^{-2}\right)\right]\times 1013250\left[\text{dynes}/\left(\text{cm}^2\cdot\text{atm}\right)\right]}{kT}$$

$k = 1.38054\times10^{-16}\,\text{erg/K}$

$$S = \frac{S^*\times\left(7.34\times10^{21}\right)}{T}\left[\text{cm}^{-2}\text{atm}^{-1}\right]$$

@ T=296K

$$S = S^*\times\left(2.4797\times10^{19}\right)\left[\text{cm}^{-2}\text{atm}^{-1}\right]$$

5. Line strengths

- Alternate forms – Beer's Law

$$\left(\frac{I}{I^{0}}\right)_{\nu,\omega,\lambda} = \exp\left(-k_{\nu}L\right)$$

$$= \exp\left(-n\sigma_{\nu}L\right)$$

$$= \exp\left(-\beta_{\omega}P_{i}L\right)$$

$$= \exp\left(-S\phi_{\nu}P_{i}L\right)$$

- n = number density of the absorbing species [molecules/cm^3]
- σ_v = absorption cross-section [cm^2/molec]
- S = line strength [cm^{-2}atm^{-1}] or [cm^{-1}sec^{-1}/atm]
- β_v = frequency-dependent absorption coefficient [cm^{-1}/atm]
- P_i = partial pressure of species i [atm]
- φ_v = frequency-dependent lineshape function [cm] or [s]
- α_ν = $k_\nu L$ = absorbance

Common to use atmosphere and wavenumber units in IR

$$S_{12}\left[\mathrm{cm}^{-2}/\mathrm{atm}\right] = \int \beta_{\omega}\,d\omega$$

$$= \frac{S_{12}\left[\mathrm{cm}^{-1}\mathrm{s}^{-1}\right]}{cP_{i}\left[\mathrm{atm}\right]}$$

$$= 8.82\times10^{-13}\,\frac{n_{1}}{P_{i}\left[\mathrm{atm}\right]}\,f_{12}\left(1-\exp\left(-h\nu/kT\right)\right)$$

$$= \frac{c}{8\pi\nu^{2}}\,\frac{n_{1}}{P_{i}}\,A_{21}\,\frac{g_{2}}{g_{1}}\left(1-\exp\left(-h\nu/kT\right)\right)$$

$$\beta_{\omega} = k_{\nu}/P_{i}$$

absorption coefficient per atmosphere of pressure

5. Line strengths

- Temperature dependence

Line strength in units of [cm^{-2}atm^{-1}]

$$S_i(T)=S_i(T_0)\frac{Q(T_0)}{Q(T)}\boxed{\left(\frac{T_0}{T}\right)}\exp\left[-\frac{hcE_i''}{k}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right]$$
$$\times\left[1-\exp\left(-\frac{hc\nu_{0,i}}{kT}\right)\right]\left[1-\exp\left(-\frac{hc\nu_{0,i}}{kT_0}\right)\right]^{-1}$$

Line strength in units of [cm^{-1}/(molecule·cm^{-2}]

$$S_i^*(T)=S_i^*(T_0)\frac{Q(T_0)}{Q(T)}\exp\left[-\frac{hcE_i''}{k}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right]$$
$$\times\left[1-\exp\left(-\frac{hc\nu_{0,i}}{kT}\right)\right]\left[1-\exp\left(-\frac{hc\nu_{0,i}}{kT_0}\right)\right]^{-1}$$

$$\frac{S(T)}{S(T_0)}=\frac{S_i^*(T)}{S_i^*(T_0)}\times\frac{T_0}{T}$$

5. Line strengths

- Band strength

$$S_{band} = \sum_{band} S_{lines}$$

Example: Heteronuclear Diatomic Band Strength

$$S^{1\leftarrow 0} = \sum_{J''}^{v'=1\leftarrow v''=0} \left[S^{1\leftarrow 0}_{J'\leftarrow J''}(P) + S^{1\leftarrow 0}_{J'\leftarrow J''}(R) \right]$$

$$S^{10}_{J'J''}(R) = \frac{c}{8\pi\nu^2} \underbrace{\frac{n_{J''}}{n_i kT/1.013\times10^6}}_{\frac{n_{J''}}{P_i\,,\,\mathrm{atm}}} \underbrace{\left[\frac{g_{J'}}{g_{J''}} = \frac{2J'+1}{2J''+1}\right]}_{\approx 1} \underbrace{\left[A_R^{10} \approx \frac{J''+1}{2J''+1}A^{10}\right]}_{A_P^{10} \approx \frac{J''}{2J''+1}A^{10}} \times \left(1-\exp(-h\nu/kT)\right)$$

➡ Based on normalized Hönl-London factor

$$\Rightarrow \begin{cases} S^{10}(R) = \dfrac{(1.013\times10^6)}{8\pi\nu^2 kT} A^{10} \displaystyle\sum_{J''}\left[\frac{n_{J''}}{n_i}\,\frac{J''+1}{2J''+1}\right] \\ S^{10}(P) = \dfrac{(1.013\times10^6)}{8\pi\nu^2 kT} A^{10} \displaystyle\sum_{J''}\left[\frac{n_{J''}}{n_i}\,\frac{J''}{2J''+1}\right] \end{cases} \xrightarrow{\sum_{J''}(n_{J''}/n_i)=1} \boxed{S^{10}(T) = \frac{(1.013\times10^6)cA^{10}}{8\pi\nu^2 kT}}$$

5. Line strengths

- Band strength

$$S_{band} = \sum_{band} S_{lines}$$

Example: Heteronuclear Diatomic Band Strength

$$\boxed{S^{10}(T) = \frac{\left(1.013\times10^{6}\right)cA^{10}}{8\pi\nu^{2}kT}}$$

Band strength of CO:

$$S_{CO}^{10}(273\mathrm{K}) = \frac{3.2\times10^{28}A^{10}}{\nu^{2}} \approx 280\mathrm{cm}^{-2}/\mathrm{atm}$$

$$\omega \approx 2150\mathrm{cm}^{-1} \Leftrightarrow \nu \approx 6.4\times10^{13}\mathrm{s}^{-1}$$

$$\Rightarrow \quad A^{10} \approx 36\mathrm{s}^{-1} \Leftrightarrow \tau^{10} = 0.028\mathrm{s}$$

Compare with previous example of $\tau_{Na}\approx16$ns
➡IR transitions have much lower values of A and longer radiative lifetime than UV/Visible transitions due to their smaller changes in dipole moment

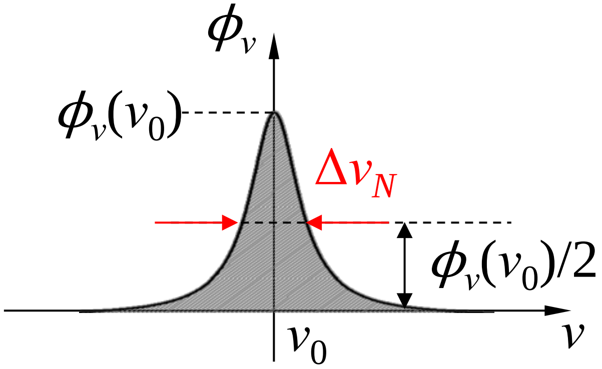
Next: Spectral Lineshapes

- Doppler, Natural, Collisional and Stark Broadening
- Voigt Profiles

Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

Lecture 6: Spectral Lineshapes

1. Background introduction
2. Types of line broadening
3. Voigt profiles
4. Uses of quantitative lineshape measurements
5. Working examples

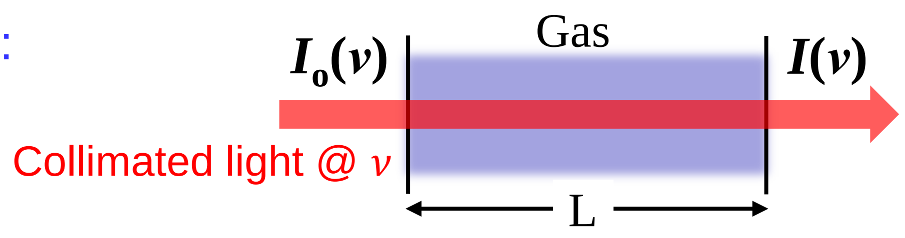


A typical lineshape function

1. Background introduction

- Beer's Law

Recall:



absorption coefficient @ ν, cm^{-1}

$$T_\nu = (I/I_0)_\nu = I_\nu / I_\nu^0 = \exp(-k_\nu L)$$

intensity or power @ ν spectral intensity @ ν

$$\boxed{k_\nu,\text{cm}^{-1} = S_{12}\left[\text{cm}^{-1}\cdot\text{s}^{-1}\right]\phi[\text{s}]}$$

$$S_{12}\left[\text{cm}^{-1}\cdot\text{s}^{-1}\right] = \left(\frac{h\nu}{c}\right) n_1 B_{12}\left(1-\exp(-h\nu/kT)\right)$$

$$= \frac{\lambda^2}{8\pi} n_1 A_{21}\left(\frac{g_2}{g_1}\right)\left(1-\exp(-h\nu/kT)\right)$$

Line strength, $\int_{line} k_\nu d\nu$

$$\boxed{\phi(\nu) = \frac{k_\nu}{\int\limits_{line} k_\nu \, d\nu}, \int_{-\infty}^{\infty}\phi(\nu)\,d\nu = 1}$$

← The lineshape function

1. Background introduction

- Alternate forms of ν, ϕ, S_{12}
  - ν $$\nu, \mathrm{s}^{-1} = \frac{c}{\lambda} = c\left(\bar{\nu}, \mathrm{cm}^{-1}\right)$$
  - ϕ $$\phi, \mathrm{cm} = c(\phi, \mathrm{s})$$
  - S_{12}
    - A common form of S

$$S_{12}, \mathrm{cm}^{-2} = \left(S_{12}, \mathrm{cm}^{-1}\mathrm{s}^{-1}\right)/c \qquad \boxed{k_\nu, \mathrm{cm}^{-1} = S_{12}\left[\mathrm{cm}^{-1}\cdot\mathrm{s}^{-1}\right]\phi[\mathrm{s}]}$$

- Another common form

Partial pressure of absorber

$$S_{12}, \mathrm{cm}^{-2}/\mathrm{atm} = \left(S_{12}, \mathrm{cm}^{-2}\right)/\left(P_i, \mathrm{atm}\right) = \frac{S_{12}, \mathrm{cm}^{-2}\mathrm{s}^{-1}}{cP_i, \mathrm{atm}}$$

$$= \frac{c}{8\pi\nu^2}\frac{n_1}{P_i, \mathrm{atm}}A_{21}\frac{g_2}{g_1}\left(1-\exp\left(-h\nu/kT\right)\right)$$

