Lecture 13 Molecular Spectroscopy

1. Long Wavelength Signatures
2. Introduction to Molecular Structure
3. Molecular Levels and Spectra
## 4. Emission and Absorption

References

- **Astro texts: Tielens, Secs 2.1-2**
  Shu I, Chs. 28-30
  Dopita & Sutherland, Ch. 1
  Palla & Stahler, Ch. 5
- **Herzberg, Molecular Spectra & Molecular Structure**
  (c. 1950, 3 volumes)
- **Herzberg, The Spectra & Structure of Simple Free Radicals**
  (Cornell 1971), esp. Parts I & II
- **Townes & Schawlow, Microwave Spectroscopy (Dover 1975)**
- **Steinfeld, Molecules and Radiation (Dover 1985)**

1. Long Wavelength Signatures of the Cool ISM

Long wavelength spectra of the ISM are dominated by *dust* and *molecules*.
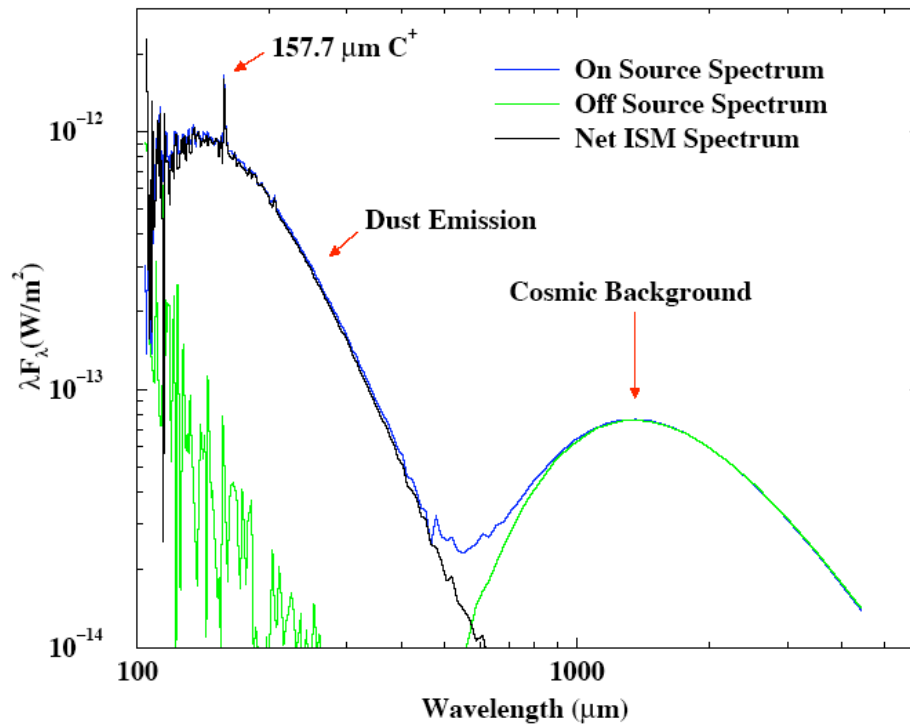
COBE 100-1000 μm
low resolution spectrum
of the Galactic plane.
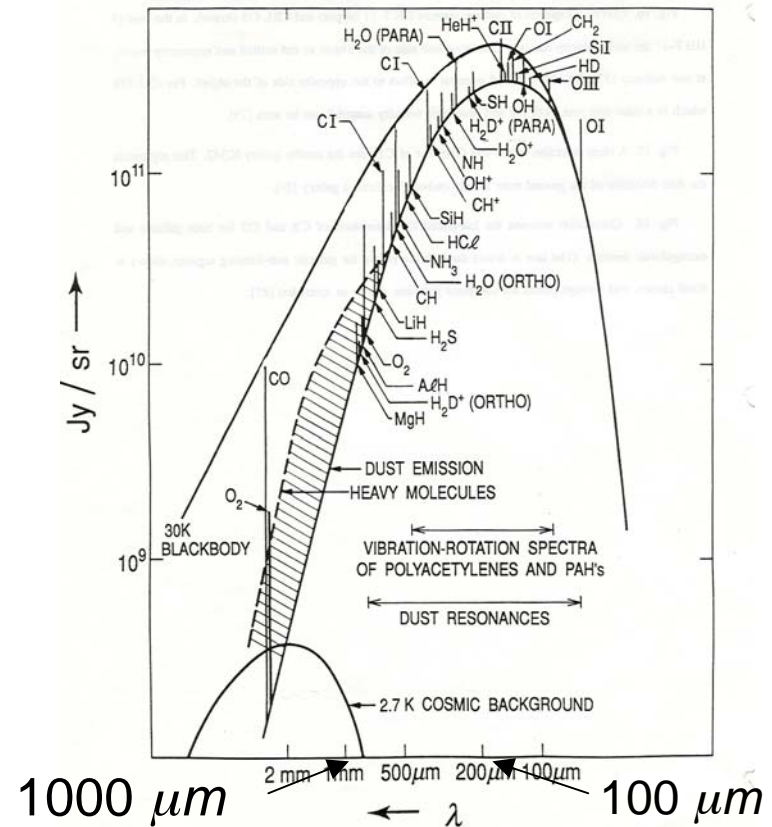
Phillips & Keene
Proc IEEE 80 1662 1992
synthetic spectrum of a
molecular cloud
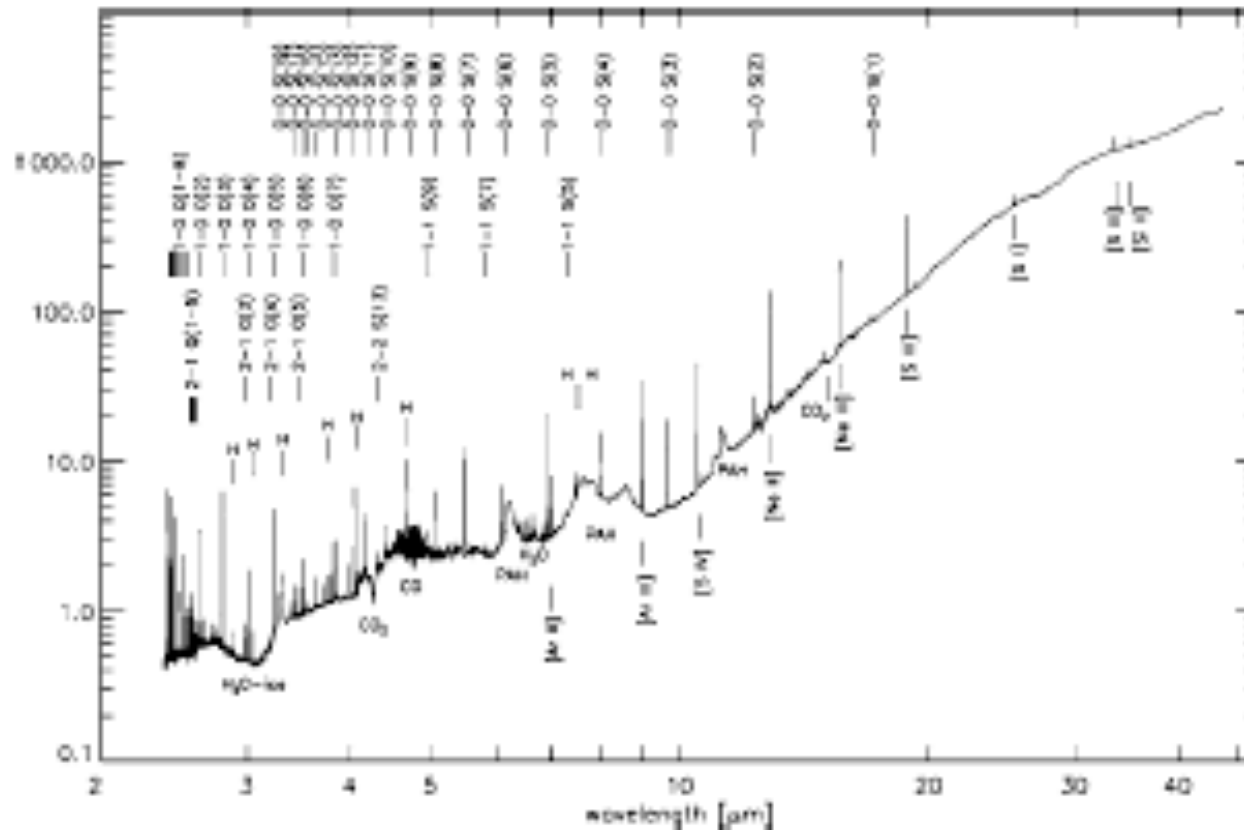
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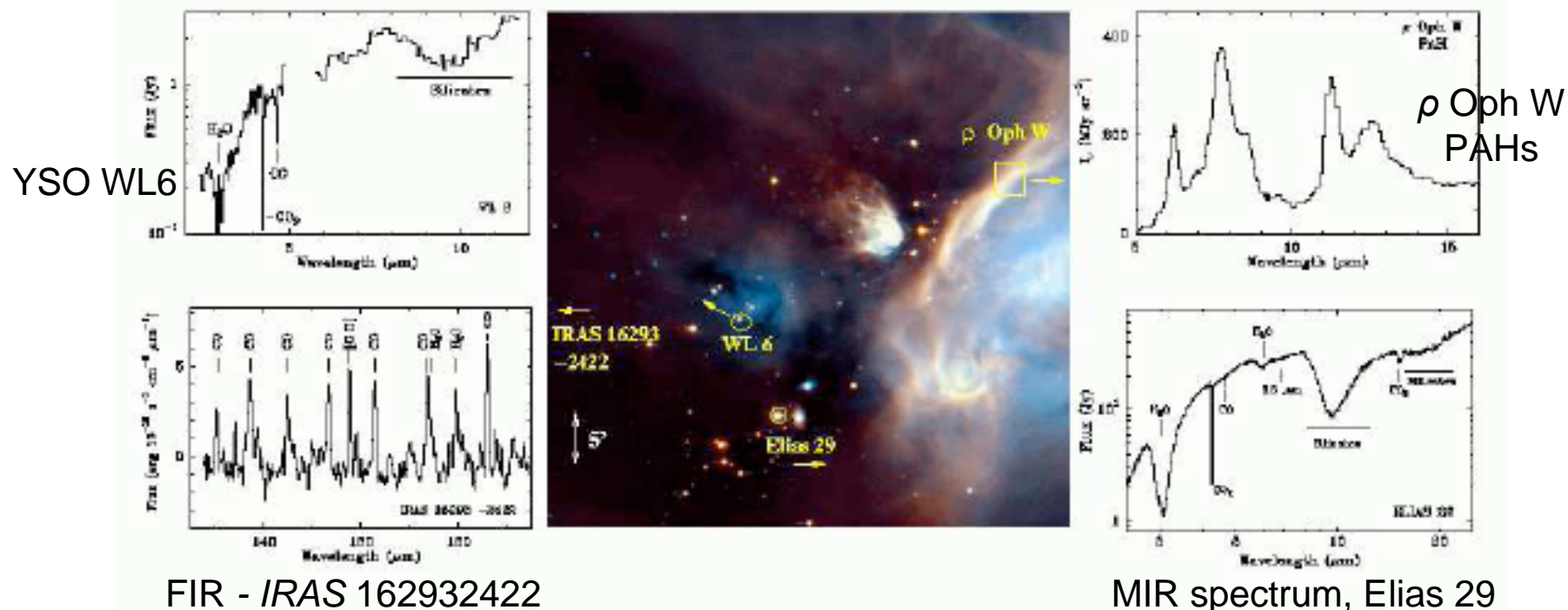# ISO NIR-MIR Spectrum of a Shock in Orion

