Motion in molecules and Spectra

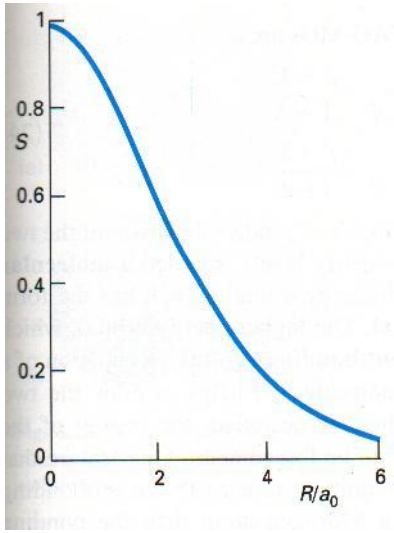
GerhardHerzberg,
Nobel 1971

"for his contributions to the knowledge
of electronic structure and geometry
of molecules,
particularly free radicals"

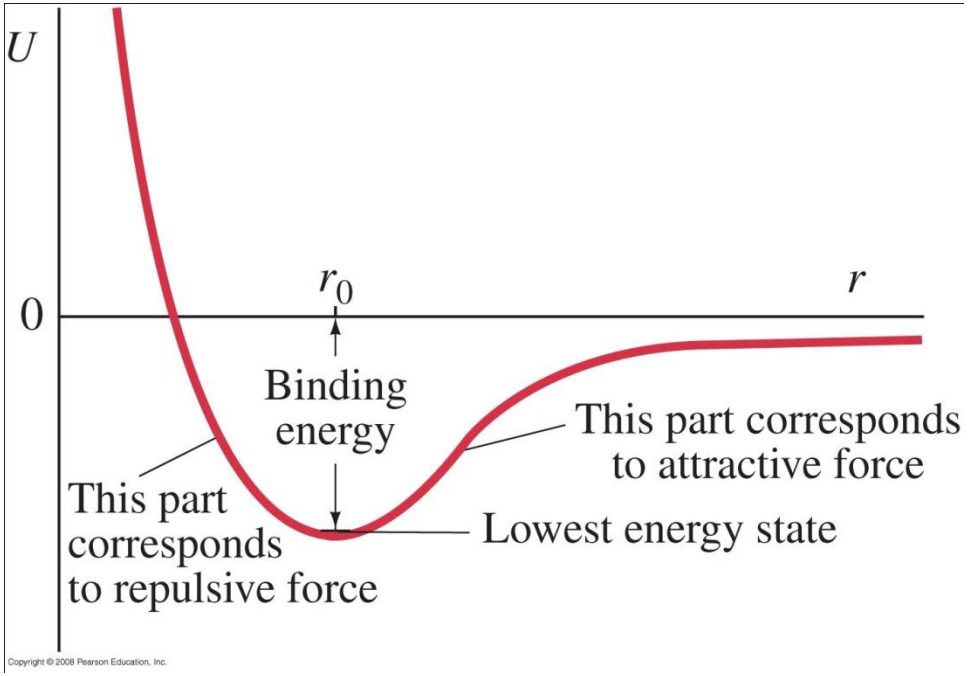
Potential-Energy Diagrams for Molecules

For the hydrogen molecule, the force between the atoms is attractive at large distances. There is a minimum in the potential.

