Lecture 18 Rotations and Vibrations

Topics
1. Vibrations of Polyatomic Molecules
2. Rotational Motion
3. Ro-vibrational Transitions

References
• Steinfeld, *Molecules and Radiation* (Dover 1985)
• Townes & Schawlow, *Microwave Spectroscopy* (Dover 1975)
• Herzberg, "Free Radicals" (Cornell, 1971)
• Herzberg*, Molecular Spectra & Molecular Structure* II:
  Infrared and Raman Spectra of Polyatomic Molecules
  (van Nostrand 1945)

1. Vibration of Polyatomic Molecules

Dense gas ⇒ Cool gas ⇒ Long wavelengths ⇒
Observations across spectrum from NIR to cm   ⇒
Rotational and vibrational transitions (*not* electronic)

• Transitions involve at least a unit change in vibrational
  quantum number, as in: **(upper) v' → (lower) v''**.

• Many transitions occur since each vibrational level has a
  manifold of rotational transitions, i.e. "band" structure.
  Transitions involve changes in *both* vibrational and rotational
  quantum numbers: **(upper) $v'J'$ → (lower) $v''J''$**, so-called
  "rotational-vibrational" transitions or ro-vibrational or just
  ro-vib transitions.

• There are usually no rules for ro-vib transitions against any
  change $v' → v''$, although the strength decreases with increasing
  $| v'\text{-}v'' |$. The change $J' → J'$ is governed by the usual angular
  momentum selection rules for dipole (or quadrupole) transitions.

Vibrational Modes of Polyatomic Molecules

Let N > 2 be the number of nuclei in a polyatomic molecule with 3N degrees of freedom. With 3 for the center-of-mass and 3 for rotation (or 2 for a linear molecule with two rotational degrees), there are 3N-6 (or 3N-5) vibrational degrees of freedom, e.g., three for N = 3 and six for N = 4, etc.

We consider the vibrational frequencies as given. Once the equilibrium configuration is known, this is a problem in classical Lagrangian mechanics. Of course high vibrational levels are subject to anharmonic corrections, as discussed in Lec. 17. See Ch. 8 of Seinfeld for a discussion of Lagrangian and more elegant methods, with explicit solutions for N = 3 and 4.

The ultimate source of accurate frequencies is spectroscopic measurements, presumably compiled and up to date at: http://physics.nist.gov/PhysRefData/MolSpec/index.html

N.B. Vibrational frequencies are in the NIR. Recall that 2 microns corresponds to 5000 cm^{-1} or ~ 7500K

Vibrations of XY$_2$ Molecules, e.g., H$_2$O and C$_2$H

symmetric stretch ν_1

ν_2 bending

(a)

Bent XY$_2$

asymmetric stretch ν_3

ν_1 symmetric stretch

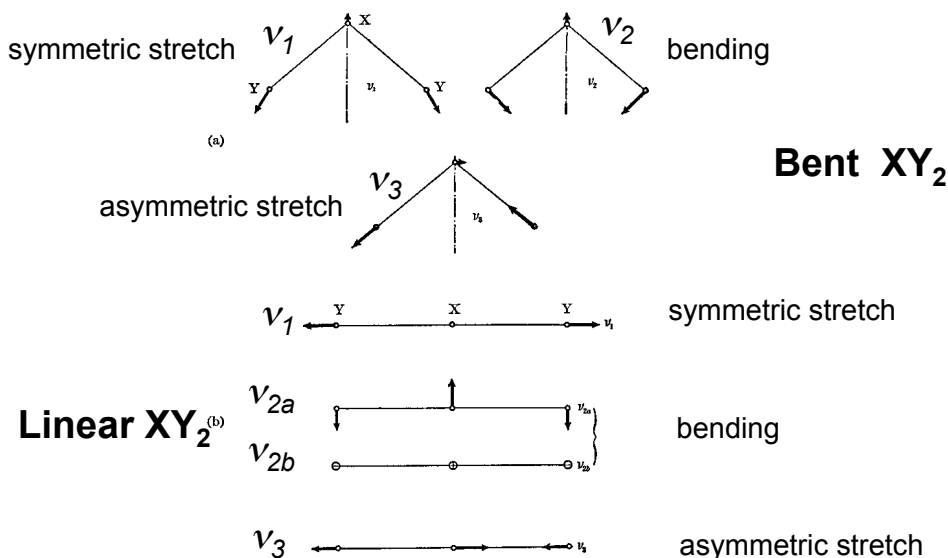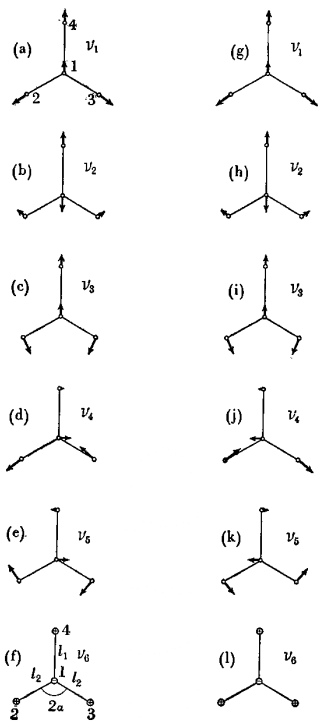**Linear XY$_2$**(b) ν_{2a} ν_{2b} bending