Figure 3   SWS grating scan of the Orion Peak 1 shock, showing a rich forest of H_2 lines and other features (Rosenthal et al. 2000).

Rich forest of H lines plus PAH features, fine structure and molecular lines
(E. van Dishoeck ARAA 42 119 2004)

Molecular Spectra of the ρ Oph Molecular Cloud
E. van Dishoeck, ARAA 42 119 2004

YSO WL6

ρ Oph W PAHs

FIR - *IRAS* 162932422

MIR spectrum, Elias 29

Major IR Space Observatories
IRAS 1983
COBE 1991
ISO 1996
Spitzer 2003
Herschel 2009

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Figure 1 (color). ISOCAM composite 7 and 15 μm image of the ρ Oph molecular cloud. The bright filaments in the west trace the hot dust illuminated by the B2V star HD 147889 located just outside the map. The dense cloud containing IRAS 16293 -2422 is to the east. The dark patches are very dense cores which are optically thick even at 15 μm, whereas the bright point sources throughout the image are low-mass YSOs. Most of the extended 7μm emission is due to PAHs (Abergel et al. 1996). Spectra of various objects in ρ Oph are indicated on the side. Left Top: PHOT-S spectrum of WL 6 (Gürtler et al., unpublished); Right Top: CAM-CVF spectrum of ρ Oph W (Boulanger et al. 2000); Left Bottom: LWS spectrum of IRAS 16293 -2422 (Ceccarelli et al. 1998a); Right Bottom: SWS spectrum of Elias 29 (Boogert et al. 2000b).

