

Interstellar Medium (ISM)

Lecture 14

2025 June 02 (Monday), 2PM

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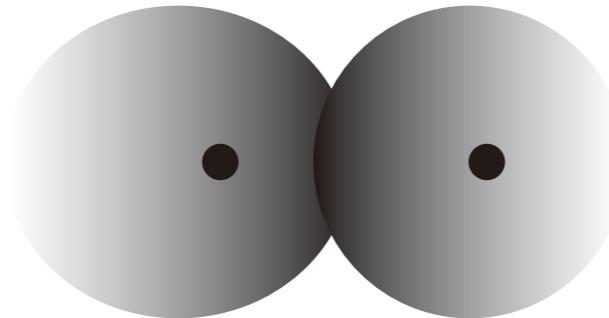
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Molecular Clouds

[Born-Oppenheimer Approximation]

- **Born-Oppenheimer approximation:**

- To a very good approximation, the motions of the electrons and nuclei could be treated separately. The electrons move much faster than the nuclei.
- *This come about because of the great difference between the masses of the electron and a typical nuclei.*
- The slowly moving nuclei only sense the electrons as a kind of smoothed-out cloud. As the nuclei move the electrons have sufficient time to adjust to adiabatically the new nuclear positions. (***It is like flies buzzing round an elephant - as the elephant moves the flies move with it.***) The nuclei then feel only an equivalent potential that depends on the internuclear distance and on the particular electronic state.

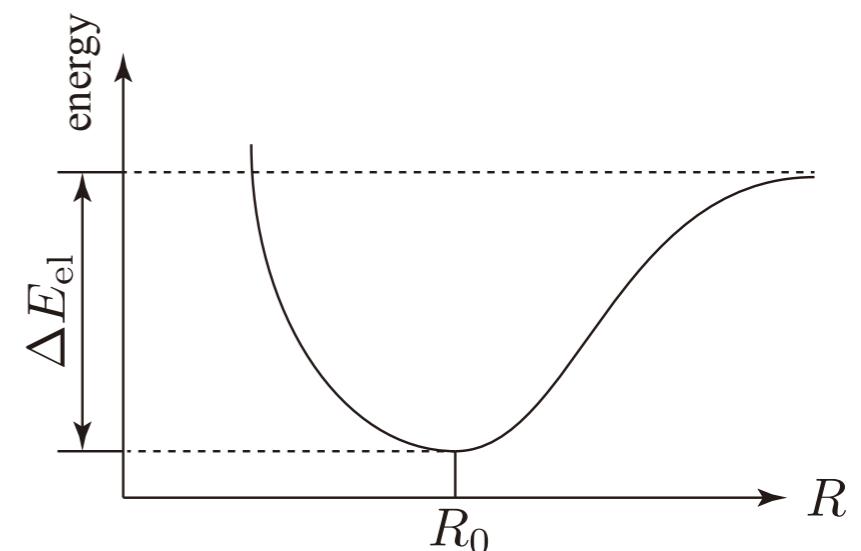


- One separates the wavefunction for the motions of electrons from the wavefunction for the motions of the nuclei. **One can then consider the electronic wavefunction separately for each position of nuclei, as if the nuclei are held fixed.**
- Due to very different energies of the **electronic, vibrational, and rotational states**, these interactions can be assumed to be decoupled. The separation of wavefunctions is referred to as the Born-Oppenheimer approximation. Under the Born-Oppenheimer approximation, the total wavefunction is a product of the nuclear, electronic, vibrational, and rotational wavefunctions.

$$\psi_{\text{tot}} = \psi_{\text{nuc}} \psi_{\text{el}} \psi_{\text{vib}} \psi_{\text{rot}}$$

- Order of magnitude of energy levels

- Electronic energy:



As the separation between the two atoms $R \rightarrow 0$ (at very small R), the overall interactions are strongly repulsive. There is repulsion due to nuclear-nuclear interaction whose potential depends on $Z_A Z_B / R$. There is also repulsion due to the electron-electron interactions, which also behave approximately as $1/R$. However, these repulsive interactions are largely cancelled by the attractive electron-nuclear interaction.

As $R \rightarrow \infty$, the molecule is pulled apart and it separates into atoms in a process known as dissociation. The energy of the system at dissociation is clearly just the sum of the atomic exchange.

At intermediate R , to get binding there must be some region of R where the molecular energy is less than the sum of the atomic energies. In this case, the electronic state is described as ‘attractive’ and there is a minimum in the potential energy curve.

For a diatomic molecule, a stable chemical bond can form between two atoms that approach within a distance of each other comparable to the Bohr radius $a_0 = \hbar^2/m_e c^2$. Then, the electron energy will be given by

$$E_{\text{elect}} \sim m_e v^2 = \frac{p^2}{m_e} \sim \frac{\hbar^2}{m_e a_0^2} \quad (\leftarrow p \times a_0 \sim \hbar, \text{ uncertainty relation}) \quad \Rightarrow \text{visible/UV (a few eV)} \\ (a \sim 1 \text{ \AA})$$

- **Vibrational energy:**

If the two nuclei are displaced from the equilibrium separation R_0 by a displacement comparable to $\xi \sim a_0$, they will vibrate about the equilibrium position with a frequency ω_{vib} such that **the vibrational energy contained in the motion and displacements of the two nuclei (of typical mass M) will be comparable to the depth of the electronic potential well.**

$$M\omega_{\text{vib}}^2 a_0^2 \sim E_{\text{elect}}$$

where ω = frequency of vibration.

M = mass of the molecule.

Then, the vibrational energy is

$$E_{\text{vib}} \sim \hbar\omega \sim \left(\frac{m_e}{M}\right)^{1/2} \frac{\hbar^2}{m_e a^2} \sim \left(\frac{m_e}{M}\right)^{1/2} E_{\text{elect}} \quad \Rightarrow \text{Near-IR / Mid-IR}$$

- **Rotational energy:**

The nuclei can also rotate about each other. Then, the energy of rotation is

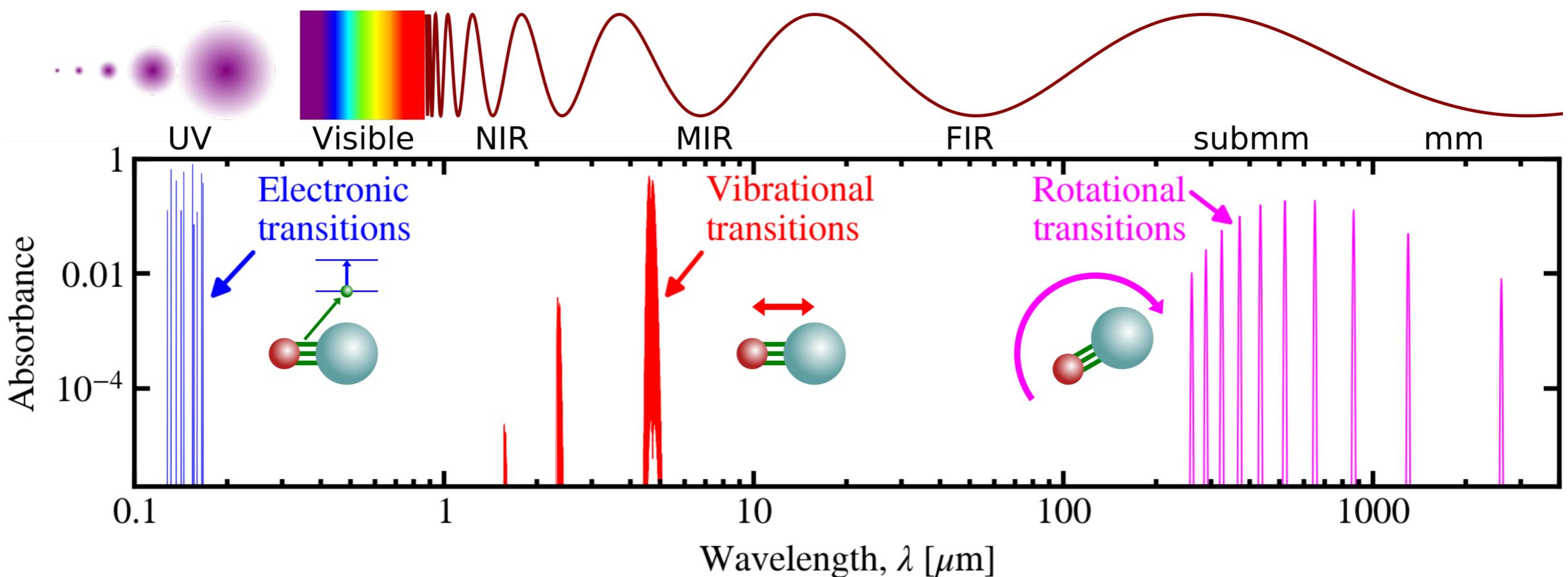
$$E_{\text{rot}} \sim \frac{L^2}{2I} \sim \frac{\hbar^2 \ell(\ell + 1)}{2I} \quad \Rightarrow \text{radio}$$

where I is the moment of inertia of the molecule: $I = Ma_0^2$. Therefore, we obtain

$$E_{\text{rot}} \sim \left(\frac{m_e}{M}\right) E_{\text{elect}}$$

In summary, $E = E_{\text{elect}} + E_{\text{vib}} + E_{\text{rot}}$

$E_{\text{elect}} : E_{\text{vib}} : E_{\text{rot}} = 1 : \left(\frac{m_e}{M}\right)^{1/2} : \left(\frac{m_e}{M}\right)$
for hydrogen ~ 0.02 ~ 0.0005



Molecular transitions.

The different types of transitions are illustrated with the CO molecule.

[credit: Frédéric Galliano]

Schrödinger equation for a diatomic molecule

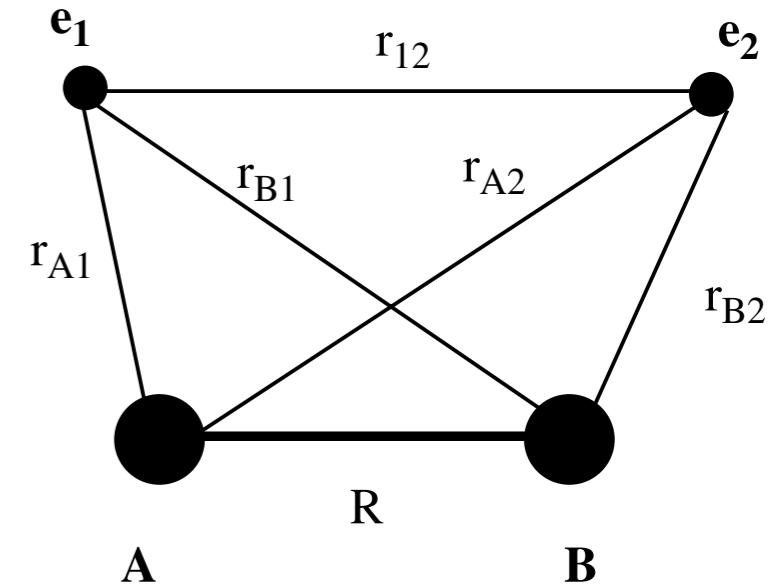
For a diatomic molecule with N electrons,

$$\left(-\frac{\hbar^2}{2M_A} \nabla_A^2 - \frac{\hbar^2}{2M_B} \nabla_B^2 - \frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + V_e - E \right) \Psi(\mathbf{R}_A, \mathbf{R}_B, \{\mathbf{r}_i\}) = 0$$

The first two terms are the kinetic energy operators for the motions of nuclei A and B, the third term gives the kinetic energy operator for the electrons, V_e is the potential and E is the total energy of the system.

The potential is given by the various Coulomb interactions within the molecule:

$$V_e = - \sum_{i=1}^N \frac{Z_A e^2}{r_{Ai}} - \sum_{i=1}^N \frac{Z_B e^2}{r_{Bi}} + \sum_{i=2}^N \sum_{j=1}^{i-1} \frac{e^2}{r_{ij}} + \frac{Z_A Z_B e^2}{R}$$



- (1) attraction of the electrons by nucleus A
 - (2) attraction of the electrons by nucleus B
 - (3) electron-electron repulsion
 - (4) nuclear-nuclear repulsion
- Born-Oppenheimer approximation: One can write the wave function as a product of electronic and nuclear wave functions.

$$\Psi(\mathbf{R}_A, \mathbf{R}_B, \{\mathbf{r}_i\}) = \psi_e(\{\mathbf{r}_i\}) \psi_n(\mathbf{R}_A, \mathbf{R}_B)$$

Then the equation becomes

$$\left[\left(-\frac{\hbar^2}{2M_A} \nabla_A^2 - \frac{\hbar^2}{2M_B} \nabla_B^2 - E \right) \psi(\{\mathbf{R}_A, \mathbf{R}_B\}) + \left[\left(-\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + V_e \right) \psi(\{\mathbf{r}_i\}) \right] \psi(\{\mathbf{R}_A, \mathbf{R}_B\}) = 0 \right]$$

- In this case the **electronic wavefunction** satisfies the following equation:

$$\left(-\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + V_e \right) \psi_e(\mathbf{r}_i) = E_e \psi_e(\mathbf{r}_i)$$

This equation is solved separately for each value of the internuclear separation R .

Then, the resulting eigenvalue E_e is the electronic energy at R and gives the electronic potential $V(R) = E_e$ upon which the nuclei move.

The equation for the wavefunction of nuclei is obtained to be

$$\left(-\frac{\hbar^2}{2M_A} \nabla_A^2 - \frac{\hbar^2}{2M_B} \nabla_B^2 + V(R) - E \right) \psi_n(\mathbf{R}_A, \mathbf{R}_B) = 0 \quad \text{where } V(R) \equiv E_e.$$

Here, E (the eigenvalue) is the total energy of the system.

-
- The Schrödinger equation for the nuclei:

$$\left(-\frac{\hbar^2}{2M_A} \nabla_A^2 - \frac{\hbar^2}{2M_B} \nabla_B^2 + V(R) - E \right) \psi_n(\mathbf{R}_A, \mathbf{R}_B) = 0 \quad \text{where } V(R) \equiv E_e.$$

The equation deals with three types of motions of the nuclei: (1) translation of the whole system, (2) vibrations, and (3) rotations. The motions can be separated into the translational motion of the center-of-mass of the system plus the internal motion of one body in a ‘central’ potential, which depends on the distance between the particles. The effective mass of this one-body problem is the reduced mass:

$$\mu = \frac{M_A M_B}{M_A + M_B}$$

The Schrödinger equation for nuclear motion, neglecting the translational motion, becomes:

$$\left[-\frac{\hbar^2}{2\mu} \nabla^2 + V(R) - E \right] \psi_n(\mathbf{R}) = 0$$

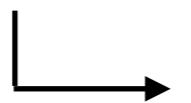
where $\mathbf{R} = (R, \theta, \phi)$. R is the internuclear separation, (θ, ϕ) is the orientation of the molecular axis relative to the laboratory z -axis.

The vibrational and rotational motion cannot be separated rigorously. However, as a good first approximation, the vibration and rotational motion may be separated.

$$\psi_n(\mathbf{R}) = \psi_{\text{vib}}(R)\psi_{\text{rot}}(\theta, \phi)$$

Then, we obtain two equations for the rotational motion and vibrational motion:

angular equation: $\left\{ -\frac{\hbar^2}{2\mu R^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] - E_r \right\} \psi_{\text{rot}}(\theta, \phi) = 0$

 the angular part of the Laplacian operator ∇^2

radial equation: $\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V(R) - E_v \right] \psi_{\text{vib}}(R) = 0$

(1) The solution of the angular equation is:

$$\psi_{\text{rot}}(\theta, \phi) = Y_{JM}(\theta, \phi) \quad \text{spherical harmonics}$$

$$E_r = \frac{\hbar^2}{2\mu R^2} J(J+1)$$

(2) The potential $V(R)$ is not a simple function and thus the radial equation has no general algebraic solution. But, we can approximate $V(R)$ about its minimum by a parabola:

$$\begin{aligned} V(R) &= V(R_e) + \frac{1}{2} \left. \frac{d^2V}{dR^2} \right|_{R=R_e} (R - R_e)^2 + \mathcal{O}((R - R_e)^3) \quad \leftarrow \quad \frac{dV}{dR} = 0 \quad \text{at} \quad R = R_e \\ &= V_0 + \frac{1}{2} k(R - R_e)^2 + \dots \end{aligned}$$

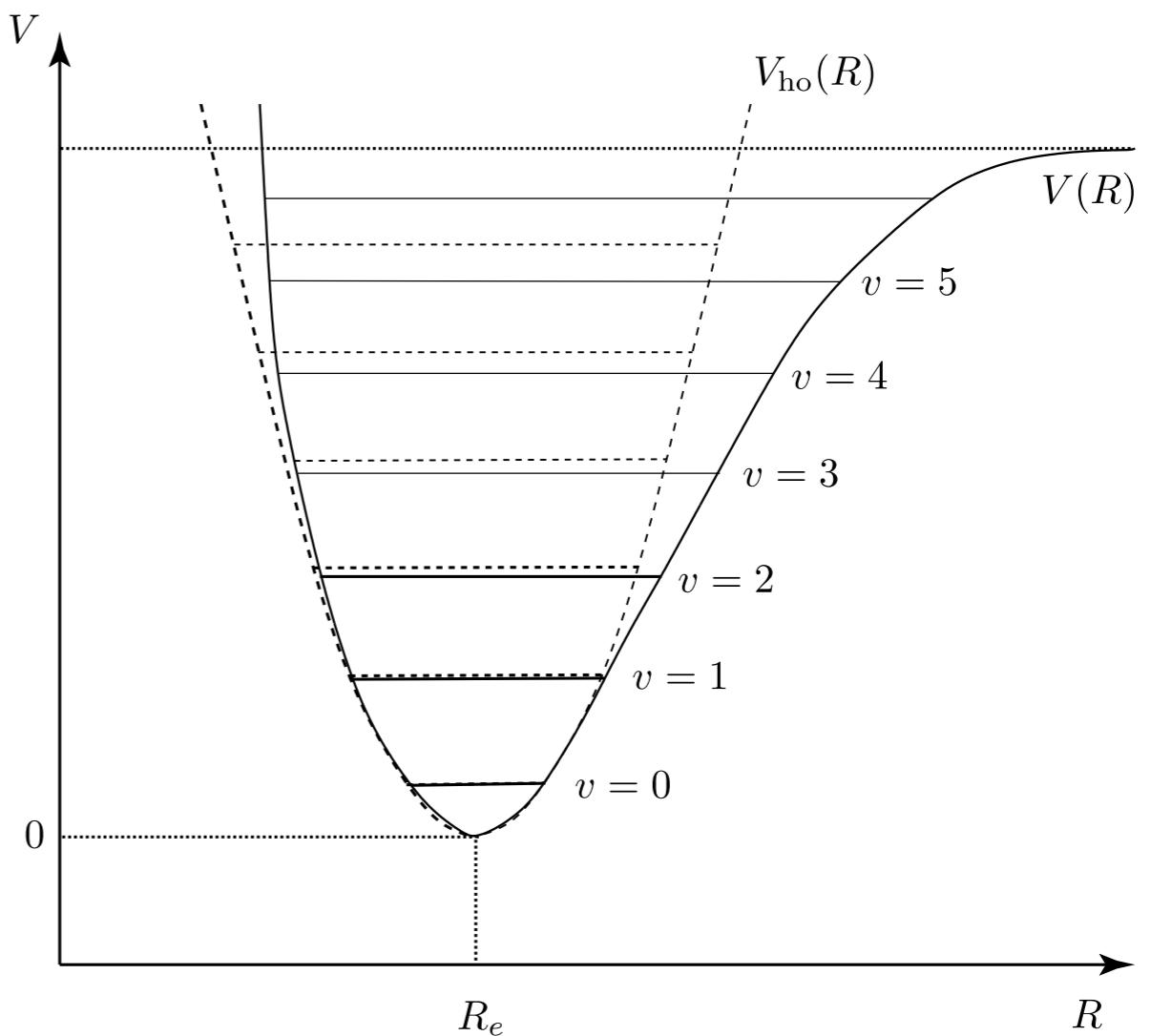
Setting the zero of energy at the minimum potential, $V_0 = V(R_e) = 0$, the radial equation becomes

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{1}{2}k(R - R_e)^2 - E_v \right] \psi_{\text{vib}}(R) = 0$$

This is the QM equation for the harmonic oscillator with the spring constant k . The energy levels of this equation are:

$$E_v = \hbar\omega \left(v + \frac{1}{2} \right)$$

$$\text{where } \omega = \left(\frac{k}{\mu} \right)^{1/2}, \quad v = 0, 1, 2, \dots$$



[Energy Levels]

- **Energy Levels**

An electronic transition consists of vibrational bands, which in turn are made up of rotational transitions.

$$E_q(v, J) = V_q(r_0) + h\nu_0 \left(v + \frac{1}{2} \right) + B_v J(J+1)$$

$$\nu_0 \equiv \frac{\omega_0}{2\pi} \quad B_v = \frac{\hbar^2}{2I} \quad I = \mu r_0^2 \quad = \text{moment of inertia of the molecule.}$$

Here, q denotes an electronic state.