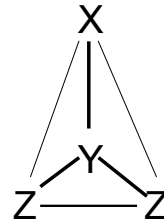ν_3 asymmetric stretch

FIG. 25. Normal vibrations of bent and linear XY$_2$ (schematic).

Fig. 25 from Herzberg, Vol. II: Normal vibrations of bent and linear XY$_2$

Vibrations of Planar XYZ_2

N = 4
3N - 6 = 6

The two panels represent reflections in the symmetry plane through XY and $\perp$ to the plane of the molecule.

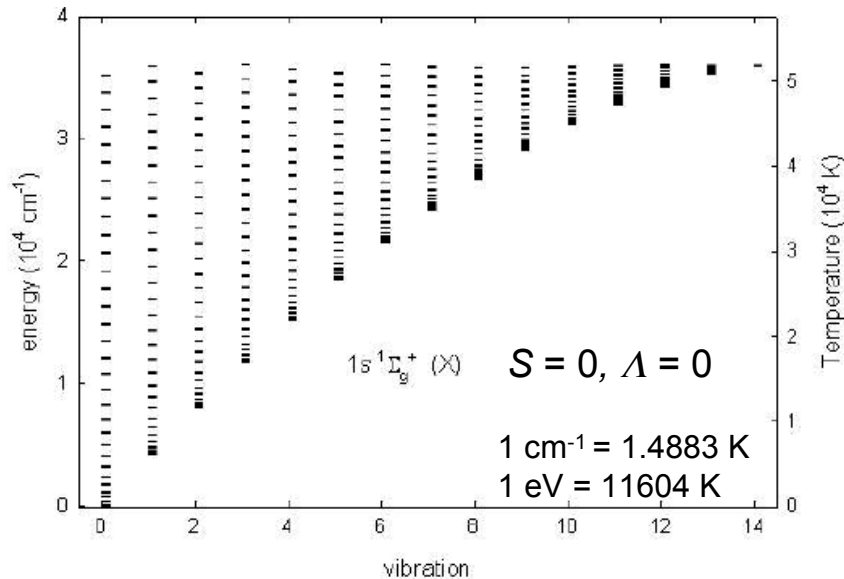In mode 6, nucleus Y moves out of the plane while the others move into the plane.

