

Astrophysics

Lecture 15

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Molecular Structure

[Introduction]

- The Make-Up of Molecules and Solids

Atoms can be combined to form molecules or solids.

The properties of these compounds depend greatly on the way their constitutive atoms are bonded together, by their electrons.

- Molecular Bonding

Chemical bonds are the result of the overlap between the outer orbitals of two atoms whose valence shell is not full.

Despite their mutual repulsion, sharing electrons leads to a lower energy state, in which a stable bonded molecule is formed.

The atomic spacing in a molecule or a solid is of the order of a few Å.

- Valence shell

The outer shell is called the valence shell. It contains the electrons responsible for molecular bonds and shaping the optical properties of solids.

The chemical bond depends on the tendency of its atoms: (i) to share electrons; (ii) to form cations, by losing one or several electrons; or (iii) to form anions, by gaining one or several electrons.

- So far, ***about 200 molecules*** have been detected in the interstellar and circumstellar medium by direct observation of their spectra. These molecules are ones which ***contain up to 13 atoms.***

- Molecules formed from two atoms are called **diatomics** while those formed from more than two atoms are described as **polyatomic**.
- Because molecular binding energies are relatively small, i.e., generally less than ionization energies, molecules are only found in cooler, or less active, astronomical environments.

Polyatomic molecules are only a significant component of matter at temperatures below about 4000 K. Diatomic systems can survive to somewhat higher temperatures and may be found in environments with temperatures up to about 8000 K.

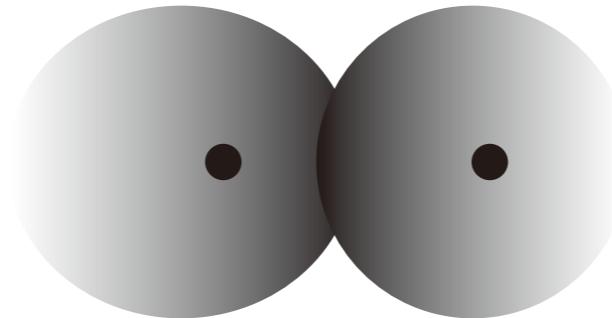
- The Structure, and hence the spectra, of molecules are more complicated than atoms in two ways:
 - There is no single charge center about which electrons move. The electronic wavefunctions therefore have lower symmetry, making them harder to calculate and harder to work with.
 - The nuclei themselves move, giving rise to both rotational and vibrational motions of the atoms within the molecule. These motions give rise to discrete spectra.

[Born-Oppenheimer Approximation]

- **Born-Oppenheimer approximation:**

Born & Oppenheimer (1927)

- 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.

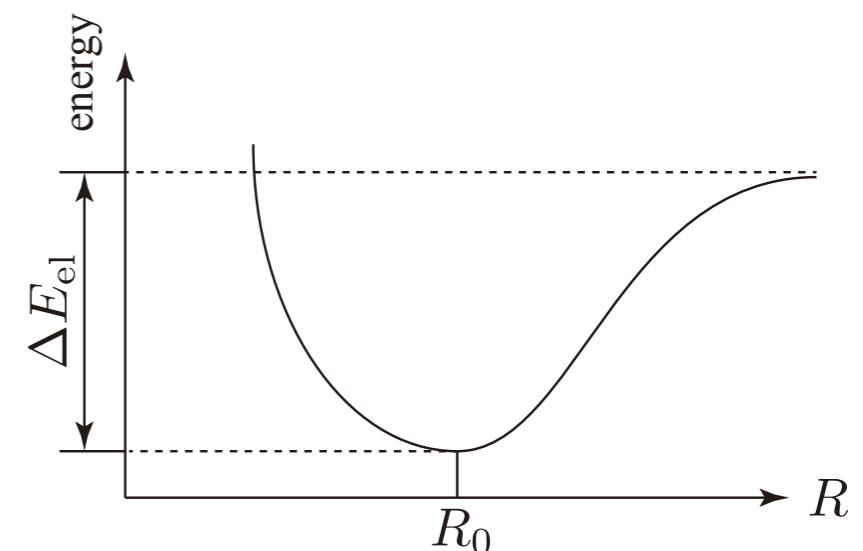


- One separates the wavefunction for the motions of electrons from the wavefunction for the motions of the nuclei. One can then consider the electronic wavefunction separately for each position of nuclei, as if the nuclei are held fixed.
- Due to very different energies of the **electronic, vibrational, 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:



- (1) 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.
- (2) 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.
- (3) 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

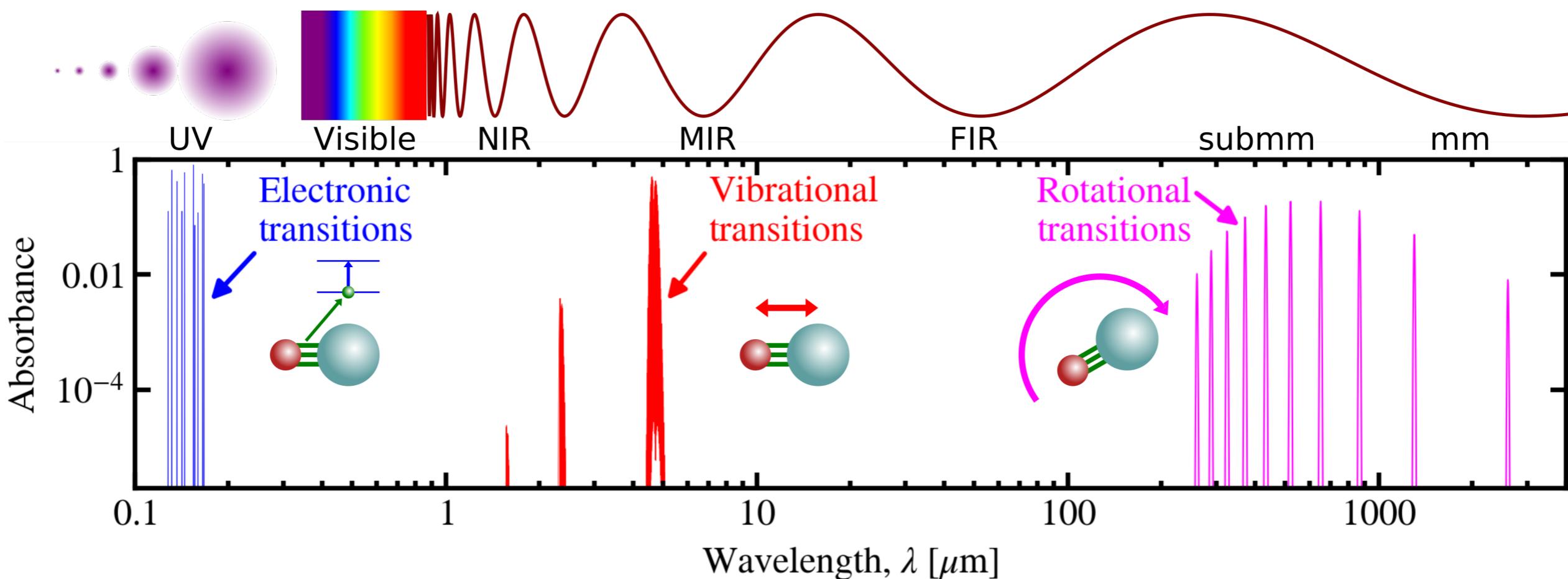
$$E_{\text{rot}} \sim \frac{L^2}{2I} \sim \frac{\hbar^2 \ell(\ell + 1)}{2I} \quad \Rightarrow \text{radio}$$

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

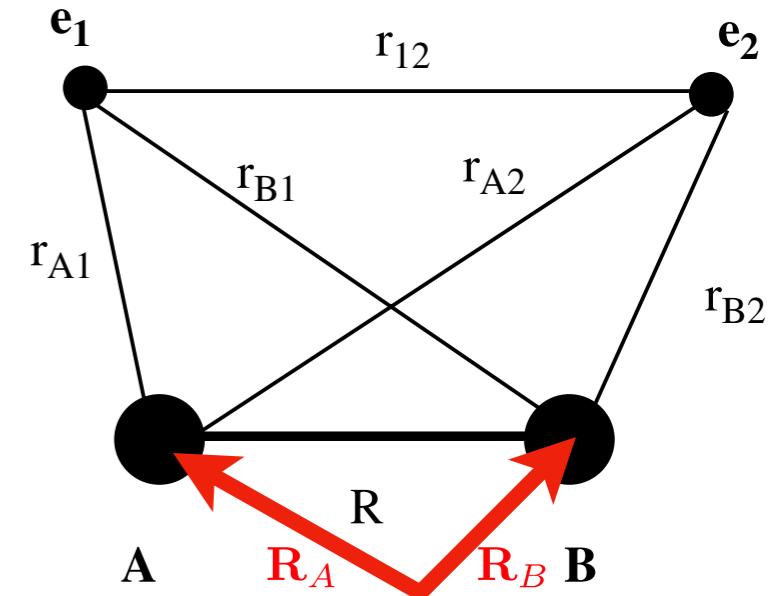
For a diatomic molecule with N electrons,

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

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.