- $$\left(S_{12}, \mathrm{cm}^{-2}\mathrm{atm}^{-1}\right)\left(P_i, \mathrm{atm}\right)$$

$$= \left(S^*, \frac{\mathrm{cm}^{-1}}{\mathrm{molec/cm^2}}\right)\left(n_i, \frac{\mathrm{molec}}{\mathrm{cm}^3}\right)$$

HITRAN database lists S* (cm/molec), usually at T_{ref} = 296K

✎Notes:

1. $$\frac{n_1}{P_i, \mathrm{atm}} = \frac{n_1}{n_i kT/1.013\times10^6\,\mathrm{dynes/cm^2 atm}} = \frac{1}{kT}\underline{\left(\frac{n_1}{n_i}\right)}10^6$$ ← Boltzmann fraction

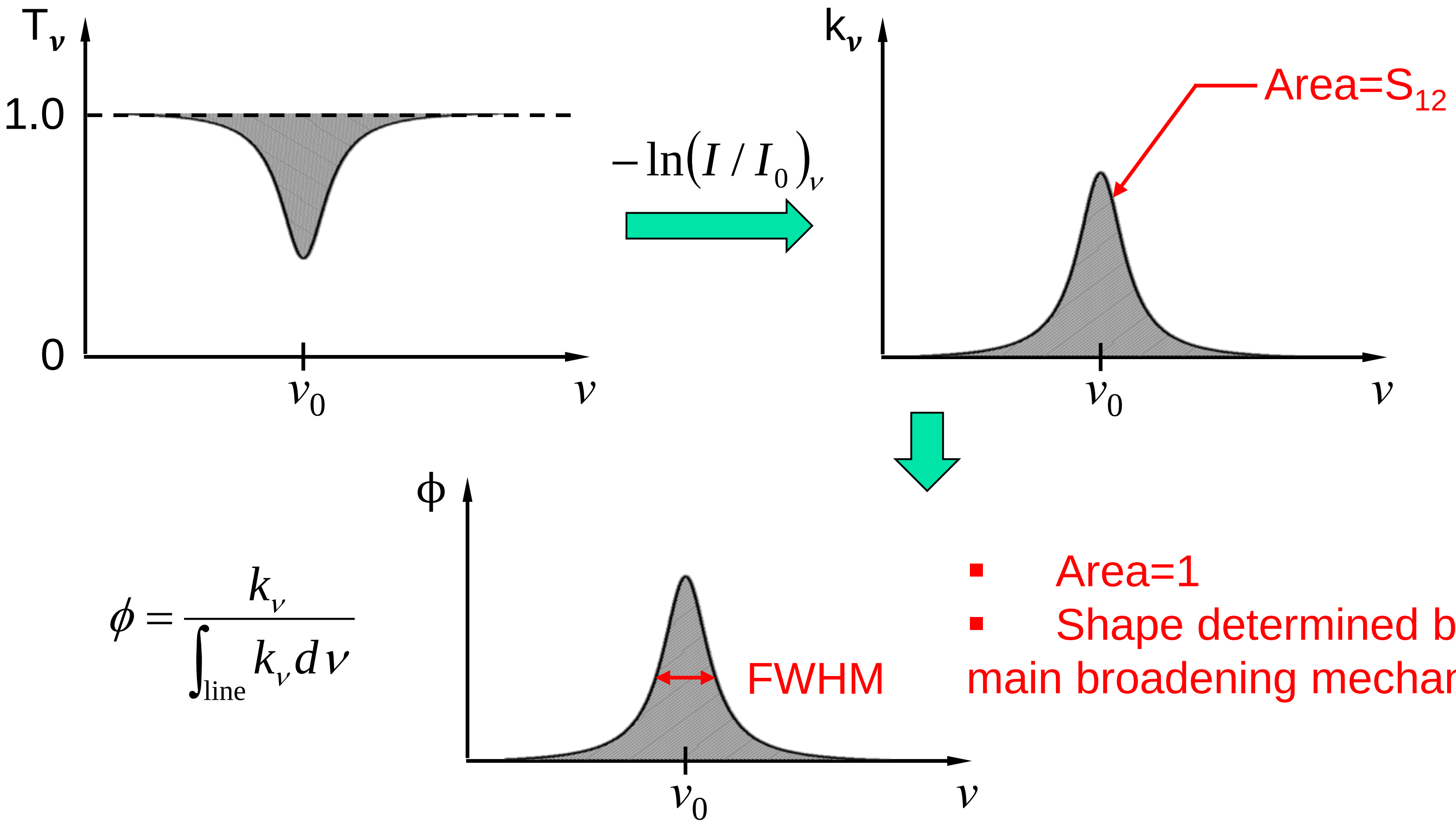
2. $$k_\nu, \mathrm{cm}^{-1} = \left(S_{12}, \mathrm{cm}^{-2}/\mathrm{atm}\right)\left(P_i, \mathrm{atm}\right)\left(\phi, \mathrm{cm}\right)$$

$$P_i, \mathrm{atm} = \left(P, \mathrm{atm}\right)\underline{\left(\chi_i\right)}$$ ← Mole fraction

1. Background introduction

- How are S_{12} and ϕ measured?

➡ High-resolution absorption experiments



$$\phi = \frac{k_\nu}{\int_{\text{line}} k_\nu d\nu}$$

- Area=1
- Shape determined by main broadening mechanism

2. Types of line broadening

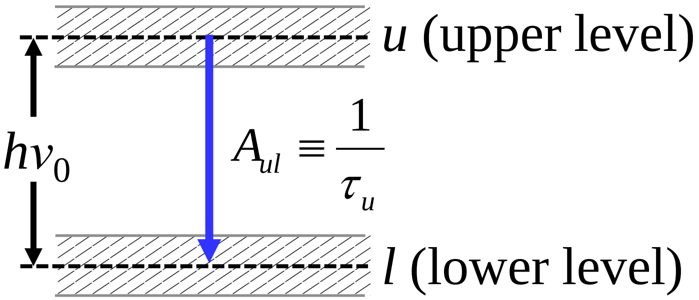
- Brief overview

Lorentzian Homogeneous (affects all molecules equally)	1. Natural broadening ➡ Result of finite radiative lifetime 2. Collisional/pressure broadening ➡ Finite lifetime in quantum state owing to collisions
Gaussian Inhomogeneous (affects certain class of molecule)	3. Doppler broadening ➡ Thermal motion
Lorentzian + Gaussian	4. Voigt profile ➡ Convolution of 1-3

2. Types of line broadening

- Natural line broadening

1. Heisenberg uncertainty principle: $\Delta E_u \Delta t_u \geq h/2\pi$



Decay rate

$\Delta E_u =$ uncertainty in energy of u

$\Delta t_u = \tau$, the uncertainty in time of occupation of u

$\Delta E_u = h\Delta\nu_u = (h/2\pi)/(\Delta t = \tau_{rad})$ ➡ $\boxed{\Delta\nu_u = 1/2\pi\tau_{rad}}$ “lifetime” limited

2. In general

$$\Delta\nu_N = \Delta\nu_u + \Delta\nu_l = \frac{1}{2\pi}\left(\frac{1}{\tau_u} + \frac{1}{\tau_l}\right)$$

0 for ground state (natural broadening)

2. Types of line broadening

- Natural line broadening
  3. Typical values
     - Electronic transitions:

$$\tau_u \sim 10^{-8}\,\mathrm{s} \rightarrow \Delta\nu_N \sim 1.6\times10^{7}\,\mathrm{s}^{-1}$$

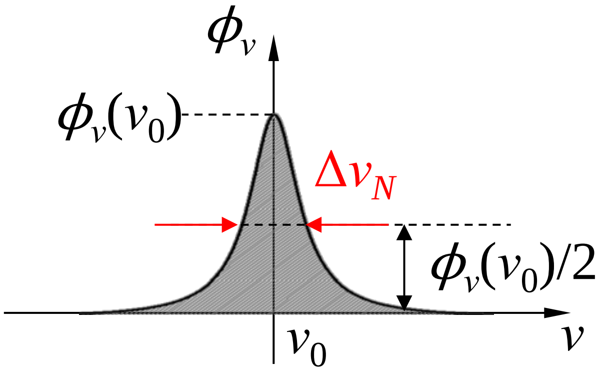
$$\Delta\omega_N,\mathrm{cm}^{-1} = \Delta\nu_N / c = 5\times10^{-4}\,\mathrm{cm}^{-1}$$

     - Vib-rot transitions

$$\tau_u \sim 10^{-2}\,\mathrm{s} \rightarrow \Delta\nu_N \sim 16\mathrm{s}^{-1}, \Delta\omega_N,\mathrm{cm}^{-1} = 5\times10^{-10}\,\mathrm{cm}^{-1}$$

     - These are typically much smaller than $\Delta\nu_D$ and $\Delta\nu_C$

  4. Lineshape function – "Lorentzian" – follows from Fourier transform



$$\phi(\nu)_N = \frac{1}{\pi}\frac{\Delta\nu_N/2}{(\nu-\nu_0)^2+(\Delta\nu_N/2)^2}$$

✐Note: a) $\phi_{\max} = \phi(\nu_0) = \frac{2}{\pi}\frac{1}{\Delta\nu_N}$

b) $\phi(\nu-\nu_0 = \Delta\nu_N/2) = \phi(\nu_0)/2$

2. Types of line broadening

- Natural line broadening

Lineshape derivation from damped oscillator model (Ref. Demtröder)