XYZ_2 can also have other isomeric forms

Fig. 24 from Herzberg, Vol. II: Normal vibrations of bent and linear XYZ_2

Vibrational Levels of H_2

$1s\,^1\Sigma_g^+\ (X)$ $S = 0,\ \Lambda = 0$

1 cm^{-1} = 1.4883 K
1 eV = 11604 K

14 vibrational levels of the ground electronic state of H_2 included in CLOUDY (Shaw et al. ApJ, 624, 674, 2005)
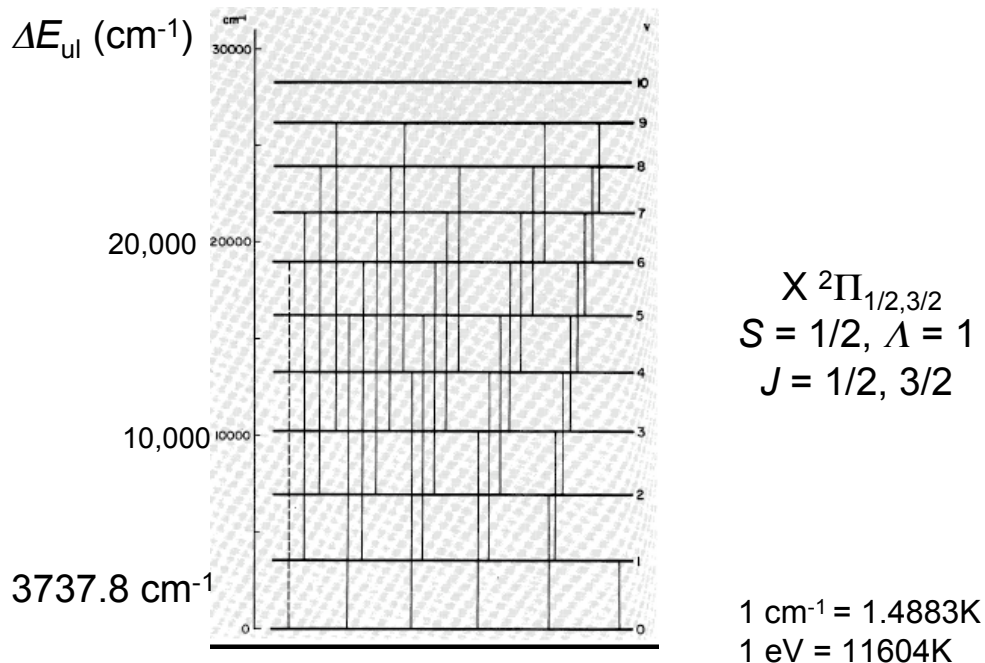
Vibrational Levels of the OH Ground State

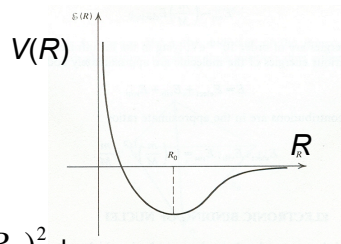ΔE_{ul} (cm^{-1})

20,000

10,000

3737.8 cm^{-1}

X $^2\Pi_{1/2,3/2}$
$S = 1/2$, $\Lambda = 1$
$J = 1/2$, $3/2$

1 cm^{-1} = 1.4883K
1 eV = 11604K

Fig. 32 Herzberg's "Radicals"

Ro-vibrational Transition Probabilities

The transition probability is determined by the matrix element of the electric dipole moment, which varies with the inter-nuclear separation R. Expand $\mu(R)$ about the minimum in the potential R_{0}:

$V(R)$

$$\mu(R) = \mu(R_0) + \mu'(R_0)(R - R_0) + \frac{1}{2}\mu''(R_0)(R - R_0)^2 + \cdots$$

Evaluating the matrix element with oscillator wave functions yields:

$\langle v \mid \mu(R_0) \mid v' \rangle \propto \delta(v', v)$ (pure rotational)

$\langle v \mid \mu'(R_0)(R - R_0) \mid v' \rangle \propto \delta(v', v \pm 1)$ (rovib fundamental)

$\langle v \mid \frac{1}{2}\mu''(R_0)(R - R_0)^2 \mid v' \rangle = \delta(v', v \pm 2)$ (rovib first overtone)

1, Ro-vib transition probabilities are determined by the derivatives of the dipole moment, and not on the permanent moment.

2. Fundamental ro-vib transitions are much stronger than overtone.

3. Molecules with small permanent dipole moments can have large ro-vib transition moments, e.g., CO.

2. Rotational Motion

The rotational motion of a molecule is determined by the
moments of inertia and the angular momenta.
- Classically, any object has three orthogonal principal moments of inertia (diagonals of the inertia tensor) with corresponding simple expressions for the rotational energy and angular momentum.
- This carries over directly to quantum mechanics.
- It is customary to classify the rotational properties of molecules according to the values of the principle moments of inertia

The principle moments of inertia are usually designated
I_a, I_b, *and* I_c *in order of increasing magnitude*

Nomenclature for Rotating Molecules

A molecule with rotational symmetry is a ***symmetric top,*** and either $I_c = I_b > I_a$ or $I_c > I_b = I_a$:
- ***prolate symmetric tops*** ($I_c = I_b > I_a$)
  example: NH_3, linear molecules ($I_a = 0$)
- ***oblate symmetric tops*** ($I_c > I_b = I_a$)
  example: planar benzene

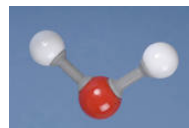A molecule with equal moments is a ***spherical top.***
   example: CH_4
A molecule with unequal moments $I_c \neq I_b \neq I_a$ is an ***asymmetric top,*** example: H_2O
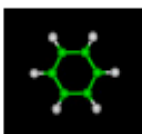
benzene   methane   water