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- 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:

$$\begin{aligned} \psi_{\text{rot}}(\theta, \phi) &= Y_{JM}(\theta, \phi) \\ E_r &= \frac{\hbar^2}{2\mu R^2} J(J+1) \end{aligned}$$

(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:

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

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

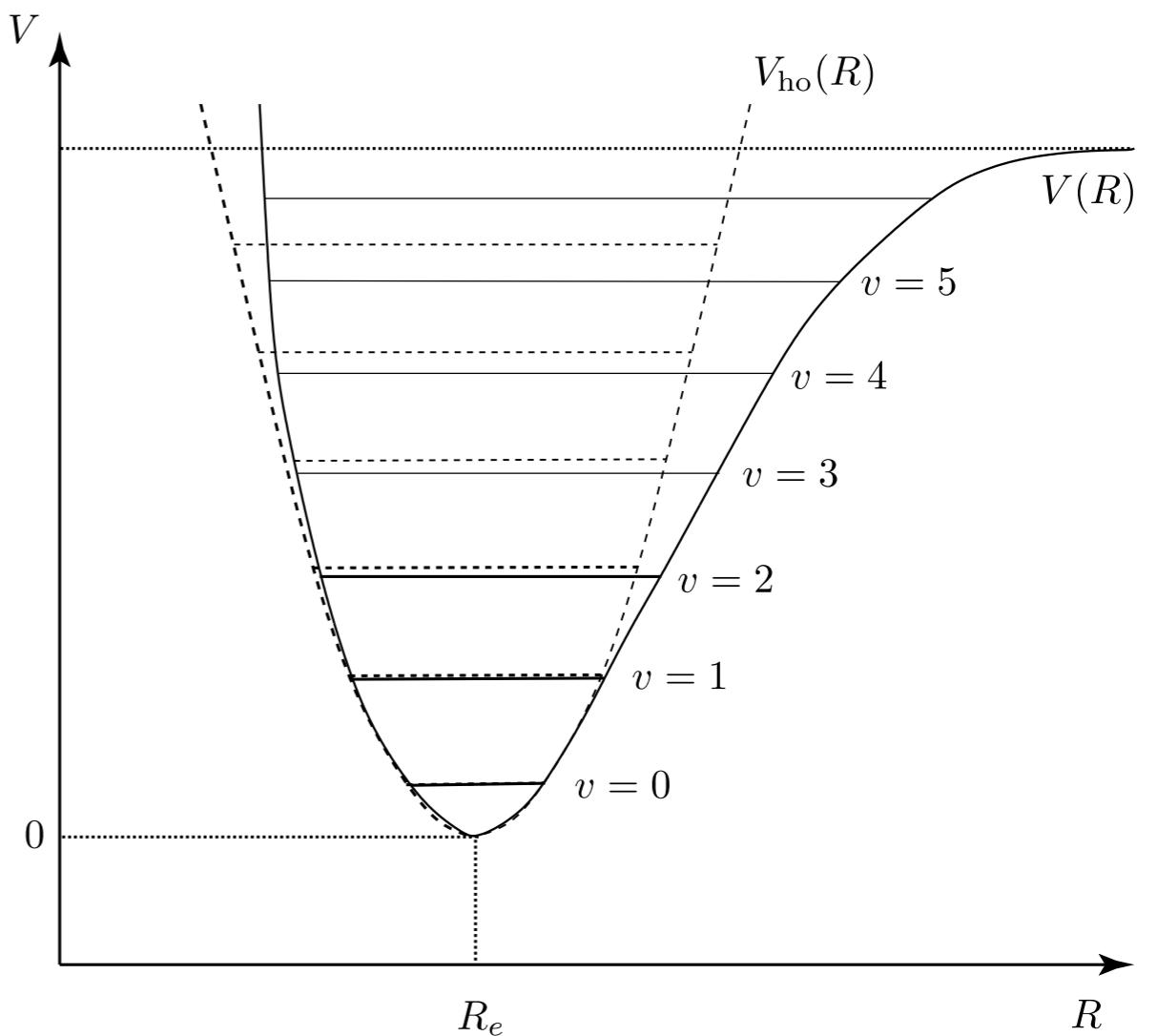
$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{1}{2}k(R - R_e)^2 - E_v \right] \psi_{\text{vib}}(R) = 0$$

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

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

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

Note that the vibrational frequency is inversely proportional to the reduced mass.



[Labelling of Electronic States of Diatomic Molecules]

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

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

S = total electronic spin

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

Ω = projection of the total electronic angular momentum onto the internuclear axis
 $= |\Lambda + S_z| \quad (S_z = -S, -S + 1, \dots, S - 1, S)$

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

$$\Lambda = \Sigma, \Pi, \Delta, \dots \quad (\text{for } L_z = 0, 1, 2, \dots)$$

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

- If the term symbol Λ 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 O₂, 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

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

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

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

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- Examples:

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

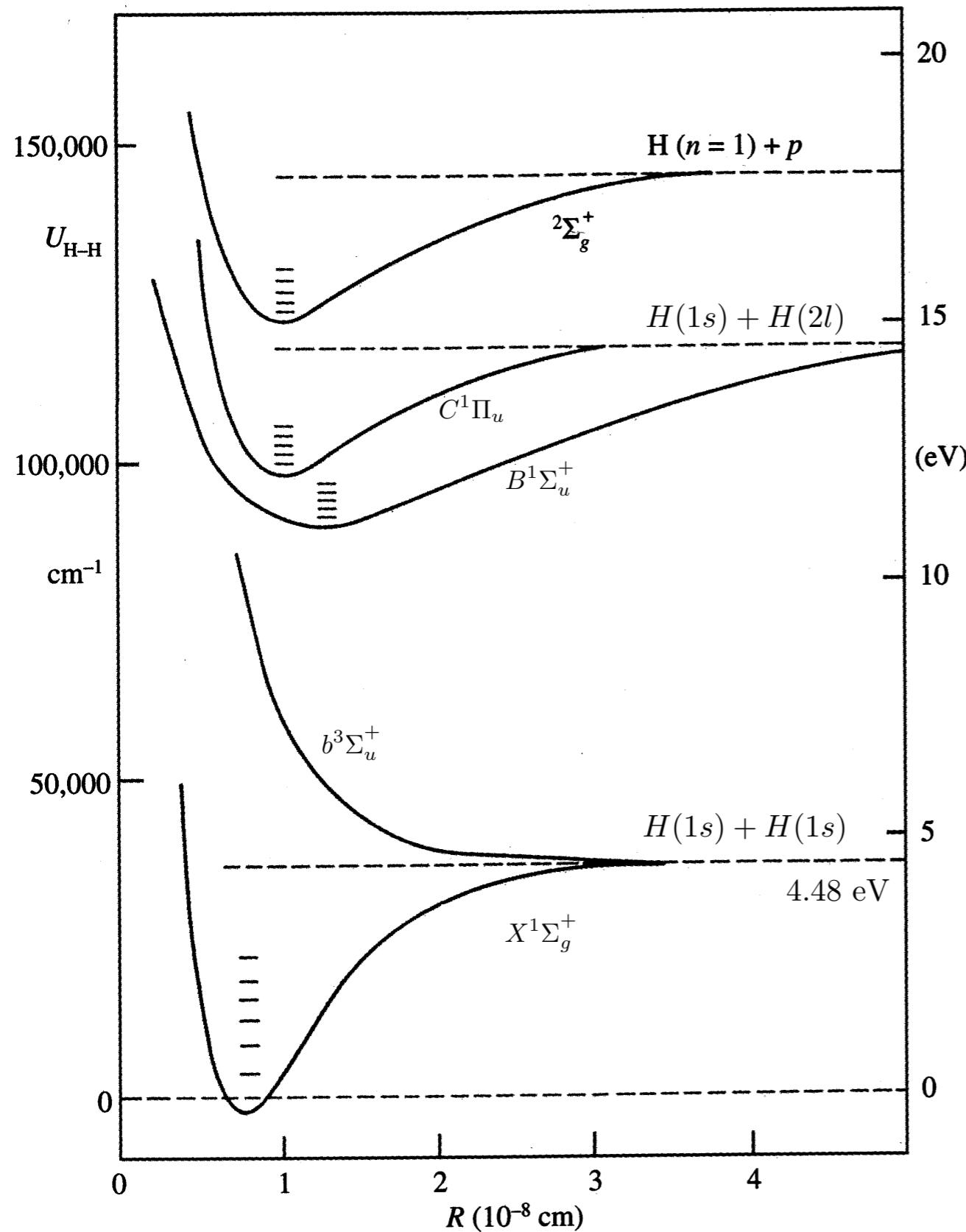
$^1\Sigma$ denotes a state with $S = 0$ and $\Lambda = 0$

$^3\Pi$ denotes a state with $S = 1$ and $\Lambda = 1$, etc
 - For most (stable) diatomic, the electronic ground state is a closed shell, meaning that it is $^1\Sigma$.
 - Examples include H_2 , N_2 and most other homonuclear diatomics. The exception is O_2 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. ($1s^22s^22p^2 + 1s^22s^22p^4$)
 - Diatomics with an odd number of electrons usually have $S = 1/2$. For example, H_2^+ , CH^+ , and CN all have $^2\Sigma$ ground state.
 - CH , OH and NO all have $\Lambda = 1$ and thus their ground states are $^2\Pi$. These molecules have extra lines in their spectra due to a process called Λ -doubling. (In this case, it is necessary to consider the coupling of the rotational motion to the spin and/or orbital angular momenta.)

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

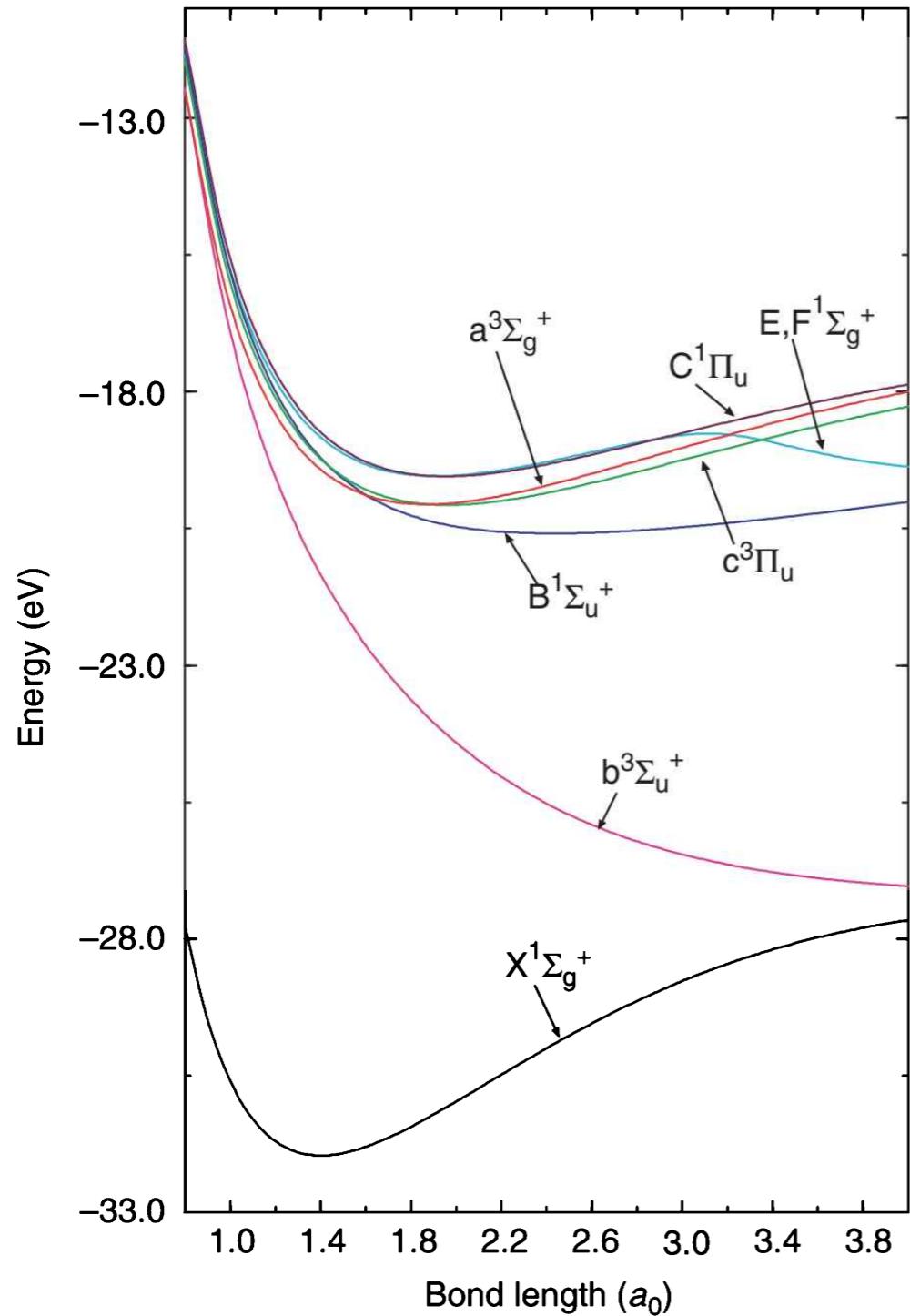
Letter designations for projected total orbital angular momentum.

