

Goals for Part II - The Dense ISM

To describe some of what's known about the dense ISM, which is relatively cool (< 100 K) and dense ($> 100 \text{ cm}^{-3}$). Its distinguishing features are

- (1) the presence and important role of molecules
- (2) star formation occurs in the dense ISM

- In the first section, *Molecular Spectroscopy and Chemistry*, we attempt to provide a molecular physics basis for both observational and theoretical studies of the dense ISM.
- In the second section, *Molecular Clouds and Star Formation*, we apply this knowledge to recent research results.

Caveat emptor - Considering the complexity of molecular physics, our treatment of molecular spectroscopy is necessarily elementary. We will often use the familiar example of a diatomic molecule to communicate basic ideas and insights.

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Lecture Plan for Part II - The Dense ISM

A. Molecular Spectroscopy and Chemistry

- Lec 17 Introduction to molecular spectroscopy
- Lec 18 Rotations and vibrations
- Lec 19 H_2 and CO
- Lec 20 Three special molecules - OH, H_2O , NH_3
- Lec 21 Introduction to interstellar chemistry
- Lec 22 Molecular ions and fractionation

B. Molecular Clouds and Star Formation

- Lec 23 Photon dominated regions
- Lec 24 CO observations of molecular clouds
- Lec 25 Physical properties of molecular clouds
- Lec 26 Clouds, clumps and cores
- Lec 27 Stability of molecular clouds and cores
- Lec 28 From cores to disks around young stellar objects

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Lecture 17 Molecular Spectroscopy I

I write about molecules with great diffidence, having not yet rid myself of the tradition that atoms are physics, but molecules are chemistry, but the new conclusion that hydrogen is abundant seems to make it likely that the above-mentioned elements C, O, and N will frequently form molecules.

Sir Arthur Eddington (1937)

Today we say, “*Atoms, molecules, and solids are astrophysics*”

Topics

1. Long Wavelength Observational Signatures
2. Introduction to Molecular Structure
3. Notation for Electronic Levels
4. First Remarks on Vibrational Levels

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Reference Texts

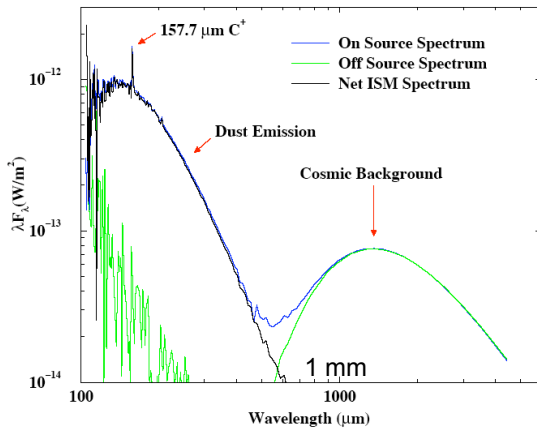
1. **Authoritative Classic** - Townes & Schawlow, *Microwave Spectroscopy* (1955, Dover 1975)
2. **Astro Texts**
Shu, *Physics of Astrophysics I*, Ch. 28-30
Rybicki & Lightman, *Radiative Processes*, Ch.11
Tielens, *Physics and Chemistry of the ISM*, Sec. 2.1-2.2
Palla & Stahler, *The Formation of Stars*, Ch. 5
3. **Molecular Physics Books**
Herzberg, *The Spectra & Structure of Simple Free Radicals* (Cornell 1971), condensation of the 3-volume classic:
Molecular Spectra & Molecular Structure (van Nostrand, 1939-1966)
Steinfeld, *Molecules and Radiation* (Dover 1985)
4. **Lecture Notes** - Lecture 17 for AY216-2006, James Graham
5. **Data base** - <http://physics.nist.gov/PhysRefData/MolSpec/index.html>

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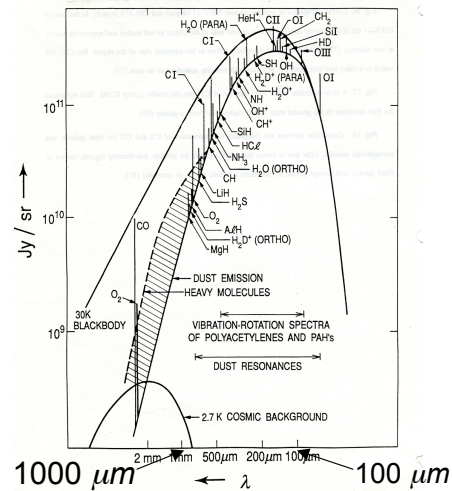
1. Long Wavelength Signatures of the Cool ISM

Long wavelength spectra of the ISM are dominated by *dust* and *molecules*.