- **Angular Momentum**

Molecules are not spherical and the orbital angular momentum of the individual electrons is no longer a conserved quantity.

- *For diatomic molecules, the total orbital angular momentum \mathbf{L} is strongly coupled to the nuclear axis.*
- It is therefore necessary to consider the components of L , designated \mathcal{L} (or Λ), along the diatomic nuclear axis which, by convention, is taken to define the z -axis of the system.
- While the value of the total orbital angular momentum in a diatomic molecule can change, its projection onto the diatomic axis is conserved.
- As the projection of \mathbf{L} onto z -axis can be either positive or negative, states with $\mathcal{L} \neq 0$ are twofold degenerate while states with $\mathcal{L} = 0$ are singly degenerate.

Excitation Temperature

- The excitation temperature for a given transition is defined as:

$$\frac{n_u}{n_\ell} = \frac{g_u}{g_\ell} e^{-h\nu_{ul}/kT_{\text{exc}}}$$

- For pure rotational transitions, the excitation temperature is often called the **rotation temperature**.
- For vibrational transitions, it is called the **vibrational temperature**.
- This nomenclature is analogous to the “spin temperature” defined for the H I 21-cm hyperfine transition.

[Labelling of Electronic States of Diatomic Molecules]

- **Heteronuclear diatomic molecule** (e.g., HD, OH, or CO): The notation of the electronic structure of a diatomic molecule is similar to that for atomic structure under *LS* coupling. Each electronic state is designated by the **term symbol**.

$$2S+1 \mathcal{L} J_{ez}$$

In some literatures, the following symbol is used.

$$2S+1 \Lambda_{\Omega}$$

S = total electronic spin

\mathcal{L} = projection of the total electronic “orbital” angular momentum along the internuclear axis
 $(\rightarrow L_z)$

J_{ez} = projection of the total electronic (orbital + spin) angular momentum onto the internuclear axis
 $= |\mathcal{L} + S_z|$ ($\rightarrow J_{ez} = L_z + S_z; S_z = -S, -S+1, \dots, S-1, S$)

- The uppercase Greek letters to denote the total “orbital” angular momentum.

$\mathcal{L} = \Sigma, \Pi, \Delta, \dots$ (for $L_z = 0, 1, 2, \dots$)

Recall S, P, D, \dots in the atomic spectroscopy.

- If the term symbol \mathcal{L} is Σ ($L_z = 0$), then additional superscript \pm is applied.

$$\pm = \begin{cases} + & \text{if symmetric under reflection through (all) planes} \\ & \text{containing the nuclei,} \\ - & \text{if antisymmetric under reflection through a plane} \\ & \text{containing the nuclei.} \end{cases}$$

Nearly all Σ states are + state Σ^+ .
One exception is O_2 , of which the lowest electronic state is ${}^3\Sigma_g^-$.

- **Homonuclear diatomic molecule:** Diatomic molecules with identical nuclei (H_2 , N_2 , O_2 , C_2) are referred to as homonuclear. The energy levels of homonuclear diatomic molecules are designated by

$$2S+1 \mathcal{L}_{u,g}$$

$$2S+1 \Lambda_{u,g}$$

$$(x, y, z) \rightarrow (-x, -y, -z)$$

$$u, g = \begin{cases} g & \text{("gerade") if symmetric under reflection through the} \\ & \text{center of mass, } \Rightarrow \text{even (계하드)} \\ u & \text{("ungerade") if antisymmetric under reflection through the} \\ & \text{center of mass. } \Rightarrow \text{odd (운계하드)} \end{cases}$$

For the special case of Σ state, a superscript + or - is added.

$$2S+1 \Sigma_{u,g}^{\pm}$$

- The ***electronic states*** of diatomic molecules are also labelled with one of the following letters, appearing in front of the term symbol.

X labels the ground electronic state

A, B, C, ... label states of same spin multiplicity as the ground state

a, b, c, ... label states of different spin multiplicity to the ground state

- Examples:

$^1\Sigma$ denotes a state with $S = 0$ and $\mathcal{L} = 0$

$^3\Pi$ denotes a state with $S = 1$ and $\mathcal{L} = 1$, etc

$S \rightarrow \Sigma$
$P \rightarrow \Pi$
$D \rightarrow \Delta$
$F \rightarrow \Phi$
$G \rightarrow \Gamma$

H: $1s^1$
C: $1s^2 2s^2 2p^2$
N: $1s^2 2s^2 2p^3$
O: $1s^2 2s^2 2p^4$

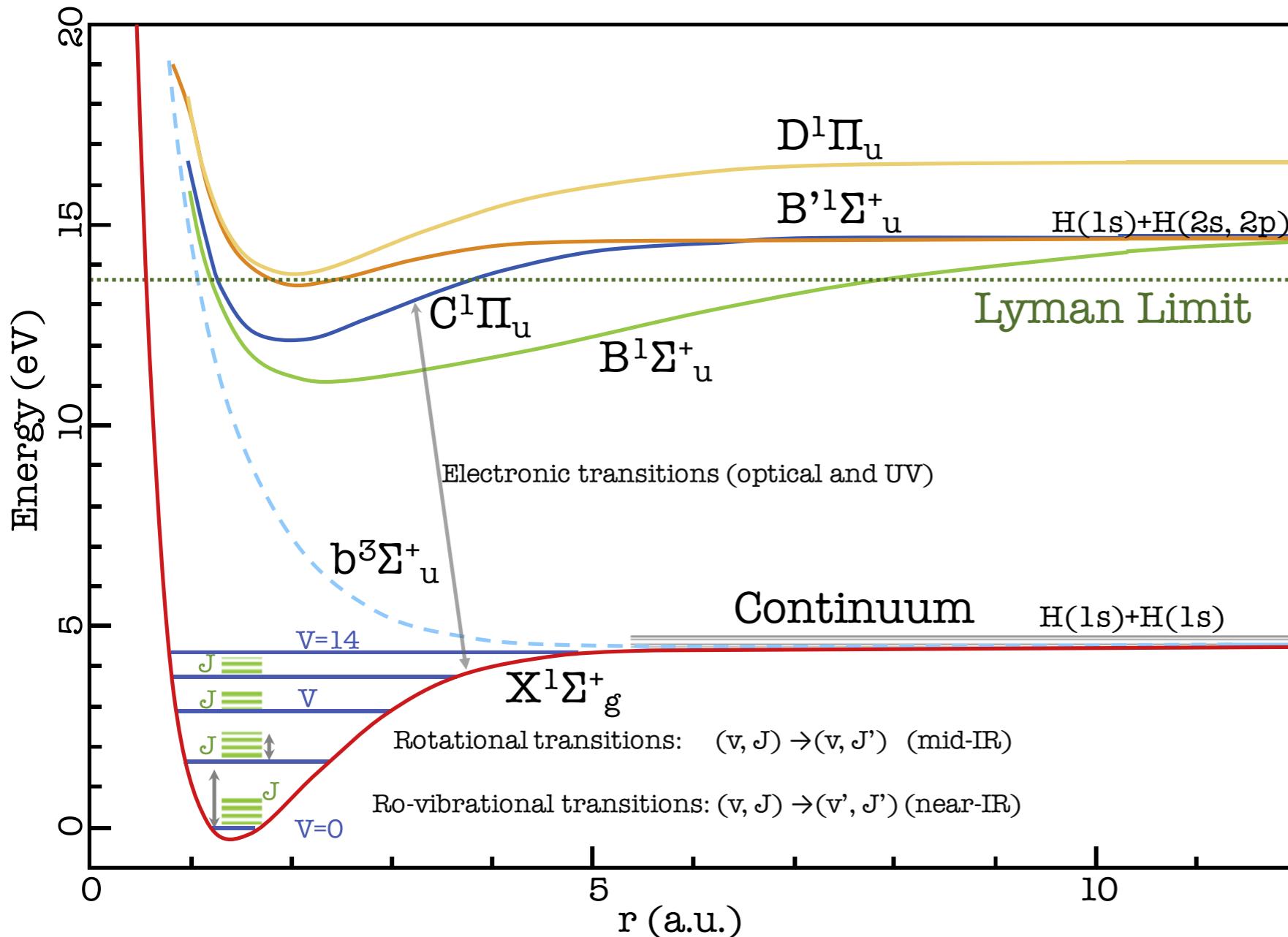
- For most (stable) diatomics, the electronic ground state is a closed shell, meaning that it is $^1\Sigma$.
 - Examples include H₂, N₂ and most other homonuclear diatomics. The exception is O₂ which has a $^3\Sigma$ ground state. (Each O has 4 valence electrons, and thus $S = 1$)
 - CO and many other heteronuclear diatomics with an even number of electrons also have $^1\Sigma$ ground states.
 - Diatomics with an odd number of electrons usually have $S = 1/2$. For example, H₂⁺ and CN have $^2\Sigma$ ground state. (Note a typo in “Astronomical Spectroscopy.” CH⁺ has $^1\Sigma$ ground state.)
 - CH, OH and NO all have $\mathcal{L} = 1$ and thus their ground states are $^2\Pi$. These molecules have extra line splitting in their spectra due to a process called Λ -doubling.

$\mathcal{L} =$	0	1	2	3	4	...
Orbitals	σ	π	δ	ϕ	γ	...
States	Σ	Π	Δ	Φ	Γ	...
Degeneracy	1	2	2	2	2	...

Λ -doubling is the splitting of rotational levels that have the same quantum numbers and differ only in their parity.

Letter designations for projected total orbital angular momentum.

[Energy levels of Molecular Hydrogen]



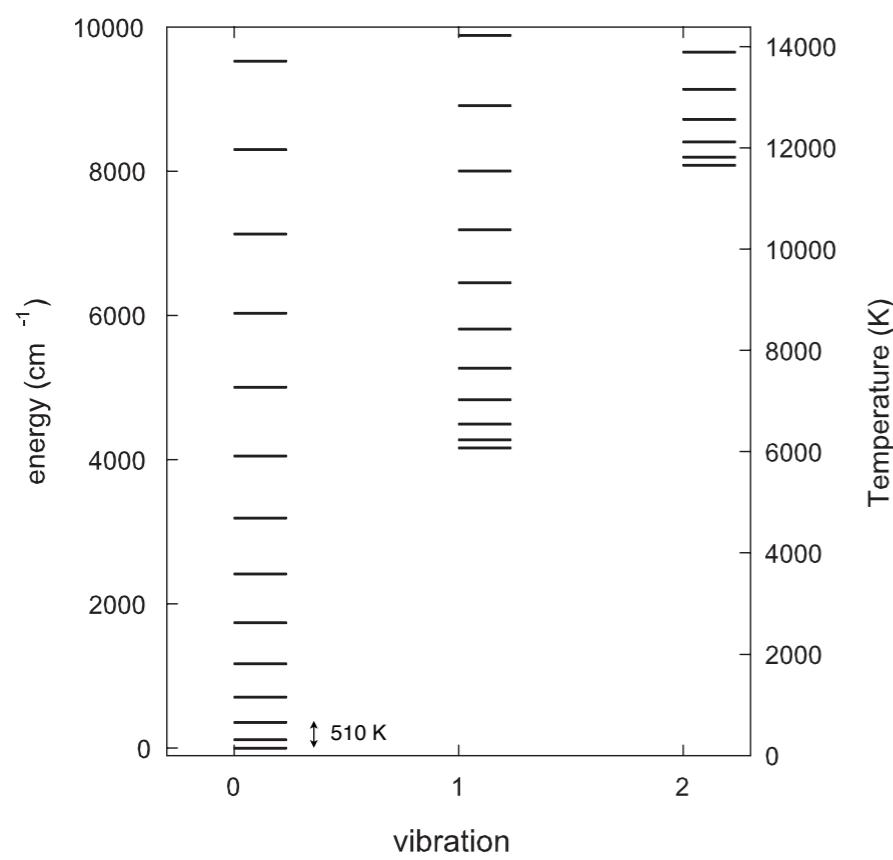
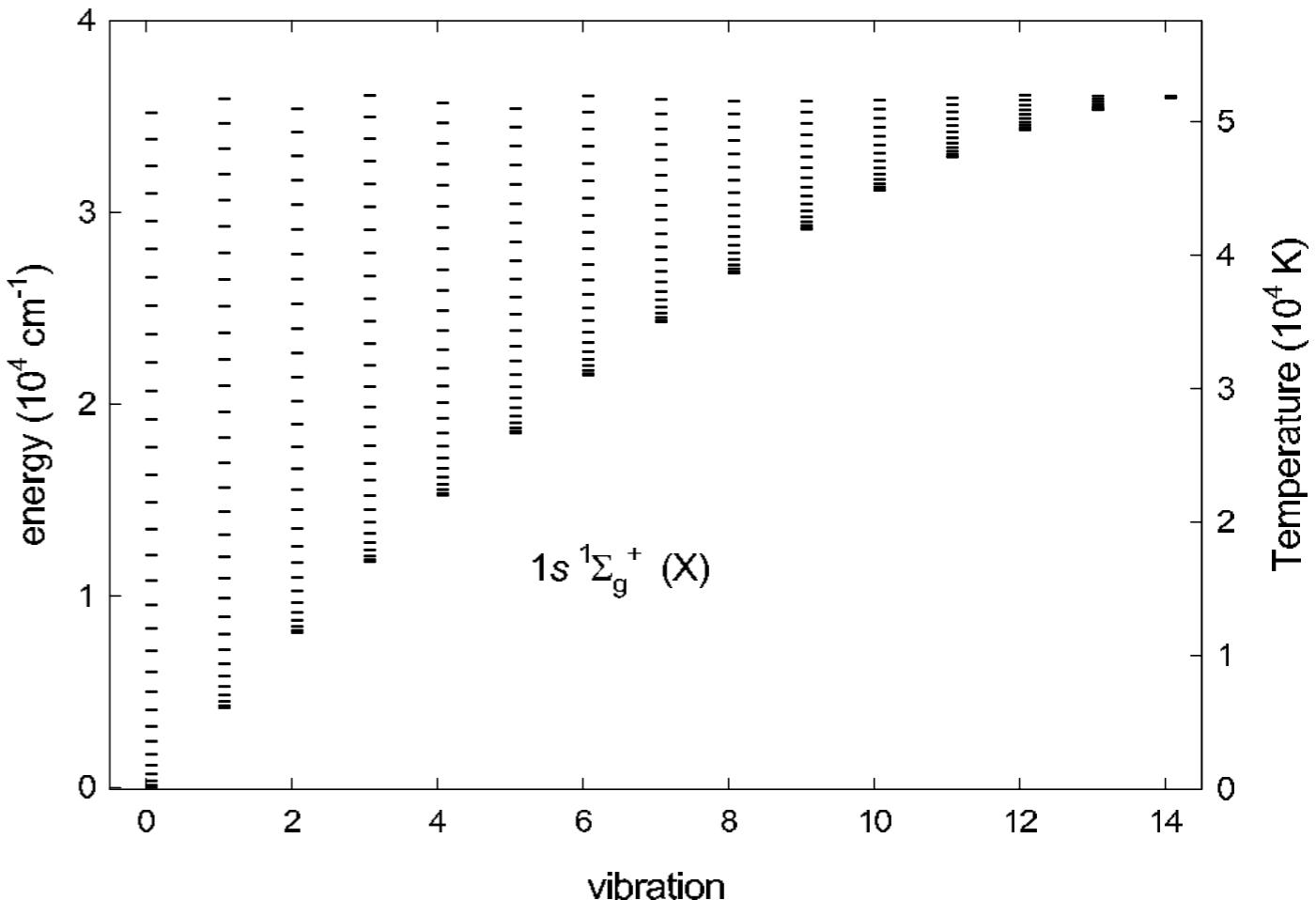
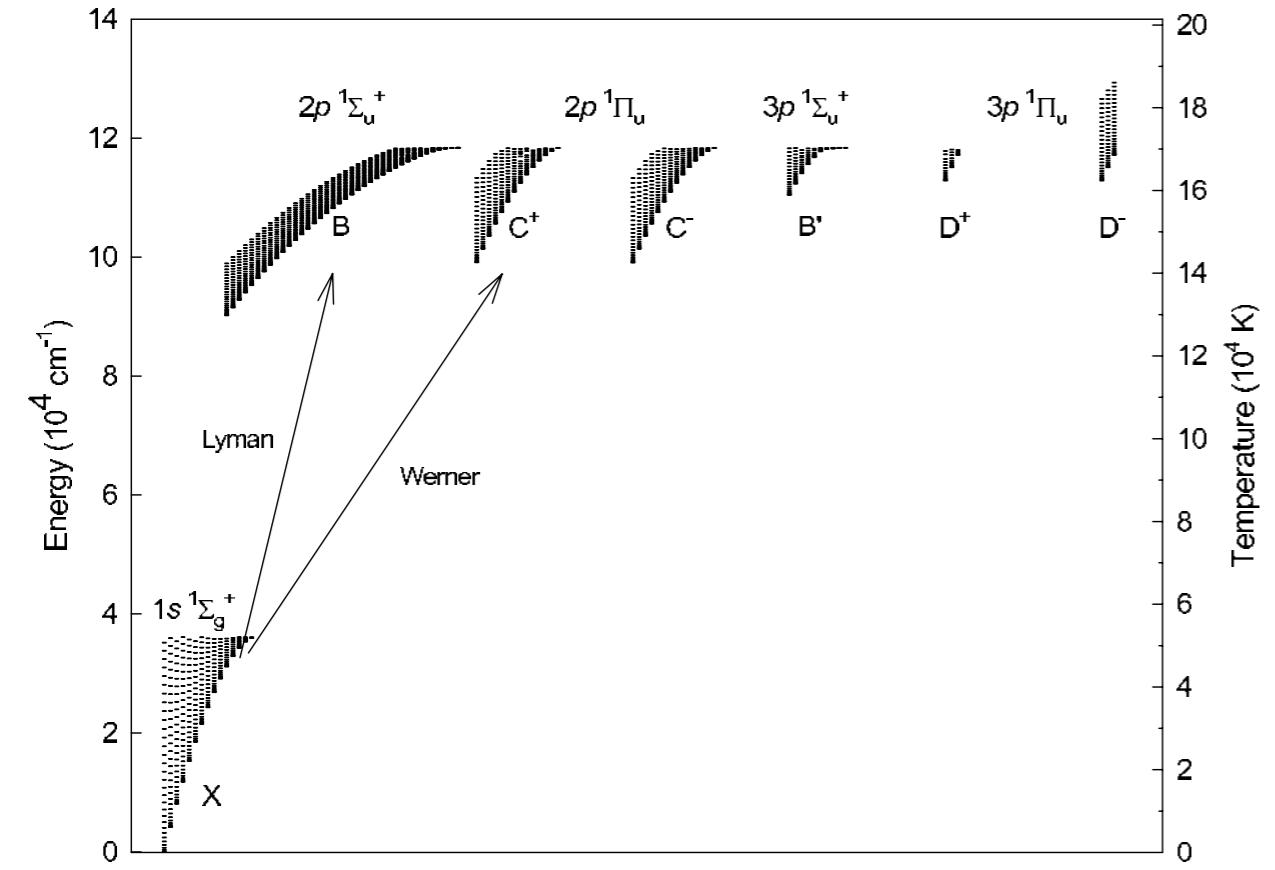
The transition from the ground state $X^1\Sigma_g^+$ to the excited states $B^1\Sigma_u^+$ and $C^1\Pi_u$ are called **Lyman and Werner bands**, respectively.

