

Interstellar Medium (ISM)

Lecture 11
June 11 (Thursday), 2020

updated 06/08, 21:38

선광일 (Kwangil Seon)
KASI / UST

Molecular Clouds 1

- Molecular Structure
- Formation and Destruction of Molecular Hydrogen
- Photodissociation Region

[Bohn-Oppenheimer Approximation]

- **Bohn-Oppenheimer approximation:**
 - The motions of the electrons and nuclei could be treated separately.
 - *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. The nuclei then feel only an equivalent potential that depends on the internuclear distance and on the particular electronic state.
 - 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:

Let a be a typical molecular size. Then, the electron energy will be given by

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

- Vibrational energy:

For stable molecules, the internuclear potential has a minimum at some point. Vibration about the minimum can occur and can be estimated roughly by comparing to a harmonic oscillator. Then, the potential energy of the harmonic oscillator must be similar to the electronic energy:

$$\frac{1}{2}M\omega^2a^2 \sim \frac{\hbar^2}{2m_e a^2}$$

where ω = frequency of vibration.
 M = mass of the molecule.

Then, the vibrational energy is

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

Recall that the energy levels of a harmonic oscillator:

$$E_{\text{osc}} = \left(n + \frac{1}{2}\right) \hbar\omega$$

- Rotational energy:

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

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

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

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

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

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

[Schrodinger equation for a diatomic molecule]

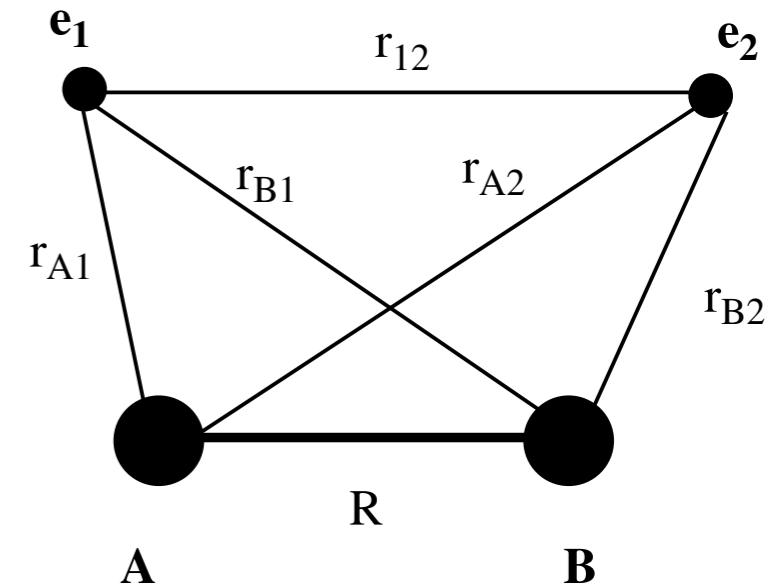
For a diatomic molecule with N electrons,

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

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

The potential terms are:

- (1) attraction of the electrons by nucleus A
- (2) attraction of the electrons by nucleus B
- (3) electron-electron repulsion
- (4) nuclear-nuclear repulsion



- Bohn-Oppenheimer approximation: We write the wave function as a product of electronic and nuclear wave functions.

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

- The **electronic wavefunction** satisfies the following equation:

$$\left(-\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + V_e - E_e \right) \psi_e(\mathbf{r}_i) = 0$$

This equation is solved separately for each value of the internuclear separation R . Then, the resulting eigenvalue E_e is given as a function of R .

-
- The nuclear wave function satisfies the Schrodinger equation:

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

There are three 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 Schrodinger 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.

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

 the angular part of the Laplacian operator ∇^2

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

(1) The solution of the angular equation is:

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

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

(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:

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

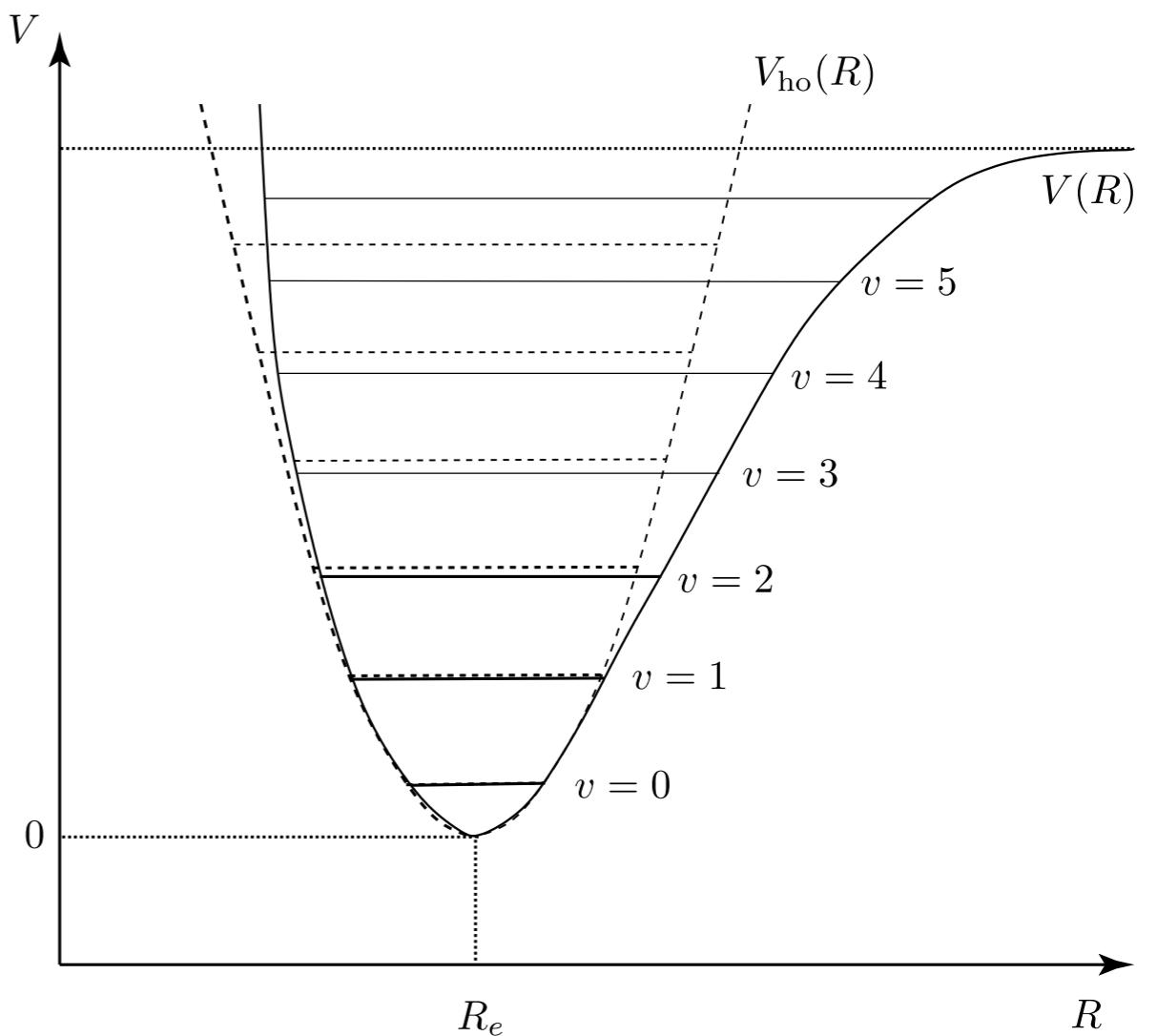
Setting the zero of energy at the minimum potential, $V_0 = V(R_e) = 0$, the radial equation becomes