Fine structure transitions

Atoms and ions with non-zero spin and orbital angular momentum have fine-structure transitions at MIR-FIR wavelengths. For the most abundant heavy atoms, the low-ionization carriers are (wavelengths in microns):

Atom	I	II	III
C ($^3P_{2,1,0}$)	370.4 609.1	157.7	
N ($^4S_{3/2}$)		120.9 205.2	57.32
O ($^3P_{0,1,2}$)	145.5 63.18		51.81 88.36

Molecular Emission

Containing more than one nucleus, molecules can have *vibrational and rotational* as well as electronic motion, with transitions extending from FUV to mm wavelengths.

Electronic bands in the Optical and UV instead of single transitions, e.g. the H_2 Lyman and Werner bands near 1100 Å, seen in UV absorption line spectra

Vibrational transitions in the NIR-MIR e.g., H_2 1-0 S(1) at 2.12 µm and CO v=1-0 at 4.6 μm

Rotational transitions in the MIR–FIR e.g., H_2 0-0 S(0) at 28.2 µm & CO J=1-0 at 2.6 mm

Early History of Interstellar Molecules

First optical detections:

CH	4300 Å	Dunham et al. (1937)
CN	3876 Å	Swings & Rosenfeld (1937)
CH^+	4235 Å	McKellar (1940)

Radio detections

[predicted by Townes & Shklovsky (1950s)]

OH	18 cm	Weinreb et al. (1963)
NH_3	1.3	Cheung et al. 1968, 1969
H_2O	1.4 cm	"
H_2CO	6.2 cm	Snyder at al. (1969)
CO	2.6 mm	Wilson, Jefferts, & Penzias (1970)

UV detection

H_2	1008 Å	Carruthers (1970)

2. Molecular Structure

The many novel and complex aspects of molecular structure are greatly simplified by the **Born-Oppenheimer Approximation**, based on the fact that because of their large mass, nuclei move much slower than the electrons.

$$E \cong E_{rot} + E_{vib} + E_{el}$$

$$E_{rot} \approx 10^{-3} - 10^{-2}\, eV, \quad E_{vib} \approx 10^{-2} - 10^{-2}\, eV, \quad E_{el} \approx 1 - 10\, eV$$

Averaging the energy over the fast electronic motion gives the nuclear potential energy as a function of the nuclear separations. This is a *frozen nucleus approximation.*
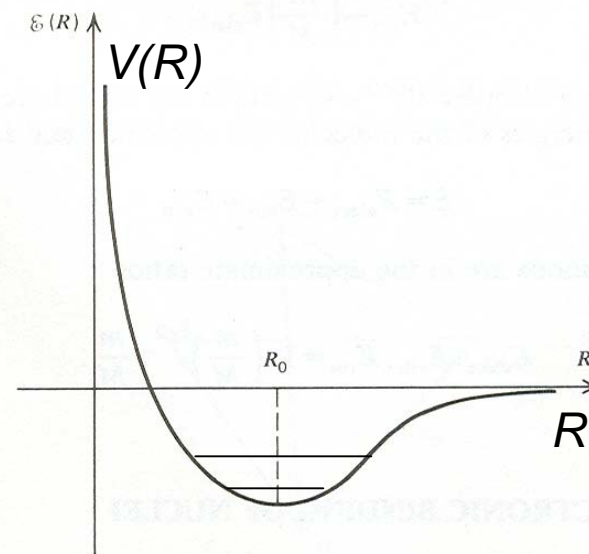

Figure: Schematic potential for a diatomic model, with asymptotic R^{-6} van der Waals interaction and anharmonic oscillator potential at minimum

Rigid Rotational Motion

The signature example of free rotation in the Born-Oppenheimer approximation is the rigid rotor, whose energy levels are given by the well-known expression

$$E_J = J(J+1)B \qquad B = \frac{\hbar^2}{2I}$$

The moment of inertia of a diatomic molecule is $I = m_{12}r_{12}^2$. With typical separations of Angstroms, I is determined mainly by the reduced mass. e.g., for the two most abundant interstellar molecules, the rotational constants are

$$m_{12}(H_2) = 0.5m_H \qquad B(H_2) = k_B \ (85.3 \ K)$$
$$m_{12}(CO) = 6.86 \ m_H \qquad B(CO) = k_B \ (2.77K)$$

The value for CO doesn't quite scale because the CO molecule is larger (by 50%) because its atoms have several electronic shells

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Going Beyond Born and Oppenheimer

According to the Born-Oppenheimer model, the nuclei rotate freely and rigidly and vibrate about their equilibrium configuration. Not only are there corrections when the rotation and vibration are fast, but interactions between orbital and spin angular momenta produce long wavelength spectral features.