γ = Damping ratio
$\gamma = \Delta\nu_n \sim 1/\Delta\tau\cdot 2\pi$
in units of s^{-1}

$$\ddot{x} + \gamma\dot{x} + \omega_0^2 x = 0,\ \ \omega_0^2 = k/m$$

$$x(0) = x_0,\ \dot{x}(0) = 0$$

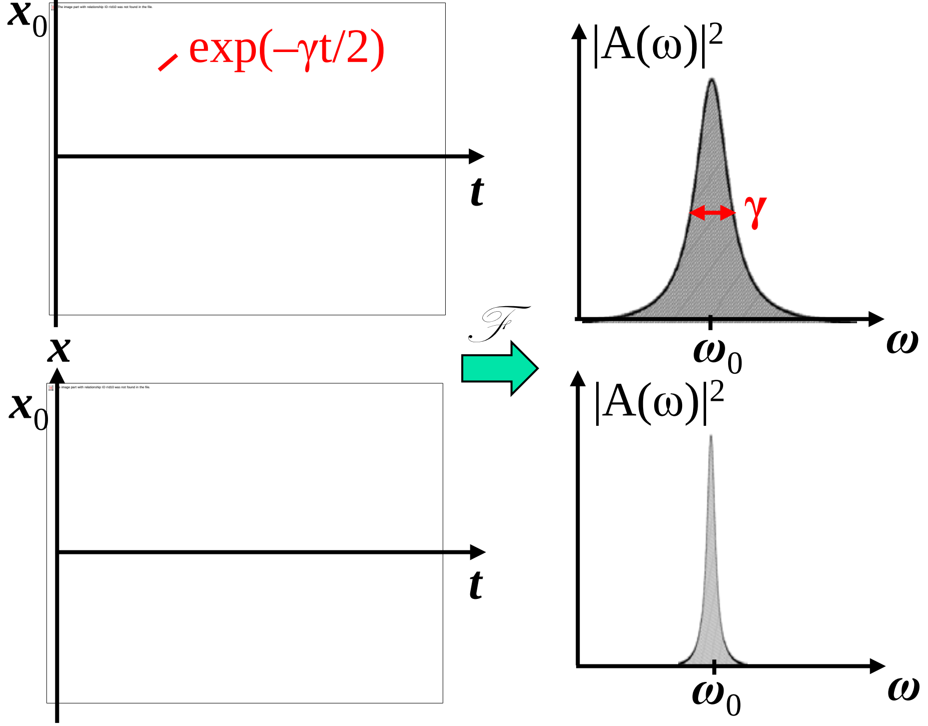
$$\Rightarrow\ x(t) = x_0 \exp(-\gamma t/2)\left[\cos\omega t + (\gamma/2\omega)\sin\omega t\right]$$

$$\omega = \left(\omega_0^2 - \gamma^2/4\right)^{1/2}$$

Small damping ($\gamma \ll \omega_0$) $\Rightarrow$

$$x(t) = x_0 \exp(-\gamma t/2)\cos\omega_0 t$$

Amplitude of x(t) decrease ➡ frequency of emitted radiation is no longer monochromatic



$$x(t) = \frac{1}{2\sqrt{2\pi}}\int_0^\infty A(\omega)\exp(i\omega t)\,d\omega$$

$$A(\omega) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^\infty x(t)\exp(-i\omega t)\,dt$$

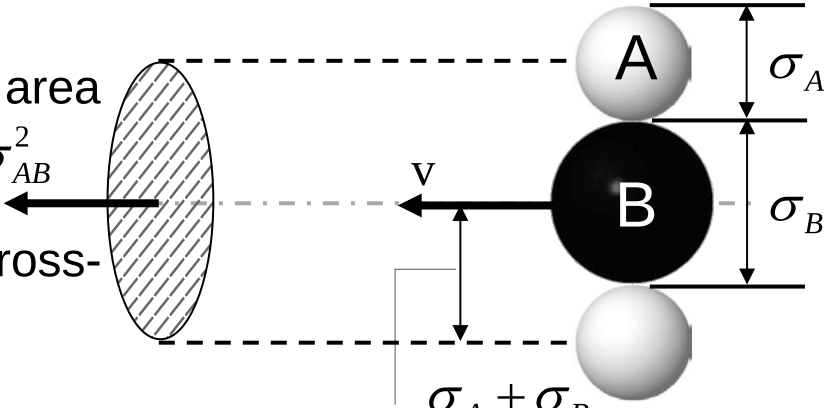
$$= \frac{x_0}{\sqrt{8\pi}}\left(\frac{1}{i(\omega-\omega_0)+\gamma/2} + \cancel{\frac{1}{i(\omega+\omega_0)+\gamma/2}}\right)$$

$$\Downarrow\ \ I(\omega) \propto A(\omega)A^*(\omega),\ L = I/I_0$$

$$\boxed{L(\omega-\omega_0) = \frac{1}{\pi}\frac{\gamma/2}{(\omega-\omega_0)^2 + (\gamma/2)^2}}$$

2. Types of line broadening

- Collision broadening
  1. Also lifetime limited – time set by collision time interval



Effective area

$A = \pi\sigma_{AB}^2$

Optical cross-section

σ_A

σ_B = optical collision diameter of B

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}$$

$$Z_{BA} = \#\,\text{collision/s of a single B with all A}$$

#/cc

$$= n_A \cdot \pi\sigma_{AB}^2 \cdot \left(\bar{c} = \sqrt{\frac{8kT}{\pi\mu_{AB}}} \right)$$

$$\mu_{AB} = \frac{m_A m_B}{m_A + m_B}$$

⇨

For a mixture,

$$Z_B = \sum_A n_A \cdot \pi\sigma_{AB}^2 \cdot \sqrt{\frac{8kT}{\pi\mu_{AB}}}$$

$$= P \sum_A X_A \cdot \pi\sigma_{AB}^2 \cdot \sqrt{\frac{8}{\pi\mu_{AB} kT}}$$

$$P,\text{dynes/cm}^2 = 1.013 \times 10^6 \left(P,\text{atm}\right)$$

2. Types of line broadening

- Collision broadening

1. Also lifetime limited – time set by collision time interval

$$Z_B = \sum_A n_A \cdot \pi\sigma_{AB}^2 \cdot \sqrt{\frac{8kT}{\pi\mu_{AB}}} = P\sum_A X_A \cdot \pi\sigma_{AB}^2 \cdot \sqrt{\frac{8}{\pi\mu_{AB}kT}}$$

Since

$$\Delta\nu_C, \mathrm{s}^{-1} = \frac{1}{2\pi}\left(\frac{1}{\tau_{coll,upper}} + \frac{1}{\tau_{coll,lower}}\right) \cong \frac{Z_B}{\pi}$$

$$= (P, \mathrm{atm})\sum_A X_A \cdot \underbrace{\sigma_{AB}^2 \cdot \sqrt{\frac{8}{\pi\mu_{AB}kT}} \cdot 1.013\times10^6}_{2\gamma_A, \mathrm{s}^{-1}/\mathrm{atm}}$$

$$\Delta\nu_C, \mathrm{s}^{-1} = (P, \mathrm{atm})\sum_A X_A 2\gamma_A$$

$2\gamma_A$ = colli. halfwidth, i.e., FWHM per atm. pressure

Notes:

$$\Delta\nu_C, \mathrm{cm}^{-1} = \Delta\nu_C, \mathrm{s}^{-1}/c$$

$$2\gamma, \mathrm{cm}^{-1}/\mathrm{atm} = 2\gamma, \mathrm{s}^{-1}/\mathrm{atm}/c$$

2. Lineshape function – Lorentzian $\phi(\nu)_{coll} = \dfrac{1}{\pi}\dfrac{\Delta\nu_C/2}{(\nu-\nu_0)^2 + (\Delta\nu_C/2)^2}$

3. Crude approximation $\underset{\mathrm{cm}^{-1}/\mathrm{atm}}{2\gamma(T)} = \underbrace{2\gamma^{300}}_{\approx 0.1\mathrm{cm}^{-1}/\mathrm{atm}}(300/T)^n \leftarrow$ n=1/2 for hard sphere

2. Types of line broadening

- Collision broadening

$$\Delta\nu_C, \mathrm{cm}^{-1} = (P, \mathrm{atm}) \sum_A X_A 2\gamma_A$$

with $2\gamma_A$ in cm^{-1}/atm

Example: Pressure broadening of CO

R(9) line of CO's 2nd overtone, 50ppm in Air, 300K, 1.0atm
Species population: 77% N_2, 20% O_2, 2% H_2O (85% humidity) 380ppm CO_2

Species, A	**Mole Fraction, X_A**	**$2\gamma_{CO\text{-}A}$ (300K) cm^{-1}/atm**
N_2	0.77	0.116
H_2O	0.02	0.232
CO	50e-6	0.128
CO_2	380e-6	0.146
O_2	0.21	0.102

$$\begin{aligned}\Delta\nu_C &= P\Big(X_{N_2}\cdot 2\gamma_{CO-N_2} + X_{H_2O}\cdot 2\gamma_{H_2O-N_2} + X_{CO}\cdot 2\gamma_{CO-CO} \\ &\quad + X_{CO_2}\cdot 2\gamma_{CO-CO_2} + X_{O_2}\cdot 2\gamma_{CO-O_2}\Big) \\ &= 0.115\mathrm{cm}^{-1}\end{aligned}$$

2. Types of line broadening

- Collision broadening

Some collisional broadening coefficients 2γ [cm^{-1}/atm] in Ar and N_2 at 300K

Species	Wavelength [nm]	Ar	N_2
Na	589	0.70	0.49
K	770	1.01	0.82
Rb	421	2.21	1.51
OH	306	0.09	0.10
NH	335	0.038	
NO	225	0.50	0.58
NO	5300	0.09	0.12
CO	4700	0.09	0.11
HCN	3000	0.12	0.24

Some collisional broadening coefficients 2γ [cm^{-1}/atm] in Ar and N_2 at 2000K

Species00	Wavelength [nm]	Ar	N_2
NO	225	0.14	0.14
OH	306	0.034	0.04
NH	335	0.038	

2. Types of line broadening

- Doppler broadening

1. Moving molecules see different frequency (Doppler shift)

$$\left|\nu_{app}-\nu_{act}\right| = \nu_{act} u/c = u/\lambda \Rightarrow \nu_{app} = \nu_{act}\left(1-u/c\right)$$

↳ molec. velocity along beam path

2. Gaussian velocity distribution function (leads to Gaussian $\phi(\nu)$)

$$\phi(\nu) = \underbrace{\frac{2\sqrt{\ln 2}}{\sqrt{\pi}\Delta\nu_D}}_{\phi(\nu_0)} \exp\left[-\left(\frac{2\sqrt{\ln 2}}{\Delta\nu_D}(\nu-\nu_0)\right)^2\right]$$

$$\boxed{\begin{aligned}\Delta\nu_D(\mathrm{FWHM}) &= 2\sqrt{\frac{2kT\ln 2}{mc^2}}\,\nu_0 \\ \Delta\nu_D(\mathrm{FWHM}) &= 7.17\times10^{-7}\,\nu_0\sqrt{\frac{T}{M}}\end{aligned}}$$

g/mole of emitter/absorber

- Aside:

Maxwellian velocity distribution

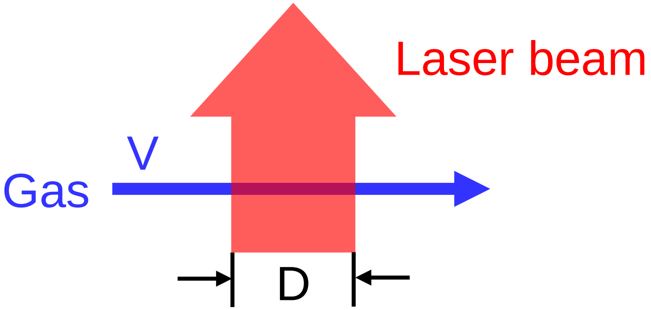
$$f(U_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} \exp\left(-\frac{mU_x^2}{2kT}\right)$$

2. Types of line broadening

- Stark broadening
  - Important in charged gases, i.e., plasmas.
  - Coulomb forces perturb energy levels