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

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

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

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



[Electronic Structures of Diatomic Molecules]

- 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 most 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 angular momentum onto the internuclear axis
 $= \mathcal{L} + S_z$ ($\rightarrow J_{ez} = L_z + S_z$)

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

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

- 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 states are + state Σ^+ .
One exception is O₂, of which the lowest electronic state is ${}^3\Sigma_g^-$.

- The electronic states of diatomic molecules are also labelled with letters:

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

- Diatomc 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

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

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

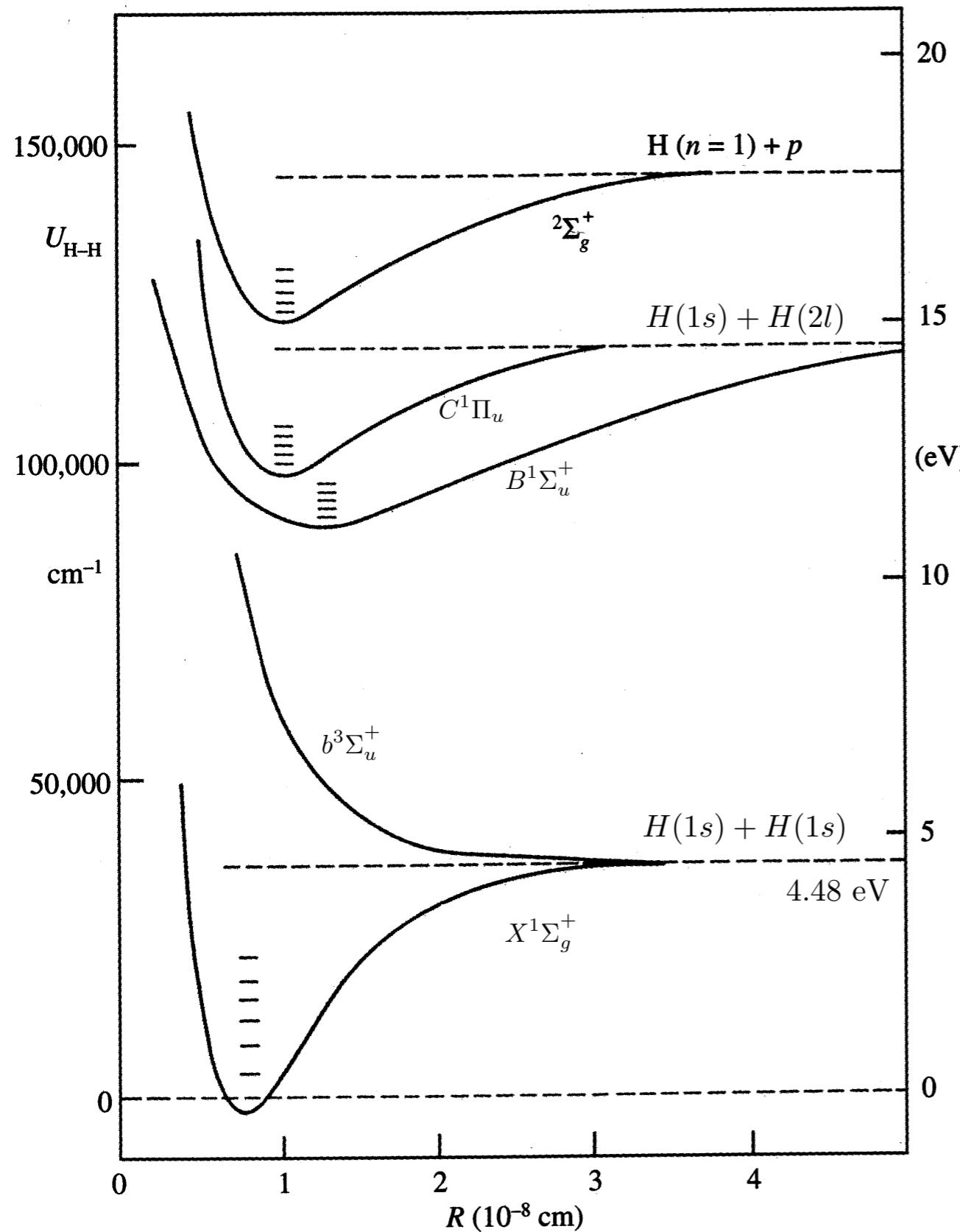
- For the special case of Σ state, a superscript + or - is added.

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

- In the case of a heteronuclear diatomic molecule (e.g., HD, OH, or CO), the energy levels are designated:

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

[Energy levels of Molecular Hydrogen]



- The short horizontal lines in each of the bound states indicate the vibrational levels.
- 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**.

Werner band: $C^1\Pi_u - X^1\Sigma_g^+$ at about 1100 Å;
 Lyman band: $B^1\Sigma_u^+ - X^1\Sigma_g^+$ at about 1010 Å.

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	$^1\Sigma_0^+$

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 2 *p* electrons contributed by C and 4 *p* electrons contributed by O; together, these 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. The reduced mass of CO is $(12 \times 16/28)$ amu \approx 6.9 amu. The C=O

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.

[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) $g \longleftrightarrow u$
- Electric-dipole selection rule for ro-vibrational transitions:
 $\Delta v = \text{any}$
 $\Delta J = 0, \pm 1$ not $J = 0 \leftrightarrow 0$
- But, note that H_2 has no electric-dipole. The electric-quadrupole are allowed for $\Delta J = \pm 2$.