Rotational Energy of a Symmetric Top

Classically the energy of rotation is

$$E = \tfrac{1}{2}I_x\omega_x^2 + \tfrac{1}{2}I_y\omega_y^2 + \tfrac{1}{2}I_z\omega_z^2 = \frac{J_x^2}{2I_x} + \frac{J_y^2}{2I_y} + \frac{J_z^2}{2I_z}$$

The symmetry axis is *z*. For an oblate rotor $I_x = I_y = I_b$, and since $J^2 = J_x^2 + J_y^2 + J_z^2$

$$E = \frac{J^2}{2I_b} + J_z^2\left(\frac{1}{2I_c} - \frac{1}{2I_b}\right) \quad \text{(oblate)}$$

Similarly for a prolate rotor, $I_x = I_y = I_b$ still holds and

$$E = \frac{J^2}{2I_b} + J_z^2\left(\frac{1}{2I_a} - \frac{1}{2I_b}\right) \quad \text{(prolate)}$$

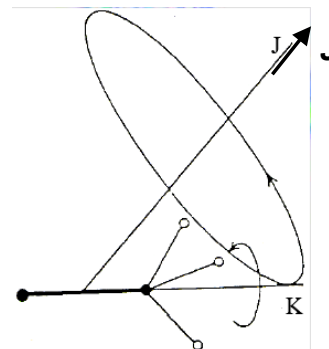The next step is to quantize these classical expressions.

Rotational Energy of Symmetric Tops

The square of the angular momentum and its projection on the symmetry axis are good quantum numbers.

NB The projection on a fixed axis is also conserved; it is usually denoted M_z and enters into the Zeeman effect.

$$J^2 = J(J+1)\hbar^2 \quad \text{and} \quad J_z = K\hbar$$

$$J = 0,\ 1,\ 2\ \cdots \quad K = 0,1,2\ \cdots$$

rotating vector diagram

$$E = \frac{\hbar^2}{2I_b}J(J+1) + \left(\frac{\hbar^2}{2I_c} - \frac{\hbar^2}{2I_b}\right)K^2 = BJ(J+1) + (C-B)K^2 \quad \text{(oblate)}$$

$$E = \frac{\hbar^2}{2I_b}J(J+1) + \left(\frac{\hbar^2}{2I_a} - \frac{\hbar^2}{2I_b}\right)K^2 = BJ(J+1) + (A-B)K^2 \quad \text{(prolate)}$$

in terms of the rotational constants, $A = \dfrac{\hbar^2}{2I_a}$, $B = \dfrac{\hbar^2}{2I_b}$, $C = \dfrac{\hbar^2}{2I_c}$

Rules of the Game for Symmetric Tops

- *J* can have any integral value
- As a projection of **J**, *K* has $(2J+1)$ values,

  $$+J, J-1, \ldots -J+1, -J$$

- The energy depends on $|K|$, so there are only
  $J+1$ distinct values, and the levels start at $J = K$
- For a prolate top (cigar) $A > B$: levels increase with K
  For an oblate top (pancake) $C < B$: levels decrease
  with K -- see the diagram *on* the next slide
- The simple rotational ladder of a linear molecule is
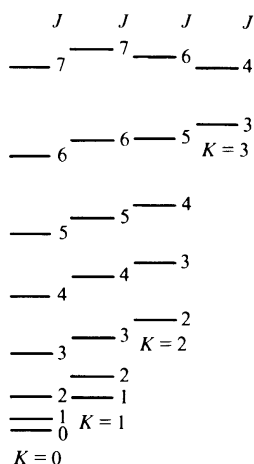 recovered for $K = 0$ (slide 27)

  **For *asymmetric tops* (all unequal moments): Only *J* and *E* are
  conserved. The states are labeled by *J* and (K_-K_+) -- conserved
  projections in the limit of prolate & oblate symmetric tops .
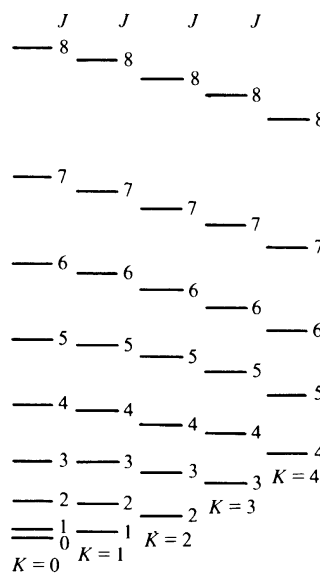 To be discussed later in connection with the water molecule.**

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Energy Levels of a Symmetric Top

Prolate, $A > B$

Oblate, $C < B$

Allowed transitions are up and down fixed *K* ladders.