- Types of instrument broadening
  - Instruments have insufficient resolution
  - Powerful lasers can perturb populations away from equilibrium (saturation effect)
  - Transit-time broadening

- Another type of lifetime-limited broadening is transit-time broadening



Transit time $\approx D/V$

$$\therefore \Delta\nu_{transit} \approx V/D$$

for apparent broadening of an abs. line

Reference: Demtröder p.85-p.88

2. Types of line broadening

- Examples

1st Example:

T = 300K, M = 30g/mole, P = 1atm

- Electronic transition
  (λ=600nm, $v=5x10^{14}s^{-1}$)

$$\Delta\nu_D = 1.1\times10^9\,\mathrm{s}^{-1} \sim 0.04\,\mathrm{cm}^{-1}$$

$$\Delta\nu_D >> \Delta\nu_N \sim 10^7\,\mathrm{s}^{-1}$$

$$\Delta\nu_C \sim 3\times10^9\,\mathrm{s}^{-1} = 0.1\,\mathrm{cm}^{-1}$$

$$\therefore \Delta\nu_D < \Delta\nu_C$$

- Vib-rot transition
  (λ=6μm, $v=5x10^{13}s^{-1}$)

$\rightarrow \lambda_{IR}=10\lambda_{vis}$

$$\Delta\nu_D \sim 1.1\times10^8\,\mathrm{s}^{-1} \sim 0.004\,\mathrm{cm}^{-1}$$

$$\Delta\nu_C \sim 3\times10^9\,\mathrm{s}^{-1} = 0.1\,\mathrm{cm}^{-1}$$

$$\therefore \Delta\nu_D << \Delta\nu_C$$

2nd Example:

T = 2700K, M = 30g/mole, P = 1atm

- Electronic transition
  (λ=600nm, $v=5x10^{14}s^{-1}$)

$$\underbrace{\Delta\nu_D}_{\sim T^{1/2}} \sim 0.11\,\mathrm{cm}^{-1} > \underbrace{\Delta\nu_C}_{\sim T^{-1/2}} \sim 0.03\,\mathrm{cm}^{-1}$$

- Vib-rot transition
  (λ=6μm, $v=5x10^{13}s^{-1}$)

$$\Delta\nu_D \sim 0.01\,\mathrm{cm}^{-1} < \Delta\nu_C \sim 0.03\,\mathrm{cm}^{-1}$$

2. Types of line broadening

- Conclusions
  - Doppler broadening most significant at:

    Low P, high T, small λ

  - Collision broadening most significant at:

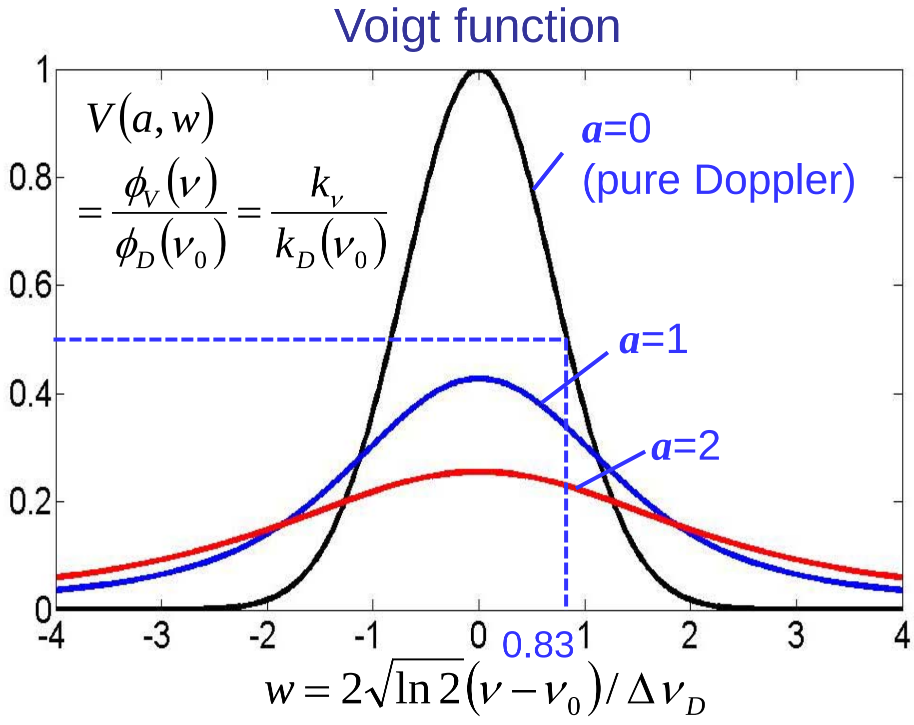
    High P, low T, large λ

  - Many conditions require consideration of both effects

    Together ➡ Voigt profile!

3. Voigt Profiles

1. Dominant types of broadening
    - Collision broadening
    - Doppler broadening
2. Voigt profile
3. Line-shifting mechanisms



3. Voigt profiles
3.1. Dominant types of broadening

- Collision broadening review
  - $$\phi_C(\nu)=\frac{1}{\pi}\frac{\Delta\nu_C/2}{(\nu-\nu_0)^2+(\Delta\nu_C/2)^2}$$ Lorentzian form “lifetime limited”
  - $$\Delta\nu_C,\mathrm{s}^{-1}=\left(\sum_A X_A \underline{2\gamma_A}\right)(P,\text{atm of mixture})$$

    mole fraction of A

    coll. width/atm for A as coll. partner, $\propto\sqrt{1/T}$
  - Typical value of $2\gamma_A$ ~ $0.1\mathrm{cm}^{-1}$/atm (or $0.3\times10^{10}\mathrm{s}^{-1}$/atm)

    - Aside: $2\gamma_A,\mathrm{s}^{-1}=\frac{1}{c}1.013\times10^6\sigma_{AB}^2\cdot\sqrt{\frac{8}{\pi\mu_{AB}kT}}\propto\sqrt{\frac{1}{T}}$

      if σ_{AB} is constant

      $$0.1\mathrm{cm}^{-1}/\mathrm{atm}\cdot3\times10^{10}\,\mathrm{cm/s}=0.3\times10^{10}\,\mathrm{s}^{-1}/\mathrm{atm}$$
  - A type of “Homogenous broadening”, i.e., same for all molecules of absorbing species

3. Voigt profiles
3.1. Dominant types of broadening

- Doppler broadening review
  - $$\phi(\nu) = \underbrace{\frac{2\sqrt{\ln 2}}{\sqrt{\pi}\Delta\nu_D}}_{\phi(\nu_0)} \exp\left[-\left(\frac{2\sqrt{\ln 2}}{\Delta\nu_D}(\nu - \nu_0)\right)^2\right]$$ Gaussian form
  - $$\Delta\nu_D, \mathrm{s}^{-1} = 2\left(\frac{2kT\ln 2}{mc^2}\right)^{1/2}\nu_0 = 7.17\times10^{-7}\nu_0\sqrt{T/M}$$

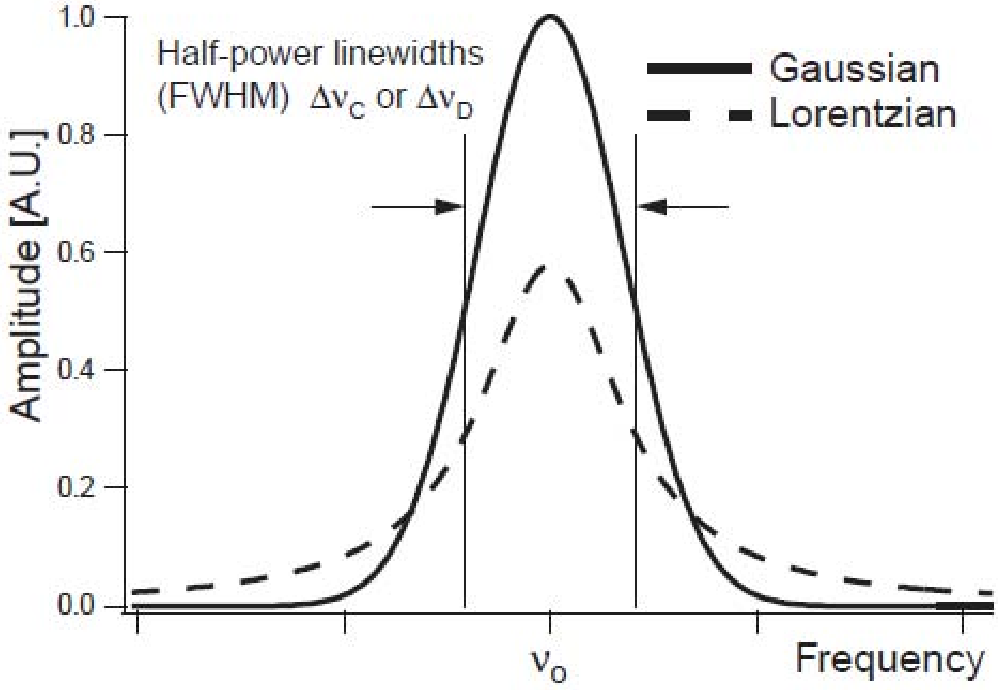
    FWHM

    g/mole of absorber/emitter
  - Typical value

    $$\Delta\nu_D(\lambda = 600\mathrm{nm}, M = 30) = 0.35\times10^{10}\mathrm{s}^{-1}(3000\mathrm{K}) \approx 0.12\mathrm{cm}^{-1}$$
    $$= 0.1\times10^{10}\mathrm{s}^{-1}(300\mathrm{K}) \approx 0.03\mathrm{cm}^{-1}$$
  - This is a type of “Inhomogenous broadening”, i.e., depends on specific velocity class of molecule

3. Voigt profiles
3.1. Dominant types of broadening

- Comparison of ϕ_D and ϕ_C (for same $\Delta\nu$(FWHM))



- Both have same area (unity)
- Peak heights

$$\phi(\nu_0)_{Dopp} = \frac{2\sqrt{\ln 2}}{\sqrt{\pi}\Delta\nu_D} = 0.94/\Delta\nu_D$$

$$\phi(\nu_0)_{coll} = \frac{2}{\pi}\frac{1}{\Delta\nu_C} = 0.637/\Delta\nu_C$$

⇨ for $\Delta\nu_C/\Delta\nu_D = 1$

$$\phi(\nu_0)_{Dopp} = 1.48\phi(\nu_0)_{coll}$$

- Gaussian: higher near peak
- Lorentzian: higher in wings

- Some exceptions/improved models
  - Collision narrowing (low-pressure phenomenon)

    ➡ Galatry profiles, others, with additional parameters
  - Stark broadening ➡ Plasma phenomenon

Ready to combine Doppler & collision broadening; done via Voigt profile

3.2. Voigt profile

- Physical argument

The physical argument employed in establishing the Voigt profile is that the effects of Doppler & collision broadening are decoupled. Thus we argue that every point on a collision-broadened lineshape is further broadened by Doppler effects.