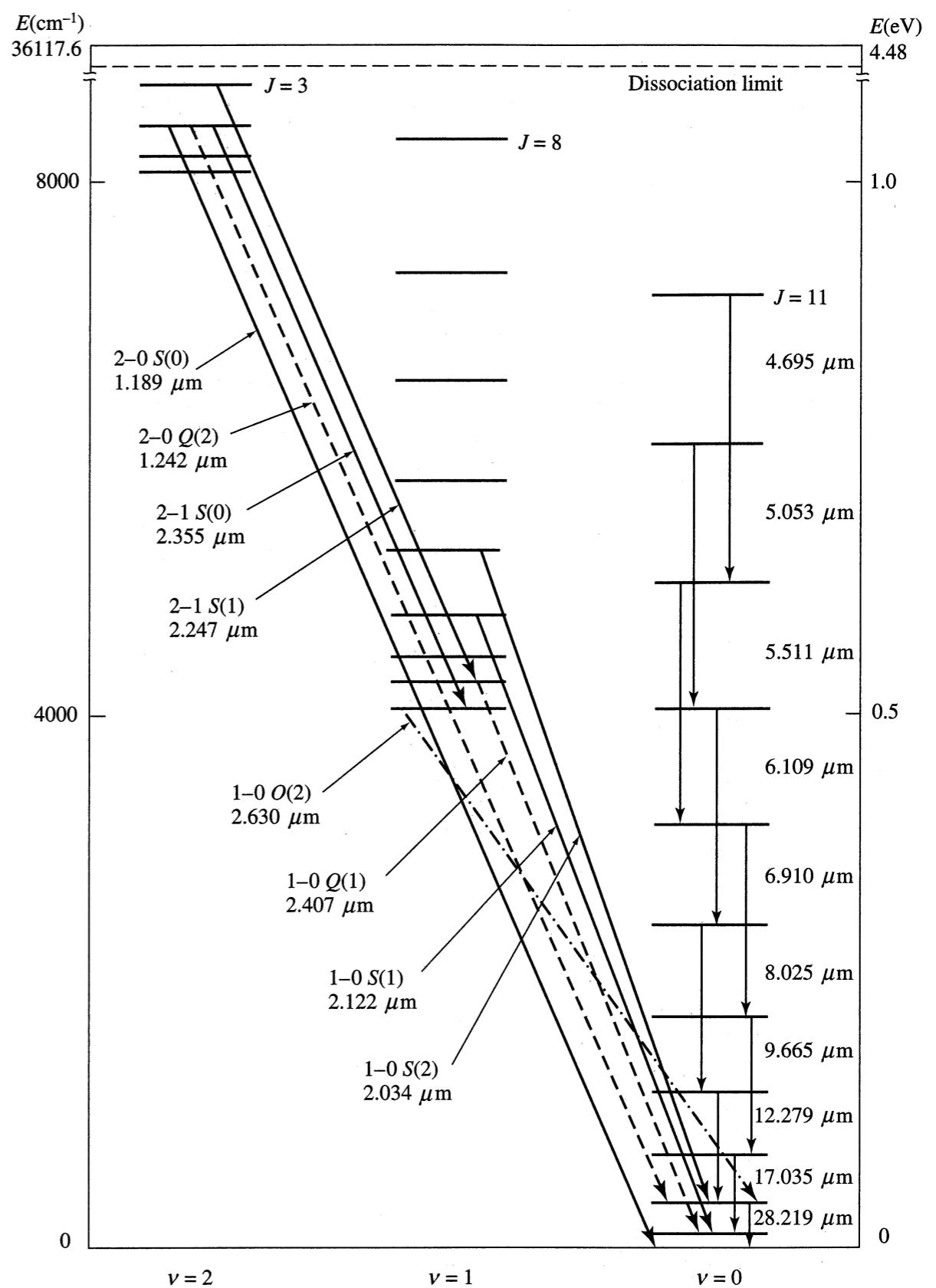
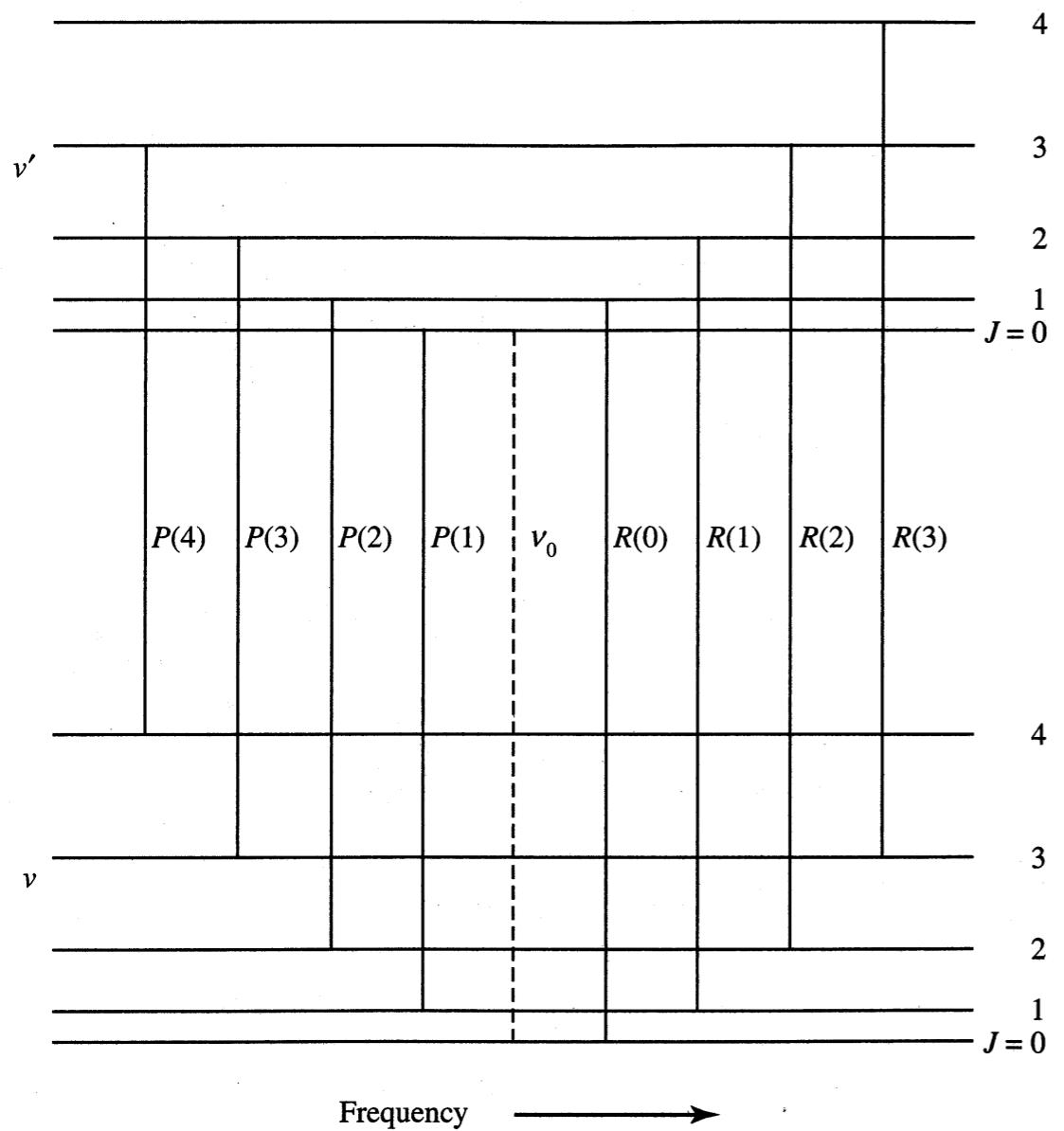
O, P, Q, R, and S transitions