COBE 100-1000 μm
low resolution spectrum
of the Galactic plane.

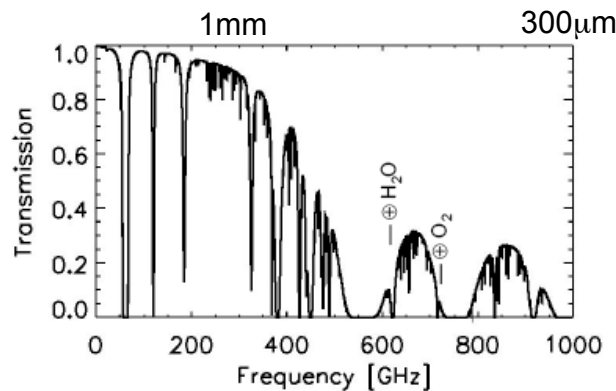
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Phillips & Keene
Proc IEEE 80 1662 1992
synthetic spectrum of a
molecular cloud

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The Problem of Atmospheric Transmission



Sub-mm transmission from Mauna Kea with 1mm H₂O
The 300-1000 μm band covers the maximum of the galactic emission

For more detailed Mauna Kea transmission factors:
<http://www.submm.caltech.edu/cso/weather/atplot.shtml>

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Milestones in Infrared Space Astronomy

Major IR space observatories of the last 25 years:

Kuiper Airborne Observatory	1974	(0.9m)
IRAS	1983	(0.6m)
COBE	1990	(0.2m)
ISO	1995	(0.6m)
<i>SPITZER</i>	2003*	(2.4m)
<i>HERSCHEL</i>	2009	(3.5m)
SOFIA	2011	(2.5m)
<i>WEBB</i> (NGST)		(6.5m)

* Same size as HST

An important goal of these systems is the detailed study of **small particles** (dust and aromatic polycyclic hydrocarbons, or PAHs) and **molecules** in the ISM.

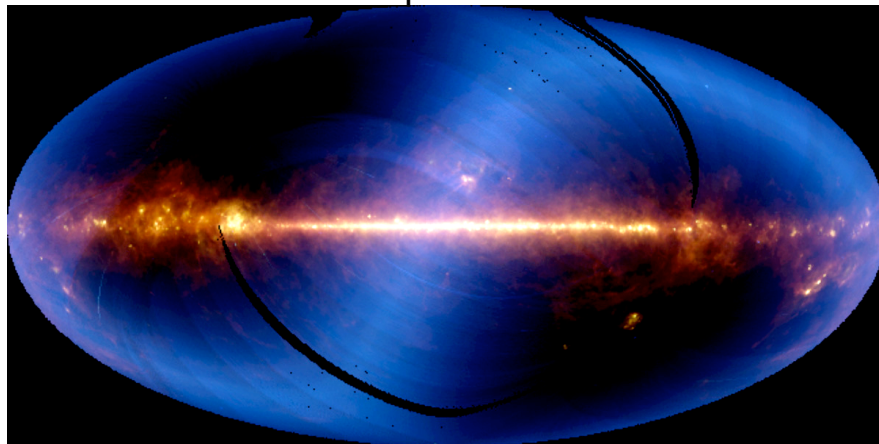
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IRAS All Sky Image of the Milky Way

(0.5° resolution)

Ophiuchus



Zodiacal light (S - shape)