Overlap integral is a function of R

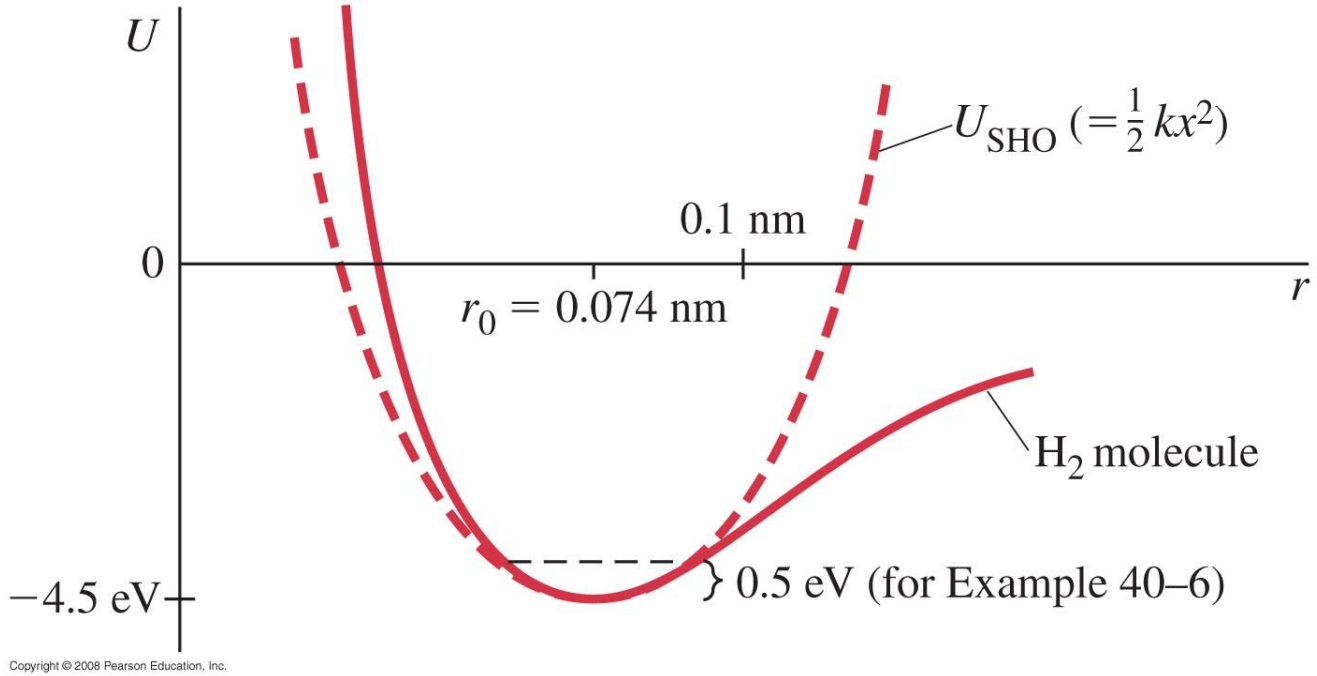


Also account for repulsion of nuclei



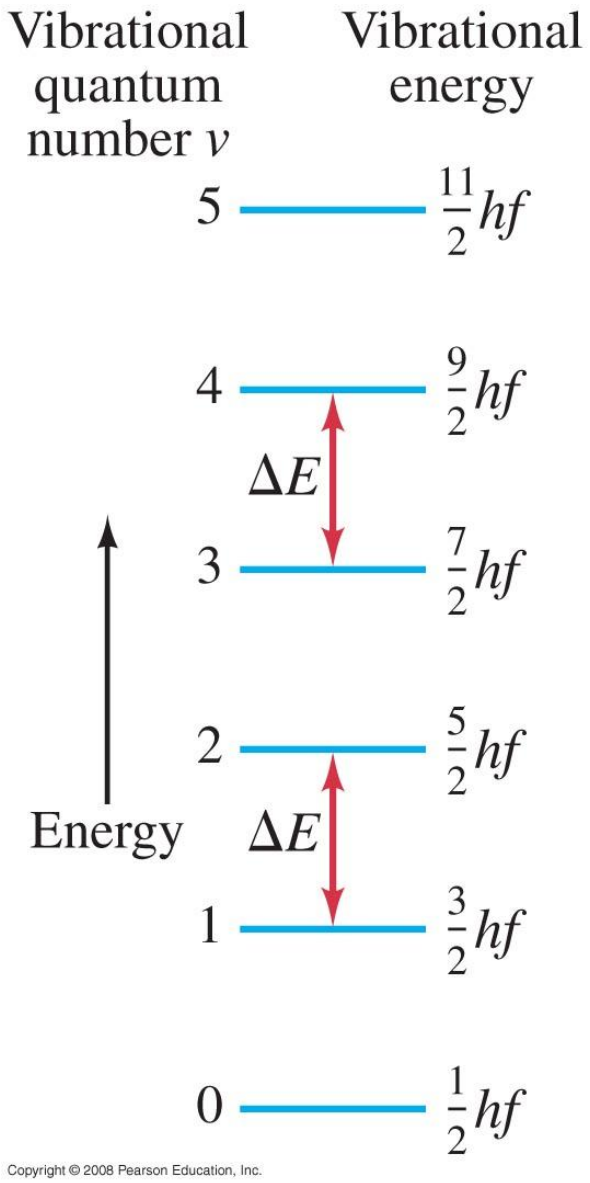
Molecular Spectra

Small-amplitude vibrations of a diatomic molecule will be simple harmonic. Again, the energy is quantized.