- 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 $0, \pm 1$ or ± 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.

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

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



[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**

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) or total spin 0 (antiparallel).

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 involving even values 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 involving odd values 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.**
 - 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 $J = 0 \leftrightarrow J = 0$)

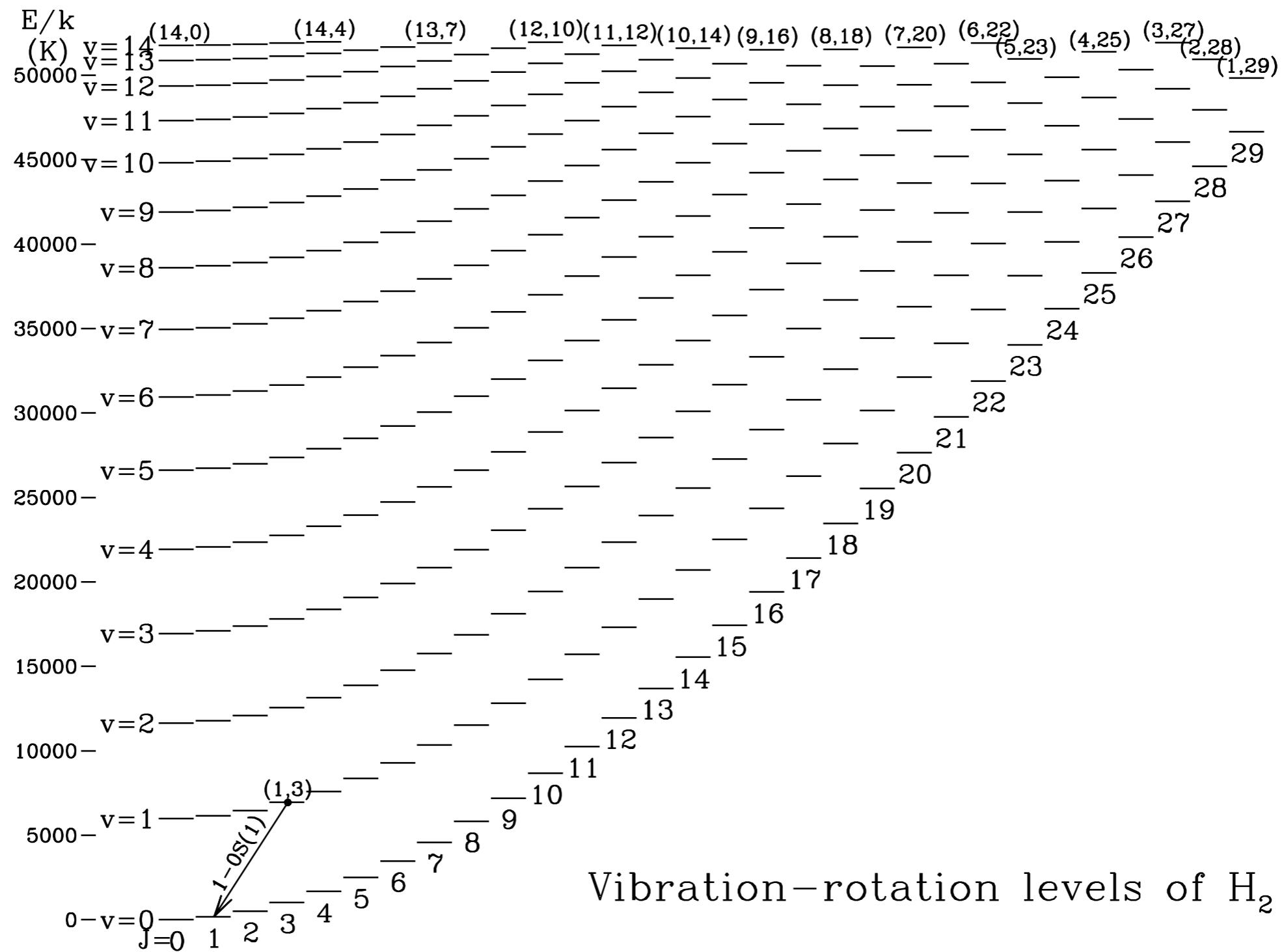
The vibration-rotation emission spectrum of H₂ therefore consists of electric quadrupole transitions. Therefore, the H₂ emission lines are faint and hard to detect. The downward transitions are identified by

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

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 $S_{\text{nucleus}} = 0$]



Vibration–rotation energy levels of the ground electronic state of H_2 with $J \leq 29$. The $(v, J) = (1, 3)$ level and $1-0\text{S}(1)$ $\lambda = 2.1218 \mu\text{m}$ transition are indicated.

Ortho/Para Ratios

- The ortho state of a molecule is defined as having the larger of two 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.
 - ▶ Since $g = 2I + 1$, the usual ortho to para ratio is $(2x1+1)/(2x0+1) = 3$ 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.

- 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 photo dissociate 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

D_0 = dissociation energy

r_0 = speration

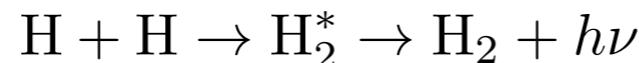
$$B_0 \equiv \frac{\hbar^2}{2I}$$

$\omega_0 = \sqrt{k/\mu}$ fundamental frequency of vibration

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:

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

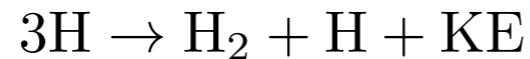
Rate for the electric quadrupole transition:

$$A_{ul} \sim 10^{-11} \text{ s}^{-1}$$

Probability of emitting a photon before it breaks apart: $p \sim A_{ul} (2\pi/A_{ul}) \sim 10^{-25}$

- 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 H₂ 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 H₂.