Convolution: $\phi_V(\nu) = \phi_D(\nu) * \phi_C(\nu) = \int_{-\infty}^{\infty} \phi_D(u)\phi_C(\nu - u)\,du$

$$\Rightarrow \phi_V(\nu) = \int_{-\infty}^{\infty}\left[\frac{1}{\pi}\frac{\Delta\nu_C/2}{(\Delta\nu_C/2)^2+(\nu-\nu_0-\delta)^2}\right]\left[\frac{2\sqrt{\ln 2}}{\sqrt{\pi}\,\Delta\nu_D}\exp\left[-\left(\frac{2\sqrt{\ln 2}}{\Delta\nu_D}\delta\right)^2\right]\right]d\delta$$

$$\Rightarrow \boxed{\phi_V(\nu) = \underbrace{\frac{2\sqrt{\ln 2}}{\sqrt{\pi}\,\Delta\nu_D}}_{\phi_D(0)}\left\{\frac{a}{\pi}\int_{-\infty}^{\infty}\frac{\exp(-y^2)\,dy}{a^2+(w-y)^2} \equiv \underset{\uparrow}{V}(a,w)\right\}}$$

the “Voigt function” (V≤1)

where $a = \sqrt{\ln 2}\left(\Delta\nu = \Delta\nu_C + \Delta\nu_N\right)/\Delta\nu_D \approx \sqrt{\ln 2}\,\Delta\nu_C/\Delta\nu_D$

$w = 2\sqrt{\ln 2}\,(\nu-\nu_0)/\Delta\nu_D$

$y = 2\delta\sqrt{\ln 2}/\Delta\nu_D$ (integrated out)

3.2. Voigt profile

$$\phi_V(\nu)=\underbrace{\frac{2\sqrt{\ln 2}}{\sqrt{\pi}\Delta\nu_D}}_{\phi_D(0)}\left\{\frac{a}{\pi}\int_{-\infty}^{\infty}\frac{\exp\left(-y^2\right)dy}{a^2+(w-y)^2}\equiv V(a,w)\right\}$$

the "Voigt function" (V≤1)

✐Notes:

1. $\phi_V(\nu)=\phi_D(\nu_0)V(a,w)$, so that

2. $k_\nu=k_0V(a,w)$

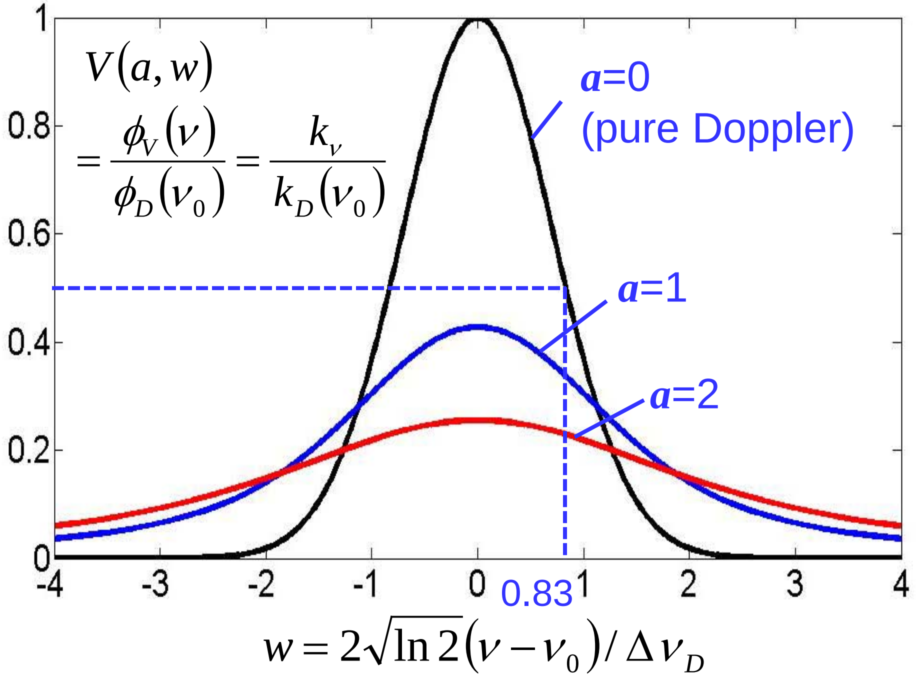
Spec. abs. coeff.

$k_D(\nu_0)$, the line-center spec. abs. coeff. for Doppler broadening

Recall: $k_\nu=S\phi$

3. $V(a,0)=\exp\left(a^2\right)\text{erfc}(a)$

$\therefore\phi_V(\nu_0)=\phi_D(\nu_0)\cdot\exp\left(a^2\right)\text{erfc}(a)$

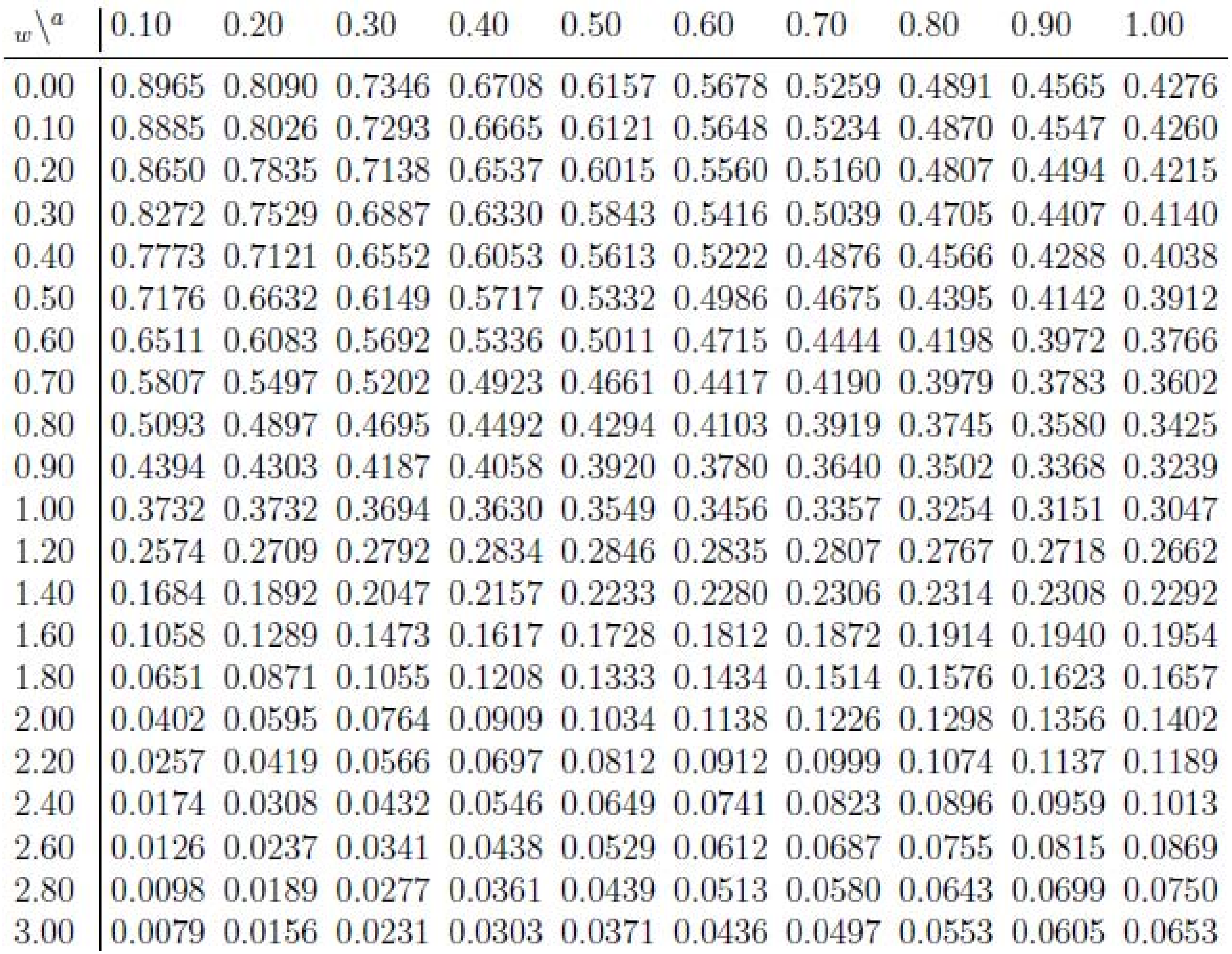


a=1: $\exp\left(a^2\right)\text{erfc}(a)=0.43$

a=2: $\exp\left(a^2\right)\text{erfc}(a)=0.257$

3.2. Voigt profile

- Voigt table



$w \backslash a$	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
0.00	0.8965	0.8090	0.7346	0.6708	0.6157	0.5678	0.5259	0.4891	0.4565	0.4276
0.10	0.8885	0.8026	0.7293	0.6665	0.6121	0.5648	0.5234	0.4870	0.4547	0.4260
0.20	0.8650	0.7835	0.7138	0.6537	0.6015	0.5560	0.5160	0.4807	0.4494	0.4215
0.30	0.8272	0.7529	0.6887	0.6330	0.5843	0.5416	0.5039	0.4705	0.4407	0.4140
0.40	0.7773	0.7121	0.6552	0.6053	0.5613	0.5222	0.4876	0.4566	0.4288	0.4038
0.50	0.7176	0.6632	0.6149	0.5717	0.5332	0.4986	0.4675	0.4395	0.4142	0.3912
0.60	0.6511	0.6083	0.5692	0.5336	0.5011	0.4715	0.4444	0.4198	0.3972	0.3766
0.70	0.5807	0.5497	0.5202	0.4923	0.4661	0.4417	0.4190	0.3979	0.3783	0.3602
0.80	0.5093	0.4897	0.4695	0.4492	0.4294	0.4103	0.3919	0.3745	0.3580	0.3425
0.90	0.4394	0.4303	0.4187	0.4058	0.3920	0.3780	0.3640	0.3502	0.3368	0.3239
1.00	0.3732	0.3732	0.3694	0.3630	0.3549	0.3456	0.3357	0.3254	0.3151	0.3047
1.20	0.2574	0.2709	0.2792	0.2834	0.2846	0.2835	0.2807	0.2767	0.2718	0.2662
1.40	0.1684	0.1892	0.2047	0.2157	0.2233	0.2280	0.2306	0.2314	0.2308	0.2292
1.60	0.1058	0.1289	0.1473	0.1617	0.1728	0.1812	0.1872	0.1914	0.1940	0.1954
1.80	0.0651	0.0871	0.1055	0.1208	0.1333	0.1434	0.1514	0.1576	0.1623	0.1657
2.00	0.0402	0.0595	0.0764	0.0909	0.1034	0.1138	0.1226	0.1298	0.1356	0.1402
2.20	0.0257	0.0419	0.0566	0.0697	0.0812	0.0912	0.0999	0.1074	0.1137	0.1189
2.40	0.0174	0.0308	0.0432	0.0546	0.0649	0.0741	0.0823	0.0896	0.0959	0.1013
2.60	0.0126	0.0237	0.0341	0.0438	0.0529	0.0612	0.0687	0.0755	0.0815	0.0869
2.80	0.0098	0.0189	0.0277	0.0361	0.0439	0.0513	0.0580	0.0643	0.0699	0.0750
3.00	0.0079	0.0156	0.0231	0.0303	0.0371	0.0436	0.0497	0.0553	0.0605	0.0653