AY216-09

Order of Magnitude of the Rotational Energy

The rotational energy is determined by the moments of inertia, e.g, for an oblate asymmetric top

$$E = \frac{\hbar^2}{2I_b}J(J+1) + \left(\frac{\hbar^2}{2I_c} - \frac{\hbar^2}{2I_b}\right)K^2 = BJ(J+1) + (C-B)K^2$$

And $I \sim ma^2$ where m is a typical atomic mass and a is a typical nuclear separation. The order of magnitude of the rotational energy is, using these constants for a hydride,

$h/2\pi = 1.05 \times 10^{-27}$ erg s,　　$m \sim 2 \times 10^{-24}$ g,　　$a \sim 10^{-8}$ cm,

$(h/2\pi)^2/2I \sim 5 \times 10^{-15}$ erg $\sim 3 \times 10^{-3}$ eV

Converting to Kelvins, this rough estimate gives ~ 40 K for H and smaller values for heavier atoms. Recall from Lec. 17 that $B(H_2) = 85$K and $B(CO) = 2.77$K

Radiative Transitions

Rotational Transitions – Molecules with a ***permanent dipole moment*** can generate a strong pure rotational spectrum.
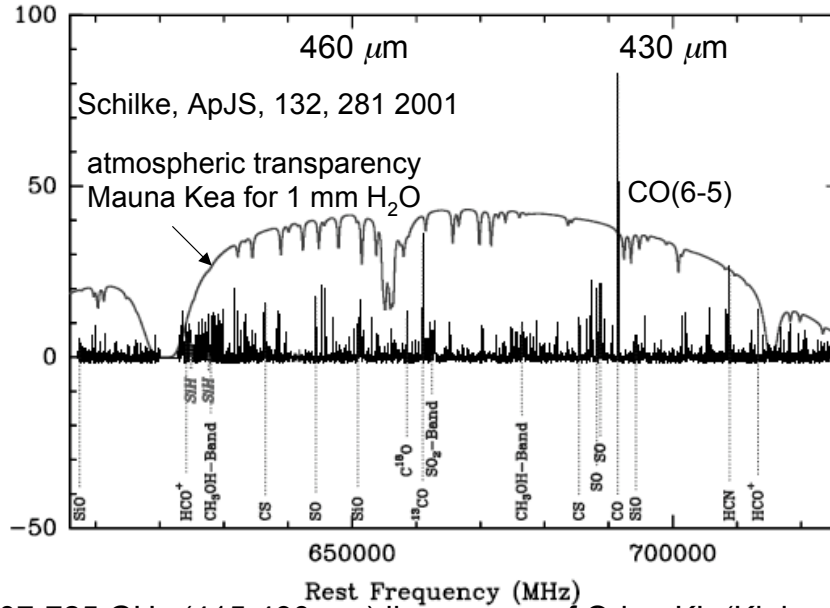Symmetric molecules like H_2, C_2, O_2, CH_4 and C_2H_2 have weak rotational spectra generated by the electric quadrupole moment.
For H_2, the $\Delta J = 2$ transitions start at $\lambda(2 \to 0) = 28$ μm.

Selection Rules – The general rules apply, albeit in new forms dictated by molecular symmetry.

For a ***symmetric top***, the dipole moment lies along the symmetry axis. The radiation field cannot exert a torque along this axis, so the selection rule for a pure rotational transition is $\Delta K = 0$ (and $\Delta J = \pm 1$). Levels with J=K are metastable.
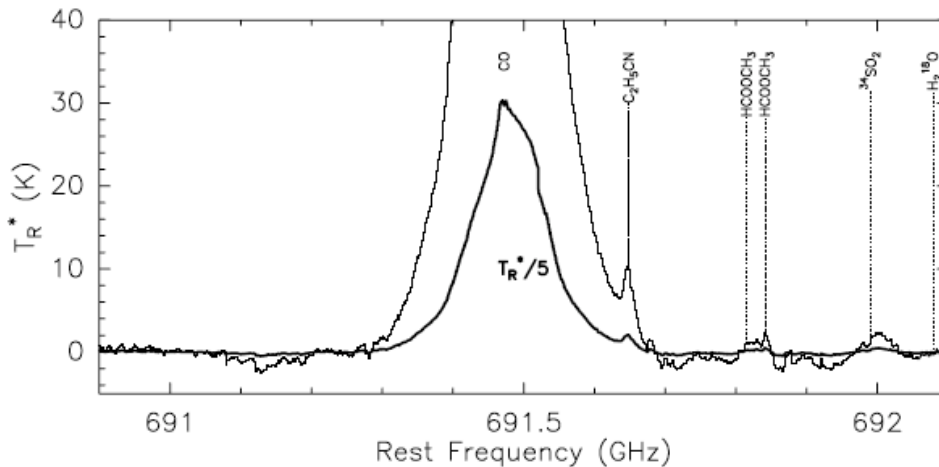
Observed Rotational Transitions