- ***Formation of negative hydrogen ion by radiative association followed by formation of H₂ by associative detachment:***

- First step:



- Second step:



This is an exothermic 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.



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

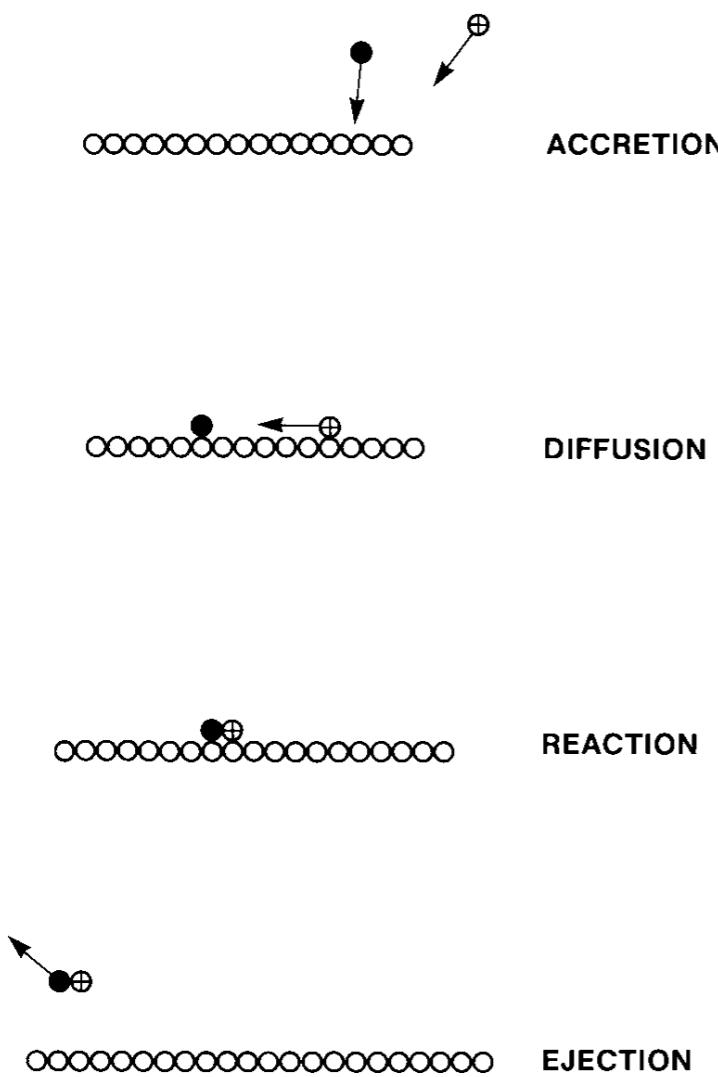
The photodetachment needs only $I = 0.77 \text{ eV}$ to take away one of its electrons.

- ***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

$$n_{\text{HI}} > \frac{\zeta_{\text{pd}}}{k_{\text{ad}}} \approx 120 \text{ cm}^{-3}$$

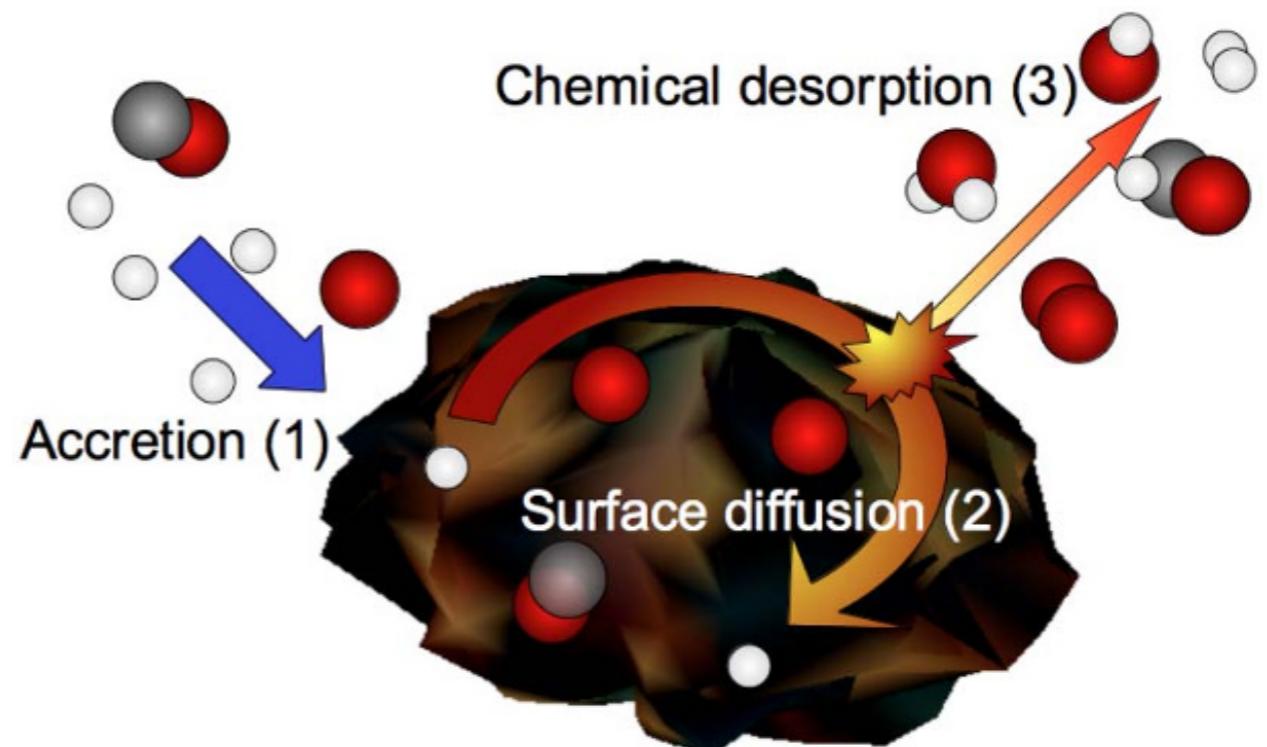
Grain Catalysis of H₂

- The dominant process of H₂ formation in the Milky Way and other galaxies is via grain catalysis.
 - The surface of a dust grain acts as a lab of chemical activity.
 - **Adsorption:**
 - ▶ 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 $a \sim 0.1\mu\text{m}$
 - **Diffusion & 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:**
 - ▶ 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.