Lyman band: $B^1\Sigma_u^+ - X^1\Sigma_g^+$ at $\lambda \approx 930 - 1240\text{\AA}$

Werner band: $C^1\Pi_u - X^1\Sigma_g^+$ at $\lambda \approx 970 - 1650\text{\AA}$

In principle, states are labelled alphabetically in ascending energy order. However, there are many exceptions.

The lowest triplet state of H_2 is the $b^3\Sigma_u^+$ with the $a^3\Sigma_g^+$ lying somewhat higher.



Other molecules

	Ground term
H ₂	$^1\Sigma_g^+$
CH	$^2\Pi_{1/2,3/2}$
CH ⁺	$^1\Sigma_0^+$
OH	$^2\Pi_{3/2,1/2}$
CN	$^2\Sigma_{1/2}^+$
CO	$^1\Sigma_0^+$
SiO	$^1\Sigma_0^+$
CS	$^1\Sigma_0^+$

H(1): $1s^1$
 C(6): $1s^2 2s^2 2p^2$
 N(7): $1s^2 2s^2 2p^3$
 O(8): $1s^2 2s^2 2p^4$
 Si(14): $1s^2 2s^2 2p^6 3s^2 3p^2$
 S(16): $1s^2 2s^2 2p^6 3s^2 3p^4$

The electronic ground state of H₂ (two electrons) has zero electronic orbital angular momentum ($L_e = 0$), has zero electron spin ($S_e = 0$), is symmetric under reflection through the center of mass (g), and is symmetric under reflection through planes containing the nuclei (+). The ground state is X $^1\Sigma_g^+$.

CO has two (2) *p* electrons contributed by C and four (4) *p* electrons contributed by O; together these six (6) *p* electrons fill the 2*p* subshell, and as a result, the ground electronic state of CO has zero electronic angular momentum and zero electronic spin: $^1\Sigma_0^+$, just like H₂.

OH is an example of a molecule with the ground electronic state having nonzero electronic orbital angular momentum: with seven electrons, the OH ground state has $L_{ez} = 1$ and $S_{ez} = 1/2$, and is therefore designated by $^2\Pi_{1/2,3/2}$. The electron spin and orbital angular momenta can couple to give $J_e = 1/2$ or $3/2$, with energies that are separated due to spin-orbit coupling (i.e., fine-structure splitting in atoms or ions); the $J_e = 3/2$ state has the lower energy.

[Pure rotational & ro-vibrational transitions]

- **Energy Levels**

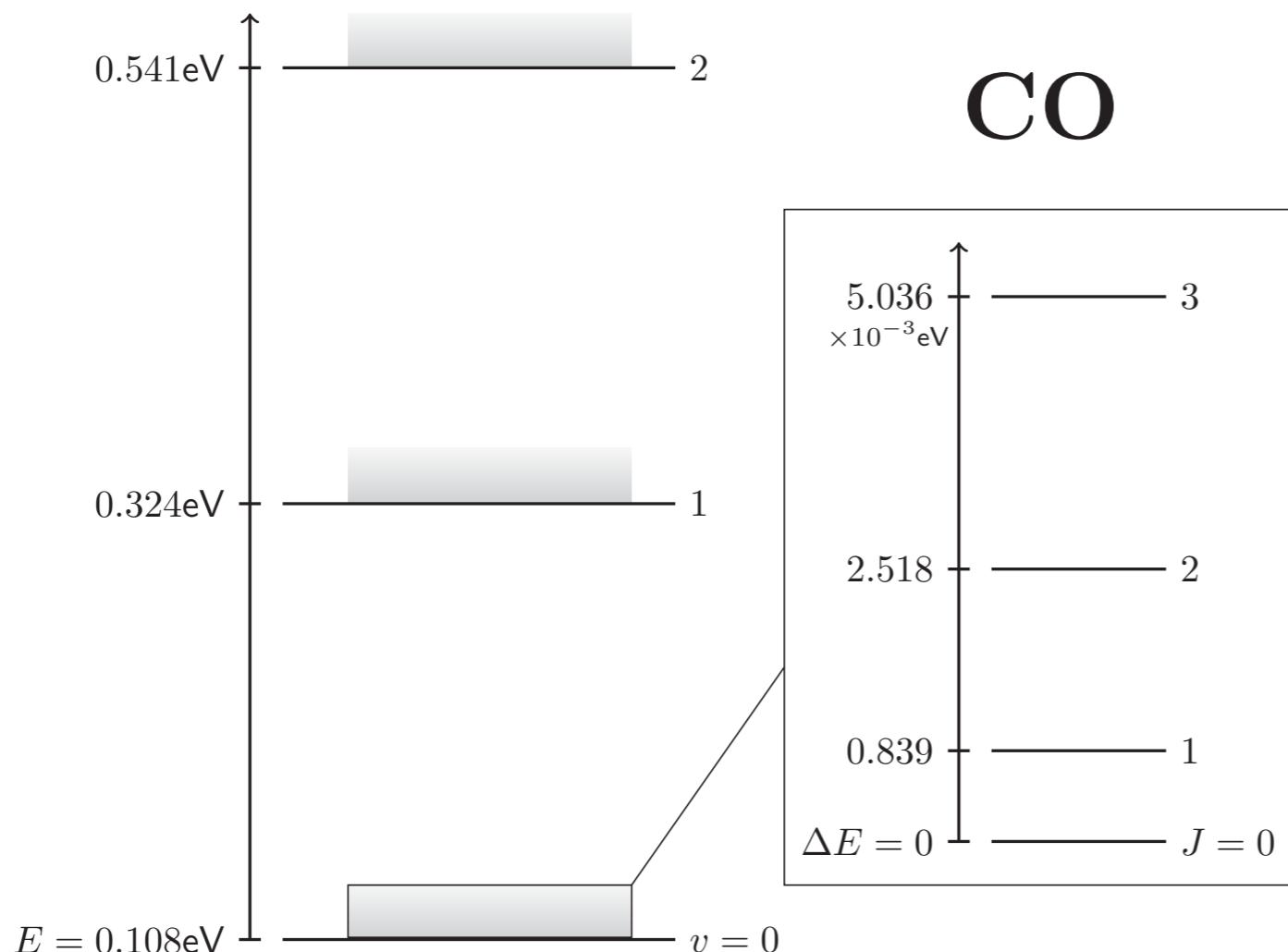
An electronic transition consists of vibrational bands, which in turn are made up of rotational transitions.

$$E_q(v, J) = V_q(r_0) + h\nu_0 \left(v + \frac{1}{2} \right) + B_v J(J+1)$$

$$\nu_0 \equiv \frac{\omega_0}{2\pi} \quad B_v = \frac{\hbar^2}{2I} \quad I = \mu r_0^2 \quad = \text{moment of inertia of the molecule.}$$

Here, q denotes an electronic state.

- **Pure rotational spectrum:** In the lowest vibrational and electronic states, it is possible to have transitions solely among the rotational states. Such transitions give rise to a pure rotational spectrum.
- **Rotational-vibration spectrum:** Because the energies required to excite vibrational modes are much larger than those required to excite rotation, it is unlikely to have a pure vibrational spectrum in analogy to the pure rotational spectrum. The transitions then yield a rotation-vibrational spectrum, in which both the vibrational state and the rotational state can change together.



The rotational and vibrational energy levels for CO. The left side show the vibrational energy for each level ν . The rotational transitions are illustrated by the gray shading at each level. The rotational energies are about 100 times smaller than the vibrational and the inset on the right hand side shows a zoomed-in region of the J-ladder.

[Selection Rules]

- Electric-dipole selection rules for electronic transitions in a diatomic molecule.

- (1) $\Delta\mathcal{L} = 0, \pm 1$, e.g., $\Sigma - \Sigma$, $\Pi - \Sigma$, $\Delta - \Pi$, etc.
- (2) $\Delta S = 0$
- (3) $\Delta J_z = 0, \pm 1$
- (4) $\Sigma^+ - \Sigma^+$, $\Sigma^- - \Sigma^-$, but not $\Sigma^+ - \Sigma^-$
- (5) $g \longleftrightarrow u$

- $\Delta\Lambda = 0, \pm 1$, e.g., $\Sigma - \Sigma$, $\Pi - \Sigma$, $\Delta - \Pi$, etc.
- $\Delta S = 0$
- $\Delta\Omega = 0, \pm 1$
- $\Sigma^+ - \Sigma^+$, $\Sigma^- - \Sigma^-$, but not $\Sigma^+ - \Sigma^-$
- $g \leftrightarrow u$

- Electric-dipole selection rule for ro-virational transitions:

$$\Delta v = \text{any}$$

$$\Delta J = 0, \pm 1 \text{ not } J = 0 \leftrightarrow 0$$

- **Note that H₂ has no permanent electric-dipole moment.**

The electric-quadrupole are allowed for $\Delta J = \pm 2$ within the ground electronic state.

O, P, Q, R, and S transitions

- The rotational levels of diatomic molecules are specified by a single vibrational quantum number v and rotational quantum number J .
 - Transitions will change J by either $0, \pm 1, \pm 2$.**
 - It is customary to identify transitions by specifying the upper and lower electronic states, upper and lower vibrational states, and one of the follows: $O(J_\ell)$, $P(J_\ell)$, $Q(J_\ell)$, $R(J_\ell)$, $S(J_\ell)$
 - The usage of the symbols are shown in the following table.

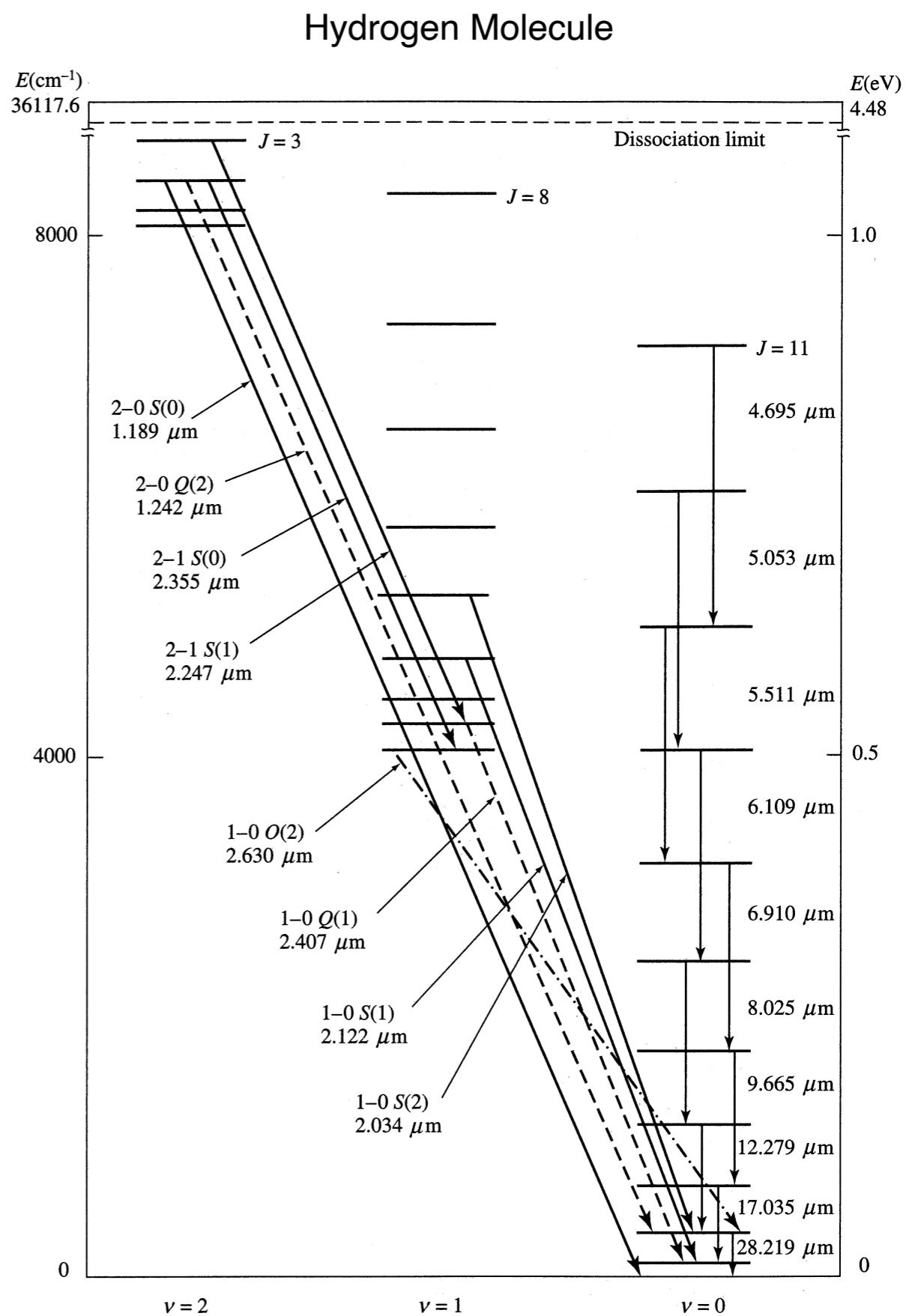
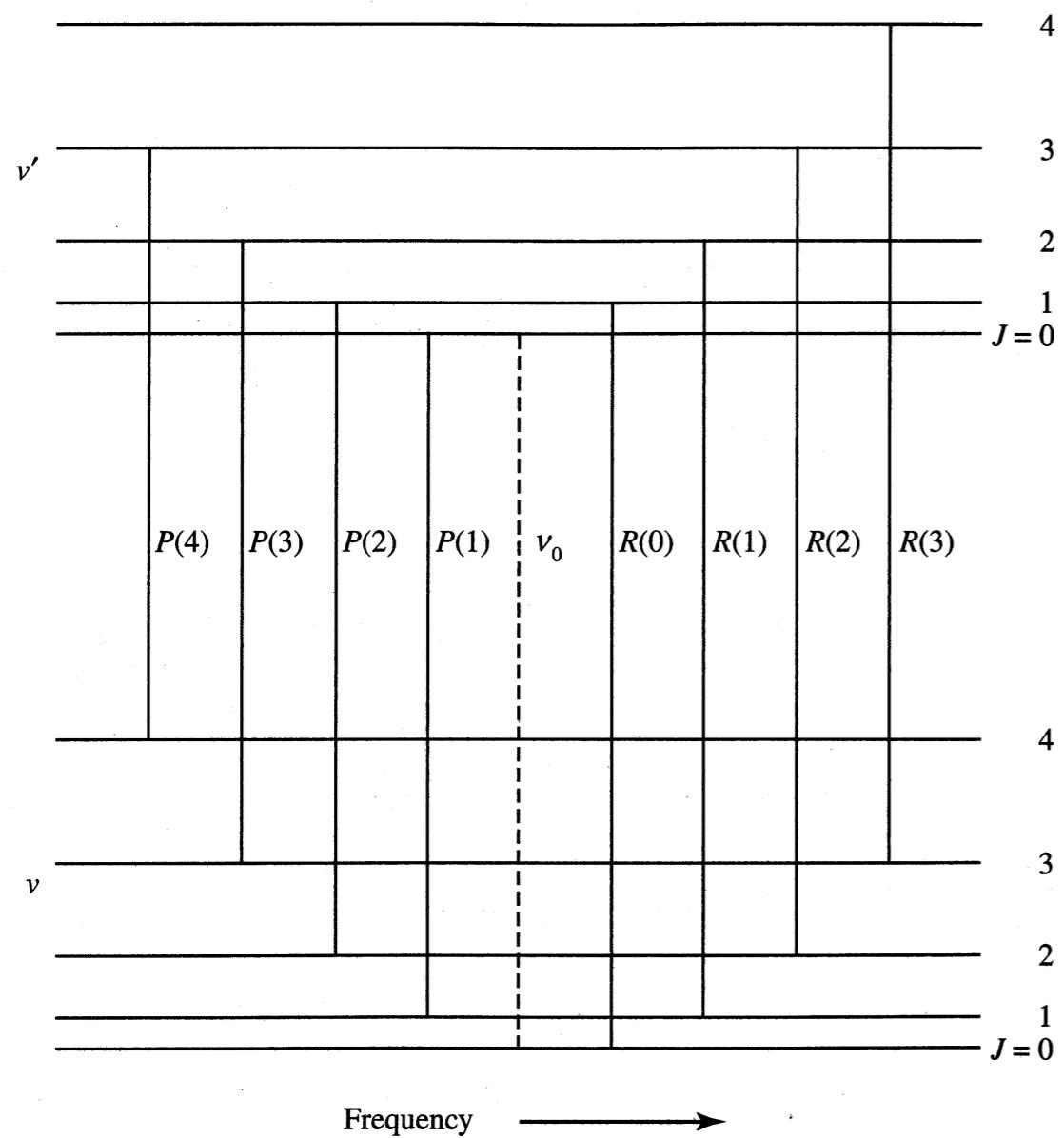
$$J_u \rightarrow J_\ell$$