[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 $\lambda \approx 970 - 1650 \text{\AA}$
 Lyman band: $B^1\Sigma_u^+ - X^1\Sigma_g^+$ at $\lambda \approx 930 - 1240 \text{\AA}$



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.

D. T. Stibbe, PhD thesis, Univ. of London (1997)

Ground Terms of 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 two *p* electrons contributed by C and four *p* electrons contributed by O; together these six *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 five electrons (one *s* and four *p* 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 (inverted case).

[Pure rotational & ro-vibrational transitions]

- **Energy Levels**

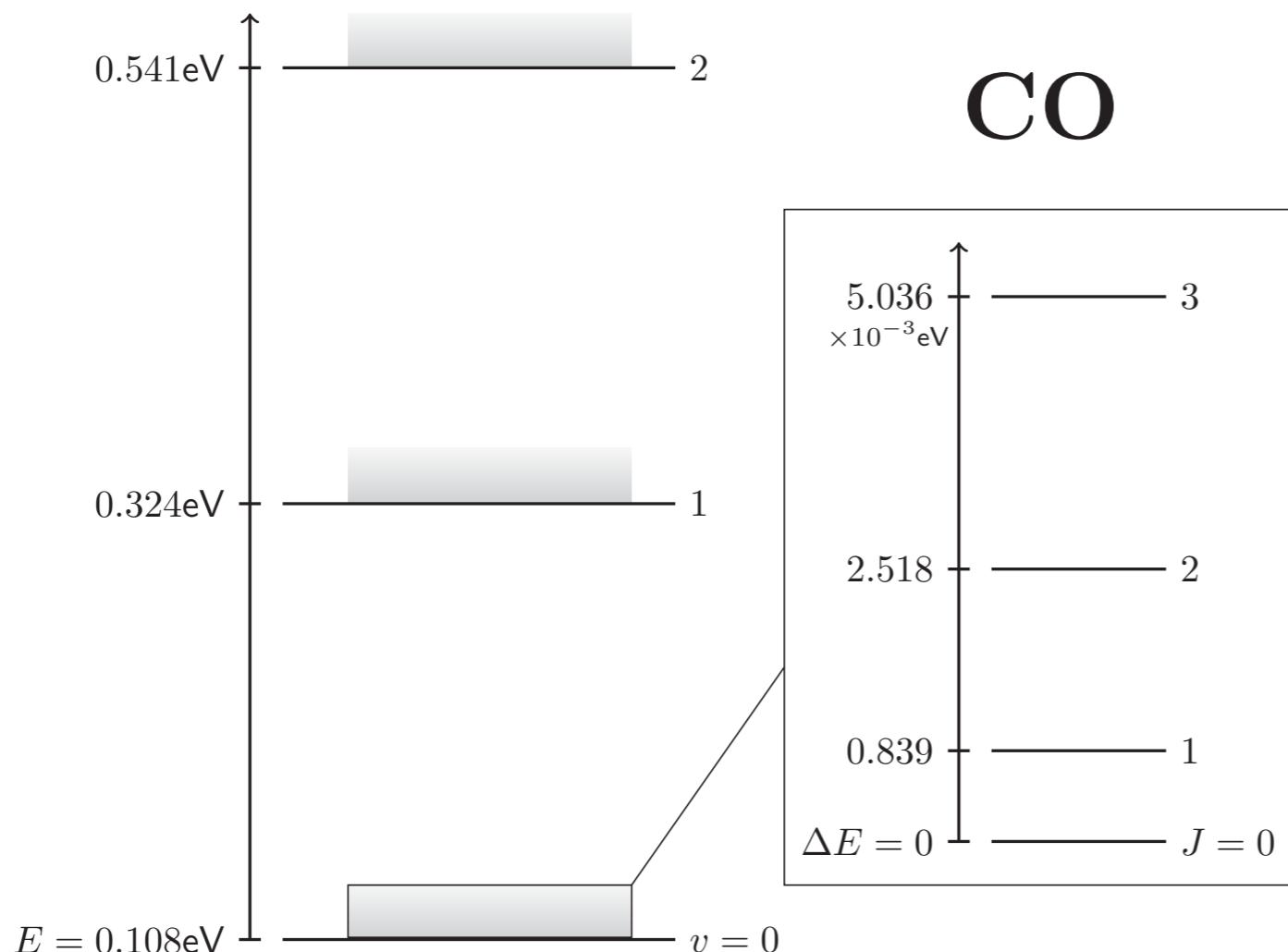
An electronic transition consists of vibrational bands, which in turn are made up of rotational transitions.

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

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

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) $\Lambda = 0, \pm 1$, e.g., $\Sigma - \Sigma$, $\Pi - \Sigma$, $\Delta - \Pi$, etc.

(2) $\Delta S = 0$

(3) $\Delta\Omega$ (or ΔJ_z) = 0, ± 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-vibrational transitions:

$\Delta v = \text{any}$

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

- But, note that **H₂ has no electric-dipole for rotational transition.**

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

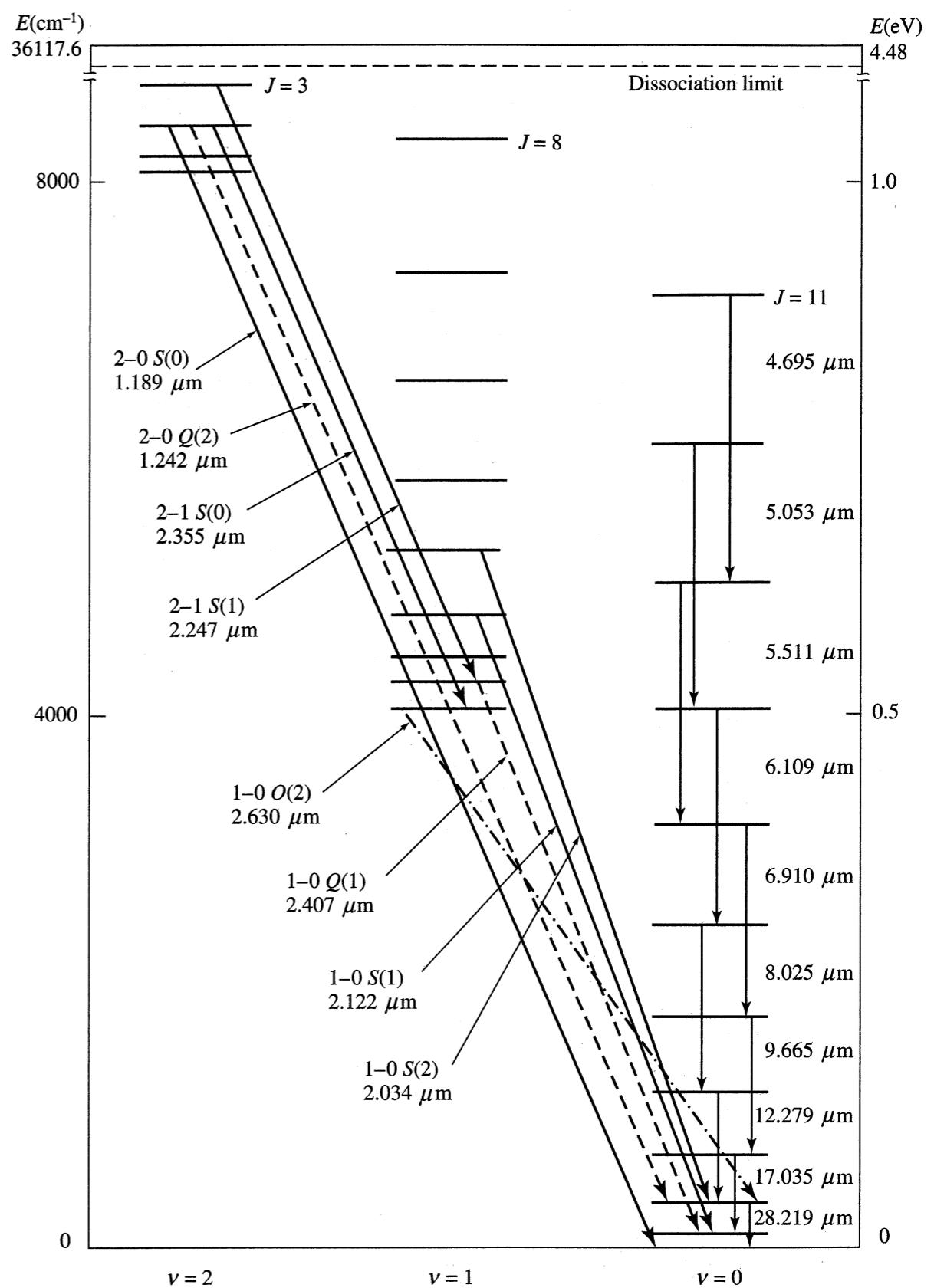
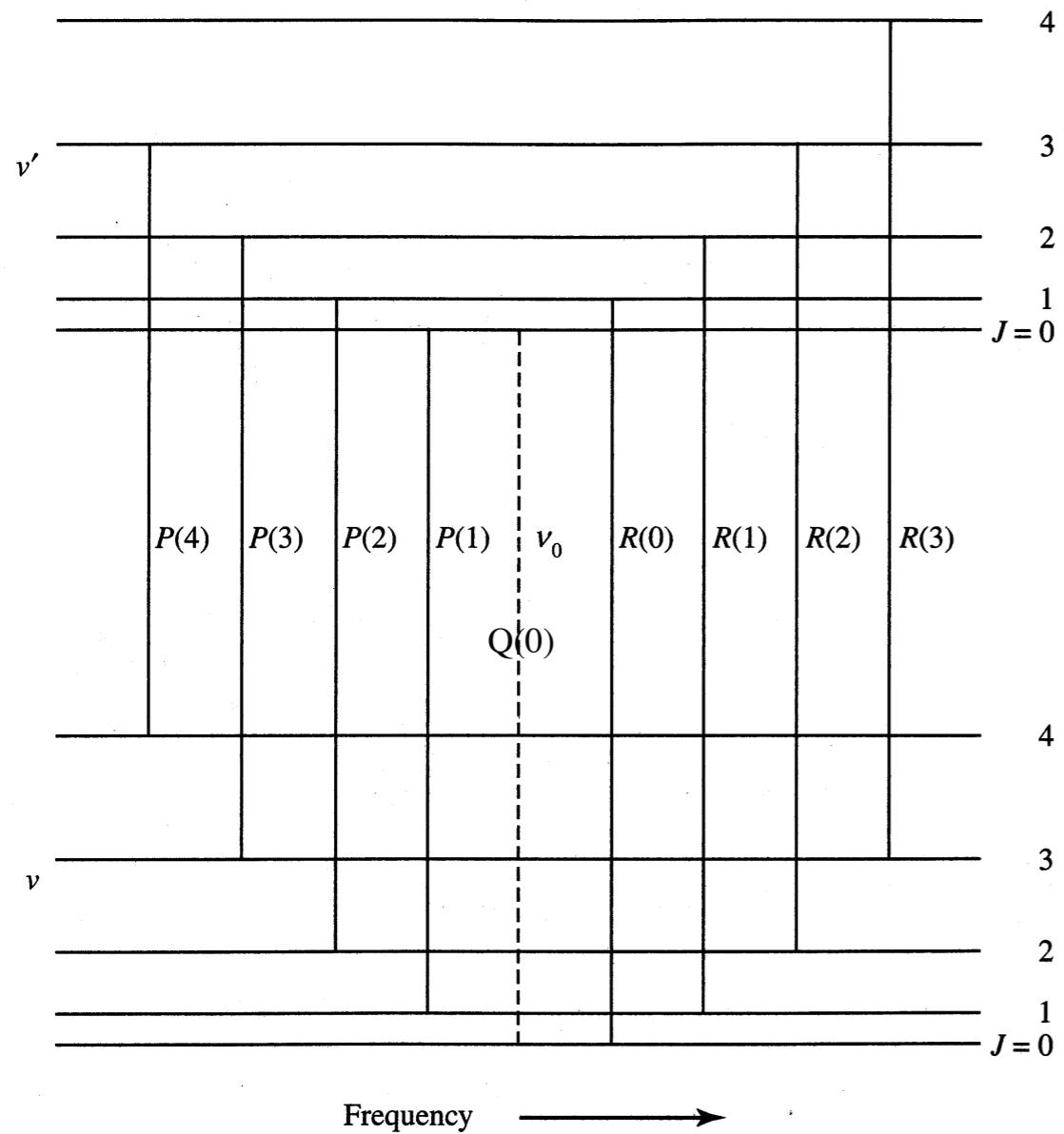
O, P, Q, R, and S transitions