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

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

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

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

$$\Sigma_{\text{gr}} \equiv \frac{1}{n_{\text{H}}} \int da \frac{dn_{\text{gr}}}{da} \pi a^2 \quad \longrightarrow \quad \Gamma_{\text{coll}} = n_{\text{HI}} n_{\text{H}} \left(\frac{8kT_{\text{gas}}}{\pi m_{\text{H}}} \right)^{1/2} \Sigma_{\text{gr}}$$

- ▶ 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.

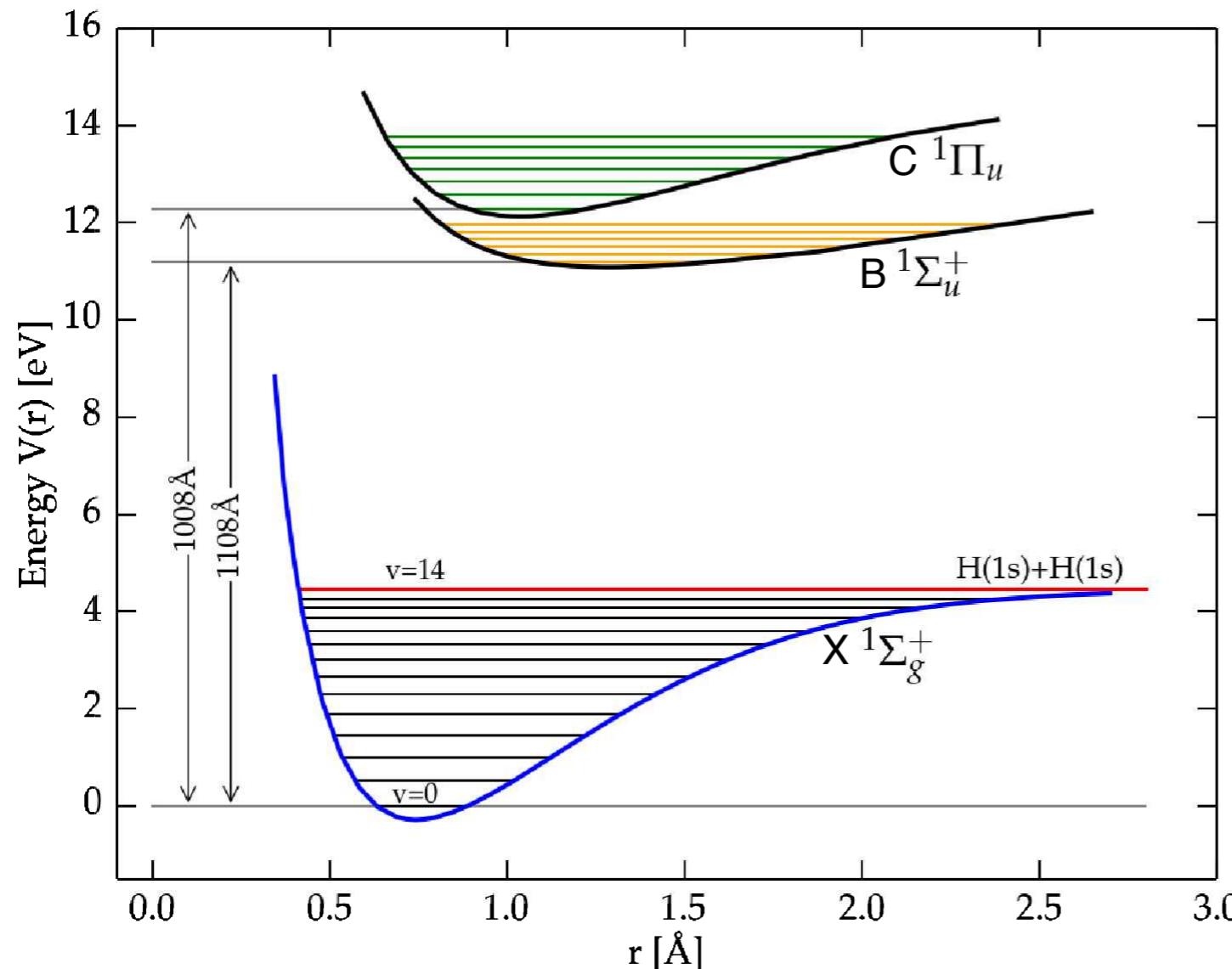
-
- Time scale of H₂ formation: dust grains are converting atomic hydrogen into molecular hydrogen on a characteristic time scale:

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

- Thus, the CNM should be filled with molecular hydrogen - unless there's a competing process that before the H₂ molecules as fast as grain surface make them.

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 11.18 - 13.60 eV.
 - The main mechanism by which H_2 is actually photodissociated is a two-step process.
 - ▶ The first step is absorption of a resonance line photon ($\lambda = 912\text{-}1108\text{\AA}$), raising the H_2 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 $\sim 85\%$ of the time. However, a fraction of $\sim 15\%$ 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

$$\zeta_{\ell \rightarrow u} = \frac{\pi e^2}{m_e c} f_{\ell u} \frac{u_\nu c}{h\nu_{\ell u}} \quad \rightarrow \quad \frac{\pi e^2}{m_e c^2 h} f_{\ell u} \lambda_{\ell u}^3 u_\lambda \quad \text{Eq (31.12) in Draine}$$

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

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

- ▶ 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:

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

- ▶ 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)]

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

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

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

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

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)

- 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. The rate of photoexcitation is given, in general, by

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

where $W_\lambda = \int d\lambda (1 - e^{-\tau_\lambda})$

$$\tau_\lambda = N_\ell \sigma_{\ell \rightarrow u} \phi_{\ell u} = N_\ell \frac{\pi e^2}{m_e c} f_{\ell u} \phi_{\ell u}$$

$\phi_{\ell u}$ = line profile

In the optical thin limit,

u_ν = radiation energy density in the absence of H₂ line absorption

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

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

$$f_{\text{shield}, \ell u} \equiv \frac{dW_\lambda/dN_\ell}{(\pi e^2/m_e c) f_{\ell u}} < 1 \quad \longrightarrow \quad \zeta_{\text{pe}, \ell \rightarrow u} = \left(\frac{u_\nu c}{h\nu} \right)_{\ell u} \left(\frac{\pi e^2}{m_e c} f_{\ell u} \right) f_{\text{shield}, \ell u}$$

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

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

- ▶ 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 dust optical depth by dust at 1000Å.