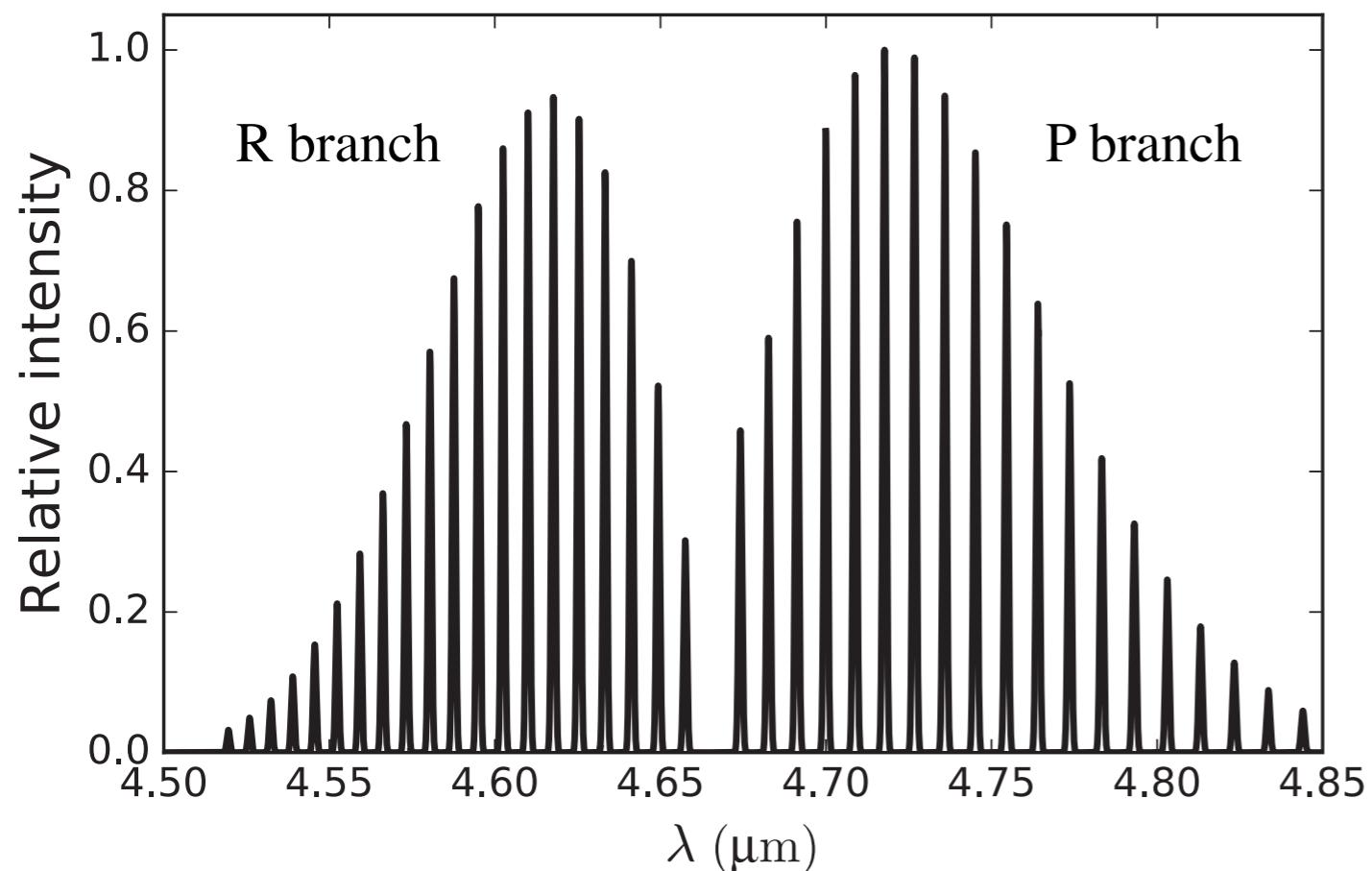
Do not be confused with
electronic transitions.

Designation	$(J_u - J_\ell)$	Note
$O(J_\ell)$	-2	Electric quadrupole transition
$P(J_\ell)$	-1	Electric dipole transition
$Q(J_\ell)$	0	Electric dipole or electric quadrupole; $Q(0)$ is forbidden
$R(J_\ell)$	+1	Electric dipole transition
$S(J_\ell)$	+2	Electric quadrupole transition

- For instance, a transition from the the $v_\ell = 0, J_\ell = 1$ level of the ground electronic state to the $v_u = 5, J_u = 2$ level of the first electronic excited state would be written to be

B-X 5-0 $R(1)$





Model spectrum of ro-vibrational lines for CO $\nu = 1 - 0$, illustrating the two branches corresponding to a positive or negative change in J and a central gap at $\Delta J = 0$.

The R branch corresponds to a higher energy jump, $J \rightarrow J - 1$, and lies at shorter wavelengths. The P branch is a smaller energy jump, $J \rightarrow J + 1$, and is at longer wavelengths.

The envelope shape arises from the population level distribution that is small at low levels due to the degeneracy, $g_J = 2J + 1$, and at high levels due to the Boltzmann exponential, $e^{-E/kT_{\text{ex}}}$. The difference between the relative intensity of the P and R branches is due to different value of the Einstein A coefficient.

[Hyperfine Splitting & Ortho-H₂ and Para-H₂]

- **Hyperfine splitting:** If one or more nuclei have nonzero nuclear spin and $J_{ez} \neq 0$, then there will be an interaction between the nuclear magnetic moment and the magnetic field generated by the electrons, resulting in “hyperfine splitting.” The energy will depend on the orientation of the nuclear angular momentum relative to the axis.
- **Ortho-H₂ and Para-H₂ (spin isomers, 이상질체)**

In the case of H₂, the electronic wave function is required to be antisymmetric under exchange of the two electrons.

The two protons, just like electrons, are identical fermions, and therefore, the Pauli exclusion principle antisymmetric requirement also applies to **exchange of the two protons**. The protons are spin 1/2 particles - the two protons together can have total spin 1 (**parallel, ortho-**) or total spin 0 (**antiparallel, para-**).

Within the ground electronic (X) state, the consequence of the antisymmetry requirement is that

If the protons have spin 0, the rotational quantum number J must be even. \Rightarrow **para-H₂ / even J**
 (an antisymmetric nuclear spin wave function ($I = 0$) and a symmetric spatial wave function having an even value of the rotational quantum number J)

If the protons have spin 1, the rotational quantum number J must be odd. \Rightarrow **ortho-H₂ / odd J**
 (a symmetric nuclear spin wave function ($I = 1$) and an antisymmetric spatial wave function having an odd value of the rotational quantum number J)

Because the nuclear spins are only weakly coupled to the electromagnetic field, **ortho-H₂ and para-H₂ behave as almost distinct species.**

H₂ has no permanent electric dipole moment.

- Thus, the vibrational states and the rotational states radiate very weakly, via the time-variation of the electric quadrupole moment and the molecule vibrates or rotates.
- Because the nuclear spin state does not change, the ro-vibrational radiative transitions of H₂ must have

$\Delta J = 0$ or $\Delta J = \pm 2$, i.e., ortho \rightarrow ortho or para \rightarrow para
 (not $J = 0 \leftrightarrow J = 0$)

The vibration-rotation emission spectrum of H₂ therefore consists of electric quadrupole transitions. Therefore, **the H₂ emission lines are faint and hard to detect**. The downward transitions are identified by

$$\begin{aligned} v_u - v_\ell \ S(J_\ell) &\quad \text{if } J_\ell = J_u - 2 , \\ v_u - v_\ell \ Q(J_\ell) &\quad \text{if } J_\ell = J_u , \\ v_u - v_\ell \ O(J_\ell) &\quad \text{if } J_\ell = J_u + 2 . \end{aligned}$$

Neither P nor Q transitions are available.

For example, 1-0 S(1) refers to the transition $(v = 1, J = 3) \rightarrow (v = 0, J = 1)$.

- Spin-exchange collisions with H⁰ or H⁺, and a process in which H₂ is captured on a grain surface can cause an ortho-para conversion.
- The statistical weight of an ortho-H₂ rotational level J is $3(2J+1)$ [because $S_{\text{nucleus}} = 1$].
 For a para-H₂ it is $(2J+1)$ [because $S_{\text{nucleus}} = 0$].

Ortho/Para Ratios

- The ortho state of a molecule is defined as having the larger statistical spin weights and para as having the smaller weight.
- Since the typical energy separation between the ortho and para states of a molecule is comparable to the gas and dust temperature in the ISM and *much smaller than the energy released in formation reactions*, **it is expected that the abundance ratio between the two states will reflect the equilibrium values at high temperatures, that is, the ratio of their statistical weight.**

$$\frac{E_{J=1} - E_{J=0}}{k_B} \approx 174.98 \text{ K} \quad \text{for H}_2$$

- ▶ Since $g = 2I + 1$, the usual ortho to para ratio is $(2 \times 1 + 1)/(2 \times 0 + 1) = 3$ for spin 1/2 systems such as H₂.
- If a molecule cannot be converted from ortho to para (or vice versa) by radiative or collisional processes, the two states can effectively be considered as two separate molecules. In this case, **the ortho to para ratio at the time of molecule formation will be preserved.**

Interstellar Molecules

- Interstellar Molecules

- Interstellar molecules were first discovered in the late 1930s through the identification of optical lines seen in absorption against background starlight with electronic transitions of molecules.

- The molecules first detected were CN ($B^2\Sigma^+ - X^2\Sigma^+$ at 3876.84\AA), CH ($A^2\Delta - X^2\Pi$ at 4300.30\AA) and CH^+ ($A^1\Pi - X^1\Pi^+$ at 4232.54\AA)

- To date, over 330 interstellar molecules have been detected.
(<http://molecules-in.space/>)

Interstellar molecules listed by number of atoms

Diatom	Triatomic	Four atoms	Five atoms	Six atoms	Seven atoms	Eight atoms	
H ₂	C ₃	c-C ₃ H	C ₅	C ₅ H	C ₆ H	CH ₃ C ₃ N	
AlF	C ₂ H	<i>l</i> -C ₃ H	C ₄ H	<i>l</i> -H ₂ C ₄	CH ₂ CHCN	HCOOCH ₃	
AlCl	C ₂ O	C ₃ N	C ₄ Si	C ₂ H ₄	CH ₃ C ₂ H	CH ₃ COOH(?)	
C ₂	C ₂ S	C ₃ O	<i>l</i> -C ₃ H ₂	CH ₃ CN	HC ₅ N	C ₇ H	
CH	CH ₂	C ₃ S	<i>c</i> -C ₃ H ₂	CH ₃ NC	HCOCH ₃	H ₂ C ₆	
CH ⁺	HCN	C ₂ H ₂	CH ₂ CN	CH ₃ OH	NH ₂ CH ₃	CH ₂ OHCHO	
CN	HCO	CH ₂ D ⁺ (?)	CH ₄	CH ₃ SH	<i>c</i> -C ₂ H ₄ O	CH ₂ CHCHO	
CO	HCO ⁺	HCCN	HC ₃ N	HC ₃ NH ⁺	CH ₂ CHOH		
CO ⁺	HCS ⁺	HCNH ⁺	HC ₂ NC	HC ₂ CHO			
CP	HOC ⁺	HNCO	HCOOH	NH ₂ CHO			
CSi	H ₂ O	HNCS	H ₂ CHN	C ₅ N			
HCl	H ₂ S	HOOC ⁺	H ₂ C ₂ O	HC ₄ N			
KCl	HNC	H ₂ CO	H ₂ N ₂ CN				
NH	HNO	H ₂ CN	HNC ₃				
NO	MgCN	H ₂ CS	SiH ₄				
NS	MgNC	H ₃ O ⁺	H ₂ COH ⁺				
NaCl	N ₂ H ⁺	NH ₃					
OH	N ₂ O	SiC ₃					
PN	NaCN	C ₄	Nine atoms	Ten atoms	Eleven atoms	Twelve atoms	Thirteen atoms
SO	OCS						
SO ⁺	SO ₂		CH ₃ C ₄ H	CH ₃ C ₅ N(?)	HC ₉ N	CH ₃ OC ₂ H ₅	HC ₁₁ N
SiN	<i>c</i> -SiC ₂		CH ₃ CH ₂ CN	(CH ₃) ₂ CO			
SiO	CO ₂		(CH ₃) ₂ O	NH ₂ CH ₂ COOH			
SiS	NH ₂		CH ₃ CH ₂ OH	CH ₃ CH ₂ CHO			
CS	H ₃ ⁺		HC ₇ N				
HF	SiCN		C ₈ H				
SH	AlNC						
FeO(?)	SiNC						

Table from A. Wootten (www.cv.nrao.edu/~awootten/allmols.html).

[Table 7.1, Kwok]

- Given the ubiquity of hydrogen in the ISM, and the inability of helium to form chemical bonds, we expect molecular gas in the ISM to consist primarily of H₂.
 - A hydrogen molecule, with the dissociation energy $D_0 = 4.52 \text{ eV}$, is not very tightly bound. An UV photon can photodissociate it.
 - In a gas with temperature $T > D_0/k \sim 50,000 \text{ K}$, collisions with other gas particles can collisionally dissociate it. Thus, **we expect molecular hydrogen to survive for long periods of time only in cold regions of the ISM that are shielded from UV radiation.**
 - Hydrogen has the lowest, reduced mass of any molecule, $\mu = m_{\text{H}}/2$, hence, hydrogen molecules have a particularly high fundamental frequency of vibration compared to other diatomic molecules.

Properties of some diatomic molecules [Table 7.1, Ryden]

Molecule	D_0 [eV]	r_0 Å	B_0 [meV]	$\hbar\omega_0$ [eV]	μ_0 [debye]
H ₂	4.52	0.74	7.36	0.516	0.000
CO	11.1	1.13	0.24	0.269	0.110
CH	3.51	1.12	1.76	0.339	1.406
OH	4.39	0.97	2.30	0.443	1.668
CN	7.57	1.17	0.23	0.253	0.557

μ_0 = permanent dipole moment
 1 debye = $10^{-18} \text{ statC cm}$

D_0 = dissociation energy
 r_0 = speration
 $B_0 \equiv \frac{\hbar^2}{2I}$
 $\omega_0 = \sqrt{k/\mu}$ fundamental frequency of vibration

CO

- For any molecule to have a dipole-allowed rotational spectrum it must have an asymmetric charge distribution which gives rise to a permanent dipole moment.

Heteronuclear diatomics poses a permanent dipole moment but homonuclears, such as H₂, do not.

- CO

Carbon monoxide, CO, is a particularly important species for astronomical observations.

CO is the most stable diatomic molecule.

It has a dissociation energy D_0 of 11.1 eV, which is more than double the D_0 value found for most other diatomic molecules.

As a result, in astronomical environments where molecules form, C and O usually combine to form CO, which is very stable and long-lived.

The wavelengths of the first few rotational transitions are 1-0 at $\lambda = 2.60$ mm, 2-1 at 1.30 mm, and 3-2 at 0.87mm.

The J = 1-0 transition of CO is the second most important spectral line in radio astronomy after the hydrogen 21 cm line.

CO is widely distributed in the interstellar medium and maps of the CO J = 1-0 transition are a standard tool for investigating the ISM.

One reason for this is that cold H₂ is very difficult to observe directly because its pure rotational transitions are not only very weak but lie in the near-infrared where ground-based observations are not possible. **The abundance of CO is therefore often used to estimate the total amount of molecular gas present in a given environment.** It is generally assumed that the number density of CO is approximately 10⁻⁴ of that of H₂.

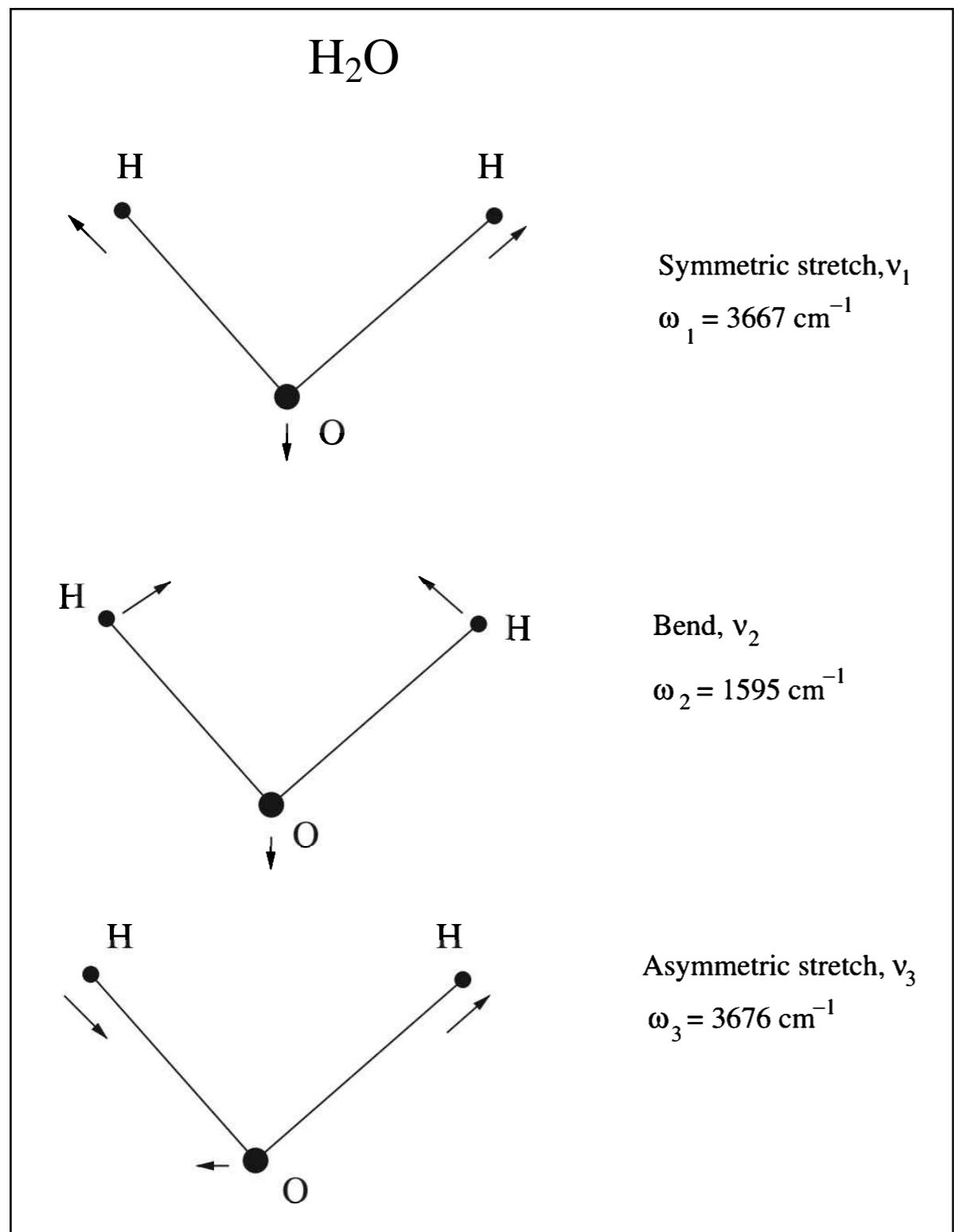
$$n(\text{CO}) \approx 10^{-4}n(\text{H}_2)$$

If, as often happens, the CO 1-0 line is optically thick, one can use higher transitions such as the CO 2-1 line instead.