LMC

Orion

Blue: 12 μm
Green: 60 μm
Red: 100 μm

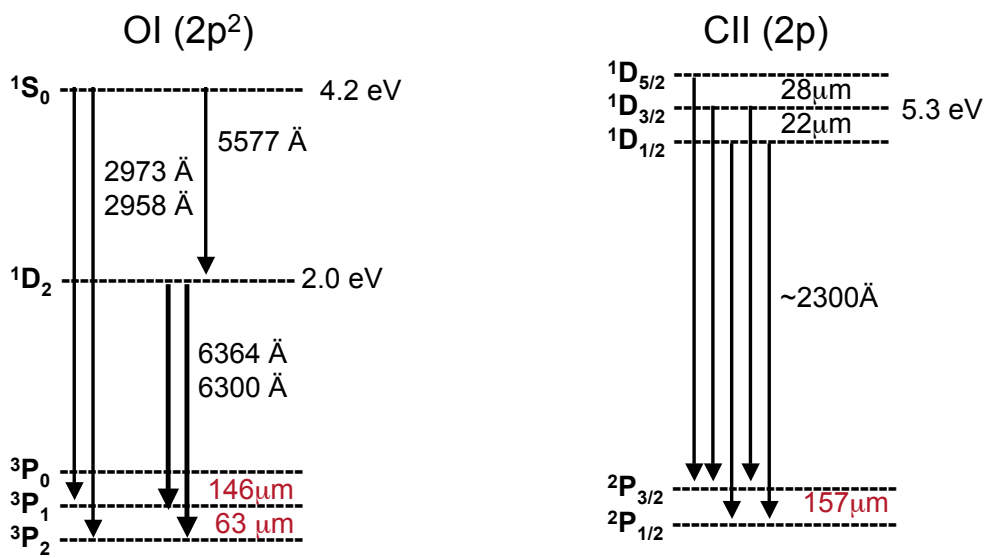
Notice the wide distribution of 100 μm "cirrus" emission just outside of the Milky Way plane.

Galactic coordinates with $l = 0$ at center

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Examples of Fine Structure



The order of magnitude of the fine-structure splitting is $\alpha = 1/137$
 ~ 0.01 times the separation of the electronic energies, or ~ 0.01 eV

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Molecular Transitions

With more than one nucleus in a molecule, the nuclei undergo *vibrational and rotational* motion and generate long wavelength transitions from the NIR- mm.

Electronic bands in the Optical and UV -

Electronic transitions develop a band structure, e.g. the H₂ Lyman and Werner bands seen in absorption line spectra below 1100 Å

Vibrational transitions in the NIR-MIR e.g., H₂ 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., H₂ 0-0 S(0) at 28.2 μm & CO J=1-0 at 2.6 mm

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Early Record 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*

OH	18 cm	Weinreb et al. (1963)
NH ₃	1.3	Cheung et al. 1968, 1969
H ₂ O	1.4 cm	"
H ₂ CO	6.2 cm	Snyder et al. (1969)
CO	2.6 mm	Wilson, Jefferts, & Penzias (1970)

* predicted by Townes & Shklovsky (1950s)

UV detection

·	H ₂	1008 Å	Carruthers (1970)
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2. Introduction to Molecular Structure

The presence of several *nuclei* makes molecules more complicated than atoms:

1. The electrons move in an average potential with several force centers that is no longer spherically symmetric.
2. The symmetry of the wave-function is reduced.
3. The nuclear degrees of freedom can be described in semi-classical terms as rotation and vibration.

Using just the nuclear separation a and the Uncertainty Principle, Shu (I, Ch, 28) and Rybicki & Lightman (Ch. 11) show that the characteristic energies for the motions of the electrons (mass m) and nuclei (mass M) have these ratios:

$$E_{\text{rot}} : E_{\text{vib}} : E_{\text{el}} \approx \frac{m}{M} : \left(\frac{m}{M}\right)^{1/2} : 1$$

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

These frequencies increase as powers of $(M/m)^{1/2} \gg 1$.

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Born-Oppenheimer Approximation

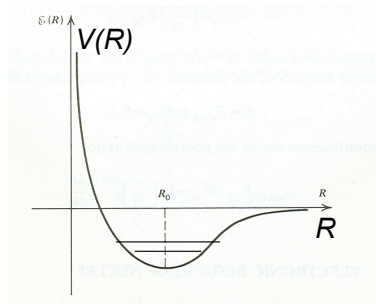
The disparate time scales mean that the three motions are quasi-independent and that the overall molecular state (wave function) can be written as three factors. Shu Ch. 28 (and other texts) derive the three wave equations, which in first approximation are:

Rotation - Quantized motion of a rigid rotor

Vibration - Slightly anharmonic motion about equilibrium

Electronic - Independent electrons moving in the non-spherical average electrical field of the nuclei and the other electrons.