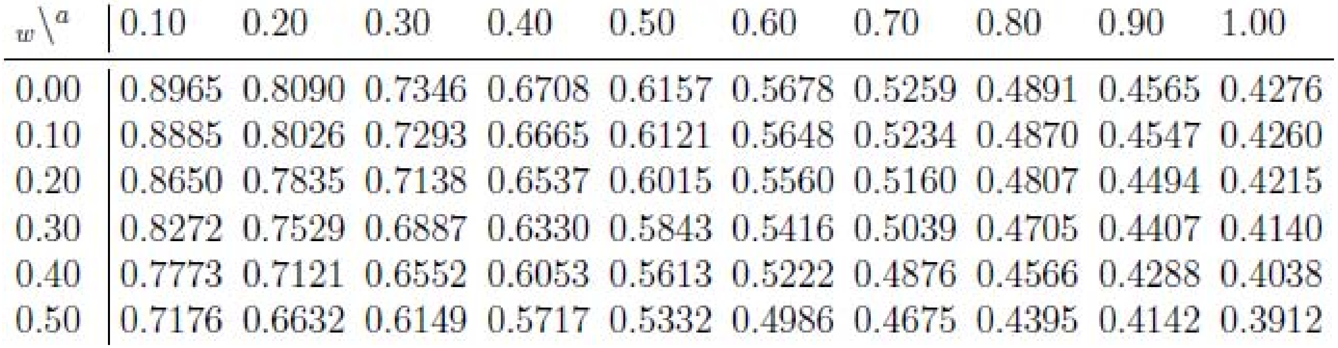
3.2. Voigt profile

- Procedure
  - Given: T, M, ν_0, P, σ, or 2γ
  - Desire: $\phi(\nu)$

$$\phi_V(\nu) = \underbrace{\frac{2\sqrt{\ln 2}}{\sqrt{\pi}\Delta\nu_D}}_{\phi_D(0)} \left\{ \frac{a}{\pi}\int_{-\infty}^{\infty} \frac{\exp(-y^2)\,dy}{a^2+(w-y)^2} \equiv \underset{\uparrow}{V}(a,w) \right\}$$

the “Voigt function” (V≤1)

1. Compute: $\Delta\nu_D$ and $\phi_D(\nu_0)$
2. Compute: $\Delta\nu_C$
3. Compute: $a = \sqrt{\ln 2}\Delta\nu_C / \Delta\nu_D$
4. Pick w, enter table (for a) and obtain $k_\nu / k_D(\nu_0) = \phi / \phi_D(\nu_0)$
5. Solve for $\nu - \nu_0$ (and hence ν) for that w
6. Results: $\phi(\nu)$ vs $\nu - \nu_0$



$w \backslash a$	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
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3.2. Voigt profile

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the "Voigt function" ($V \le 1$)

1. Compute: $\Delta\nu_D$ and $\phi_D(\nu_0)$
2. Compute: $\Delta\nu_C$
3. Compute: $a = \sqrt{\ln 2}\Delta\nu_C / \Delta\nu_D$
4. Pick w, enter table (for a) and obtain $k_\nu / k_D(\nu_0) = \phi / \phi_D(\nu_0)$
5. Solve for $\nu - \nu_0$ (and hence ν) for that w
6. Results: $\phi(\nu)$ vs $\nu - \nu_0$

- Refinements
  - Galatry profiles (collision narrowing)
  - Berman profiles (speed-dependent broadening)

3. Voigt profiles
3.3. Line-shifting mechanisms

- Pressure shift of absorption lines
  - Interaction between two collision partners can have a perturbing effect on the intermolecular potential of the molecule
    - ➡ differences in the energy level spacings
    - ➡ pressure shift

$$\Delta\nu_S = P\sum_A X_A\delta_A$$

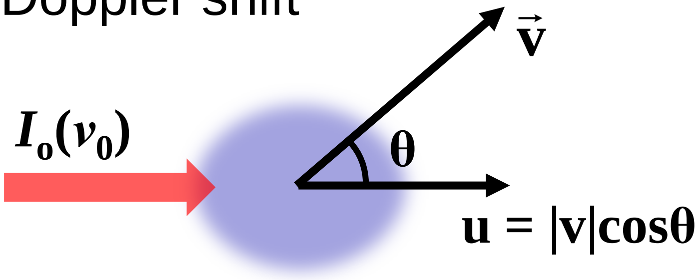
↳ cm^{-1}/atm

$$\delta_A(T) = \delta_A(T_0)\left(\frac{T_0}{T}\right)^M$$

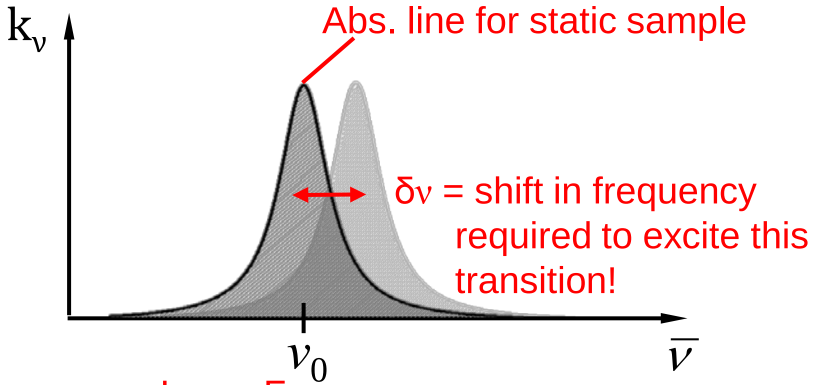
✐Notes:

1. While $2\gamma>0$, δ can be + or –
2. E.g., average values for IR H_2O spectra: δ = –0.017cm^{-1}/atm, M=0.96

- Doppler shift



$$\delta\nu = \nu_0(u/c)$$



Abs. line for static sample

$\delta\nu$ = shift in frequency required to excite this transition!

Laser Frequency

4. Uses of quantitative lineshape measurements

- Species concentration and pressure
  - Integrated absorbance area

$$A_i = \int_{-\infty}^{\infty} \alpha(\nu)\,d\nu = S_i P X_j L$$

Line strength of the transition

Pressure

Species mole fraction

Pathlength

➡ $X_j = \dfrac{A_i}{S_i P L}$

➡ $P = \dfrac{A_i}{S_i X_j L}$

- Temperature
  - FWHM of lineshape gives T in Doppler-limited applications
  - Two-line technique with non-negligible pressure broadening

$$R = \frac{S(T,\nu_1)}{S(T,\nu_2)} = \frac{S(T_0,\nu_1)}{S(T_0,\nu_2)} \exp\left[-\left(\frac{hc}{k}\right)\left(E_1'' - E_2''\right)\left(\frac{1}{T}-\frac{1}{T_0}\right)\right]$$

➡ $$T = \frac{\frac{hc}{k}\left(E_1''-E_2''\right)}{\ln R + \ln\frac{S_2(T_0)}{S_1(T_0)} + \frac{hc}{k}\frac{\left(E_1''-E_2''\right)}{T_0}}$$

T sensitivity:

$$\frac{1}{R}\frac{dR}{dT}[\%/K] = \left(\frac{hc}{k}\right)\frac{\left(E_1''-E_2''\right)}{T^2}\times 100$$

Large ΔE" for higher sensitivity;
Absorbance: 0.1<α<2.3
➡ Tradeoff between acceptable absorbance and T sensitivity.

4. Uses of quantitative lineshape measurements

- Examples

- 1st Example: Spectrally resolved absorption of sodium (Na) in a heated cell

What is P_{Na}?

λ = 589nm, T = 1600K, P = 1atm

1) Find $k_{\nu_0} = (-1/L)\ln(I/I^0)_{\nu_0}$

2) Find $\phi(\nu_0)$

3) Find P_i

$$\Delta\nu_C = P \cdot 2\gamma(1600\text{K})$$

$$= P \cdot 2\gamma(300\text{K})\sqrt{\frac{300}{1600}} = 0.21\text{cm}^{-1}$$

$$(589\times10^{-7}\,\text{cm})^{-1} = 16978\text{cm}^{-1}$$

$$\Delta\nu_D = (7.17\times10^{-7})(16978\text{cm}^{-1})\left(\frac{1600}{23}\right)^{1/2}$$

$$= 0.10\text{cm}^{-1}$$

$$a = \frac{\sqrt{\ln 2}\,\Delta\nu_C}{\Delta\nu_D} = \frac{\sqrt{\ln 2}(0.21)}{0.10} = 1.75$$

Interpolate Voigt table ⇩

$$V(a,w) = V(1.75,0) = 0.2852$$

$$\phi_D(\nu_0) = \frac{2}{\Delta\nu_D}\sqrt{\frac{\ln 2}{\pi}} = \frac{2}{0.10}\sqrt{\frac{\ln 2}{\pi}} = 9.39\text{cm}$$

$$\phi(\nu_0) = \phi_D(\nu_0)V(0)$$

$$= 9.39\times0.2852 = 2.68\text{cm}$$

⇨ Solve for P_i using $P_i = \dfrac{k_\nu}{S\phi(\nu_0)}$

Could also have solved for T from lineshape data

4. Uses of quantitative lineshape measurements

- Examples
  - 2nd Example: Atomic H velocity

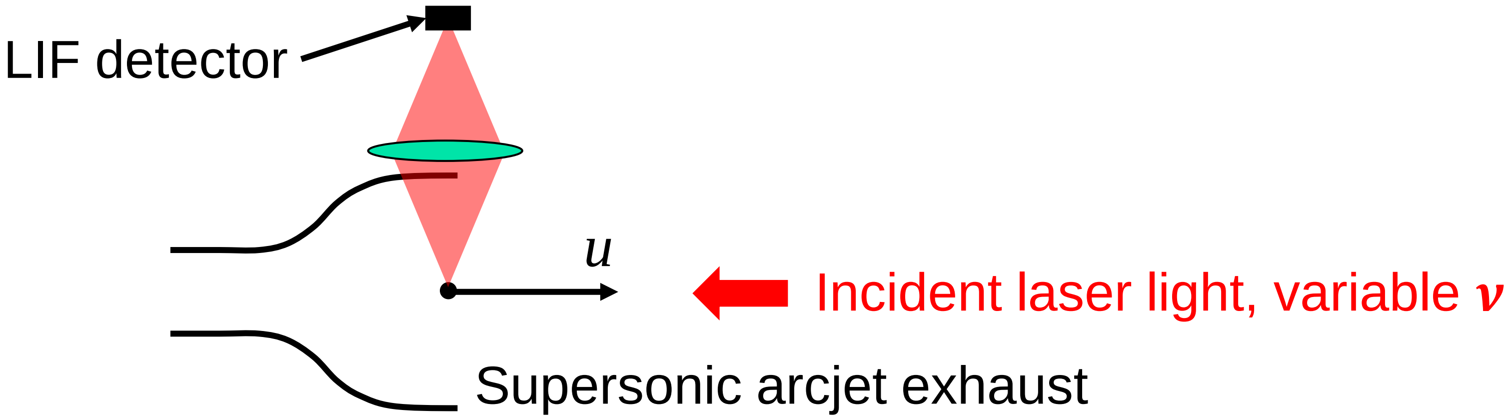
LIF (Laser Induced Fluorescence) in an arcjet thruster is used to measure the Doppler shift of atomic hydrogen at 656nm.