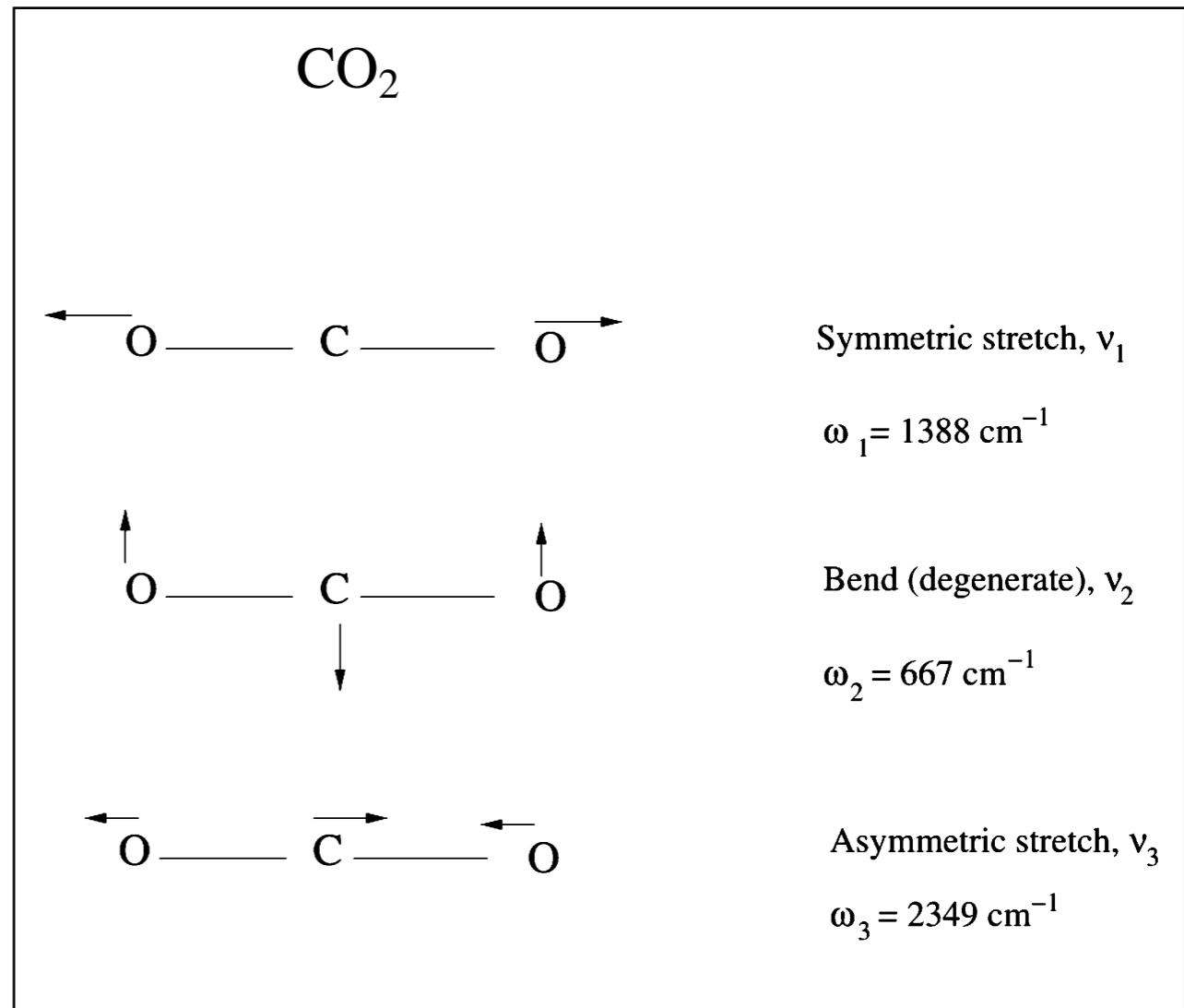
Another option to avoid the effects of optical thickness is to observe an isotopologue ¹³CO, which is present with much lower densities and whose transitions are therefore much less optically thick.

An isotopologue is a molecule that consists of at least one less abundant isotope of its constituent elements. They have the same transitions at nearby frequencies with similar decay and excitation rates. **The main difference is in their abundance and observations of the rarer species help diagnose conditions in dense regions where lines from the primary species are optically thick.**

Vibrations in Polyatomic Molecules



Three vibrational modes of the **water molecule**

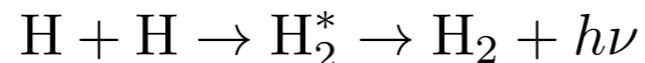


The vibrational modes of **carbon dioxide**; note that the bending mode is doubly degenerate as the motion can occur in the plane of the page, as drawn, or identically, perpendicular to the plane of the page.

[H₂ formation] (1) Gas-Phase Formation of H₂

- ***Direct Radiative Association***

- When two free H atoms collide with each other, they create an excited hydrogen molecule that is unbound.



- It must emit a photon carrying away enough energy to leave it a bound state, or it will break apart again. There is no electric dipole moment. As a result, there is no dipole radiation that could remove energy from the system and leave the two H atoms in a bound state. Electric quadrupole transitions are possible, but the rates are very low.

The lifetime of the excited hydrogen molecule until it breaks apart would be roughly one period of vibration:

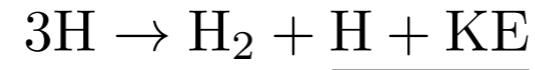
$$\frac{2\pi}{\omega_0} = \frac{h}{E_{\text{vib},0}} = \frac{6.626 \times 10^{-27} \text{ cm}^2 \text{ g s}^{-1}}{0.516 \text{ eV}} \sim 8 \times 10^{-15} \text{ s}$$

Rate for the electric quadrupole transition is: $A_{u\ell} \sim 10^{-11} \text{ s}^{-1}$

Therefore, the probability of emitting a photon before it breaks apart is: $p \sim A_{u\ell} (2\pi/\omega_0) \sim 10^{-25}$

- As a consequence, the rate coefficient for direct radiative association of H₂ is so small that this reaction can be ignored in astrochemistry.

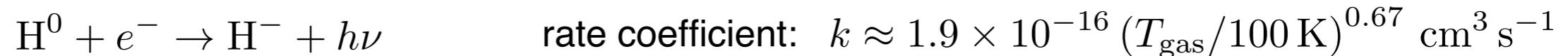
- ***Three-body reaction***



- The reaction can occur, when the third body carrying off the energy released when H_2 is formed, but the rate for this three-body reaction is negligible at interstellar or intergalactic densities.
- At the high densities of a protostar or protoplanetary disk, the three-body reaction is able to convert H to H_2 .

- ***Formation of negative hydrogen ion by radiative association followed by formation of H_2 by associative detachment:***

- First step:



- Second step:



This is an exothermic (발열) ion-molecule reaction.

- The density of negative H ion is very low because the formation rate of H^- (first step) is slow while there are many, rapid processes that destroy H^- .

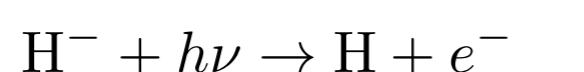
-
- ▶ H^- can be destroyed by reaction with protons:



- ▶ H^- can be destroyed by reaction with other positive ions:



- ▶ In the diffuse ISM, $n(\text{H}^+) \approx 0.01 \text{ cm}^{-3}$ or lower. Most of H^- is destroyed by ***photodetachment***, which is the inverse process to radiative association.



reaction rate: $\zeta_{\text{pd}} \approx 2.4 \times 10^{-7} G_0 \text{ s}^{-1}$

Here, G_0 is the strength of radiation in units of the interstellar radiation field (ISRF).

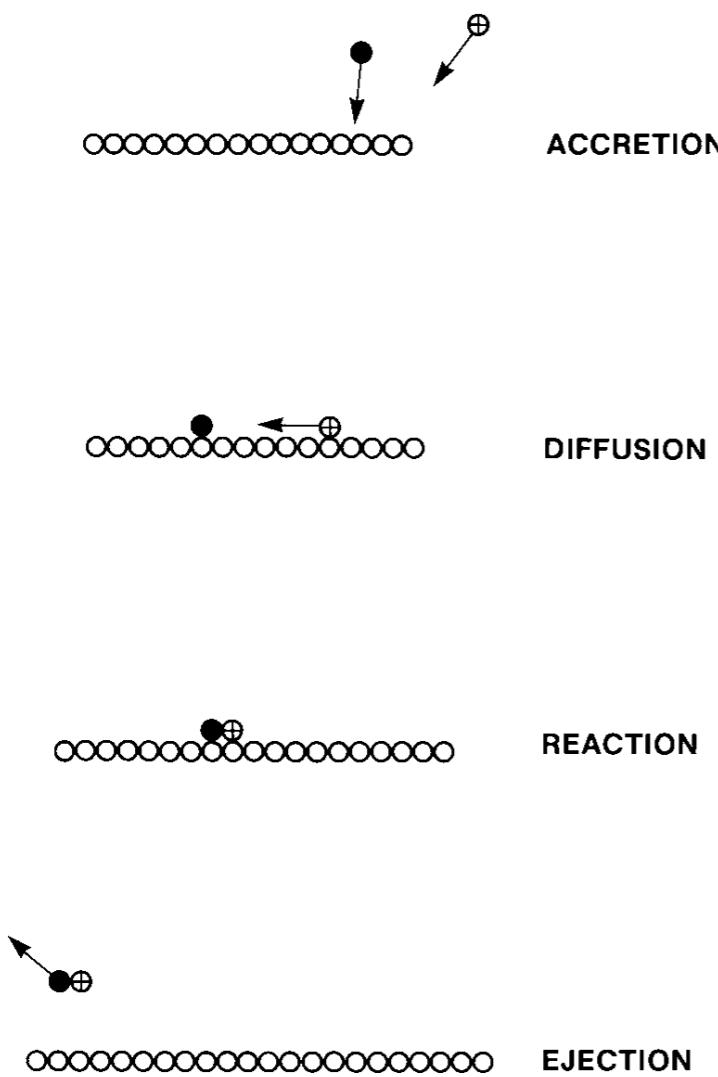
The photodetachment needs only $I = 0.77 \text{ eV}$ to take away one of its electrons.

- ***In the absence of dust (e.g., in the early universe), $\text{H}^- + \text{H} \rightarrow \text{H}_2 + e^-$ is the dominant channel for forming H_2 .***
- ▶ Associative detachment and the resulting production of H_2 will only dominate over photodetachment when

$$n_{\text{HI}} > \frac{\zeta_{\text{pd}}}{k_{\text{ad}}} \approx 180 G_0 \text{ cm}^{-3}$$

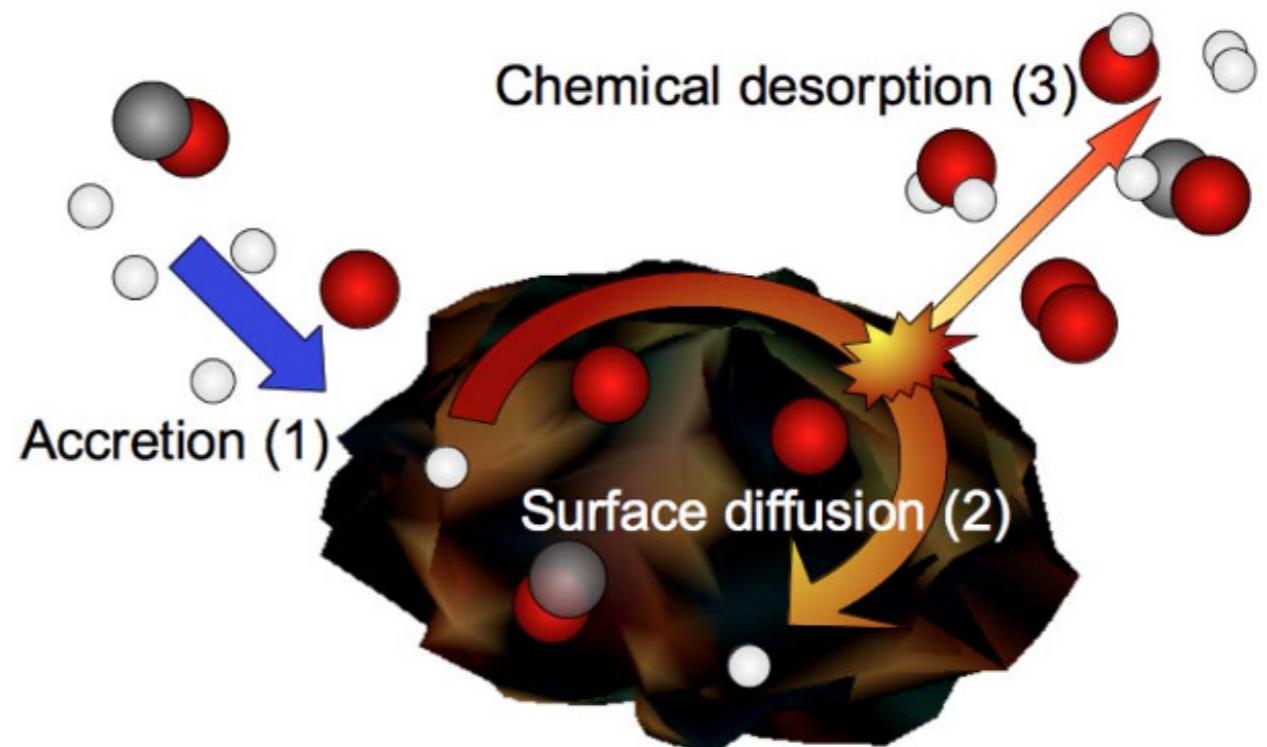
[H₂ formation] (2) Grain Catalysis of H₂

- **Langmuir-Hinshelwood mechanism:** the dominant process of H₂ formation in the Milky Way and other galaxies is via grain catalysis (촉매 작용).
 - The surface of a dust grain acts as a lab of chemical activity.
 - **Adsorption (흡착):**
 - ▶ A H atom colliding with a dust grain has some probability of sticking (bounding) to the grain.
 - ▶ The sticking probability depends (1) on the atom's speed (slower atoms are more likely to stick), (2) on the grain's temperature (hot grains are less sticky), (3) on the grain's size (smaller grains are less sticky), and (4) on the grain's composition.
 - ▶ Sticking probability: $p_s \approx 0.3$ for grains with $a \sim 0.1\mu\text{m}$
 - **Surface Diffusion & Bimolecular Reaction:**
 - ▶ Initially, the binding may be weak enough that the H atom is able to diffuse (i.e., random-walk) some distance on the grain surface, until it happens to arrive at a site where it is bound strongly enough that it becomes "trapped."
 - ▶ Subsequent H atoms arrive at random locations on the grain surface and undergoes their own random walks until they also become trapped, but eventually one of the newly arrived H atoms encounters a previously bound H atom before itself becoming trapped.
 - ▶ When the two H atoms encounter one another, they react to form H₂.
 - **Desorption (탈착):**
 - ▶ The energy released when two free H atoms react to form H₂ in the ground state is $\Delta E = 4.5 \text{ eV}$. This energy is large enough to overcome the forces that were binding the two H atoms to the grain, and the H₂ molecule is ejected from the grain surface.
- **Eley-Rideal mechanism:** a surface reaction where one H atom is adsorbed onto the surface, while the other reacts directly with it from the gas phase.



A schematic of the formation of molecules on grain surfaces.

[Fig 4.1, Tielens]



Sketch that illustrates the chemical desorption process. Species coming from the gas accrete on the dust surface can meet each other to form other species. For some reactions, the formed product is ejected in the gas.

[Fig 1, Dulieu, 2003, Scientific Reports]

Formation rate of H₂

- Formation rate

- ▶ The rate per unit volume at which H atoms collide with grains, averaged over the distribution of grain radii would be:

$$\Gamma_{\text{coll}} = n_{\text{HI}} \left(\frac{8kT_{\text{gas}}}{\pi m_{\text{H}}} \right)^{1/2} \int_{a_{\min}}^{a_{\max}} \frac{dn_{\text{gr}}}{da} \pi a^2 da$$

Recall the mean speed of the Maxwell distribution

$$\langle v \rangle = \int_0^\infty v f(v) d^3v = \sqrt{\frac{8kT}{\pi m}}$$

$$f(v) = \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-mv^2/2kT}$$

- ▶ It is customary to define *the total grain geometric cross section per H nucleon*.

$$\Sigma_{\text{gr}} \equiv \frac{1}{n_{\text{H}}} \int da \frac{dn_{\text{gr}}}{da} \pi a^2$$

$$\Gamma_{\text{coll}} = n_{\text{HI}} n_{\text{H}} \left(\frac{8kT_{\text{gas}}}{\pi m_{\text{H}}} \right)^{1/2} \Sigma_{\text{gr}}$$

- ▶ Suppose that a fraction ϵ_{gr} of the H atoms that collide with a grain depart from the grain as H₂. The rate for H₂ formation via grain catalysis would then be

$$\frac{dn(\text{H}_2)}{dt} = \frac{1}{2} n_{\text{HI}} n_{\text{H}} \left(\frac{8kT_{\text{gas}}}{\pi m_{\text{H}}} \right)^{1/2} \int da \frac{dn_{\text{gr}}}{da} \pi a^2 \epsilon_{\text{gr}}(a)$$

or
$$\frac{dn(\text{H}_2)}{dt} = R_{\text{gr}} n_{\text{H}} n_{\text{HI}}$$

The factor 1/2 is because two H atoms are required to form H₂, and the “**rate coefficient**” is given by

$$R_{\text{gr}} = \frac{1}{2} \left(\frac{8kT_{\text{gas}}}{\pi m_{\text{H}}} \right)^{1/2} \langle \epsilon_{\text{gr}} \rangle \Sigma_{\text{gr}}$$

Here, the **formation efficiency** averaged over the grain surface area is:

$$\langle \epsilon_{\text{gr}} \rangle \equiv \frac{1}{\Sigma_{\text{gr}}} \int da \frac{dn_{\text{gr}}}{da} \pi a^2 \epsilon_{\text{gr}}(a)$$

- Numerical values

- ▶ Total grain geometric cross section per H nucleon: We note that

$$C(\lambda = 0.1\mu\text{m}) \approx 2 \times 10^{-21} \text{ cm}^2/\text{H} \quad \text{suggests that} \quad \Sigma_{\text{gr}} \gtrsim 10^{-21} \text{ cm}^2/\text{H}$$

The silicate-graphite-PAH grain model of Weingartner & Draine (2001) gives

$$\Sigma_{\text{gr}} \approx 6.0 \times 10^{-21} \text{ cm}^2/\text{H}$$

- ▶ The rate coefficient for H_2 formation is then

$$R_{\text{gr}} = 7.3 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1} \left(\frac{T_{\text{gas}}}{100 \text{ K}} \right)^{1/2} \langle \epsilon_{\text{gr}} \rangle \left(\frac{\Sigma_{\text{gr}}}{10^{-21} \text{ cm}^2 \text{ H}^{-1}} \right)$$

Jura (1975) used UV spectroscopy of diffuse clouds with $T_{\text{gas}} \approx 70 \text{ K}$ and determined that

$$R_{\text{gr}} \approx 3 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$$

The observed rate coefficient indicates

$$\langle \epsilon_{\text{gr}} \rangle \approx 0.08$$

This average is the result of a very low value of ϵ_{gr} for the PAHs, which dominate the surface area, and $\epsilon_{\text{gr}} \gtrsim 0.5$ for the $a \gtrsim 0.01\mu\text{m}$ “classical” silicate and carbonaceous grains.