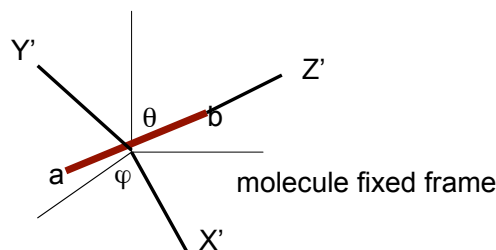
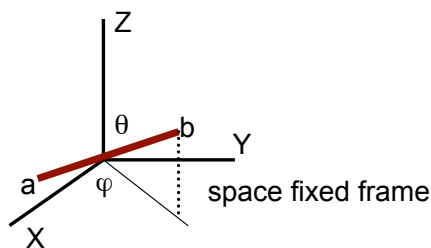
Example of a neutral diatomic molecule:
Averaging the total potential energy over the fast electronic motion gives the nuclear potential energy as a function of the separation R : Strongly repulsive at small R , anharmonic oscillator near the minimum, and $V(R) \sim R^{-6}$ (van der Waals) at large R



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Diatomic Molecules



The internuclear separation in a diatomic molecule defines a symmetry axis. The wave function for a simple rotor with two degrees of freedom (θ, φ) is the spherical harmonic $Y(\theta, \varphi)_{JM}$ with energy $BJ(J+1)$.

More generally, the symmetry of the energy determines the conserved quantities and the good quantum numbers.

The energy of a diatomic molecule has cylindrical symmetry.

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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.

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

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. For the two most abundant interstellar molecules, the rotational constants are

$$m_{12}(\text{H}_2) = 0.5m_{\text{H}} \quad B(\text{H}_2) = k_{\text{B}} (85.3 \text{ K})$$
$$m_{12}(\text{CO}) = 6.86 m_{\text{H}} \quad B(\text{CO}) = k_{\text{B}} (2.77\text{K})$$

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

N.B. The rotational spectra of more complicated molecules will be discussed in subsequent lectures.

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Conserved Quantities for a Diatomic Molecule

1. Invariance under rotations of the space-fixed frame implies conservation of total angular momentum and its z component J, J_z with quantum numbers $J = 0, 1, 2 \dots$ and $M = -J, -J+1 \dots J$.
2. There is no rotation about the symmetry axis; $J_z^{\text{rot}} = 0$.
3. Other conserved quantities: in the absence of magnetic interactions, the total nuclear spin and its z component (I, I_z), e.g., for two half-integral spins like H_2 , $I = 0$ ("para"), 1 ("ortho").
4. Under the same restrictions, the electronic spin angular and its z' projection are conserved.
5. The total *orbital* angular momentum of the electrons is not conserved (cylindrical potential), only the z' component denoted by Λ .

N.B. For the symmetric tops discussed in the next lecture, the z' component of rotational angular momentum on the symmetry axis J_z is conserved. Its values are $K = -J, -J+1 \dots +J$ (or $K = 0, \pm |1|, \pm |2| \dots$).

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H₂⁺ - The Simplest Molecule

The angular momentum of the nuclei is described by nuclear spin states, $I = 0$ (para) and 1 (ortho). Nuclear exchange involves $\theta \rightarrow \pi - \theta$, $\varphi \rightarrow \varphi + \pi$, which changes $Y(\theta, \varphi)_{JM}$ by $(-1)^J$. Thus para (ortho) states must have even J (odd J).

The electron's potential energy is

$$V = -\frac{e^2}{|r - R_a|} - \frac{e^2}{|r - R_b|} + \frac{e^2}{R_{ab}}$$

Close to a nucleus, this is H-like; far from both, He⁺-like. The ground-state energy is determined by how close the electron gets to the nuclei.

A standard way of estimating the ground state energy uses linear combinations of scaled H ground state wave functions ψ_0 for the electron wave function (Rybicki & Lightman, Sec. 11.2)

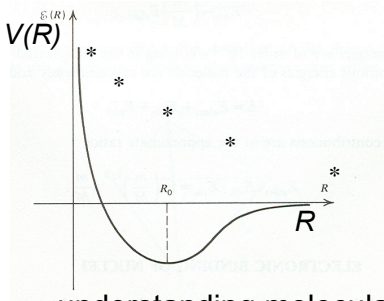
$$\psi_{\pm}(r) = C_{\pm} [\psi_0(\eta | r - R_a |) \pm \psi_0(\eta | r - R_b |)]$$

These wave functions have been chosen to have well defined symmetry under inversion, i.e., even (+) or odd (-) parity; η is a variational parameter.