1. **Hyperfine Transitions** – Clouds with molecules are partially atomic, so the classic H I 21-cm transition remains relevant. In addition, molecules with non-zero nuclear spin add hyperfine structure to molecular spectra, the primary examples being the main nitrogen isotope ^{14}N ($I = 1$) and the isotopes of carbon and oxygen ^{13}C ($I = 1/2$) and ^{17}O($I = 1/2$),

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2. **Λ-Doubling** – A form of molecular spin-orbit coupling. Λ is the projection of the orbital angular momentum on the symmetry axis of a molecule. The splitting in OH has a convenient wavelength of ~ 18 cm.

3. **Inversion Splitting -** Pyramidal molecules may undergo tunneling inversion at a specific wavelength, e.g., ~ 1 cm in NH_3. It provides an excellent thermometer for molecular regions.

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4. **Radio-Recombination Lines** – Transitions between atomic levels of high principal quantum number (Rydberg states) range form cm to mm wavelengths (for n > 50 and n < 30). The small A-values may be compensated by a tendency for masing. OH and H_2O can make strong interstellar masers

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3. Molecular Levels and Spectra

A. Electronic Levels - The levels are determined by the electrical potential, which differs profoundly from atoms. Some general perspective comes from *symmetry* considerations, often formalized by group theory. For example, the spherical symmetry of atoms is replaced by *cylindrical symmetry* for linear molecules, which includes the important case of diatomic molecules such as CO and H_2.

A useful starting point for diatomic molecules is the **unified atom** concept (c.f., Herzberg 1971), e.g., H_2^+ looks like He^+ at large distance (they should have the same Rydberg high excitation levels). In this case, the electrons have the usual hydrogenic *nl* level sequence*:*

$$1s; \ 2s,2p; \ 3s,3p,3d; \ \text{etc.}$$

In the presence of strong electric fields along the axis of the diatomic molecule, only the projection of the orbital angular momentum is conserved (now called λ), and values of this projection are labeled by the Greek letters corresponding to the atomic *s, p*, d, etc., as in

$$1s\sigma; \ 2s\sigma, \ 2p\sigma, \ 2p\pi; \ 3s\sigma, 3 \ p\pi, 3d\sigma, 3d\pi, 3d\delta; \ \text{etc.}$$

Electronic Levels

In the sequence,

1sσ; 2sσ, 2pσ, 2pπ; 3sσ,3 pπ,3dσ,3dπ,3dδ; etc.

$\lambda = 0$ for σ states and $\lambda = \pm 1$ for π states, etc., so the number of sub-states is preserved.

NB An alternate description of the electronic wave functions is to express them as linear superpositions of the *isolated atom* wave functions, so-called *molecular orbitals*. See Lecture17-06 for an illuminating discussion of molecular orbitals.

The total orbital angular momentum *projection* is the sum of the individual values of λ. It is represented by the symbol Λ, and it may be considered as a vector along the symmetry axis. Again, in analogy with atomic spectra, the magnitudes of the projections are labeled by the sequence ($|\Lambda| = 0$, 1, 2, etc):

$$\Sigma, \Pi, \Delta, \text{ etc}$$

The states for $|\Lambda| > 0$ are doubly degenerate.

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Spectroscopic Notation for the Electronic Levels

The total electronic angular momentum is the sum of orbital and spin, $\Lambda + S$. The spins are unaffected by the spatial symmetry so there are the usual $2S+1$ sub-levels. Thus electronic states are denoted as

$$^{2S+1}\Lambda \quad \text{or} \quad {}^{1,3}\Sigma, \, {}^{1,3}\Pi, \, {}^{1,3}\Delta, \text{ etc}$$

A parity symbol may be added to indicate whether the wave function is even or odd under inversion in the plane perpendicular to the symmetry axis, as in $^{2S+1}\Lambda^{\pm}$. For homonuclear molecules the behavior of the spatial wave function under inversion, as in the case of H_2, is indicated by the label g or u, for the German gerade (even) or ungerade (odd), as in $^{2S+1}\Lambda^{\pm}_{g,u}$.

Finally, electronic states are ordered roughly in energy by letters, with the ground state being X and excited states with letters starting at the beginning of the alphabet. For example, the ground state of H_2 is $X \, ^1\Sigma^+_g$.

B. 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 inertia tensor) with corresponding simple expressions for the rotational energy and angular momentum.