- ▶ Ryden provides a crude approximation for the 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} ,

$$\begin{aligned} \frac{n(\text{H}_2)}{n_{\text{HI}}} &= \frac{R_{\text{gr}} n_{\text{H}}}{\zeta_{\text{diss}}} \\ &\approx 6 \times 10^{-4} \left(\frac{n_{\text{H}}}{1000 \text{ cm}^{-3}} \right) \left(\frac{1}{f_{\text{shield,diss}}} \right) \end{aligned}$$

the ratio of H₂ molecules to H atoms becomes equal to one when the gas is self-shielded by a column density:

$$N_{\text{H}} \gtrsim 1.5 \times 10^{18} \text{ cm}^{-2}$$

This corresponds to an outer shelf-shielding skin to the cloud that is just $4 \times 10^{-4} \text{ pc}$.

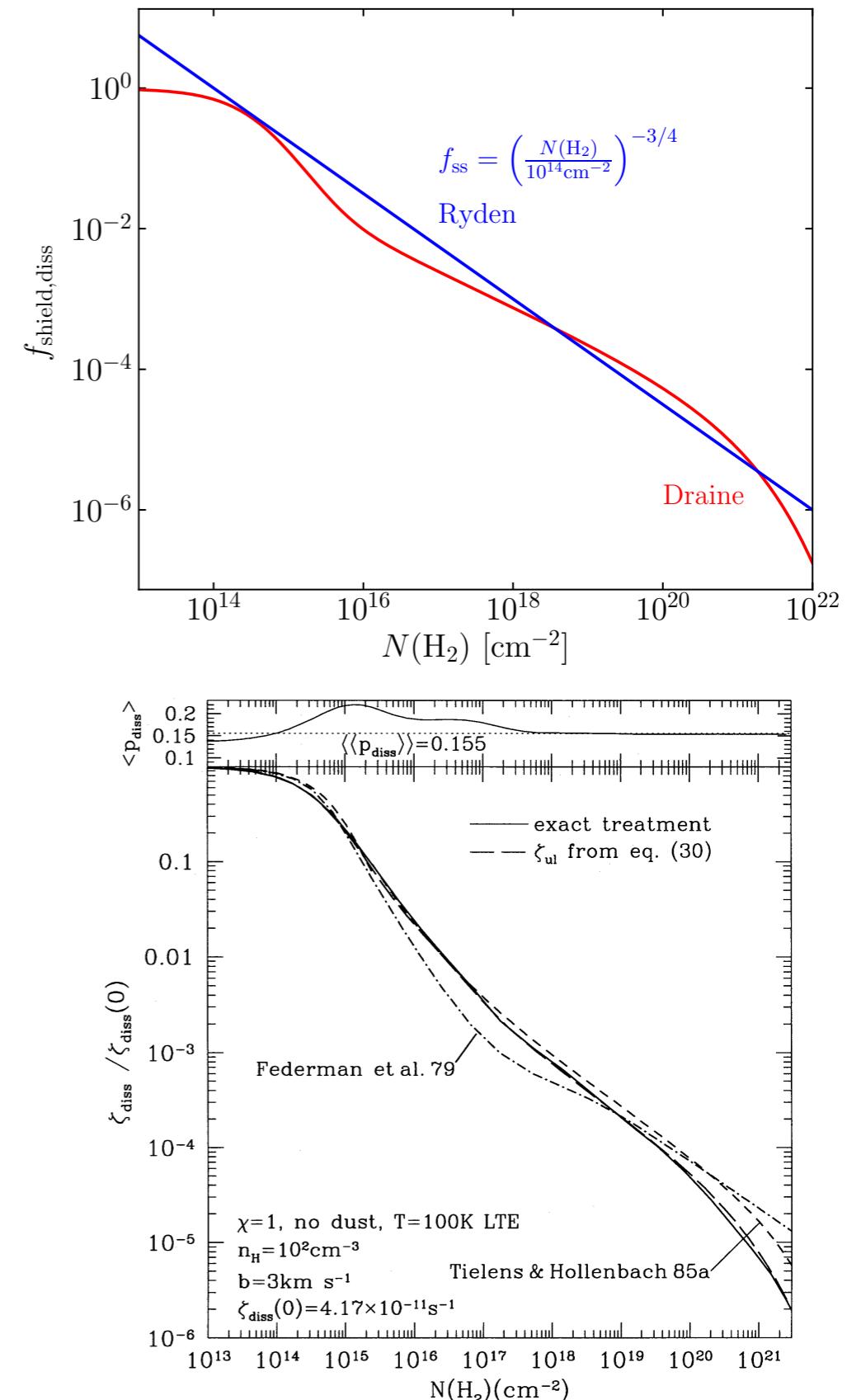


Fig 1, Draine & Bertoldi (1996)

-
- **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:

$$\frac{A_V}{N_{\text{H}}} \approx 5.3 \times 10^{-22} \text{ cm}^2 \quad \frac{A_{1100}}{A_V} \approx 4$$

- ▶ 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

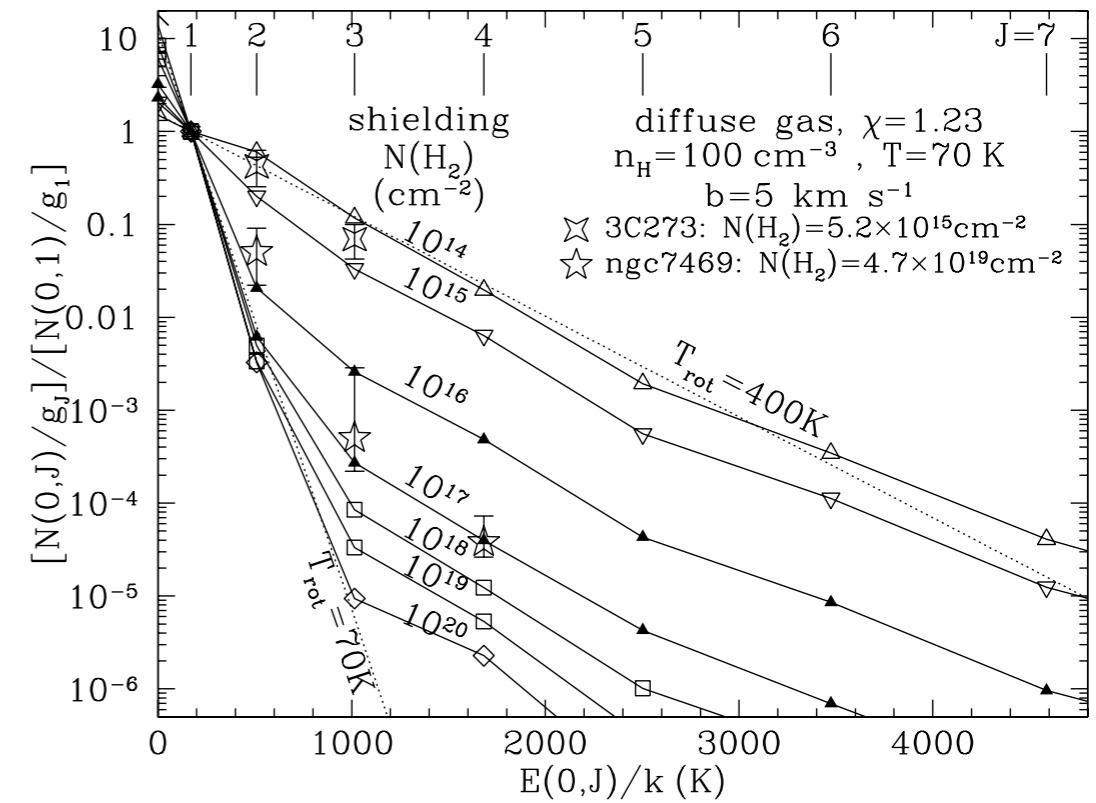
$$\frac{A_{1100}}{N(\text{H}_2)} \approx \frac{4A_V}{N_{\text{H}}/2} \approx 4.2 \times 10^{-21} \text{ cm}^2$$