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Nuclear Potential Energy Curves for H₂⁺ and H₂



Averaged over the ψ_{\pm} , the results are:
solid curve - *symmetric* wave function with no nodes producing binding
dotted curve - *anti-symmetric* wave function with node between the nuclei that prevents binding

The case of H₂⁺ points the way to understanding molecular binding, i.e., the “nature of the chemical bond”, in terms of electron wave functions that maximize the role of the electron-nucleus attraction.

With one electron, H₂⁺ is weakly bound: $B = 2.65$ eV and $a = 1.1$ Å.

The two electrons in H₂ produce $B = 4.48$ eV and $a = 0.74$ Å.

The potential energy curves for H₂ are similar to those for H₂⁺.

The binding potential has a symmetric spatial wave function ($S = 0$); the repulsive potential has an anti-symmetric spatial wave function ($S = 1$). Two shared electrons define the “covalent” chemical bond.

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3. Electronic Levels

The electronic energy levels are determined by the electrical potential. Considerable insight comes from symmetry considerations, often systematized by group theory (see Seinfeld's text). For linear molecules like H_2^+ and H_2 (plus many others of astrophysical interest) spherical symmetry of atoms is replaced by *cylindrical symmetry*.

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 have the same "Rydberg" or high excitation levels). In this case, the electrons have the usual hydrogenic n/l level sequence:

1s; 2s, 2p; 3s, 3p, 3d; etc.

An alternate description of the electronic wave basis functions uses linear superpositions of the *isolated atom* wave functions, so-called *molecular orbitals*. These were used above for H_2^+ . Lecture 17 of Ay216-2006 contains an illuminating discussion of molecular orbitals by James Graham.

N.B. The energy levels of H_2 will be discussed in detail in Lecture 19

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Nomenclature for Molecular Orbitals

In the presence of strong electric fields along the axis of a diatomic molecule, only the projection of the orbital angular momentum is conserved (generically called λ). The values of this projection are included as Greek letters while retaining the original atomic s , p , d , etc., notation, as in

1s σ ; 2s σ , 2p σ , 2p π ; 3s σ , 3p π , 3d σ , 3d π , 3d δ ; etc.

Thus, $\lambda = 0$ for σ states and $\lambda = \pm 1$ for π states, etc. The number of sub-states is preserved, e.g., the $2p\sigma$ and $2p\pi$ levels together have the three sub-states associated with $l = 1$.

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):

Σ, Π, Δ , etc.

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

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Spectroscopic Notation for Electronic Levels

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

$^{2S+1}\Lambda$ or more specifically: $^1\Sigma, ^3\Sigma; ^1\Pi, ^3\Pi; ^1\Delta, ^3\Delta$; 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 $^{2S+1}\Lambda_{g,u}^\pm$.

Finally, electronic states are ordered roughly in energy by letters, with the ground state being X and excited states having letters starting at the beginning of the alphabet. For example, the ground state of H_2 is **X** $^1\Sigma_g^+$, i.e., even under both inversion and reflection.

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4. The Vibrational Excitations

The vibrational levels correspond to relative motions of the nuclei. They are determined by the spatial location of the nuclei and the electrical forces between them. Otherwise they are unaffected by the overall symmetry of the molecule, e.g., the vibrational energy is a quadratic function and therefore symmetric under the parity operation.

Recalling the quantum oscillator, the energy levels have the form

$$E(\nu) = (\nu + 1/2) h\nu$$

where ν is the fundamental frequency of the oscillator. For polyatomic molecules with F (> 3) vibrational degrees of freedom, one solves the normal mode problem using techniques from classical mechanics. Labeling the modes with the index k , the vibrational energy is

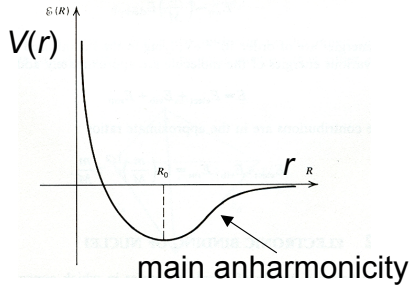
$$E_{\text{vib}} = \sum_k (\nu_k + 1/2) h\nu_k$$

The main problem with this seemingly straightforward use of the Born-Oppenheimer approximation is that, for large amplitude oscillations (large ν) - the anharmonicity of the nuclear potential is significant.