Treat this potential with the Schrödinger Equation
Think about the meaning of the wave function !!

Molecular Spectra



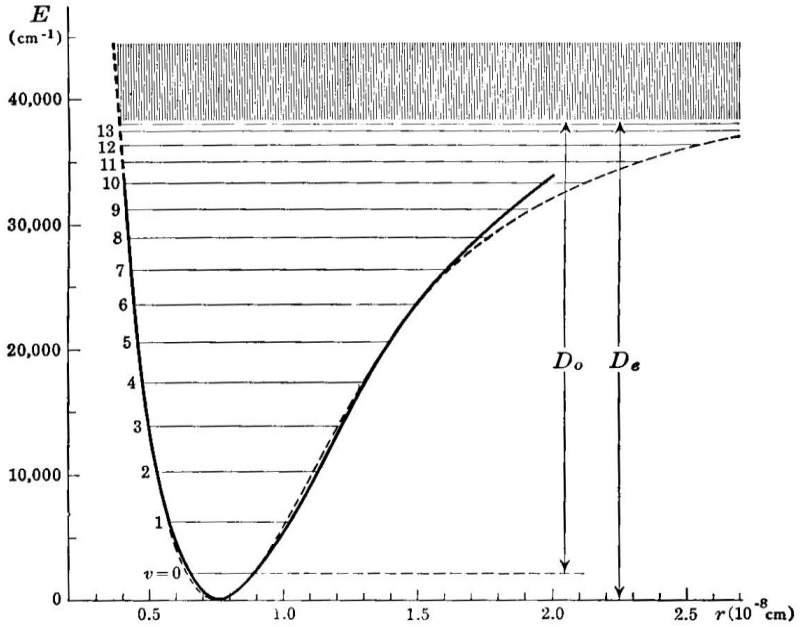
Here are some vibrational energy levels in a diatomic molecule, and the allowed transitions.

Quantum jumps between levels of vibrational energy give rise to an additional spectrum:
vibrational spectroscopy

→Infrared spectra

(Study the magnitude of frequency separations in vibrations)

Potential energy curve of a real molecule: H_2



H_2 has 14 bound vibrational energy levels.
D_2 has 17.

$$P(\mathrm{v}) = \frac{e^{-E(\mathrm{v})/kT}}{Z} = \frac{e^{-\omega_e(\mathrm{v}+1/2)/kT}}{Z}$$

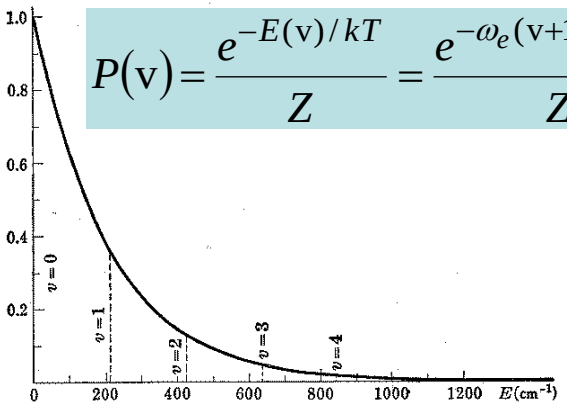
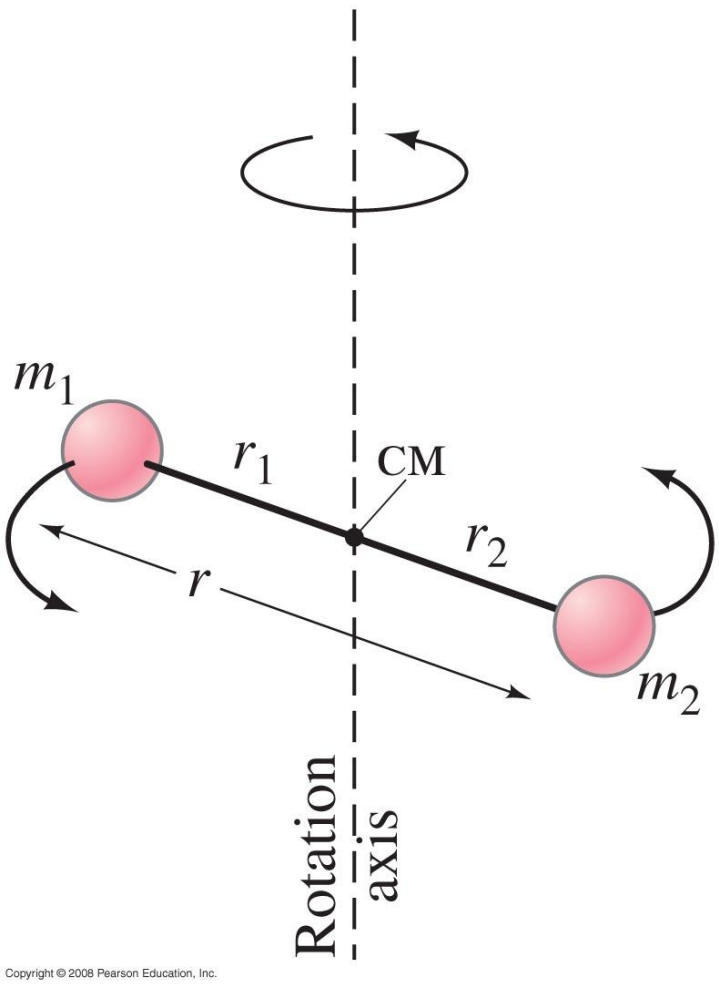