460 μm

430 μm

Schilke, ApJS, 132, 281 2001

atmospheric transparency
Mauna Kea for 1 mm H_2O

CO(6-5)

Rest Frequency (MHz)

607-725 GHz (415-490 μm) line survey of Orion-KL (Kleinman-Low Nebula) dominated by CO, CS, SO, SO_2 and CH_3OH.
Note the relatively high transparency in this FIR/submm band

Observed Rotational Transitions

1 GHz slice of the spectrum from the 607-725 GHz line survey of Orion-KL (Schilke et al. 2001) centered on the strongest line, CO(J=6-5).
For the Odin satellite observations of this spectral region, see Olofsson et al. A&A, 476, 791 & 807, 2007

A-value for Dipole Radiation From a Simple Rotor

The standard atomic formulae are slightly changed:

$$A(v'J' \rightarrow v''J'') = \frac{64\pi^4}{3h}(\frac{v}{c})^3 \frac{S(J',J'')}{2J'+1}|(v''J''|M|v'J')|^2$$

The upper level is ($v'J'$) and the lower level is ($v''J''$).
$S(J',J'')$ is the Honl-London factor.
($v''J''|M|v'J'$) is the dipole matrix element

$$S(J',J'') = \frac{1}{2}|J'(J'+1) - J''(J''+1)|$$

$$= J' \quad \text{for } J'= J''+1 \ (R) \quad \text{and} \quad J'+1 \quad \text{for } J'= J''-1 \ (P)$$

The absorption cross section is

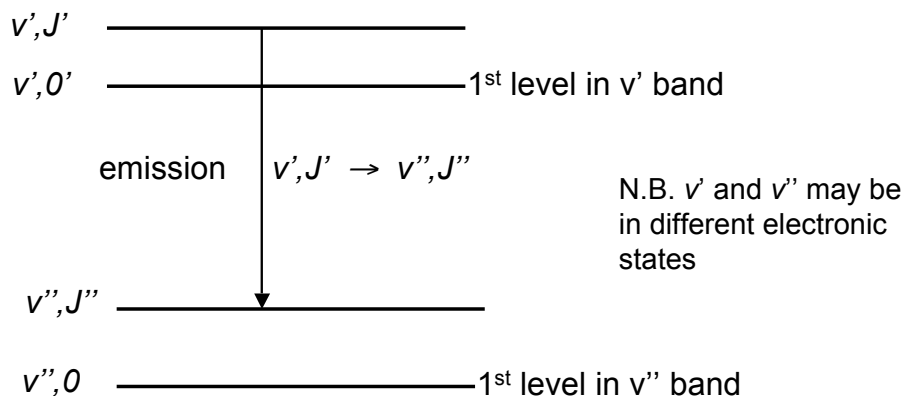$$\sigma(v'J',v''J'') = f(v'J',v''J'')\frac{\pi e^2}{m_e c}\varphi(\Delta v)$$

$$f(v'J',v''J'') = \frac{2J'+1}{3(2J''+1)}\left(\frac{\lambda(v''J'',v'J')}{\lambda(00,01)}\right)^2 \frac{A(v'J',v''J'')}{A(01,00)}$$

3. Ro-Vibrational Transitions

Convention: lower level has double, upper level has single prime.

The standard dipole transition selection rule, $\Delta J = 0, \pm 1$ allows three possibilities:

        P-transitions: _J'=J''-1_,   i.e., 0-1, 1-2, etc.
        Q-transitions _J'=J''_,   i.e., 1-1, 2-2, etc.
        R-transition: _J'=J''+1_,   i.e., 1-0, 2-1, etc

Ro-Vibrational Energies for a Diatomic Molecule

The energy in a ro-vibrational transition of a **diatomic molecule** is, ignoring the centrifugal terms discussed in Lec. 17 (slide 27),

$$\Delta E(v'J',v''J'') = \Delta E(v',v'')_{vib} + B'J'(J'+1) - B''J''(J''+1)$$

Keeping v' *and* v'' fixed (and also the first term, denoted E_0 below), the energy changes for the three types of ro-vibrational transitions are,

P branch - $J'' = J' - 1$

$$\Delta E(J)_P = E_0 - (B'+B'')J + (B'-B'')J^2$$

Q branch - $J'' = J'$

$$\Delta E(J)_Q = E_0 + (B'-B'')J(J+1)$$

R branch - $J'' = J' + 1$

$$\Delta E(J)_R = E_0 + 2B' + (3B'-B'')J + (B'-B'')J^2$$

where now everywhere J stands for J''

Unlike pure rotational transitions, ro-vib transitions depend quadratically on rotational quantum number.