- – This carries over to quantum mechanics, and 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 designated

I_a, I_b, *and* I_c *in order of increasing magnitude*

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Linear Molecules & Symmetric Tops

- A molecule which is linear or has an axis of rotational symmetry is called a ***symmetric top***

- Either $I_c = I_b > I_a$ or $I_c > I_b = I_a$

  - Linear molecules have a small I about the axis of the molecule so they are of the first type and are called ***prelate symmetric tops***

  - Other molecules, e.g., benzene, have the largest moment of inertia about the symmetry axis & are called ***oblate symmetric tops***

  - Molecules which are spherically symmetric, e.g, methane have three equal moments of inertia and are called ***spherical tops***

- Molecules with $I_c \neq I_b \neq I_a$ are ***asymmetric tops***

Energy of a Symmetric Top

- Classically, the energy of rotation is

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

$$= \frac{J_x^2}{2I_x} + \frac{J_y^2}{2I_y} + \frac{J_z^2}{2I_z}$$

- Suppose $I_x = I_y = I_b$. Since $J^2 = J_x{}^2 + J_y{}^2 + J_z{}^2$

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

The next step is to quantize these classical expressions.

Energy of a Symmetric Top

Both the square & the *projection* on the symmetry axis
of the angular momentum are good quantum numbers.

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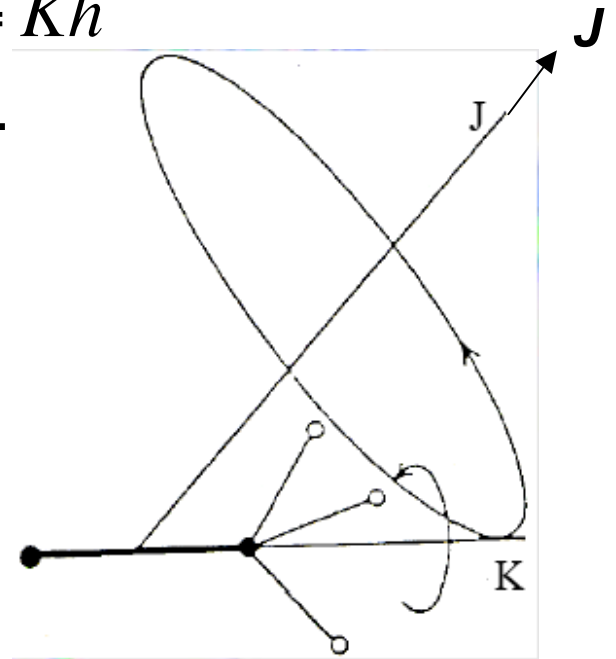usually denoted M_z and enters into the Zeeman effect.

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

$J = 0, 1, 2\dots, \qquad |K| = 0, 1, 2, ..$

Hence the rotational energy is

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

$$E = BJ(J+1) + (C-B)K^2$$

on introducing the *rotational constants B & C.*

Facts of Life 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) $C-B > 0$: levels increase with K
- For an oblate top (pancake) $C-B < 0$: levels decrease with K
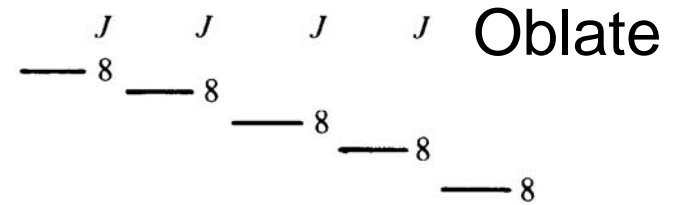- $K=0$ reduces to the simple rotational ladder of a linear molecule

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 .

Energy Levels for Symmetric Tops

Prolate

Oblate

J
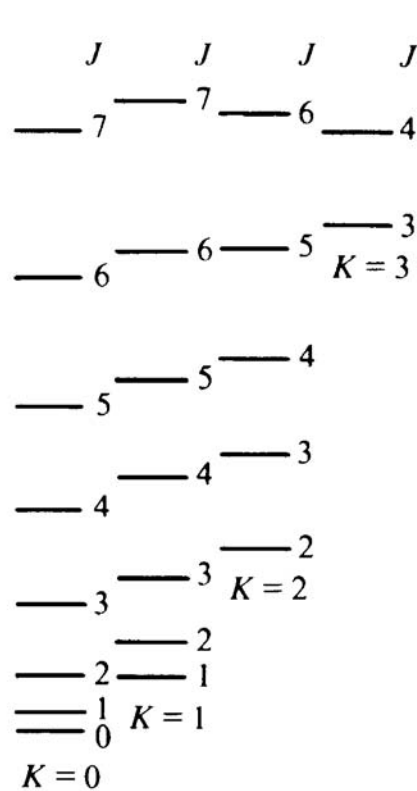
Allowed transitions are up and down fixed K ladders (slide 22).