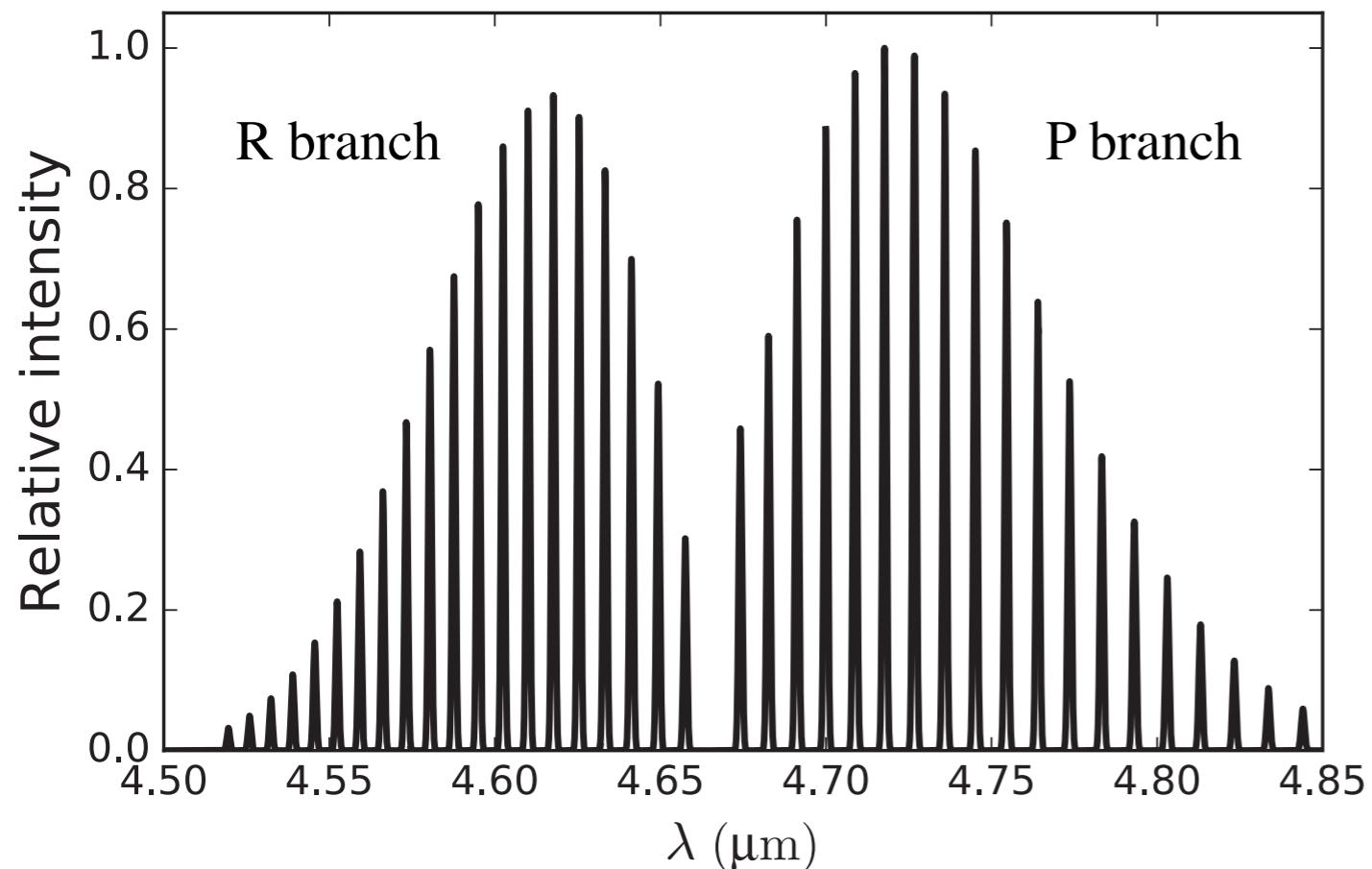
- The rotational levels of diatomic molecules are specified by a single vibrational quantum number v and rotational quantum number J .
 - Transitions will change J by either $0, \pm 1, \pm 2$.**
 - It is customary to identify transitions by specifying the upper and lower electronic states, upper and 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.

$$J_u \rightarrow J_\ell$$

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.

$$E_J = B_v J(J + 1)$$

$$\begin{aligned} \Delta E_J &= B_v J(J + 1) - B_v (J - 1)J \\ &= 2B_v J \quad \text{for } J \rightarrow J - 1 \text{ (R branch)} \end{aligned}$$

$$\begin{aligned} \Delta E_J &= B_v J(J + 1) - B_v (J + 1)(J + 2) \\ &= -2B_v (J + 1) \quad \text{for } J \rightarrow J + 1 \text{ (P branch)} \end{aligned}$$

[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 antisymmetry 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

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

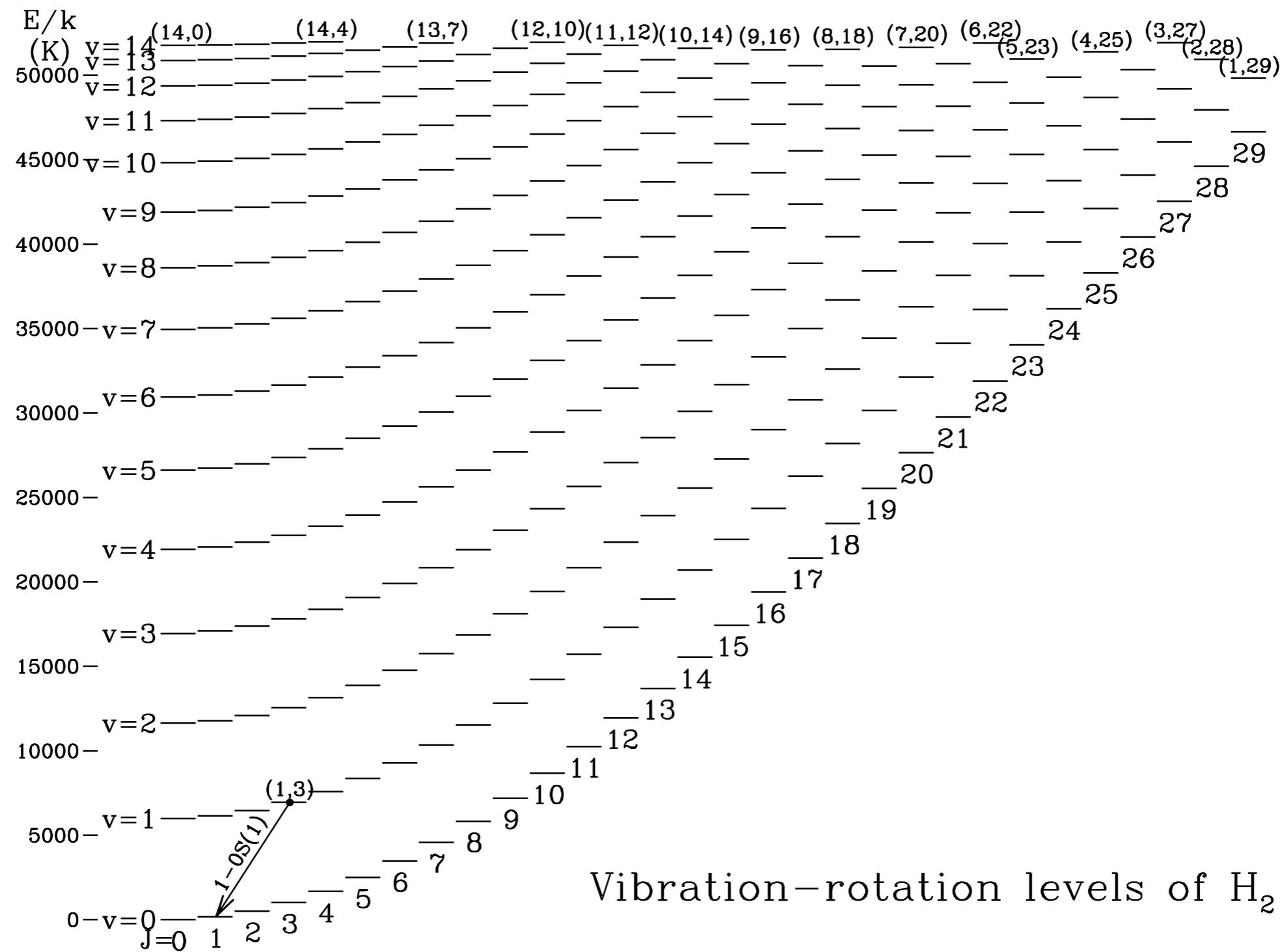
For example, 1-0 S(1) refers to the transition $(v = 1, J = 3) \rightarrow (v = 0, J = 1)$.