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Anharmonic Oscillator



The simplest way to deal with the anharmonicity is to expand the potential around the minimum in a power series in the displacement from the minimum:

$$V = 1/2 k(r - r_0)^2 - g(r - r_0)^3 + \dots \quad (g \ll k)$$

This leads to a series expansion in the energy,

$$E_v = h\nu \left[(v + 1/2) - x(v + 1/2)^2 + y(v + 1/2)^3 \right] \quad (y \ll x \ll 1)$$

We follow Herzberg's notation and measure energy (differences) in wave numbers k (cm^{-1}) [$h\nu = ch/\lambda = chk$]:

$$G_v = \omega_e \left[(v + 1/2) - x_e(v + 1/2)^2 + y_e(v + 1/2)^3 \right]$$

For CO as an example, $\omega_e = 2170 \text{ cm}^{-1}$, $x_e = 0.0622$ and $y_e \sim 10^{-5}$

A Step Beyond Born and Oppenheimer

So far, we have taken the Born-Oppenheimer approximation at face value and considered the electronic, vibrational and rotational motions as completely independent. Other than magnetic interactions, the most important correction is *centrifugal stretching*, which reduces the rotational frequencies for large J . A simple derivation starts by writing the vibrational and rotational energies as:

$$V_{\text{vib}} = 1/2 k(r - r_0)^2, \quad V_{\text{rot}} = \frac{J^2}{2mr^2}$$

Balancing the centrifugal force against the oscillator restoring force,

$$k(r_c - r_0) = \frac{J^2}{mr_c^3}, \quad \text{or} \quad r_c = r_0 + \frac{2}{kr_0} E_0, \quad \text{with} \quad E_0 = \frac{J^2}{2mr_c^2}$$

Replacing J^2 by $J(J+1)$ and substituting r_c into V_{rot} leads to a reduction in the rotational energy

$$V_{\text{rot}} = \frac{J(J+1)}{2mr_c^2} = \frac{J(J+1)}{2m(r_0 + 2E_0/kr_0)^2} \cong E_0(1 - 4E_0/kr_0^2 + \dots)$$

Centrifugal Stretching

Herzberg expresses this last result as a series in $J(J+1)$:

$$F_v(J) = E_v(J)/ch = B_v J(J+1) - D_v [J(J+1)]^2 + \dots$$

D_v is small, and the stretching is small for small J , but not necessarily negligible considering spectroscopic accuracy.

For CO, $B_v = 1.922529 \text{ cm}^{-1}$ and $D_v = 6.1206 \times 10^{-6} \text{ cm}^{-1}$.

Note on units and notation: The functions G and F are part of general usage in molecular spectroscopy. Including all three energies for a diatomic molecule, the energy in cm^{-1} is written as

$$E_{\text{tot}} = T_e + G_v + F_v(J)$$

The quantum numbers for the electronic state have been suppressed.

Conversion to other energy units: $1 \text{ cm}^{-1} = 1.4883 \text{ K}$, $1 \text{ eV} = 11604 \text{ K}$.

Brief Summary

- The dense ISM requires long- λ measurements of atomic fine-structure and molecular transitions.
- FIR atmospheric opacity requires space observations.
- Frequencies of electronic, vibrational and rotational transitions decrease with $(m_e/M)^{1/2}$, justifying the Born-Oppenheimer approximation.
- Symmetry plays a key role for rotational spectra.
- J , J_z , are conserved for the rigid rotor; $E_{\text{rot}} = BJ(J+1)$.
- The ground electronic state of H_2 has $S = 0$.
- Electronic states are labeled $^{2S+1}\Lambda$ with $\Lambda = \Sigma, \Pi$, etc.
- Anharmonicity makes the vibrational level spacing decrease with v .
- Centrifugal distortion decreases the rotational spacing for large J .