C. Vibrational Energies

The rotation and and vibration changes the rotational and vibrational frequencies, especially for large J and v. In addition to the anharmonicity of the vibrational potential energy, the vibrations and rotations change the moment of inertia. These effects are well illustrated by the formulae employed by Herzberg to make precision fits to molecular spectra (in wave numbers):

$$k = F(v) + G(v)$$

$$F_v(J) = B_v J(J+1) - D_v [J(J+1)]^2 + \cdots$$

$$G(v) = \omega_e (v + \tfrac{1}{2}) - \omega_e x_e (v + \tfrac{1}{2})^2 + \cdots$$

$$B_v = B_e - \alpha_e (v + \tfrac{1}{2}) + \cdots$$

# 4. Radiative Properties of Molecules

Rotational Transitions – Only molecules with a *permanent dipole moment* can generate a rotational spectrum. Molecules like H_2, C_2, O_2, CH_4, C_2H_2, do not have strong rotational spectra. For symmetric molecules like H_2, only quadrupole transitions ($\Delta J = 2$) occur, e.g. $\lambda(2 \to 0) = 28$ µm.

b. 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.

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Ro-Vibrational Transitions

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

v',J' ———————————|——————

$v',0'$ —————————— 1st level in v' band

v'',J'' ————————▼————————

$v'',0$ —————————— 1st level in v'' band
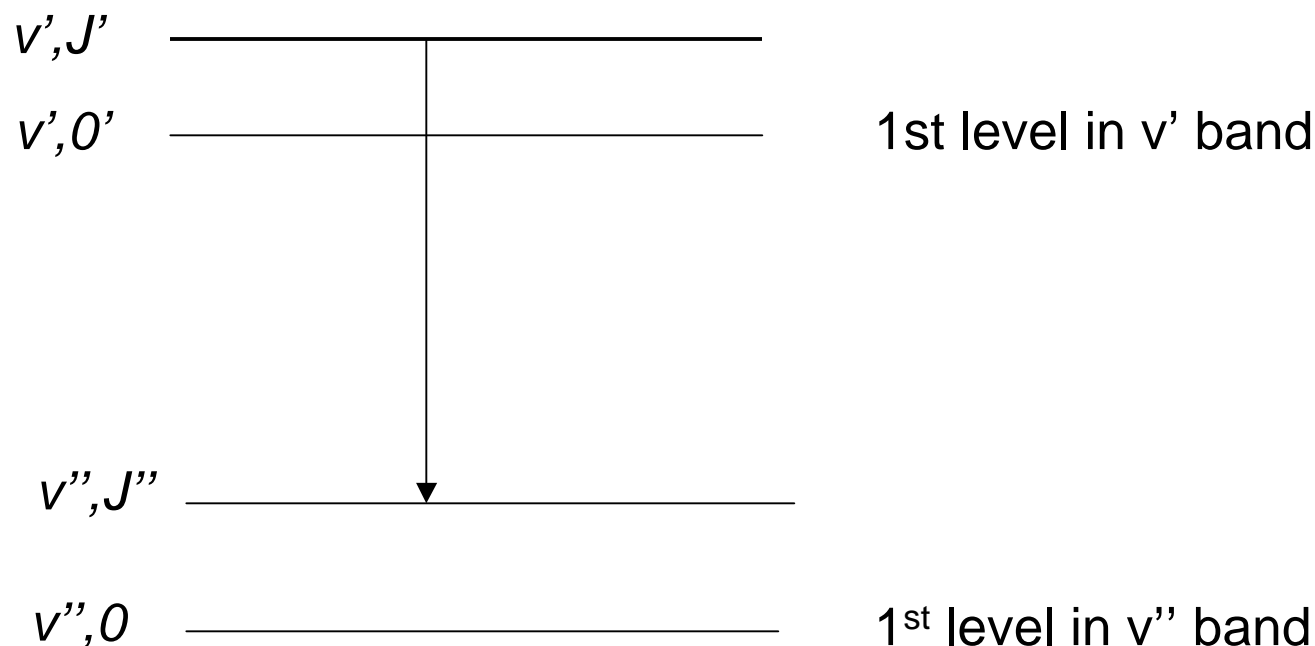
For dipole transitions, $\Delta J = 0,\ \pm 1$ allows three possibilities:
P-transitions: $J'=J''-1$, i.e., 0-1, 1-2, etc.
R-transition: $J'=J''+1$, i.e., 1-0, 2-1, etc,
Q-transitions $J'=J''$, i.e., 1-1, 2-2, etc,

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A-value for Dipole Radiation From a Simple Rotor

The standard atomic formulae are slightly changed:

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

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

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

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

Rotational Transition Progression

For the *pure rotational spectrum* of a rigid rotor, the photon energy in the transition *J'=J→ J''=J-1,*

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

generates the sequence 2*B*, 4*B*, 6*B* ... . For the *ro-vibrational spectrum*, the transitions involve the fixed energy difference between the vibrational levels (and the electronic levels for an optical or UV transition) plus the difference in rotational energies:

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

For no change in the electronic state, *B'* & *B''* are about the same. Substituting the appropriate changes for *R* and *P* transitions, *J'=J''+1* & *J'=J''-1* respectively, yields:

$$\Delta E(v'J', v''J'')_R = \Delta E(v', v'')_{vib} + 2BJ'$$

$$\Delta E(v'J', v''J'')_P = \Delta E(v', v'')_{vib} - 2B(J'+1)$$

The *R*-transitions generate a sequence of rovib transition energies just like a simple rigid rotor, with energies laddered on top of the reference energy (the difference between the first level in each vibrational energy potential).

The *P*-transitions generate the opposite sequence of rovib transition energies with energies laddered below the reference energy

<center>

-6*B*   -4*B*   -2*B*   0   2*B*   4*B*   6*B*

P-transitions   *R*-transitions

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P and R Branch Transitions
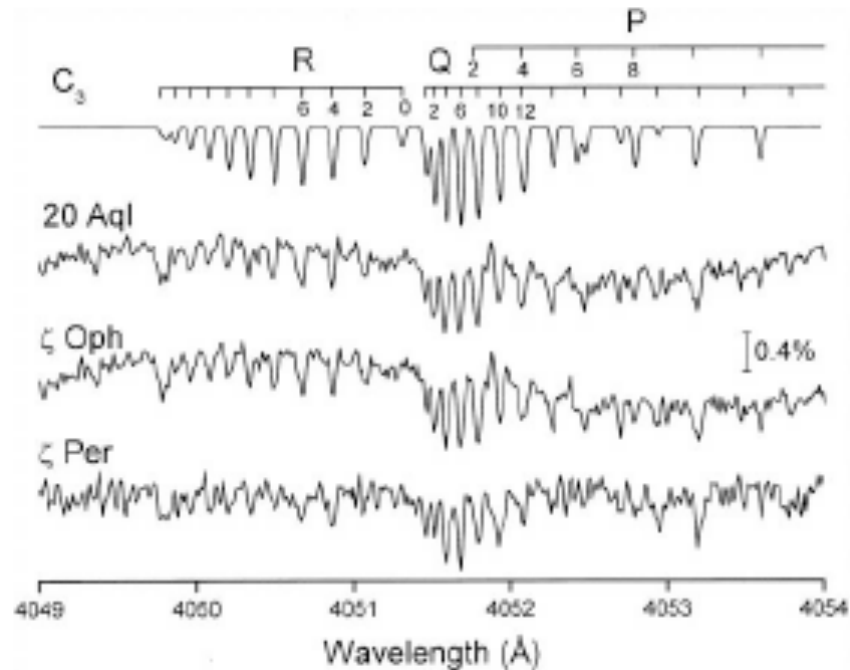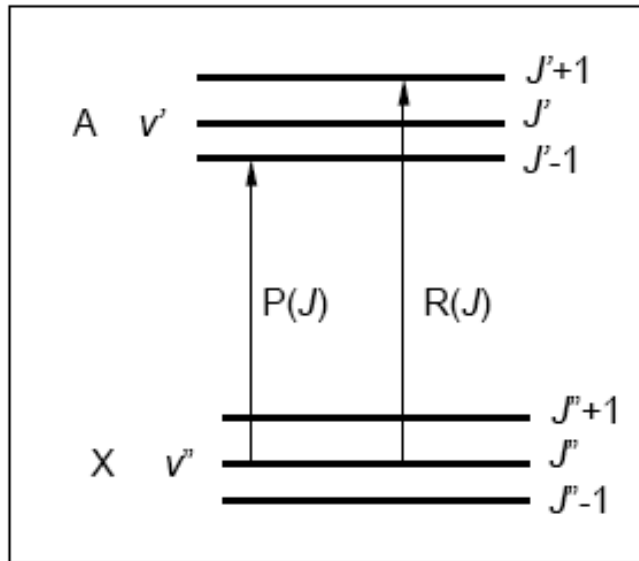
Interstellar absorption lines of C_3 for the X $^1\Sigma_g$ --> A $^1\Pi_u$ transition.
Top is a synthetic spectrum for $T = 80$ K and spectral resolution of 10^5.