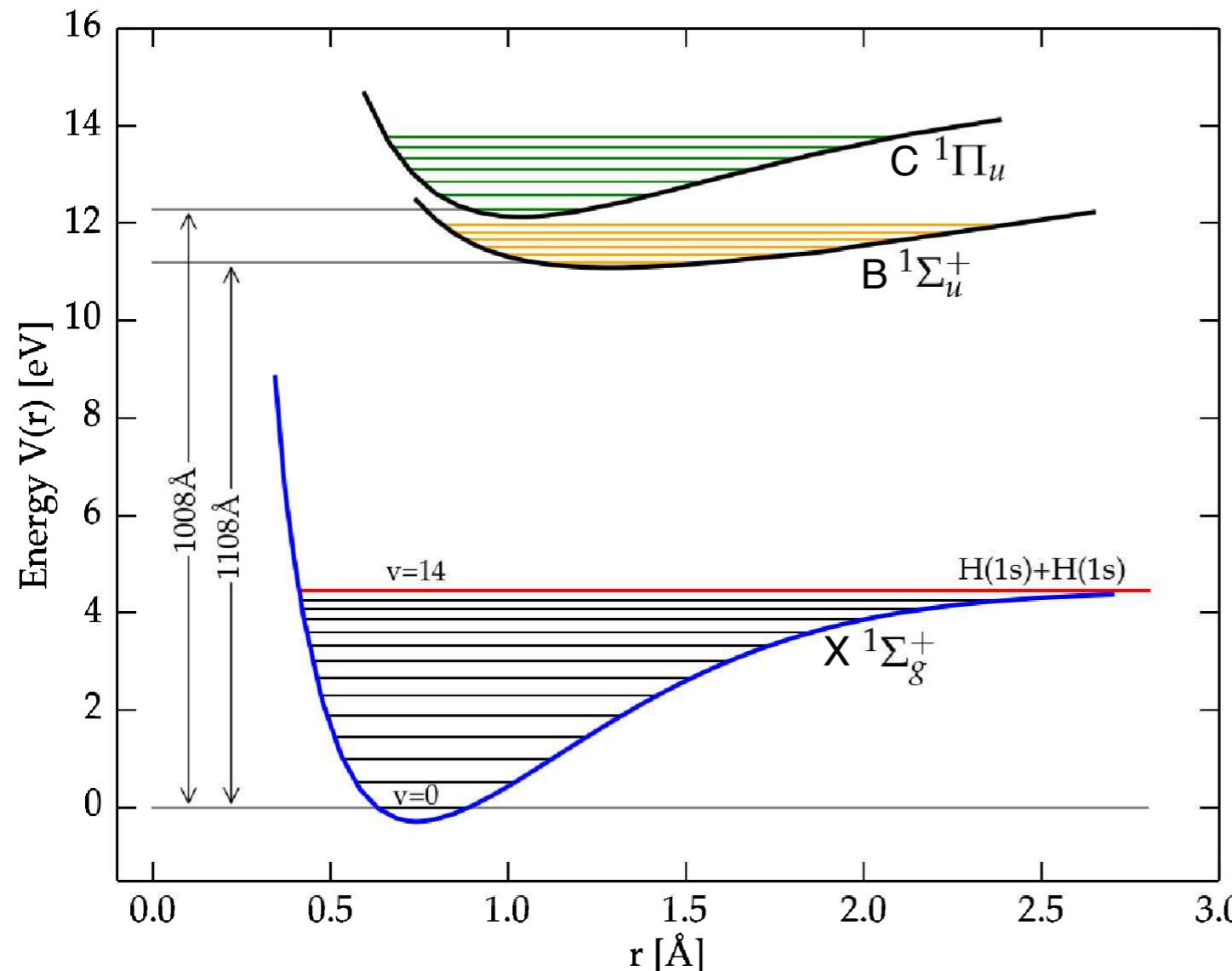
- Time scale of H₂ formation: dust grains are converting atomic hydrogen into molecular hydrogen on a characteristic time scale:

$$\begin{aligned}
 t_{\text{H}_2 \text{ form}} &\approx \frac{\frac{1}{2}n_{\text{HI}}}{R_{\text{gr}} n_{\text{H}} n_{\text{HI}}} \\
 &\approx 15 \text{ Myr} \left(\frac{n_{\text{H}}}{30 \text{ cm}^{-3}} \right)^{-1} \left(\frac{T_{\text{gas}}}{100 \text{ K}} \right)^{-1/2} \left(\frac{\langle \epsilon_{\text{gr}} \rangle}{0.08} \right)^{-1} \left(\frac{\Sigma_{\text{gr}}}{6 \times 10^{-21} \text{ cm}^2 \text{ H}^{-1}} \right)^{-1}
 \end{aligned}$$

- Thus, **the CNM should be filled with molecular hydrogen** - unless there's a competing process that destroys H₂ molecules as fast as grain surface make them.
- *The competing process is the photodissociation near bright stars.*

Photodissociation of H₂

- Photodissociation: $\text{H}_2 + h\nu \rightarrow \text{H} + \text{H} + \text{KE}$
 - Photodissociation is the principal process destroying interstellar H₂.



In the left potential energy curves, you might think that photodissociation of H₂ is a simple task; if H₂ absorb a photon of energy $h\nu > 4.52 \text{ eV}$, it will be excited to a vibrational state (**vibrational continuum**) with quantum number $v > 14$, which will be unbound.

However, absorbing a photon to lift the molecule to a $v > 14$ vibrational state requires a quadrupole transition, which has a very small transition probability.

Schematic drawing of the potential energy curves of molecular hydrogen [Figure 7.4, Ryden]

-
- **Lyman-Werner band**
 - ▶ The energy difference between the $v = 0, J = 0$ level in the ground electronic state, and the $v = 0, J = 0$ level in the first excited electronic state is $E = 11.18 \text{ eV}$ ($\lambda = 1108 \text{ \AA}$), which is a higher energy than the 10.2 eV energy of the Ly α line in atomic hydrogen.
 - ▶ The transitions between the ro-vibrational levels in the ground electronic state and the ro-vibrational levels in the **first excited electronic states** produce a forest of lines that are referred to collectively as the **Lyman band**.
 - ▶ Emission and absorption between the ground electronic state and the **second excited electronic state** is called the **Werner band**.
 - ▶ The Lyman and Werner bands lie in the energy range 11.2–13.6 eV.
 - The main mechanism by which H₂ is photodissociated is a two-step process.
 - ▶ The first step is absorption of a resonance line photon ($\lambda = 912\text{-}1108\text{\AA}$), raising the H₂ from an initial level $X(v, J)$ to a level $B(v', J')$ or $C(v', J')$ of the first and second electronic states. This photoexcitation is via a permitted absorption line, and therefore the newly excited level is guaranteed to have electric dipole-allowed decay channels, with a large transition probability.
 - ▶ The excited level is most likely to decay to vibrationally excited bound levels $X(v'', J'')$ of the ground electronic state, and such decays occur ~85% of the time. However, a fraction of ~15% of the time, the downward spontaneous transition will be to the vibrational continuum ($v > 14$) of the ground electronic state: The two hydrogen atoms will then fly away from each other and the hydrogen molecule is dissociated.

- Photodissociation Rate:

- ▶ The probability per unit time of photoexcitation of H_2 from lower level ℓ to upper level u is given by

$$\zeta_{\ell \rightarrow u} = \frac{\pi e^2}{m_e c} f_{\ell u} \frac{u_\nu c}{h\nu_{\ell u}} \rightarrow \frac{\pi e^2}{m_e c^2 h} f_{\ell u} \lambda_{\ell u}^3 u_\lambda$$

Eq (31.12) in Draine

cross-section x radiation field

- ▶ There are many transitions out of a given lower vibration-rotation level. The total rate of photoexcitation out of ℓ is:

$$\zeta_{\text{photoexc}, \ell} = \sum_u \zeta_{\ell \rightarrow u}$$

- ▶ The photodissociation rate is obtained by summing over all of the photoexcitation channels, each multiplied by the probability $p_{\text{diss}, u}$ that the upper level will decay to the vibrational continuum:

$$\zeta_{\text{diss}, \ell} = \sum_u \zeta_{\ell \rightarrow u} p_{\text{diss}, u}$$

- ▶ The dissociation probability averaged over the photoexcitation channels is:

$$\langle p_{\text{diss}} \rangle_\ell \equiv \frac{\zeta_{\text{diss}, \ell}}{\zeta_{\text{photoexc}, \ell}}$$

- ▶ Note that the photoexcitation and photodissociation rates are nearly independent of the level ℓ .

level ℓ (v, J)	$\zeta_{\text{photoexc}, \ell} / \chi^b$ (10^{-10} s^{-1})	$\zeta_{\text{diss}, \ell} / \chi$ (10^{-11} s^{-1})	$\langle p_{\text{diss}} \rangle_\ell$
(0,0)	3.08	4.13	0.134
(0,1)	3.09	4.20	0.136
(0,2)	3.13	4.23	0.135
(0,3)	3.15	4.57	0.145
(0,4)	3.21	4.94	0.154
(0,5)	3.26	5.05	0.155

Photoexcitation and Photodissociation Rates for Unshielded H₂

[Table 31.1, Draine; Draine & Bertoldi (1996)]

Here, the intensity of interstellar radiation field near 1000Å.

$$\chi \equiv \frac{(\nu u_\nu)_{1000\text{\AA}}}{4 \times 10^{-14} \text{ erg cm}^{-3}}$$

$\chi = 1$ for the ISRF of Habing (1968)

= 1.71 for the ISRF of Draine (1978)

= 1.23 for the ISRF of Mathis et al. (1983)

- ▶ In the local diffuse neutral ISM, the H₂ photodissociation rate is:

$$\zeta_{\text{diss}} \equiv \langle p_{\text{diss}} \rangle \zeta_{\text{photoexc}} \approx 5 \times 10^{-11} \text{ s}^{-1}$$

- ▶ The typical timescale for photodissociation of H₂ is: $t_{\text{diss}} \approx 1/\zeta_{\text{diss}} \sim 640 \text{ yr}$

This is smaller by four orders of magnitude than the ~ 15 Myr timescale for creation of H₂ by grain surface catalysis in the CNM.

- Steady-state abundance of H₂
 - ▶ The steady-state abundance of molecular hydrogen is determined by a balance between formation on grains and photodissociation, resulting in a very low steady state abundance:

$$\zeta_{\text{diss}} n(\text{H}_2) = R_{\text{gr}} n_{\text{HI}} n_{\text{H}}$$

$$\begin{aligned} \frac{n(\text{H}_2)}{n_{\text{HI}}} &= \frac{R_{\text{gr}} n_{\text{H}}}{\zeta_{\text{diss}}} \\ &\approx 1.8 \times 10^{-5} \left(\frac{n_{\text{H}}}{30 \text{ cm}^{-3}} \right) \left(\frac{R_{\text{gr}}}{3 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}} \right) \left(\frac{5 \times 10^{-11} \text{ s}^{-1}}{\zeta_{\text{diss}}} \right) \end{aligned}$$

- ▶ ***In the absence of self-shielding***, diffuse H I clouds will contain only a tiny amounts of H₂. ***Molecular hydrogen shouldn't dominate over atomic hydrogen until the density reaches $\sim 3 \times 10^6 \text{ cm}^{-3}$.***
- ▶ In reality, ***observations reveal that the molecular form dominates at densities as low as $\sim 300 \text{ cm}^{-3}$.*** This is because the inner parts of molecular clouds are protected from UV light by ***self-shielding***.

Self-Shielding and Dust-Shielding

- **Self-shielding** refers to the phenomenon where the photoexcitation transitions become optically thick, so that the molecule in question is “shielded” from starlight by other molecules.
 - ▶ Self-shielding occurs on a line-by-line basis, with stronger self-shielding for the stronger lines (large oscillator strengths) from levels with large populations.
 - ▶ Recall that the equivalent width is the measure of absorbed light ($\text{EW} = \text{fraction of absorbed light}$). **The rate of photoexcitation** is given, in general, by

$$\Delta N_\ell \zeta_{\text{pe}, \ell \rightarrow u} = \left(\frac{u_\nu c}{h\nu} \right) \Delta W$$

$$\zeta_{\text{pe}, \ell \rightarrow u} = \left(\frac{u_\nu c}{h\nu} \right)_{\ell u} \frac{dW_\nu}{dN_\ell}$$

where

$$W_\nu = \int d\nu (1 - e^{-\tau_\nu}) \rightarrow \text{fraction of absorption}$$

$$\tau_\nu = N_\ell \chi_0 \phi_\nu = N_\ell \frac{\pi e^2}{m_e c} f_{\ell u} \phi_\nu$$

ϕ_ν = line profile

u_ν = radiation energy density
in the absence of H_2 line absorption

In the optical thin limit,

$$\frac{dW_\nu}{dN_\ell} = \frac{d}{dN_\ell} \int d\nu \tau_\nu = \chi_0 = \frac{\pi e^2}{m_e c} f_{\ell u}$$

Note that

$$\tau_\lambda = \tau_\nu = N_\ell \frac{\pi e^2}{m_e c} f_{\ell u} \phi_\lambda \left| \frac{d\lambda}{d\nu} \right|$$

- ▶ Therefore, the self-shielding factor is defined to be:

$$f_{\text{shield}, \ell u} \equiv \frac{dW_\nu / dN_\ell}{(\pi e^2 / m_e c) f_{\ell u}} < 1$$



$$\zeta_{\text{pe}, \ell \rightarrow u} = \left(\frac{u_\nu c}{h\nu} \right)_{\ell u} \left(\frac{\pi e^2}{m_e c} f_{\ell u} \right) f_{\text{shield}, \ell u}$$

- ▶ The photodissociation rate for H_2 in level ℓ is reduced by self-shielding:

$$\begin{aligned}\zeta_{\text{diss},\ell} &= \sum_u \zeta_{\text{pe},\ell \rightarrow u} p_{\text{diss},u} \\ &= \frac{\pi e^2}{m_e c} \sum_u f_{\ell u} \left(\frac{u_\nu c}{h\nu} \right)_{\ell u} f_{\text{shield},\ell u} p_{\text{diss},u}\end{aligned}$$

Compare with Eq. (31.24) of [Draine]

$$\begin{aligned}u_\nu &= u_\lambda \left| \frac{d\lambda}{d\nu} \right| = u_\lambda \frac{\lambda^2}{c} \\ \rightarrow \frac{u_\nu c}{h\nu} &= u_\lambda \frac{\lambda^3}{hc}\end{aligned}$$

- ▶ The photodissociation rate per H_2 is obtained by averaging the above equation over the population levels. A reasonably accurate approximation is given by Draine & Bertoldi (1996).

$$\zeta_{\text{diss}} \approx \zeta_{\text{diss},0} f_{\text{shield, diss}} e^{-\tau_{\text{d},1000}}$$

$$f_{\text{shield,diss}} \approx \frac{0.95}{(1 + x/b_5)^2} + \frac{0.035}{(1 + x)^{0.5}} \exp [-8.5 \times 10^{-4} (1 + x)^{0.5}]$$

$$x \equiv \frac{N(\text{H}_2)}{5 \times 10^{14} \text{ cm}^{-2}}, \quad b_5 \equiv \frac{b}{\text{km s}^{-1}}$$

$\zeta_{\text{diss},0}$ = the photodissociation rate in the absence of dust extinction or self-shielding

$\tau_{\text{d},1000}$ = the optical depth by dust at 1000Å.