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

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.
 - ▶ 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.



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.

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 3876.84Å), CH ($A^2\Delta - X^2\Pi$ at 4300.30Å) and CH⁺ ($A^1\Pi - X^1\Pi^+$ at 4232.54Å)

- Over 200 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]

- 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

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 undergo a pure rotation transition, it must have a permanent dipole moment, μ . This means that 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 possess a permanent dipole moment but homonuclears, such as H_2 , 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 $\lambda = 2.60 \text{ mm}$, 2-1 at 1.30 mm , and 3-2 at 0.87 mm .

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.

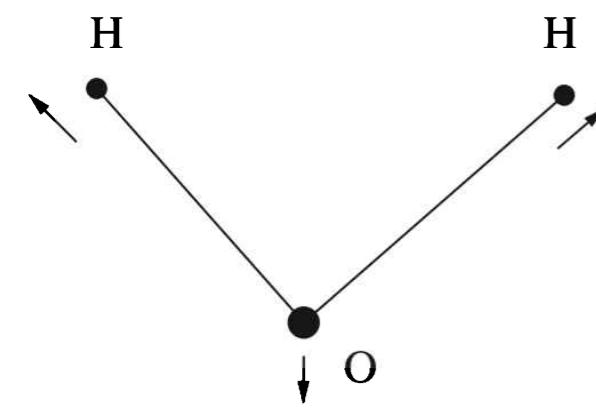
$$n(\text{CO}) \approx 10^{-4}n(\text{H}_2)$$

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.

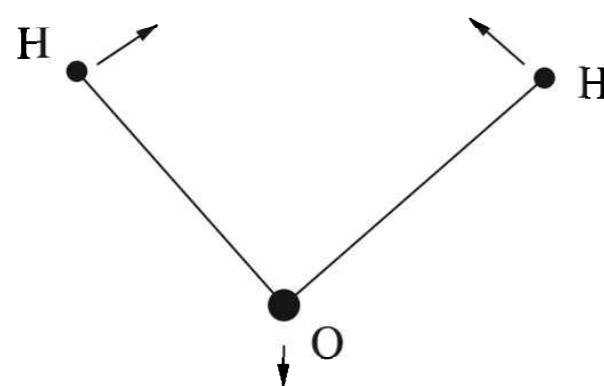
An isotopologue is a molecule that consists of at least one less abundant isotope of its constituent elements. They have the same transitions at nearby frequencies with similar decay and excitation rates. The main difference is in their abundance and observations of the rarer species help diagnose conditions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

Vibrations in Polyatomic Molecules

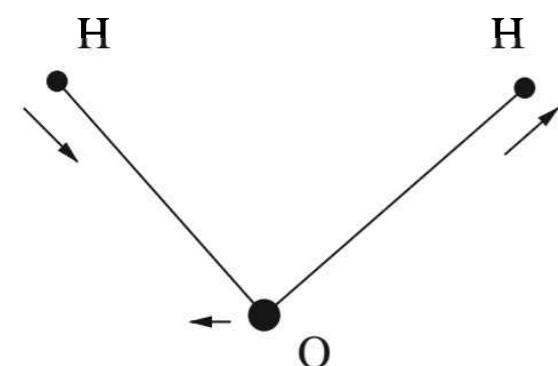
H_2O



Symmetric stretch, v_1
 $\omega_1 = 3667 \text{ cm}^{-1}$



Bend, v_2
 $\omega_2 = 1595 \text{ cm}^{-1}$



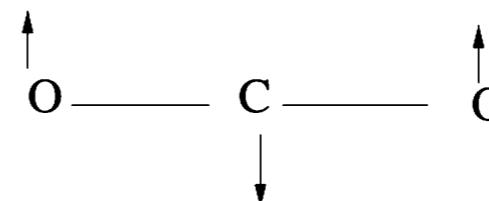
Asymmetric stretch, v_3
 $\omega_3 = 3676 \text{ cm}^{-1}$

The three vibrational modes of the water molecule

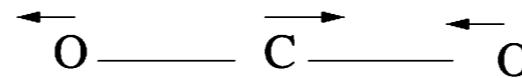
CO_2



Symmetric stretch, v_1
 $\omega_1 = 1388 \text{ cm}^{-1}$



Bend (degenerate), v_2
 $\omega_2 = 667 \text{ cm}^{-1}$



Asymmetric stretch, v_3
 $\omega_3 = 2349 \text{ cm}^{-1}$

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.

Excitation Temperature

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

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

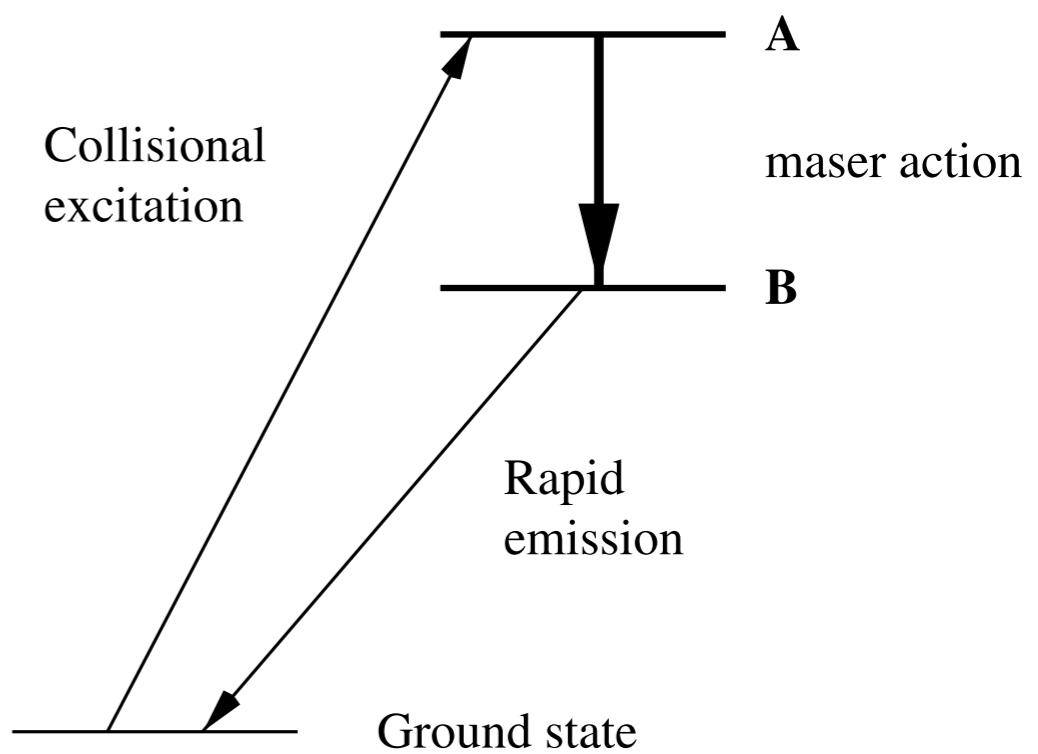
For pure rotational transitions, the excitation temperature is often called the **rotation temperature**.

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.

Maser Emissions

- Microwave amplification stimulated emission of radiation (maser) action is observed from at least 36 molecules including SiO, OH and water, usually at IR and microwave frequencies.
- The population inversion necessary to cause maser action can be created by a number of mechanisms including optical pumping, radiation trapping in certain long-lived levels and selective collisional excitation of the masing molecule.
- In the righthand side figure, the levels are vibration-rotation levels of the electronic ground state. If level A is excited in some collision process, such as scattering with H_2 , and level B is not, then the population of level A can be greater than the population of level B. The situation gives a non-thermal population and can lead to maser action.



Dust / Solid Particles

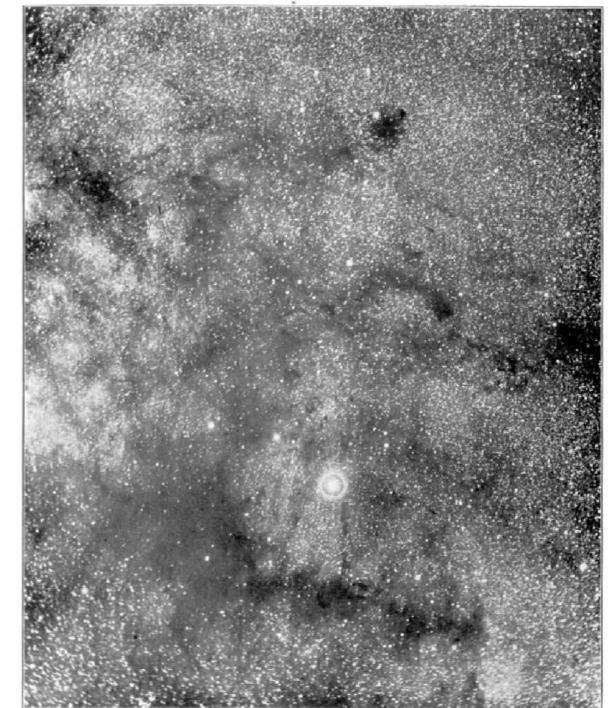
[Interstellar Dust: Observed Properties]

- Extinction = Absorption + Scattering
 - Dust particles can scatter light, changing its direction of motion. When we look at a reflection nebula, like that surrounding the Pleiades, we are seeing light from the central stars that has been scattered by dust into our line of sight.
 - Dust particles can also absorb light. The relative amount of scattering and absorbing depends on the properties of the dust grains.
- Thermal radiation from Dust
 - When dust absorbs light, it becomes warmer, so dust grains can emit light in the form of thermal radiation. Most of this emission is at wavelengths from a few microns (near IR) to the sub-mm range (Far-IR).
- Polarization
 - The polarization of starlight was discovered in 1949 (Hall 1949).
 - The degree of polarization tends to be larger for stars with greater reddening, and stars in a given region of the sky tends to have similar polarization directions.