Doppler shift: $\delta\boldsymbol{\nu} = 0.70\text{cm}^{-1}$

Use line position to infer velocity

The corresponding velocity component is found

$$u = \frac{c\delta\nu}{\nu_0} = \frac{3\times10^8\,\text{m/s}\times0.70\text{cm}^{-1}}{15.232\text{cm}^{-1}} = 13800\text{m/s}$$



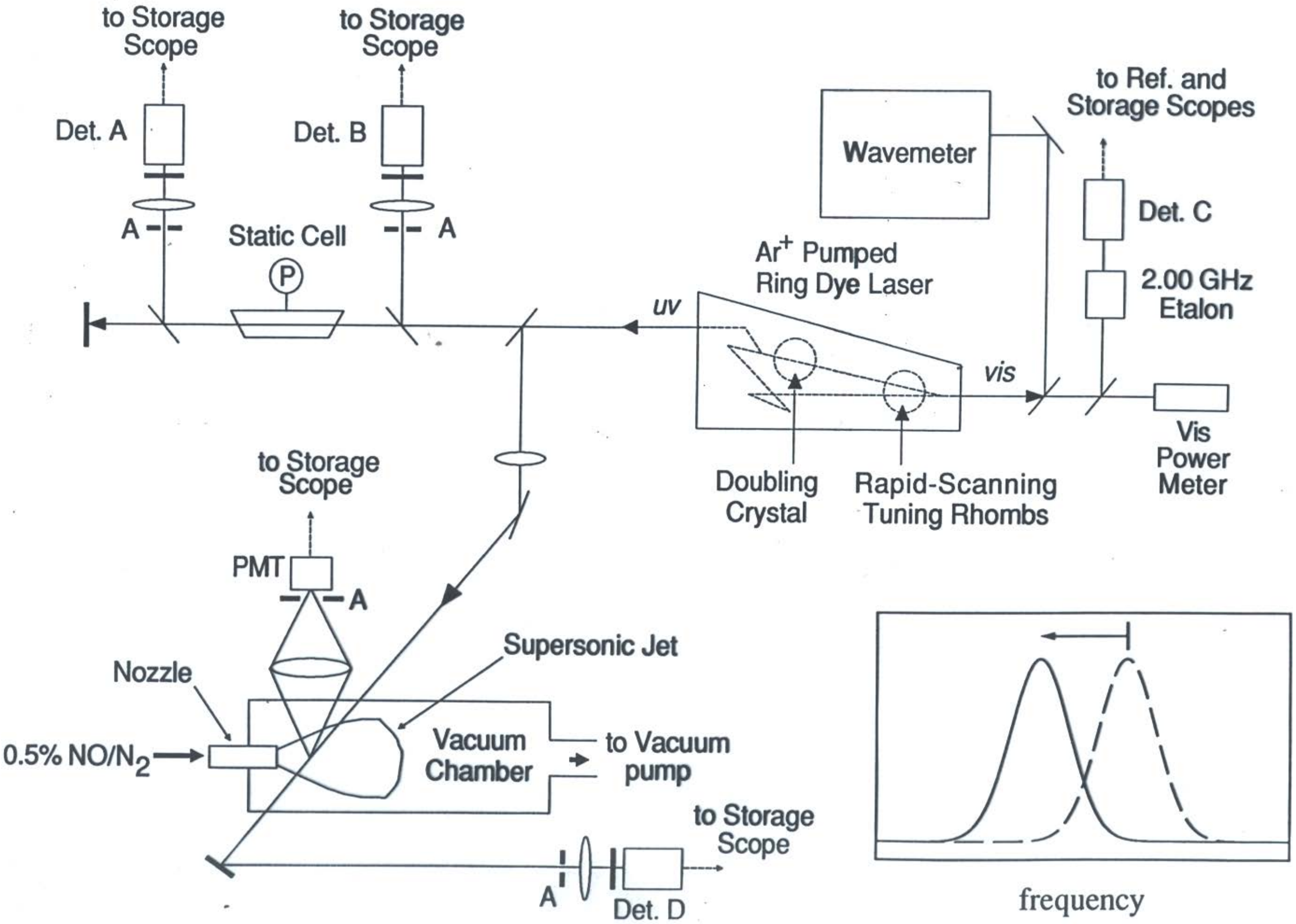
LIF detector

Incident laser light, variable $\boldsymbol{\nu}$

Supersonic arcjet exhaust

5. Working examples - 1

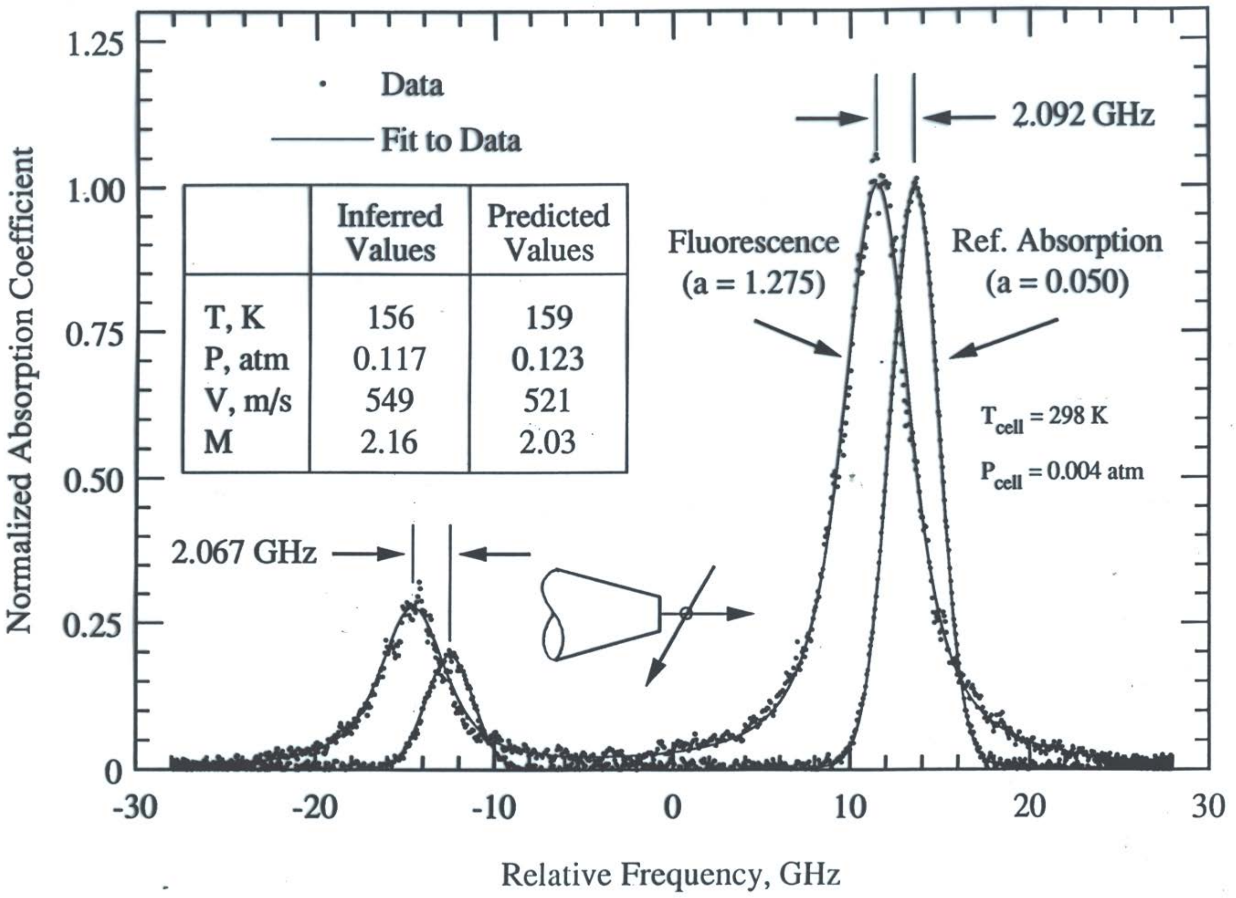
- CW laser strategies for multi-parameter measurements of high-speed flows containing NO



Schematic for NO LIF experiments

5. Working examples - 1

- CW laser strategies for multi-parameter measurements of high-speed flows containing NO