- Ryden provides a crude approximation for the above self-shielding factor:

$$f_{\text{shield,diss}} \approx \left(\frac{N(\text{H}_2)}{10^{14} \text{ cm}^{-2}} \right)^{-3/4}$$

- For a cloud with a density of 1000 cm^{-3} ,

$$\frac{n(\text{H}_2)}{n_{\text{HI}}} = \frac{R_{\text{gr}} n_{\text{H}}}{\zeta_{\text{diss}}} \quad \begin{array}{l} n_{\text{H}} = \text{number density of H nucleon} \\ n_{\text{HI}} = \text{number density of H atom} \end{array}$$

$$\approx 6 \times 10^{-4} \left(\frac{n_{\text{H}}}{1000 \text{ cm}^{-3}} \right) \left(\frac{1}{f_{\text{shield,diss}}} \right)$$

The ratio of H_2 molecules to H atoms becomes equal to one when the gas is self-shielded by a column density:

$$N_{\text{H}_2} \gtrsim 1.5 \times 10^{18} \text{ cm}^{-2} \quad \leftarrow \frac{n(\text{H}_2)}{n_{\text{HI}}} = 1$$

This corresponds to **an outer shelf-shielding skin to the cloud that is just 4×10^{-4} pc.**

$$d = \frac{N_{\text{H}_2}}{n_{\text{H}}} = 4 \times 10^{-4} \text{ pc} \left(\frac{N_{\text{H}_2}/1.5 \times 10^{18} \text{ cm}^{-2}}{n_{\text{H}}/1000 \text{ cm}^{-3}} \right)$$

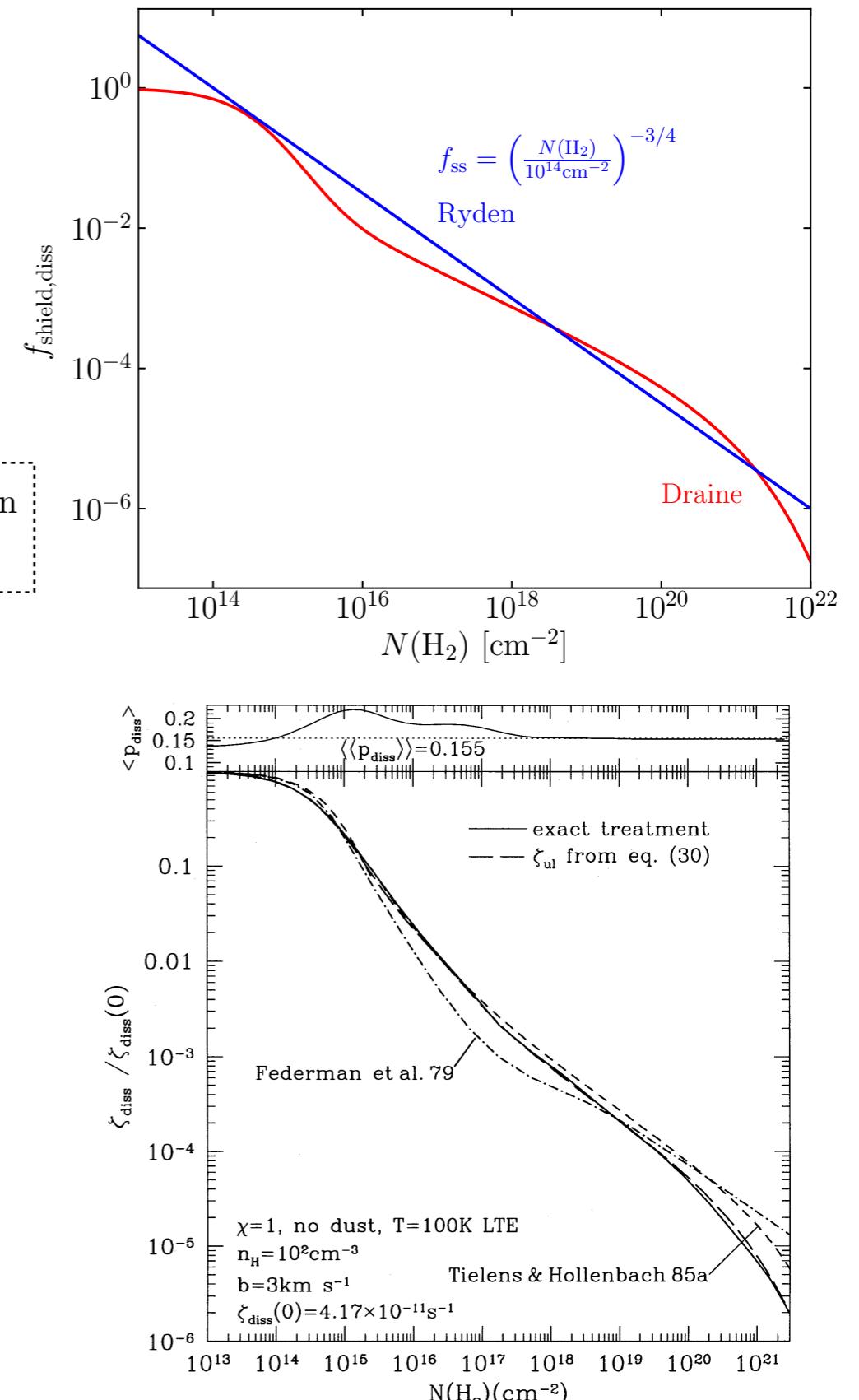


Fig 1, Draine & Bertoldi (1996)

- **Dust** can also shield molecular gas from UV light.
 - ▶ In our galaxy, the relation between dust extinction and column density of hydrogen nucleon and the ratio between extinctions 1100Å and V band are, respectively:

$$\frac{A_V}{N_{\text{H}}} \approx 5.3 \times 10^{-22} \text{ cm}^2$$

$$\frac{A_{1100}}{A_V} \approx 4$$

- ▶ When hydrogen is primarily molecular, $N(\text{H}_2) = N_{\text{H}}/2$. This results in dust extinction in the Lyman and Werner bands of

$$\frac{A_{1100}}{N(\text{H}_2)} \approx \frac{4A_V}{N_{\text{H}}/2} \approx 4.2 \times 10^{-21} \text{ cm}^2$$

$A_{1100} \gtrsim 1$

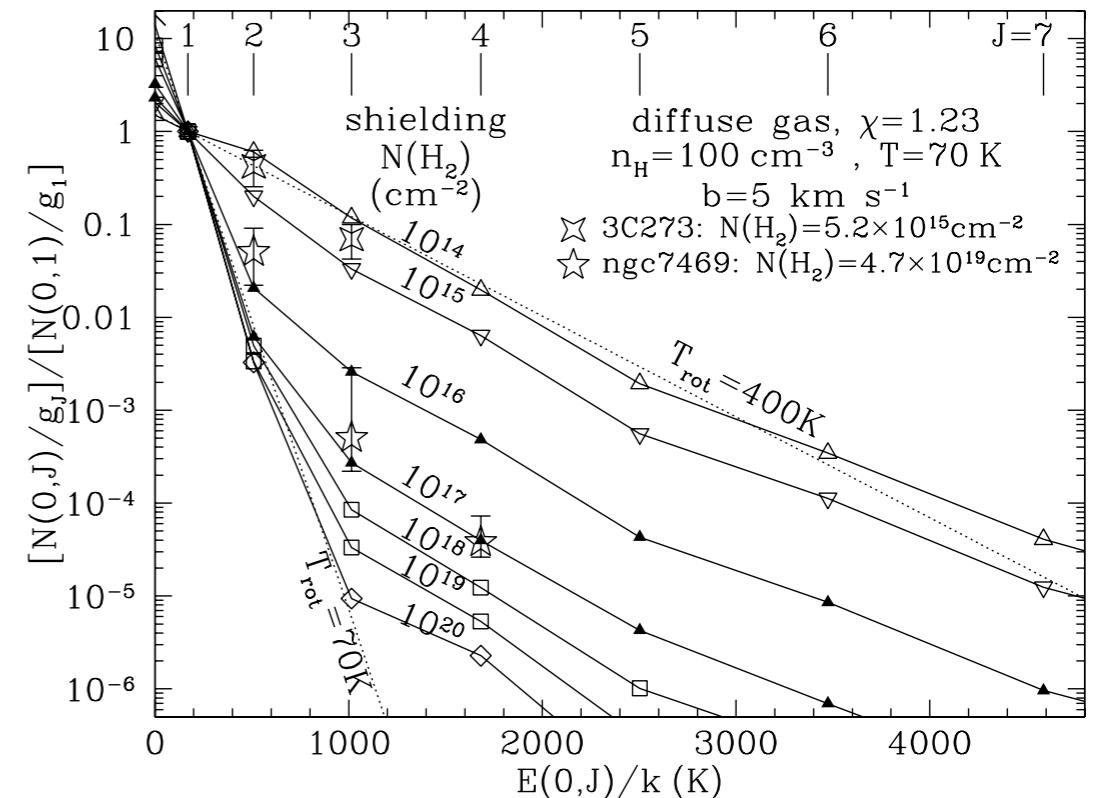
- ▶ Thus, column densities $N(\text{H}_2) \gtrsim 2.4 \times 10^{20} \text{ cm}^{-2}$ have more than one magnitude of dust extinction in the Lyman and Werner bands.
- ▶ This is 100 times higher than the H₂ column density that leads to self-shielding in typical molecular gas. Thus, **self-shielding by H₂ is much more effective than shielding by dust under ordinary circumstances.**

Vibrational and Rotational Level Population

- Vibrational Level Populations
 - Photoexcitation to some level $B(v', J')$ or $C(v', J')$ will be followed, within a few nanoseconds, by spontaneous decay to some level $X(v'', J'')$ of the ground electronic state. As a result, UV pumping of H_2 populates the vibrationally excited levels of the ground electronic state.
 - At low densities, these vibrationally excited levels will spontaneously decay to lower vibrational levels via electric quadrupole transitions. *This “radiative cascade” populates many lower levels, finally reaching the ground vibrational level.*
 - The vibrationally excited levels have radiative lifetimes of only $\sim 10^6$ sec, and collisional deexcitation by collisions with H, H_2 , or He is unlikely at densities $n_H \lesssim 10^4 \text{ cm}^{-3}$.
 - This cascade yields optical and near-infrared emission lines.

- Rotational Level Populations

- In the ground vibrational state, the lifetime of the lowest rotational levels are long enough that collisional effects can play a role in depopulating the lowest J levels. ***The populations of the lowest J levels are, therefore, sensitive to the density and temperature of the gas.***
- For ***low levels of self-shielding*** ($N(H_2) \lesssim 10^{15} \text{ cm}^{-2}$), the rotational distribution function for $J > 2$ is relatively insensitive to the gas temperature.
 - ▶ The rotational levels $J \geq 3$ have relative populations that can be approximately characterized by rotational temperature $T_{\text{rot}} \approx 400 \text{ K}$.
 - ▶ However, this has nothing to do with the actual temperature; ***it is entirely the result of the branching ratios in the vibration-rotation “cascade” that populates the high J levels.***
- As the ***shielding column density increases***, the UV pumping rates decline, and the fraction of H_2 in levels $J > 3$ declines.
- The relative populations of the lowest levels $J = 0$ and $J = 2$ can be used to estimate the gas temperature.



Rotational excitation of H_2 in diffuse clouds, for various $N(H_2)$.

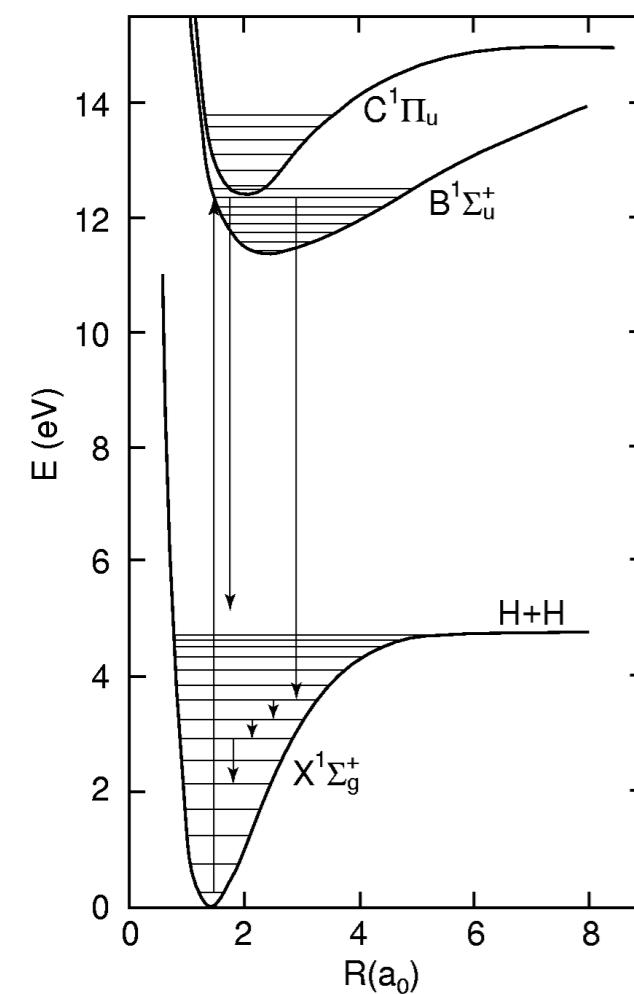
Also shown is the rotational excitation of H_2 in diffuse clouds to the sightlines of the AGNs 3C273 and NGC 7469 (Gillmon et al. 2006).

Fig 31.1, Draine

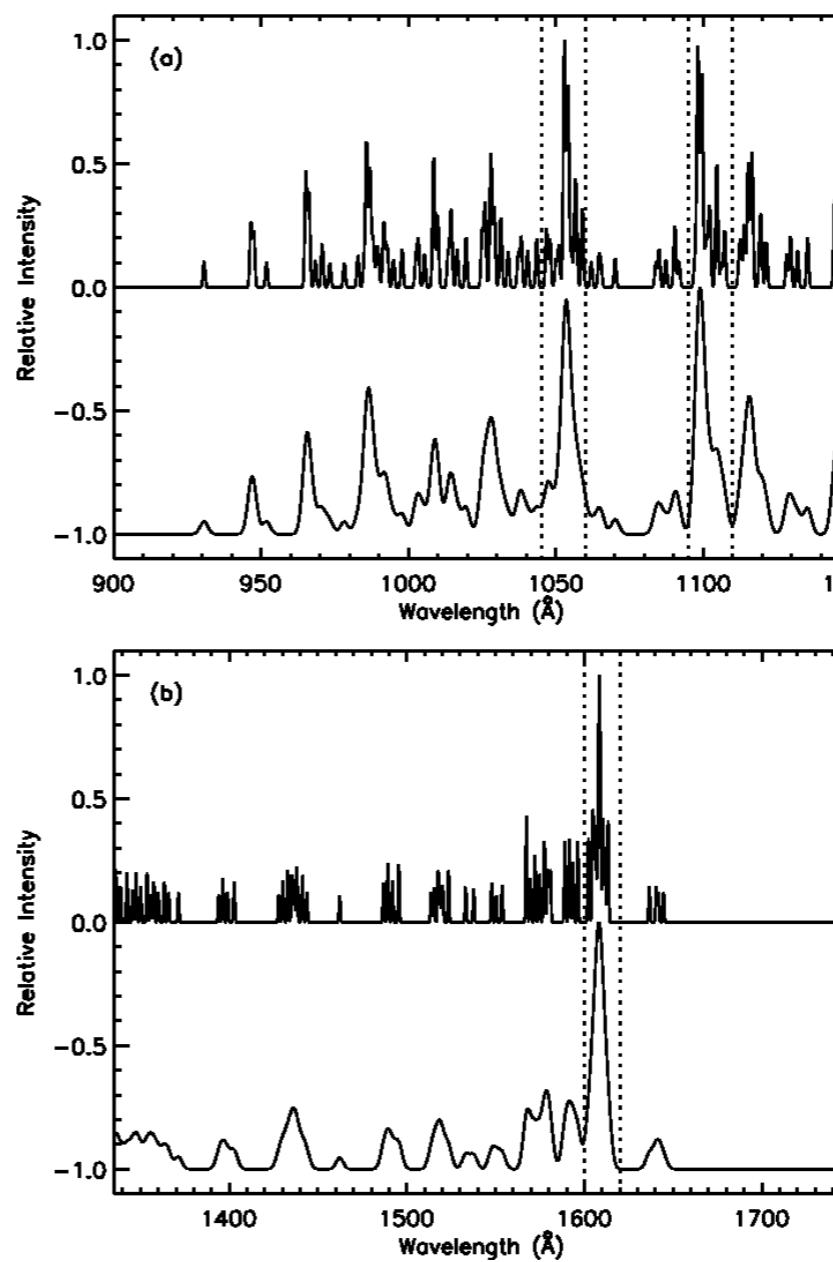
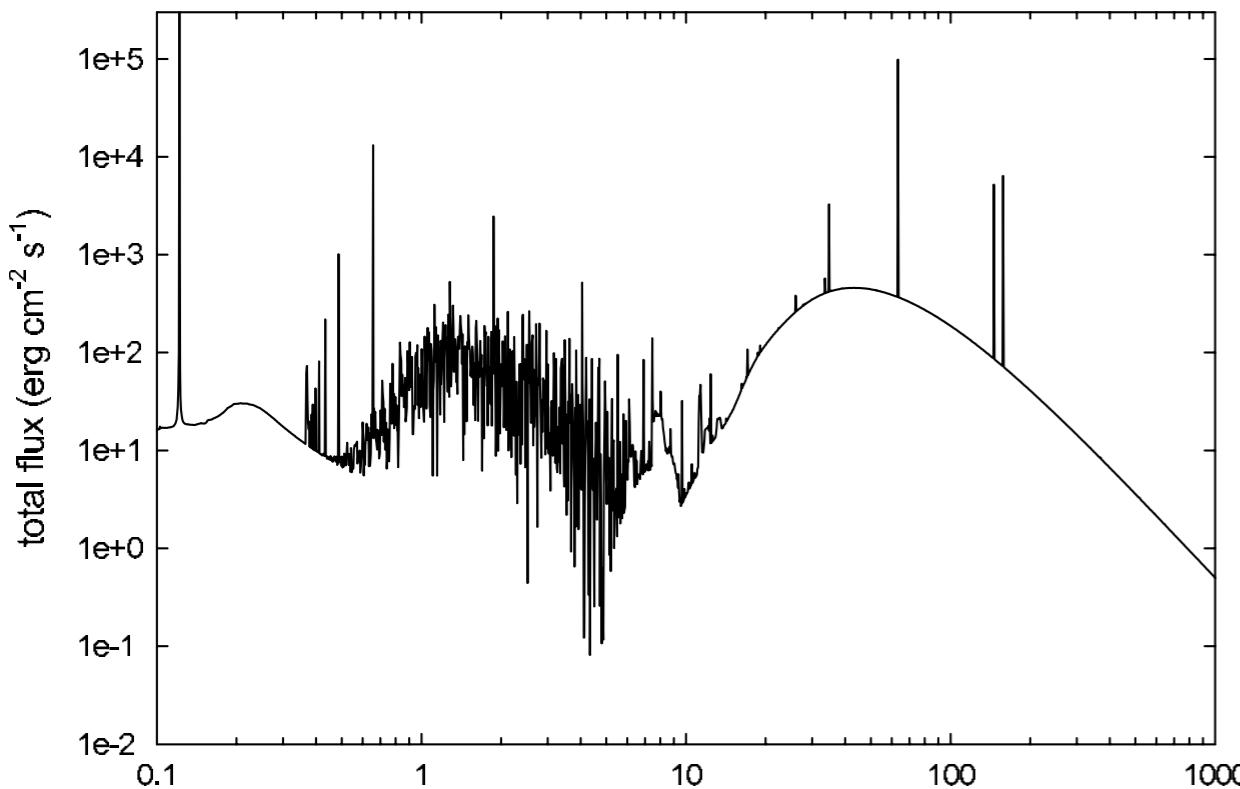
For $N(H_2) \gtrsim 10^{18} \text{ cm}^{-2}$ high column density

$$T_{\text{gas}} \approx \frac{510 \text{ K}}{\ln [5N(0,0)/N(0,2)]}$$

Molecular Hydrogen Fluorescence Lines



Energy levels of H_2
van Dishoeck (1990),
Molecular
Astrophysics



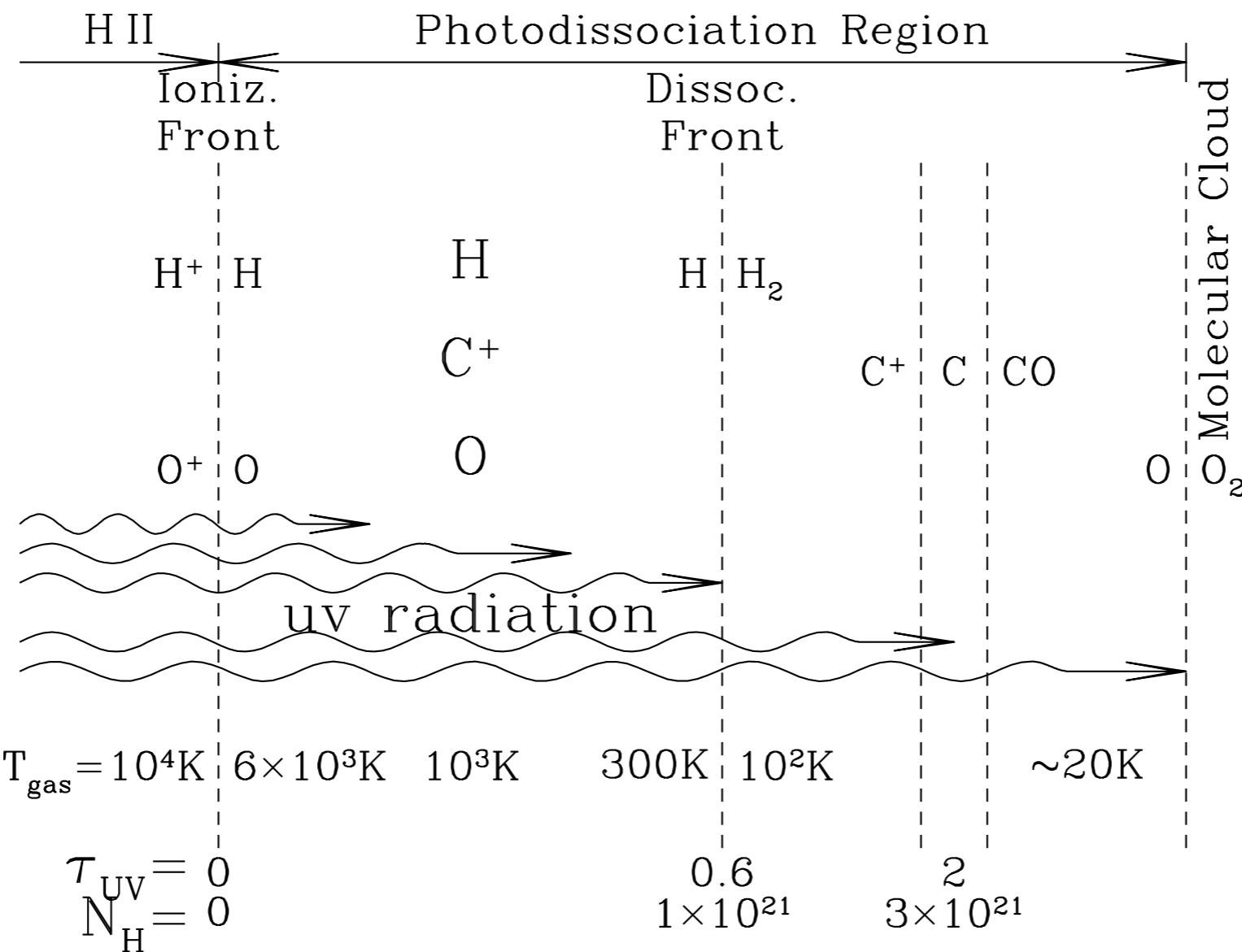
Seon et al. (2003)
 H_2 emission spectra
calculated using the
model of Sterberg
(1989).
The upper panels are
for the short-
wavelength band of
the FIMS, and the
lower panels are for
the long-wavelength
band.