The Pleiades cluster and surrounding reflection nebulae (Fig. 6.3, Ryden)

PLATE II.



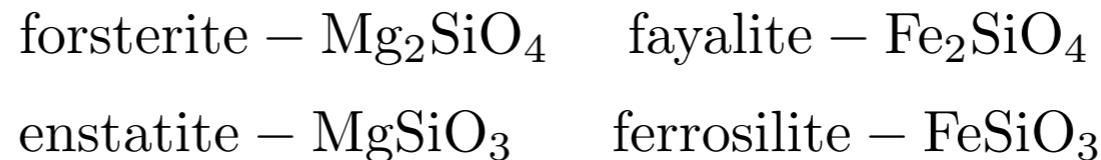
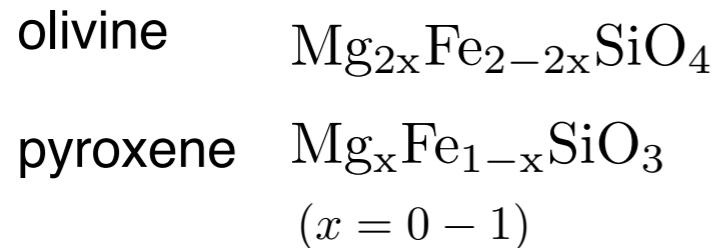
PHOTOGRAPH OF THE MILKY WAY NEAR THE STAR THETA OPHIUCHI.

The dark structures near θ Ophiuchi (Barnard 1899; Fig. 6.1, Ryden)

[Interstellar Dust]

- Silicates

- The two main types of silicates in dust are pyroxene and olivine.



[Left] Olivine is the simplest silicate structure, which is composed of isolated tetrahedra bonded to iron and/or magnesium ions. No oxygen atom is shared to two tetrahedra.

[Middle] In pyroxene, silica tetrahedra are linked together in a single chain, where one oxygen ion from each tetrahedra is shared with the adjacent tetrahedron.

[Right] Other types are possible. In amphibole structures, two oxygen ions from each tetrahedra are shared with the adjacent tetrahedra.

In mica structures, the tetrahedra are arranged in continuous sheets, where each tetrahedron shares three oxygens with adjacent tetrahedra.

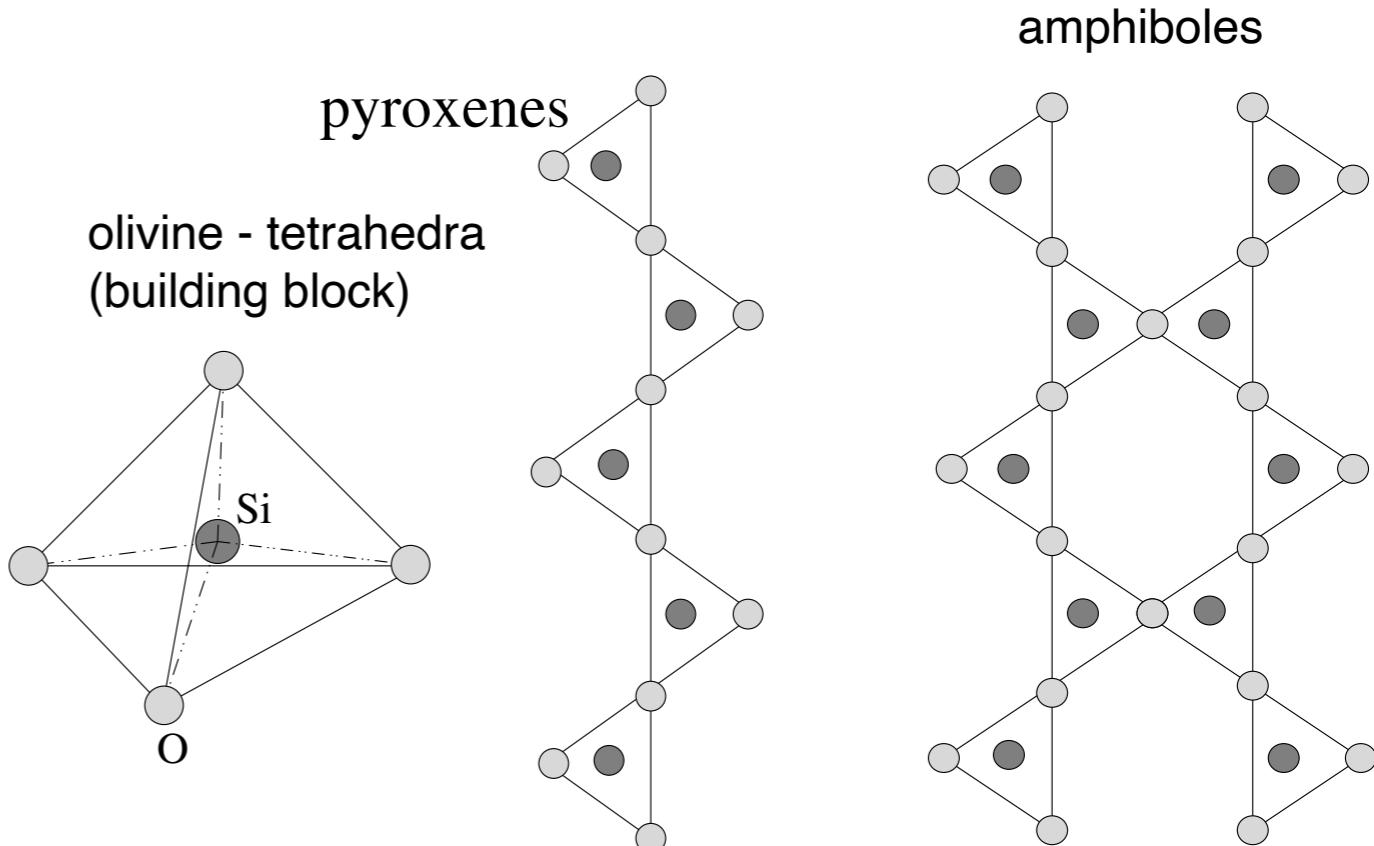
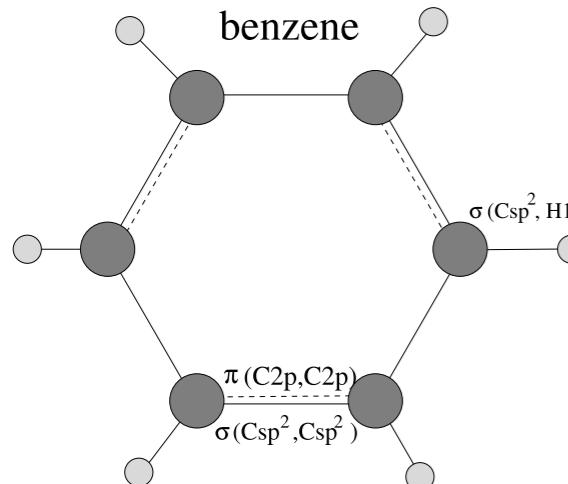


Fig 5.9 Krugel
[An Introduction to the Physics of Interstellar Dust]

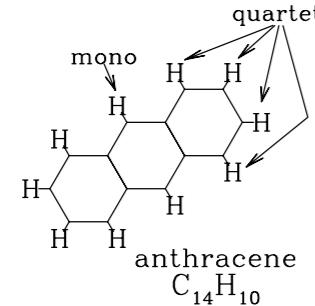
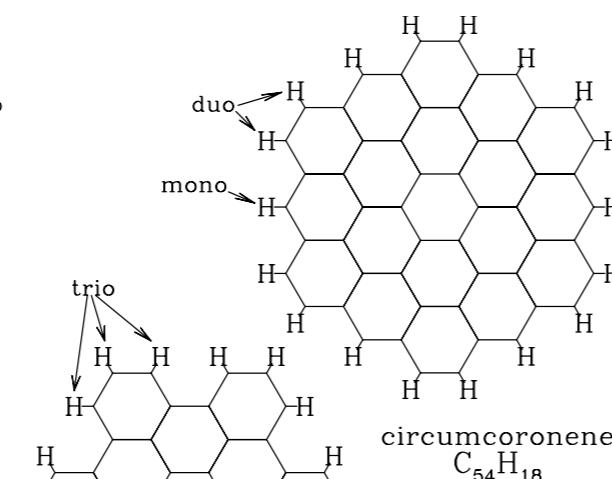
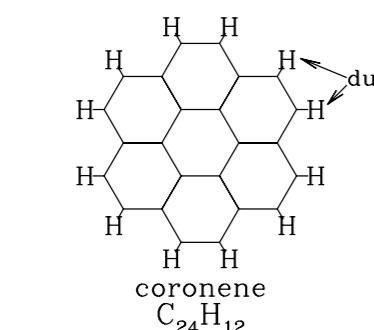
• Polycyclic Aromatic Hydrocarbons

- The IR emission spectra of spiral galaxies show emission features at 3.3, 6.2, 7.7, 8.6, 11.3, and 12.7 μm that are attributable to vibrational transitions in polycyclic aromatic hydrocarbon (PAH) molecules.
- PAH molecules are planar structures consisting of carbon atoms organized into hexagonal rings, with hydrogen atoms attached at the boundary.