Ro-vibrational Progression for a Diatomic Molecule

Unlike rotational transitions within the same vibrational band, the ro-vibrational transitions have an additional quadratic dependence $(B'-B'')J^2$. Since $B' < B''$ usually , this means that:

- **P transition frequencies are a monotone decreasing function of J and start at v_0**
- **Q transitions also start at v_0 and crowd around this frequency.**
- **R transitions start $2B'$ above v_0 and increase with J for small J.**

For large J, the quadratic term cuts in and changes the frequency from an increasing to a decreasing function of J. The maximum frequency for the P branch is given by

$$J* = \frac{3B'-B''}{2(B''-B')}$$

Because this is a stationary point, many transitions crowd around this point, which is called the *bandhead*.
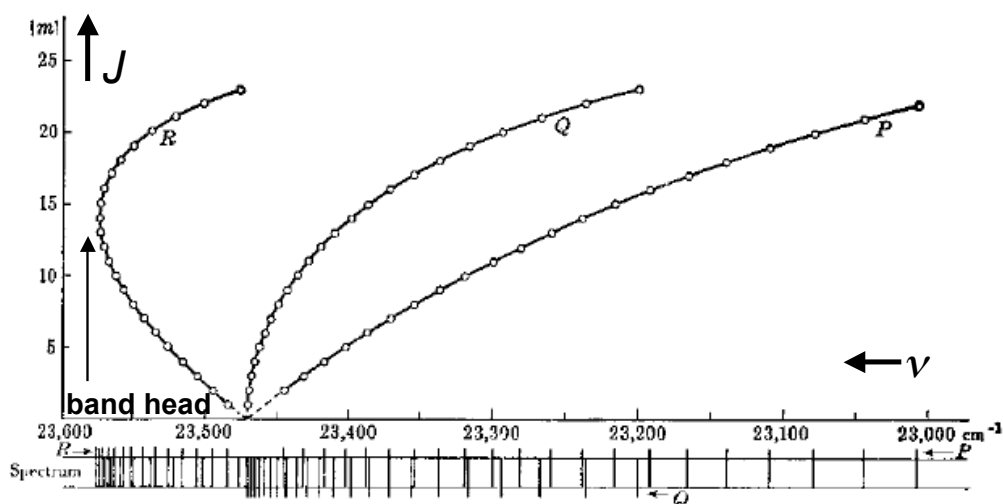
Fortrat Diagram for AlH

Figure 25 from Herzberg I(*Diatomic Molecules*) plots *J* against (decreasing) frequency. This is inverted from the previous formulae for the frequency vs. *J.*
This is an optical (electronic) transition from an excited to the ground electronic state ($^1\Pi \rightarrow\ ^1\Sigma$) so that there is a Q-branch.

Caveat on Selection Rules

We used a diatomic molecule to illustrate P, Q, and R branches, even though they rarely have Q branches in the ground electronic state. A more complete statement of the selection rules governing rotation-vibration transitions (c.f. Rybicki & Lightman, Sec. 11.5) helps clarify the situation:

ΔJ = 0, ±1 but *not* J=0→J=0
$\Delta\Lambda$ = 0, ±1
ΔJ = 0 is *not* allowed for Λ=0 → Λ=0
Δv = any positive or negative integer

Most diatomic molecules are in Λ = 0 (Σ) ground electronic states and therefore do not have Q branches. An important exception is the OH radical, to be discussed in Lec. 20.

Q branches are more commonly found in polyatomic molecules and in electronic transitions such as the $^1\Pi \rightarrow\ ^1\Sigma$ transition of AlH shown in the previous side.
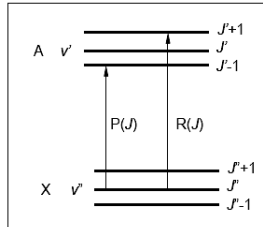
P, Q, and R Branches for C$_3$

B' ≠ B" because the moment of inertia, proportional to <v|1/R^2|v>, depends on *v*. However *B'* is only a little smaller than *B"* so that the quadratic terms are small.