FIG. 58. **Boltzmann Factor and Thermal Distribution of the Vibrational Levels.** The curve gives the function $e^{-E/kT}$ for $T = 300°$ K. with E in cm^{-1}. The broken-line ordinates correspond to the vibrational levels of the I_2 molecule.

RATIO OF THE NUMBER OF MOLECULES IN THE FIRST TO THAT IN THE ZEROTH VIBRATIONAL LEVEL FOR 300° K. AND 1000° K.

Gas	$\Delta G_{1/2}$ (cm^{-1})	$e^{-\Delta G_{1/2} hc/kT}$	
		For 300° K.	For 1000° K.
H_2	4160.2	2.16×10^{-9}	2.51×10^{-3}
HCl	2885.9	9.77×10^{-7}	1.57×10^{-2}
N_2	2330.7	1.40×10^{-5}	3.50×10^{-2}
CO	2143.2	3.43×10^{-5}	4.58×10^{-2}
O_2	1556.4	5.74×10^{-4}	1.07×10^{-1}
S_2	721.6	3.14×10^{-2}	3.54×10^{-1}
Cl_2	556.9	6.92×10^{-2}	4.49×10^{-1}
I_2	213.2	3.60×10^{-1}	7.36×10^{-1}

Molecular Spectra



A diatomic molecule can rotate around a vertical axis. The rotational energy is quantized.

Reduced mass.

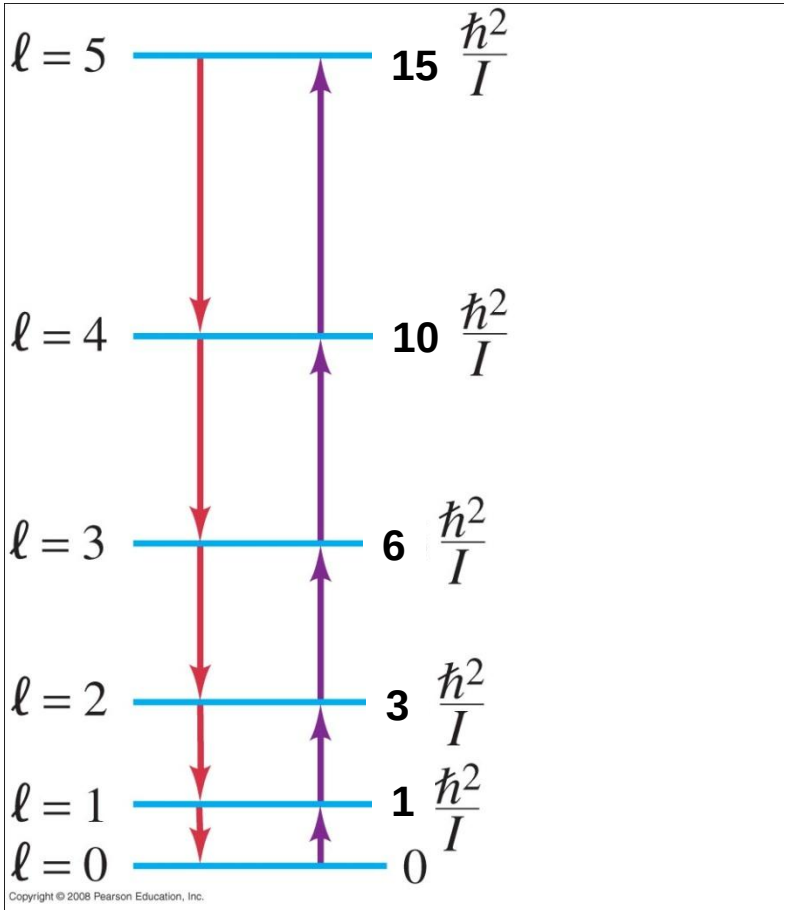
moment of inertia of a diatomic molecule rotating about its center of mass can be written