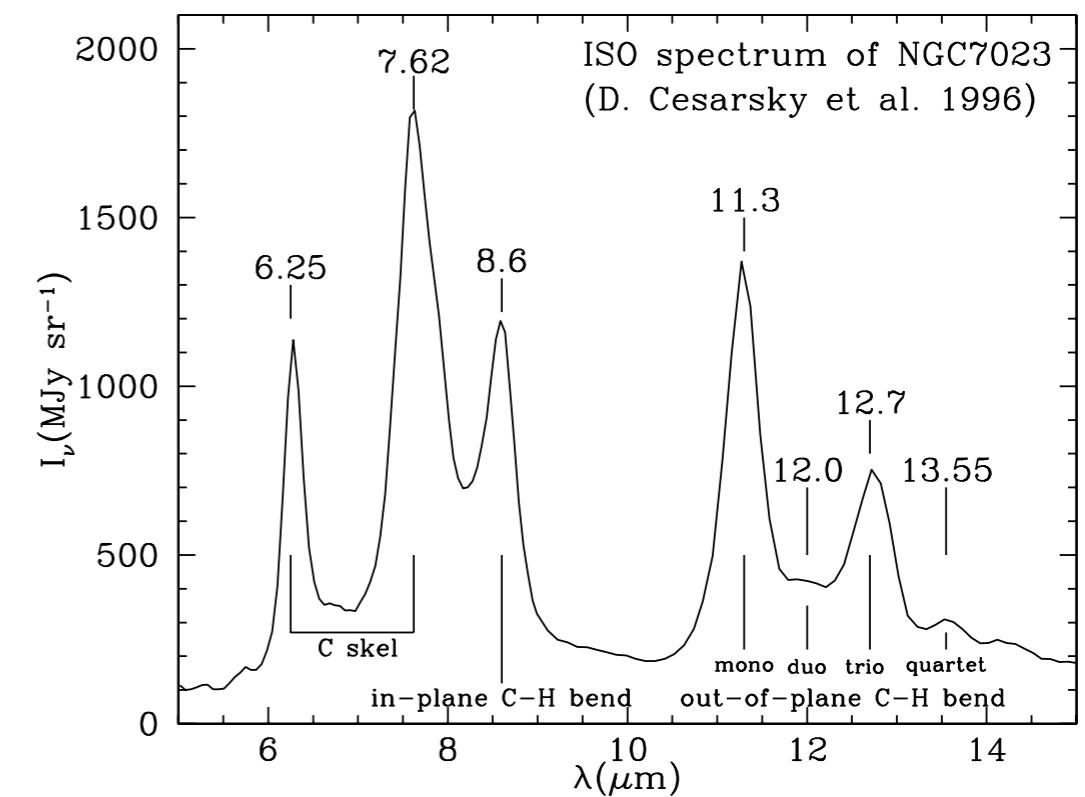


Bezene ring (C_6H_6)
The simplest type of PAHs.

[Fig 5.6 in Krugel]



Structure of four PAHs.
[Fig 23.9 in Draine]



The IR spectrum of the reflection nebula NGC 7023
(Cesarsky et al. 1996)

- Graphite (흑연)

- Graphite is the most stable form of carbon (at low pressure), consisting of infinite parallel sheets of sp^2 -bonded carbon.
 - ▶ A single (infinite) sheet of carbon hexagons is known as graphene. Each carbon atom in graphene has three nearest neighbors, with a nearest-neighbor distance of 1.421\AA .
 - ▶ Crystalline graphite consists of regularly stacked graphene sheets.
 - ▶ The sheets are weakly bound to one another by van der Waals forces.

- Nanodiamond

- Diamond consists of sp^3 -bonded carbon atoms, with each carbon bonded to four equidistant nearest neighbors (enclosed angles are 109.47°).
- Diamond nanoparticles are relatively abundant in primitive meteorites. Based on isotopic anomalies associated with them, we know that some fraction of the nanodiamond was of premolar origin.
- But, its abundance in the ISM is not known.

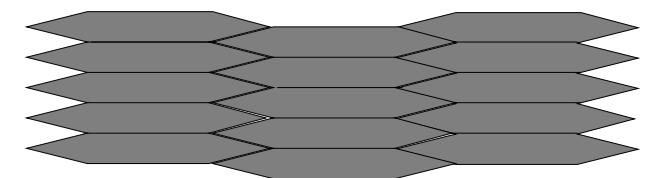
- Amorphous carbon

- Hydrogenated amorphous carbon (HAC)

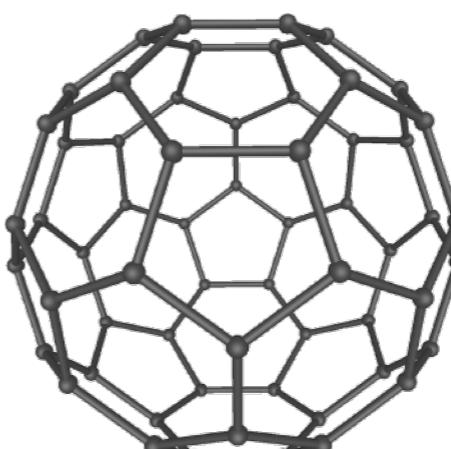
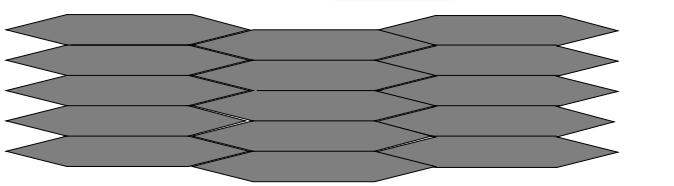
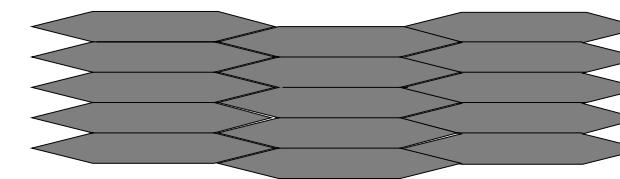
- Fullerenes



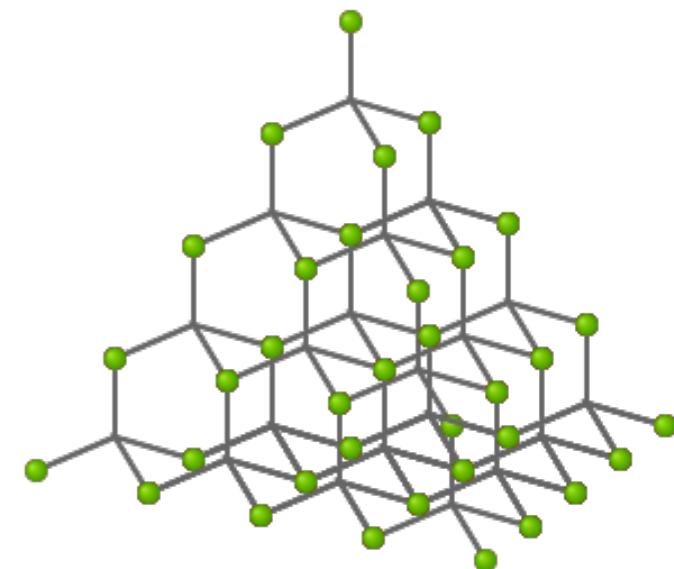
graphite sheets



3.35\AA



Buckminsterfullerene (C_{60})



Structure of diamond.

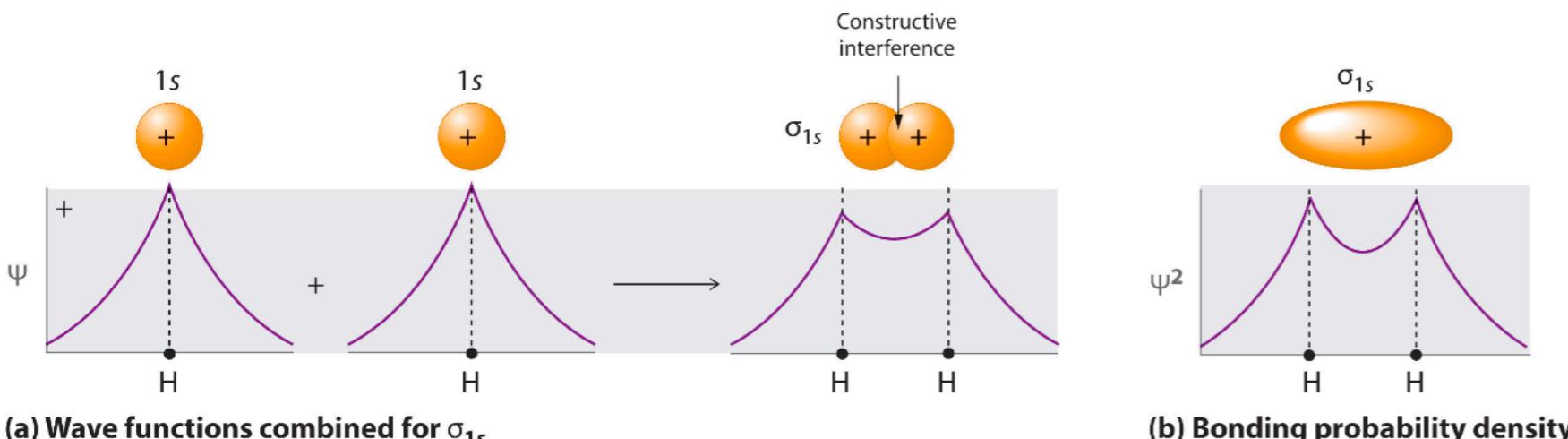
[Solid State Physics] - Bonding and Antibonding Orbitals

- **Molecular Orbital Method:** The molecular orbitals are created via the linear combinations of atomic orbitals. For instance, for a diatomic molecule,

$$|\psi\rangle = C_A|1s_A\rangle + C_B|1s_B\rangle$$

Since the two protons are identical, the probability that the electron is near A must equal the probability that the electron is near B.