- ▶ 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 H_2 column density that leads to self-shielding in typical molecular gas. Thus, self-shielding by H_2 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 $n_H \lesssim 10^4 \text{ cm}^{-3}$.

- 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 H₂ in levels $J > 3$ declines.
 - ▶ The relative populations of levels $J = 0$ and $J = 2$ can be used to estimate the gas temperature:



Rotational excitation of H₂ in diffuse clouds, for various N(H₂).

Also shown is the rotational excitation of H₂ in diffuse clouds to the sightlines of the AGNs 3C273 and NGC 7469 (Gillmon et al. 2006).

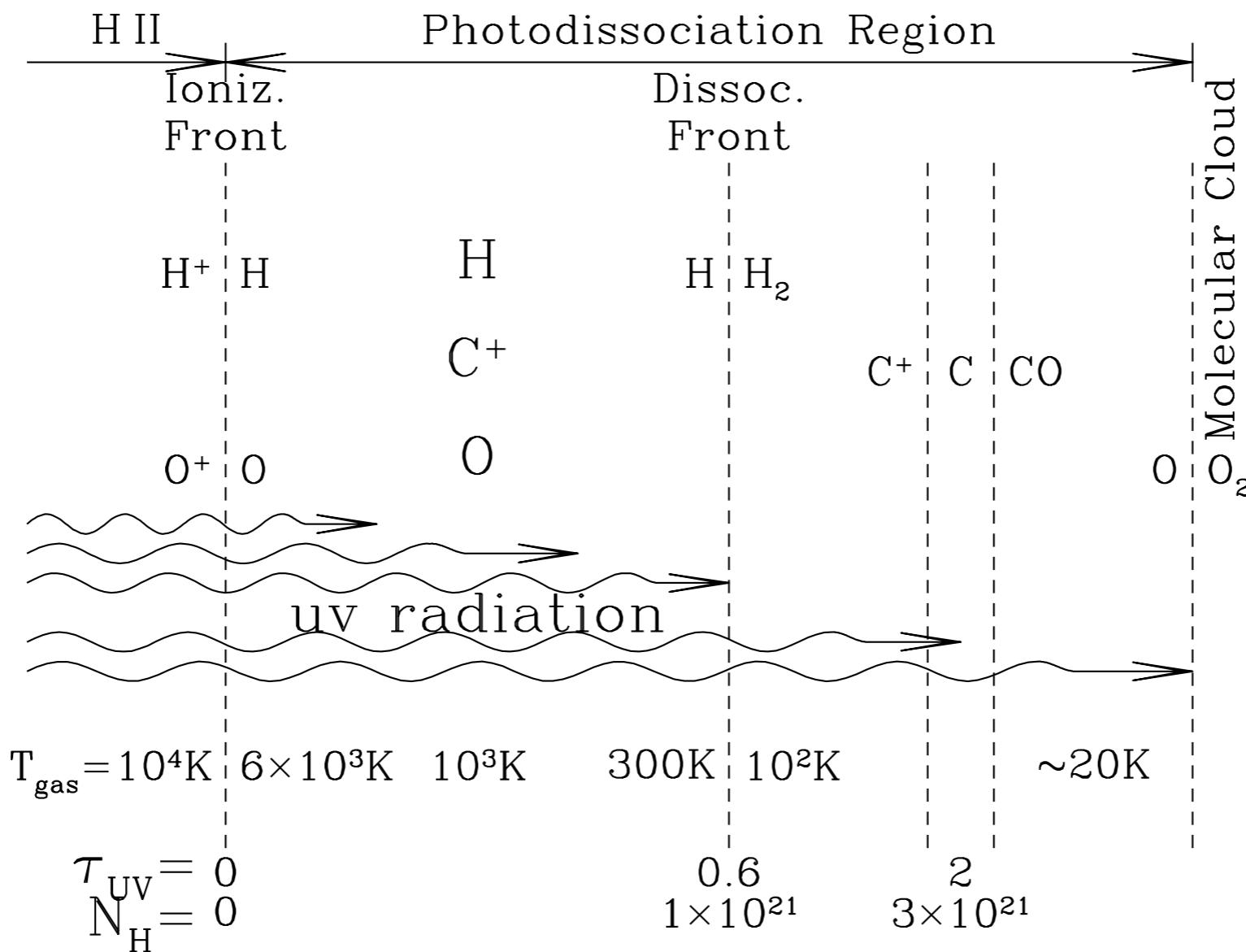
Fig 31.1, Draine

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

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

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).



Structure of a PDR at the interface between an H II region and a dense molecular cloud.

[Fig 31.2, Draine]

• 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 3876.84Å), CH ($A^2\Delta - X^2\Pi$ at 4300.30Å) and CH+ ($A^1\Pi - X^1\Pi^+$ at 4232.54Å)
- As of 2005, over 120 interstellar molecules have been detected.

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	l-C ₃ H	C ₄ H	l-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	l-C ₃ H ₂	CH ₃ CN	HC ₅ N	C ₇ H
CH	CH ₂	C ₃ S	c-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	c-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	HOCO ⁺	H ₂ C ₂ O	HC ₄ N		
KCl	HNC	H ₂ CO	H ₂ NCN			
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				
SO	OCS		Nine atoms	Ten atoms	Eleven atoms	Twelve atoms
SO ⁺	SO ₂		CH ₃ C ₄ H	CH ₃ C ₅ N(?)	HC ₉ N	CH ₃ OC ₂ H ₅
SiN	c-SiC ₂		CH ₃ CH ₂ CN	(CH ₃) ₂ CO		HC ₁₁ N
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, Kowk]