$$I = \mu r^2,$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Angular momentum $L = I\omega$

Molecular Spectra (purely rotational)



These are some rotational energy levels and allowed transitions for a diatomic molecule.

$$E = \frac{1}{2} I\omega^2 = \frac{L^2}{2I}$$

Rotation in a molecule related to angular momentum; Quantization analoguous to electron in atom

$$E = \frac{\hbar^2}{2I}\ell(\ell+1)$$

Rotational quantum number mostly given as *J*

Determination of the equilibrium separation R_e from thespectrum

Population distributions
rotational states in a diatomic molecule

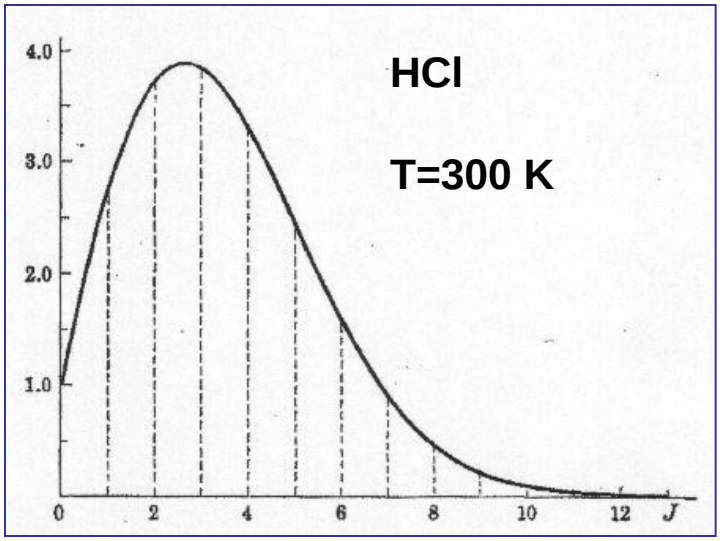
Probability of finding a molecule in a rotational quantum state:

$$P(J) = \frac{(2J+1)e^{-E_{rot}/kT}}{\sum_{J'}(2J'+1)e^{-E_{rot}/kT}}$$

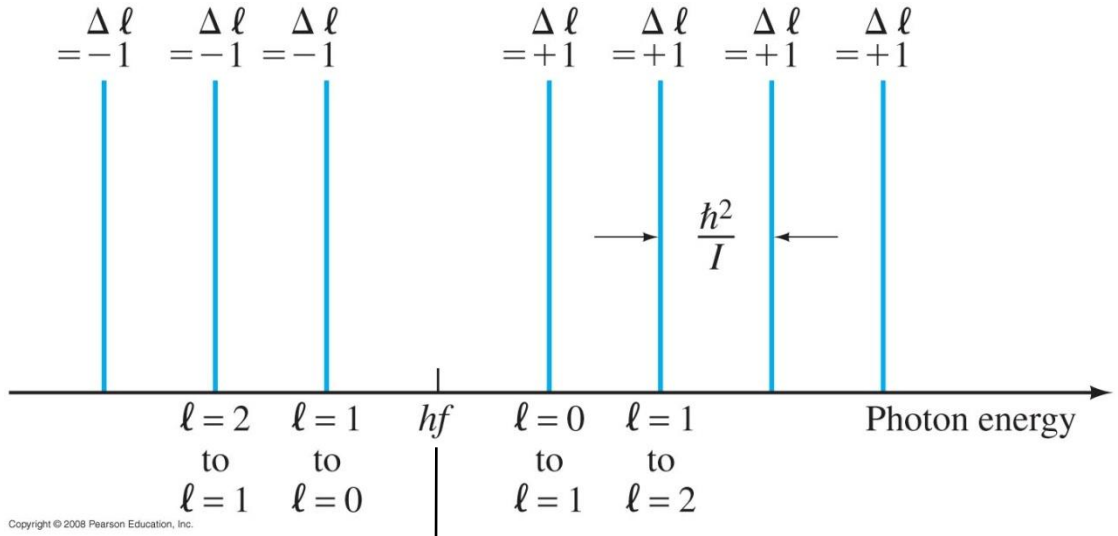
$$= \frac{1}{Z_{rot}}(2J+1)e^{-BJ(J+1)+DJ^2(J+1)^2}$$