Summary: P and R are linear in *J* for small *J* and quadratic for large *J*; Q ∝ (*B'-B"*) so the transitions crowd around *E*$_0$

Interstellar absorption spectrum of C$_3$ for the X $^1\Sigma_g$ → A $^1\Pi_u$ transition. Top: synthetic spectrum (*T* = 80 K) for spectral resolution of 10^5. Notice locations of P, Q, and R in accord with previous formulae
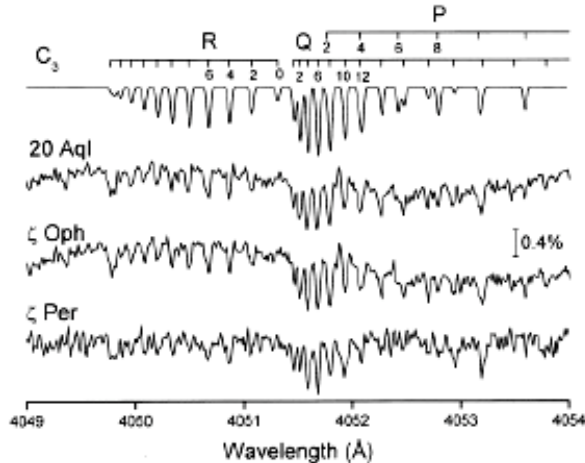
Adamkovics et al., ApJ, 595, 235, 2003

CO(v = 2-0) First Overtone Bandhead

WL16 is a young stellar object with a broad and distorted bandhead near 2.3 μm providing information about its accretion disk.

The inset shows the intrinsic line shape assumed in modeling the spectrum (solid curve) that generates the broad feature.

In 1992, the sensitivity was insufficient to detect individual ro-vib lines. The pile up of lines at the bandhead generates enough flux to have made this measurement possible.
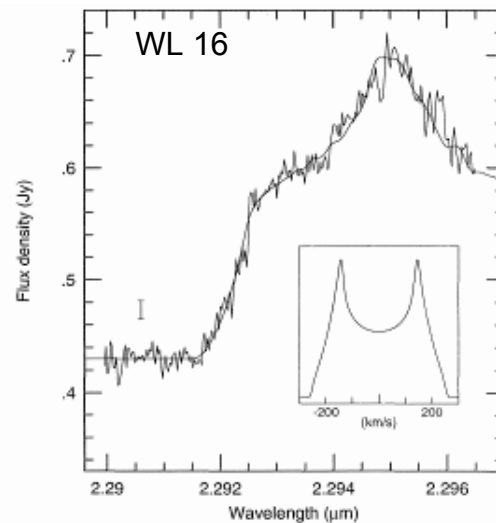
Carr et al. ApJ, 411, L37, 1993

Example of the Rigid Rotor

For the **pure rotational spectrum** of a rigid rotor, the energy emitted in the transition $J'=J \rightarrow J''=J\text{-}1$ *is* (J is upper level)

$$\Delta E_J = E(J) - E(J-1) = 2BJ$$

and leads to the sequence $2B$, $4B$, $6B$ ... .

For the **ro-vibrational spectrum**, with $B' = B''$ (J is always the lower level), the transition energies are

P branch - $J'' = J' - 1 \equiv J$

$$\Delta E(J)_P = E_0 - 2BJ$$

R branch - $J'' = J' + 1 \equiv J$

$$\Delta E(J)_R = E_0 + 2B(J+1)$$

Q branch - $J'' = J' \equiv J$

$$\Delta E(J)_Q = E_0$$

In order of increasing energy or frequency:

$$\dots \ \text{-}6B \quad \text{-}4B \quad \text{-}2B \quad 0 \quad 2B \quad 4B \quad 6B \ \dots$$

P branch Q R branch

Brief Summary

1. Vibrational frequencies are well known in most cases.
2. Ro-vib transition probabilities depend on the derivatives of the dipole moment function $\mu\ (R)$.
3. Moments of inertia are conventionally ordered $I_a < I_b < I_c$ with $I_c = I_b > I_a$ for prolate symmetric tops and $I_c > I_b = I_a$ for oblate symmetric tops
4. The selection rules for symmetric tops, $\Delta K = 0$, $\Delta J = \pm 1$. imply that transitions are up and down "K-ladders"
5. Ro-vib transitions depend quadratically on $J'' - J'$ and lead to the crowding near the bandhead frequency of P and Q branch transitions.