Shaw et al. (2005)

Thermal emission by dust dominates the IR
emission, with fine structure atomic emission
superimposed.
PAH features are present in the near IR.
A set of weak H_2 lines are present in the 1–
10 μm region.

Photodissociation Region (PDR)

- H II region + PDR
 - Stars are formed out of molecular gas, and when a massive star forms, it strongly irradiate the remaining molecular clouds with UV radiation, resulting in photoionization and photodissociation.
 - ▶ The photoionized gas, heated to $\sim 10^4$ K, will be overpressure, which will drive a compressive wave in the molecular cloud, and will also cause the ionized gas to try to flow toward lower-pressure regions nearby.
 - ▶ **The interface between the H II region and the dense molecular cloud is called a photodissociation region or PDR.**
 - ▶ PDR will be bounded by an ionization front - the surface where the hydrogen is 50% ionized - and will contain a photodissociation front - the surface where the hydrogen is 50% atomic and 50% molecular (by mass).
 - The overall physics and chemistry of PDRs is complex - see the review by Hollenbach & Tielens (1999).
- **Meudon PDR code:** a code that consider a stationary plane-parallel slab of gas and dust illuminated by a radiation field coming from one or both side of the cloud.
 - <https://ism.obspm.fr/pdr.html> (Le Petit et al. 2006, ApJS, 164, 506)



Structure of a PDR at the interface between an H II region and a dense molecular cloud.
[Fig 31.2, Draine]

[Molecular Clouds] Observations

- Cloud Structure
 - Local density estimates using line ratios often give larger densities than global mean densities found by averaging the observed molecular column densities along the line of sight.
 - The interpretation of this is that the ***clouds are very clumpy***, with the dense cores having typical sizes of < 1 pc or smaller, and densities $> 10^6 \text{ cm}^{-3}$.
 - The overall cloud extends for 3–20 pc on average, with a mean density of 10^{3-4} cm^{-3} .
 - Most molecular clouds show **a number of discernible cores**. These are often detected as sources of molecular lines with high critical densities (e.g., CS), while the general cloud is mapped using lines of lower critical density (mainly CO).
 - Within the galaxies, molecular clouds are most often seen organized into complexes with **sizes from 20 pc to 100 pc, and overall H₂ masses of $10^{4-6} M_{\text{sun}}$** . The distinction between “clouds” and “complexes” in terms of sizes and masses is somewhat artificial.
 - A more precise statement would be that ***we see a wide range of structures***, from single small clouds to large complexes of clouds, with many complexes arrayed along the spiral arms of the Galaxy.

Molecular Clouds: Cloud Categories

- Cloud Categories (based on the total surface density)
 - Individual clouds are separated into categories based on their optical appearance: diffuse, translucent, or dark, depending on the visual extinction A_V through the cloud.

Category	A_V (mag)	Examples
Diffuse Molecular Cloud	$\lesssim 1$	ζ Oph cloud, $A_V = 0.84^a$
Translucent Cloud	1 to 5	HD 24534 cloud, $A_V = 1.56^b$
Dark Cloud	5 to 20	B68 ^c , B335 ^d
Infrared Dark Cloud (IRDC)	20 to $\gtrsim 100$	IRDC G028.53-00.25 ^e

^a van Dishoeck & Black (1986).

^b Rachford et al. (2002).

^c Lai et al. (2003).

^d Doty et al. (2010).

^e Rathborne et al. (2010).

[Table 32.1, Draine]

- **Diffuse and translucent clouds** have sufficient UV radiation to keep gas-phase carbon mainly photoionized throughout the cloud.
 - Such clouds are usually pressure-confined, although self-gravity may be significant in some cases.
- The typical **dark clouds** have $A_V \sim 10$ mag, and is self-gravitating. Some dark clouds contain dense regions that are extremely opaque, with $A_V > 20$ mag.
- **Infrared Dark Clouds** are opaque even at 8 μm , and can be seen in silhouette against a background of diffuse 8 μm emission from PAHs in the ISM.

- Terminology for Cloud Complexes and Their Components

Categories	Size (pc)	n_{H} (cm^{-3})	Mass (M_{\odot})	Linewidth (km s^{-1})	A_V (mag)	Examples
GMC Complex	25 – 200	50 – 300	$10^5 – 10^{6.8}$	4 – 17	3 – 10	M17, W3, W51
Dark Cloud Complex	4 – 25	$10^2 – 10^3$	$10^3 – 10^{4.5}$	1.5 – 5	4 – 12	Taurus, Sco-Oph
GMC	2 – 20	$10^3 – 10^4$	$10^3 – 10^{5.3}$	2 – 9	9 – 25	Orion A, Orion B
Dark Cloud	0.3 – 6	$10^2 – 10^4$	5 – 500	0.4 – 2	3 – 15	B5, B227
Star-forming Clump	0.2 – 2	$10^4 – 10^5$	$10 – 10^3$	0.5 – 3	4 – 90	OMC-1, 2, 3, 4
Core	0.02 – 0.4	$10^4 – 10^6$	$0.3 – 10^2$	0.3 – 2	30 – 200	B335, L1535

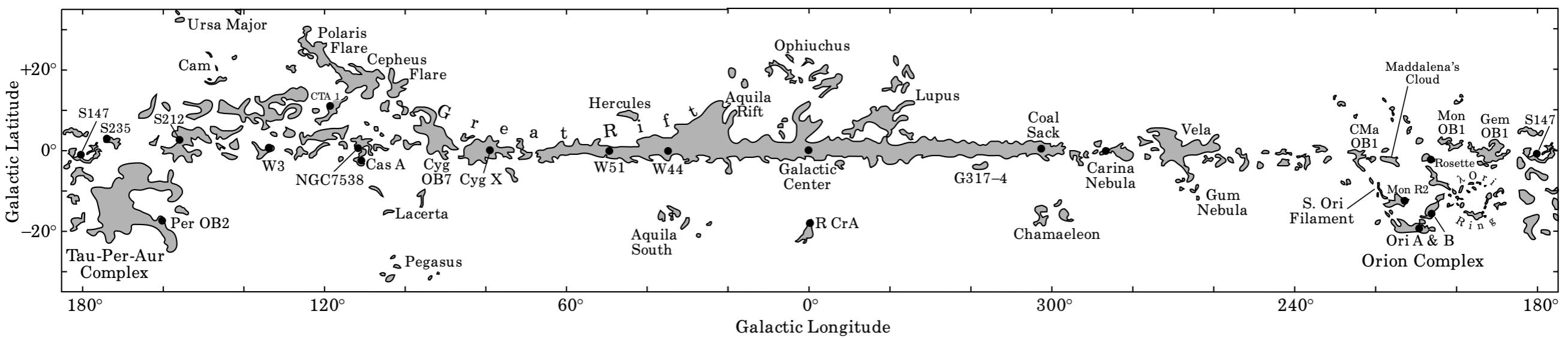
[Table 32.2, Draine]

- The **giant molecular cloud (GMC)** and **dark cloud** categories are distinguished mainly by total mass.
- Groups of distinct clouds are referred to as **cloud complexes**.
 - ▶ Molecular clouds are sometimes found in isolation, but in many cases molecular clouds are grouped together into complexes.
 - ▶ Since large clouds generally have substructure, the distinction between “cloud” and “cloud complex” is somewhat arbitrary.
 - ▶ Delineation of structure in cloud complexes is guided by the intensities and radial velocities of molecular lines (e.g., CO J = 1-0) as well as maps of thermal emission from dust at submm wavelengths.

Categories	Size (pc)	n_{H} (cm^{-3})	Mass (M_{\odot})	Linewidth (km s^{-1})	A_V (mag)	Examples
GMC Complex	25 – 200	50 – 300	10^5 – $10^{6.8}$	4 – 17	3 – 10	M17, W3, W51
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GMC	2 – 20	10^3 – 10^4	10^3 – $10^{5.3}$	2 – 9	9 – 25	Orion A, Orion B
Dark Cloud	0.3 – 6	10^2 – 10^4	5 – 500	0.4 – 2	3 – 15	B5, B227
Star-forming Clump	0.2 – 2	10^4 – 10^5	$10 - 10^3$	0.5 – 3	4 – 90	OMC-1, 2, 3, 4
Core	0.02 – 0.4	10^4 – 10^6	$0.3 - 10^2$	0.3 – 2	30 – 200	B335, L1535

[Table 32.2, Draine]

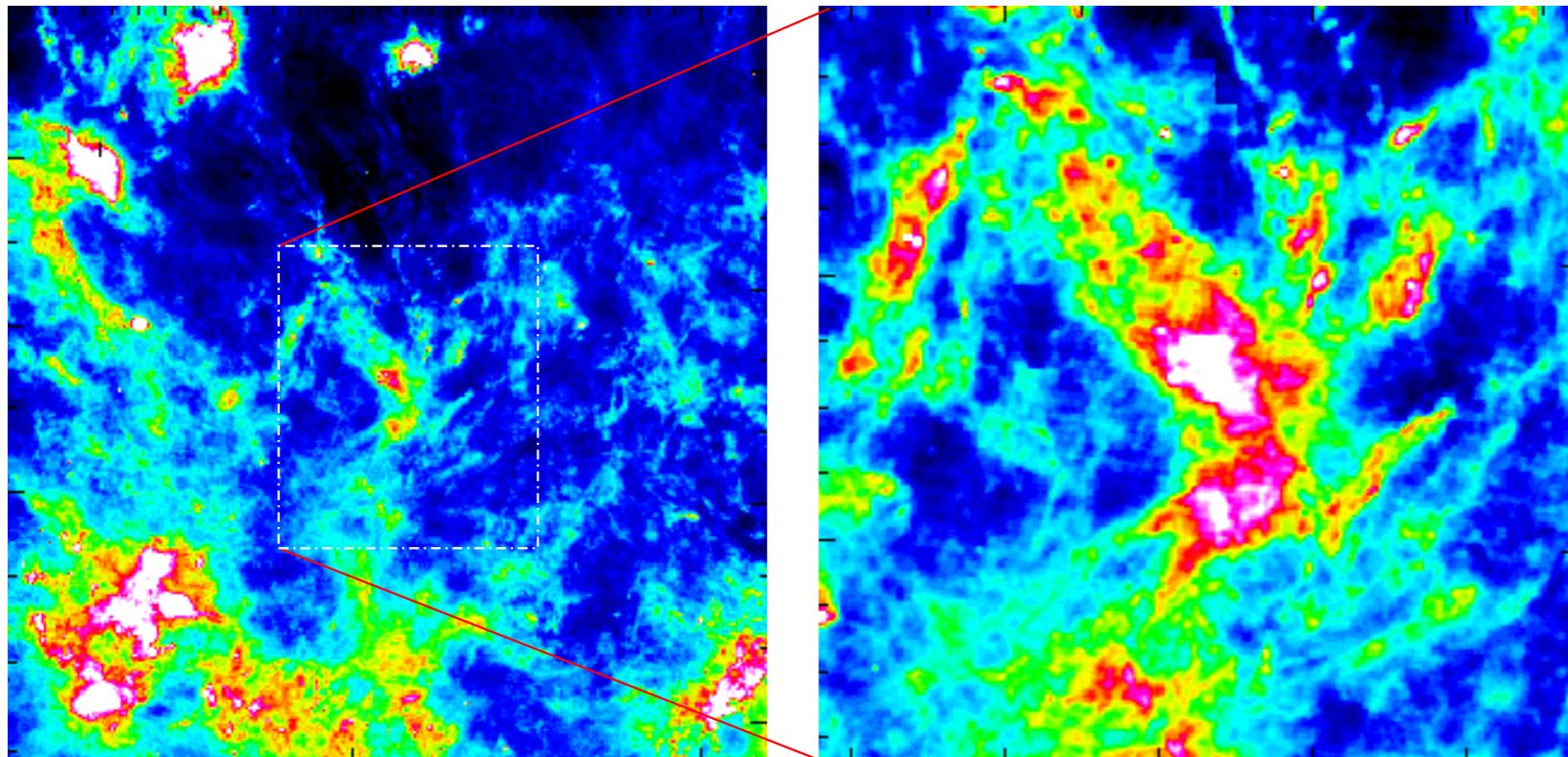
- Structures within a cloud (self-gravitating entities) are described as **clumps**.
 - ▶ Clumps may or may not be forming stars; in the former case they are termed **star-forming clumps**. **Cores** are density peaks within star-forming clumps that will form a single star or a binary star.
- GMC and GMC complex
 - ▶ Much of the molecular mass is found in large clouds known as “giant molecular clouds”, with masses ranging from $\sim 10^3 M_{\odot}$ to $\sim 2.5 \times 10^5 M_{\odot}$. These have reasonably well-defined boundaries.
 - ▶ A GMC complex is a gravitationally bound group of GMCs (and smaller clouds) with a total mass $\gtrsim 10^{5.3} M_{\odot}$.



Locations of prominent molecular clouds along the Milky Way
[Fig 32.2, Draine, Dame et al. (2001)]

The Fractal Structure of the Molecular Clouds

- Self-similarity of Clouds
 - The molecular interstellar medium is very clumpy and fragmented. Its hierarchical structure can well be described by a fractal, because of its self-similarity.
 - It has no characteristic scale. Fractals by definition are self-similar ensembles, that have a non-integer, i.e., fractional dimension.
 - ***The self-similar structures in the ISM extends over 6 orders of magnitude in scale, from about 10^{-4} to 100 pc.***
 - ▶ These are not observed for the same molecular cloud only because of technical problems, lack of spatial resolution on one side, and difficulty of mapping too large areas on the other.
 - ▶ The scaling relations all over the scales are however obtained by comparing various clouds observed with different resolutions.



IRAS 100 μm map of molecular clouds towards the Taurus complex, located at about 100 pc from the Sun. The square is $\sim 4000 \text{ pc}^2$.

Fig 14, Chap 2, Blain, Combes, Draine
[The Cold Universe]

Mass Distribution of GMCs

- Overall mass distribution of GMCs in the Milky Way
 - CO line surveys can detect GMCs at large distances, allowing the total number in the Galaxy to be estimated.
 - The overall mass distribution of GMCs in the Milky Way (excluding the molecular material within a few hundred pc of the Galactic center) can be approximated by a power-law:

$$\frac{dN_{\text{GMC}}}{d \ln M_{\text{GMC}}} \approx N_u \left(\frac{M_{\text{GMC}}}{M_u} \right)^{-\alpha} \quad \text{for } 10^3 M_{\odot} \lesssim M_{\text{GMC}} < M_u$$

$$M_u \approx 6 \times 10^6 M_{\odot}$$

$$N_u \approx 63$$

$$\alpha \approx 0.6$$

- **Most of the mass is in the most massive GMCs:**
 - ▶ $\sim 80\%$ of the molecular mass is in GMCs with $M > 10^5 M_{\odot}$.

- Star Counts
 - Molecular clouds were originally discovered by star counts.
 - ▶ Herschel (1785) noticed that there were patches along the Milky Way where very few stars were seen. He incorrectly attributed this to a real absence of stars.
 - ▶ We now understand that the apparent deficiency of stars is the result of obscuration by dusty clouds.
 - ▶ Star counts using background stars is a good way to study the cloud structure.
 - ▶ Because the visual obscuration can be very large, studies of dark clouds using star counts are now usually done in the J, H, or K bands.

Gas Surface Density in the Milky Way

- The most common way to study molecular gas is through molecular line emission, and the primary line used is the $J = 1-0$ transition (2.6 mm) of CO.
 - ▶ This transition is often optically thick, but the CO 1-0 luminosity of a cloud is approximately proportional to the total mass.
 - ▶ ***Velocity-resolved mapping of CO 1-0 together with an assumed rotation curve and an adopted value of the “CO to H₂ conversion factor” X_{CO} have been used to infer the surface density of H₂ over the Milky Way disk.***

Gas surface densities as a function of galactocentric radius. The Sun is assumed to be at $R = 8.5$ kpc.

- Surface density of H₂ estimated from CO 1-0 observations (Nakanishi & Sofue 2006), assuming

$$X_{CO} = 1.8 \times 10^{20} \text{ H}_2 \text{ cm}^{-2}/\text{K km s}^{-1}$$
- Surface density of H II derived from pulsar dispersion measures (Cordes & Lazio 2003).
- Surface density of H I from 21-cm studies (Nakanishi & Sofue 2003)

[Fig 32.4, Draine]