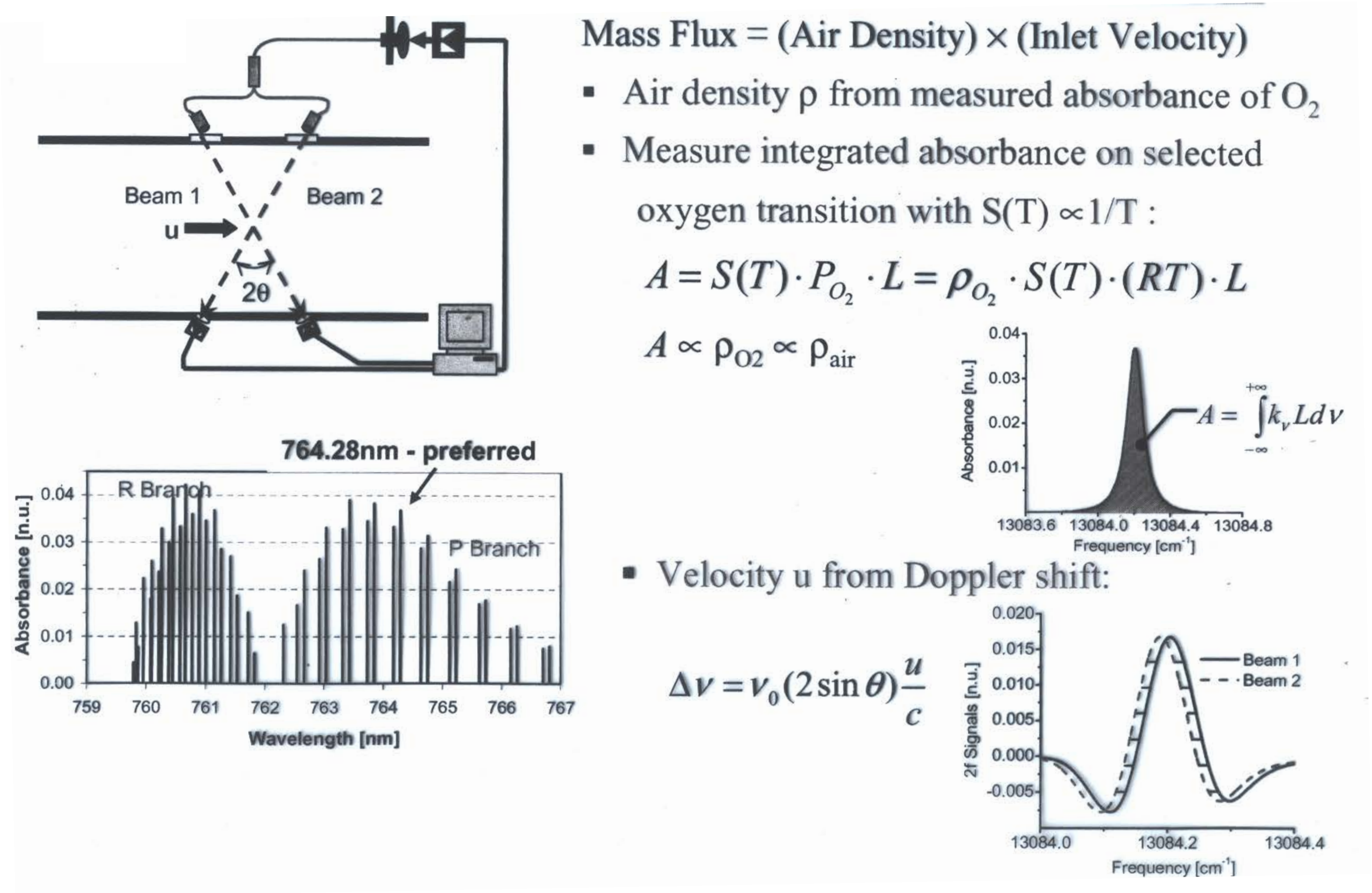
Reduced Fluorescence and Reference Absorption Signals of

NO $Q_2+R_{12}(8)$, $R_2(4)$ (226.7 nm) for Measurements at $x / D = 0.75$

	Inferred Values	Predicted Values
T, K	156	159
P, atm	0.117	0.123
V, m/s	549	521
M	2.16	2.03

5. Working examples - 2

- TDL mass flux sensor
  - Full-scale aero-engine inlet



Mass Flux = (Air Density) × (Inlet Velocity)

- Air density ρ from measured absorbance of O_2
- Measure integrated absorbance on selected oxygen transition with $S(T) \propto 1/T$:

$$A = S(T)\cdot P_{O_2}\cdot L = \rho_{O_2}\cdot S(T)\cdot(RT)\cdot L$$

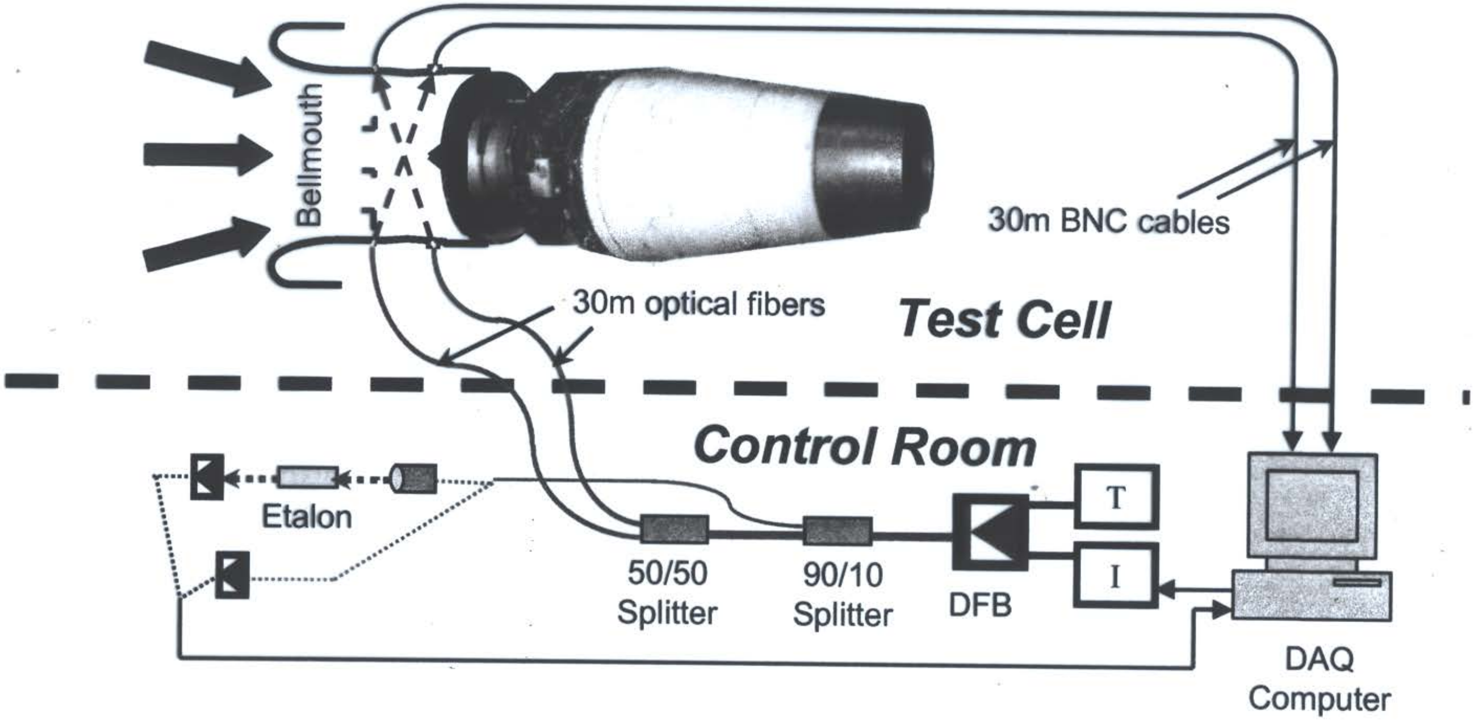
$$A \propto \rho_{O2} \propto \rho_{air}$$

- Velocity u from Doppler shift:

$$\Delta\nu = \nu_0(2\sin\theta)\frac{u}{c}$$

5. Working examples - 2

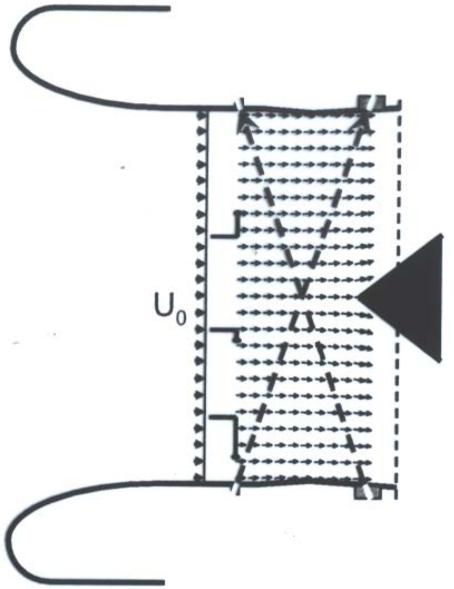
- TDL mass flux sensor
  - Sensor tests in Pratt and Whitney engine inlet

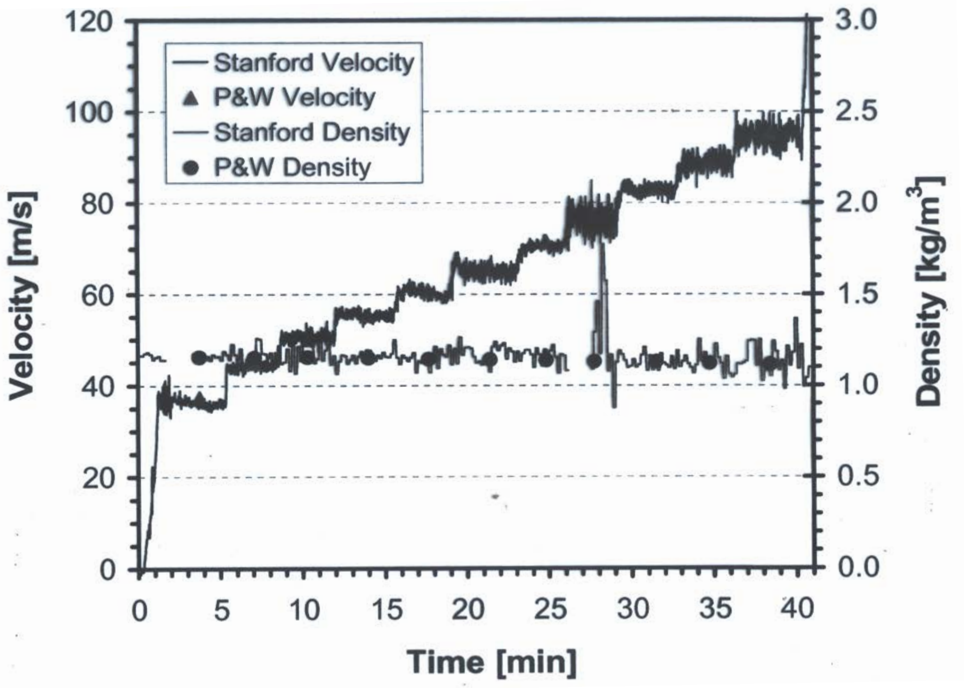


- Bellmouth installed on inlet of commercial engine (Airbus 318)
- Sensor hardware remotely operated in control room
- TDL beams mounted in engine bellmouth

5. Working examples - 2

- TDL mass flux sensor
  - P & W mass flux versus TDL sensor measurements





- TDL data agrees well (1.2% in V and 1.5% in ρ) w/ test stand instrumentation
- Flow model employed to account for non-uniformities
- Success in non-uniform flow suggest other potential applications

Next: Electronic Spectra of Diatomics

- Term Symbols, Molecular Models
- Rigid Rotor, Symmetric Top
- Hund’s Cases
- Quantitative Absorption