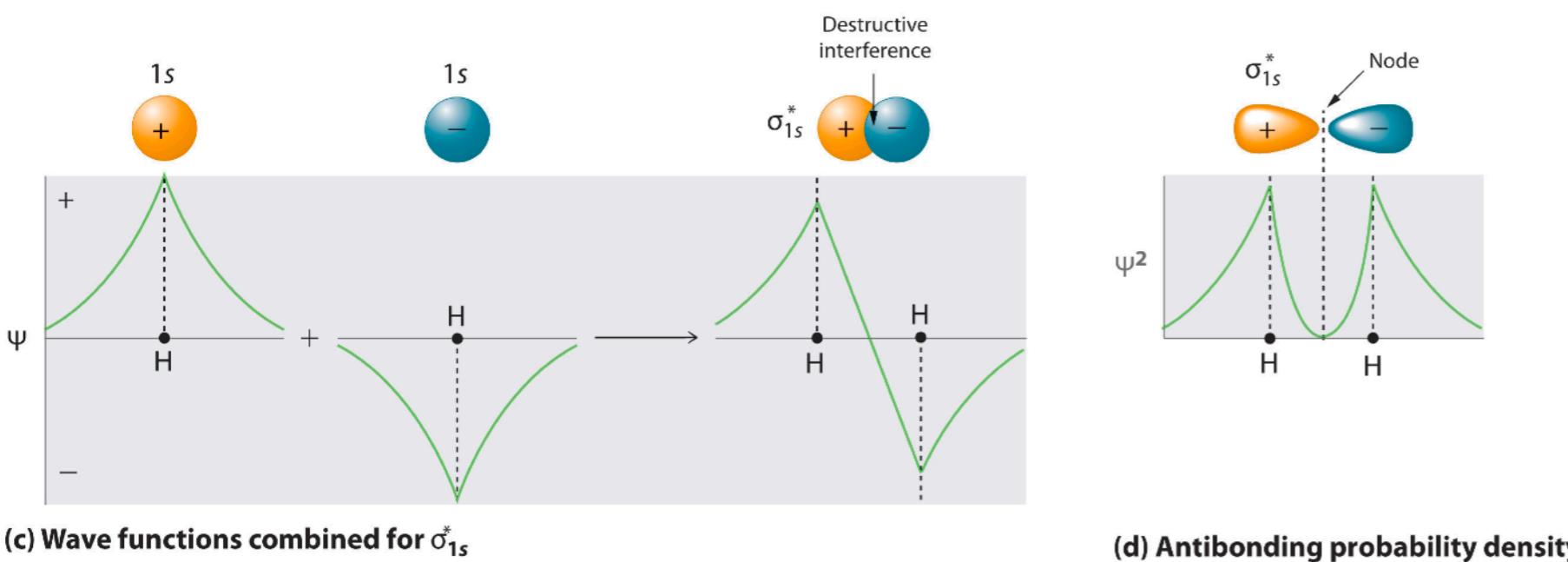
$$|C_A|^2 = |C_B|^2 \Rightarrow C_A = \pm C_B$$



We have two possibilities that satisfy the above condition.

$$|\sigma_{1s}\rangle = \frac{1}{\sqrt{2}} (|1s_A\rangle + |1s_B\rangle)$$

This is called a bonding orbital.



$$|\sigma_{1s}^*\rangle = \frac{1}{\sqrt{2}} (|1s_A\rangle - |1s_B\rangle)$$

This is called a antibonding orbital.

- **Bonding orbitals** are formed when atomic orbitals combine in ways that lead to predominantly constructive interference.

In the bonding orbitals, the electron density is found between the atoms. This leads to the idea that covalent bonding is “shared” electrons. The electrons have a high probability of being between the nuclei in the molecule.

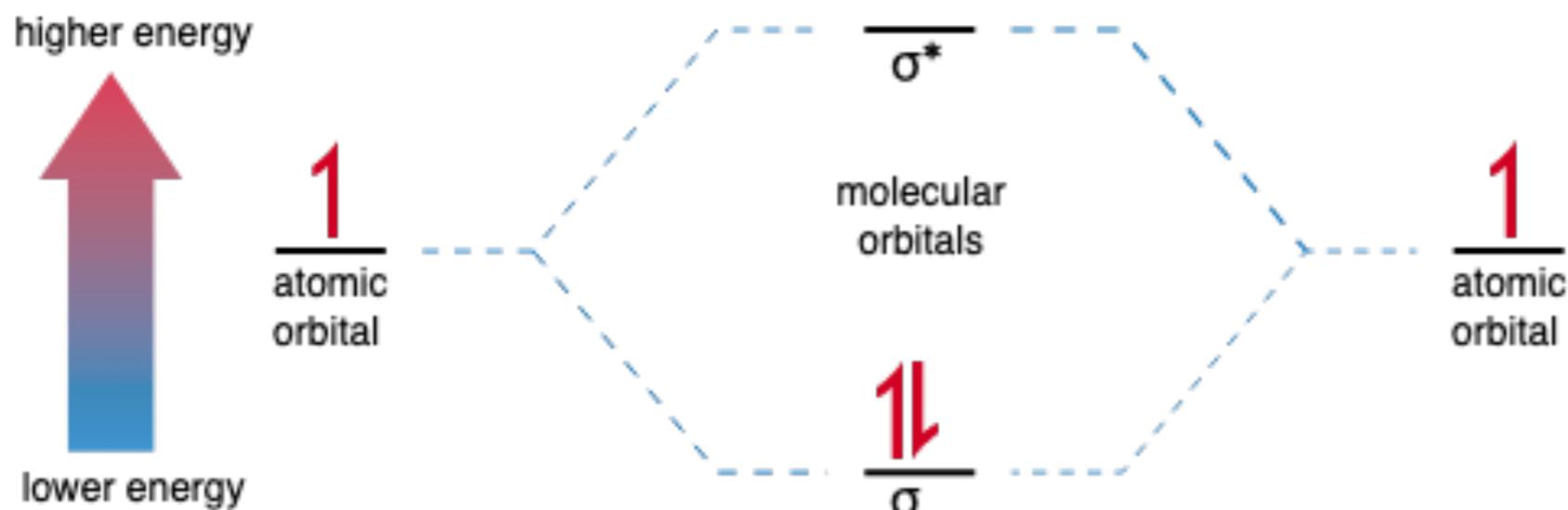
The molecular orbital has a lower energy than the separated atoms.

- **Anti-bonding orbitals** are formed when atomic orbitals combine in ways that lead to predominantly destructive interference.

In this bonding, a “node” or place of zero electron density exists between the atoms.

The molecular orbital has a higher energy than the separated atomic orbitals.

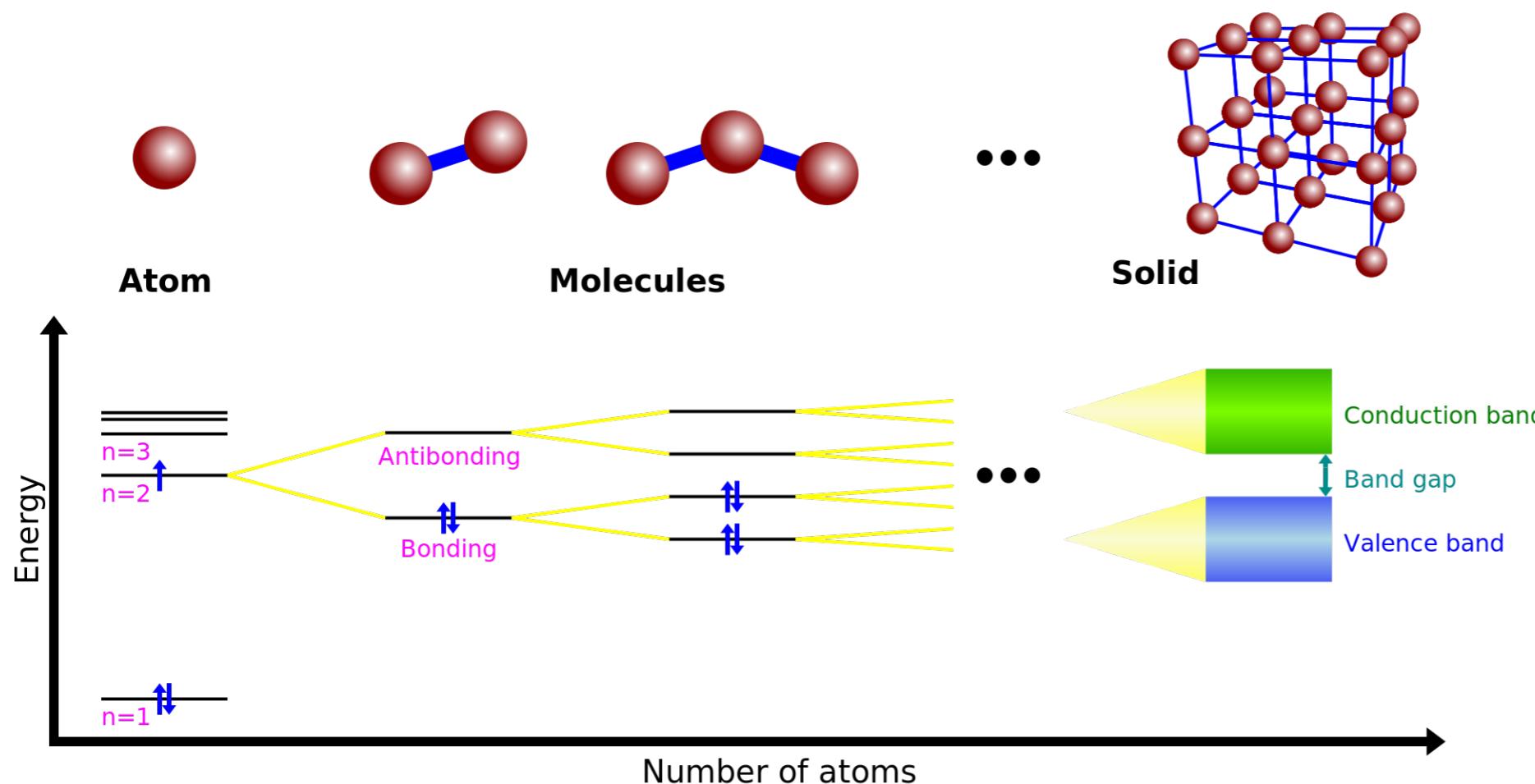
We denote anti-bonding orbitals with a * symbol.



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σ -bonding is due to the end-to-end overlap of orbitals having constructive interference (in phase). All σ -bonding is “on axis” meaning the electron density is centered directly between the two bonding nuclei.

[Band Structure of Solids]



From the left to the right, we represents: (i) typical discrete atomic levels, (ii) the successive splitting of molecular orbitals, (iii) resulting in the quasi-continuous distribution of levels in bands. Electrons are represented with a vertical blue arrow (up or down), corresponding to their spin.

[credit: Frédéric Galliano]

Origin of the band structure of a solid

A solid can be idealized as a periodic lattice of atoms bonded to each other. The permitted energy levels of a single valence electron, in the periodic electrostatic potential created by this lattice, are a series of continuous functions, also called bands. This can be viewed as a generalization of the molecular level splitting. The spacing between a large number of levels is so small that it appears continuous.

The valence band is the highest energy band populated by valence electrons (at $T = 0$ K).

The conduction band is the lowest energy band where electrons can move freely through the solid. It is the band immediately superior to the valence band.

The energy difference between them is called **the band gap** (often denoted to be E_g).