Find optimum via

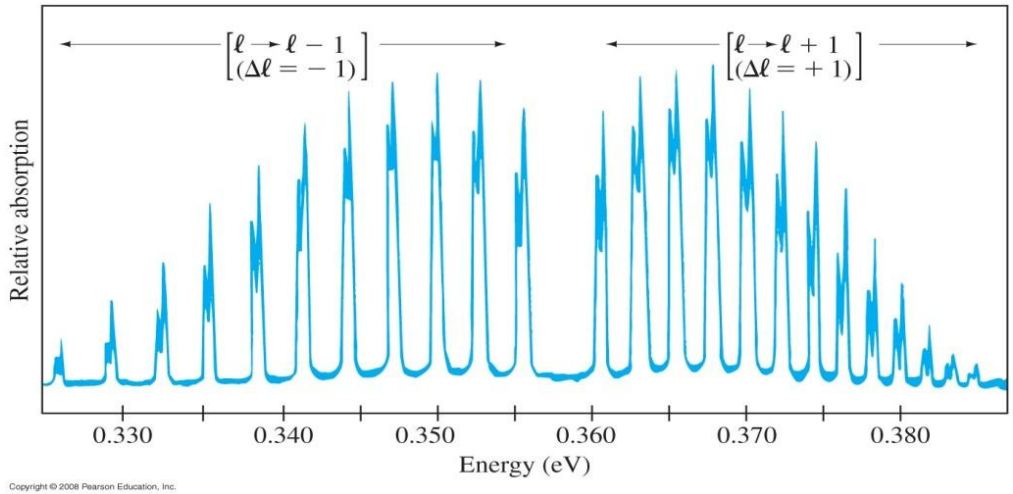
$$\frac{dP(J)}{dJ} = 0$$



Vibrational Spectra (ro-vibrational)



Location of "vibrational band origin"



Spacing between lines is

$$\Delta E = \frac{\hbar^2}{I}$$

$$R_e = \sqrt{\frac{I}{\mu}}$$

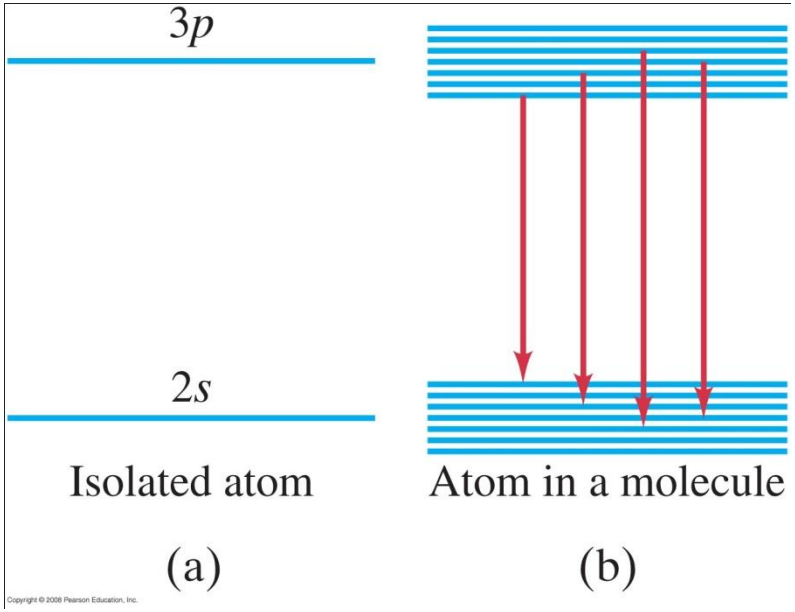
$$\mu = \frac{M_H M_{Cl}}{M_H + M_{Cl}}$$

Bond length

Molecular Spectra

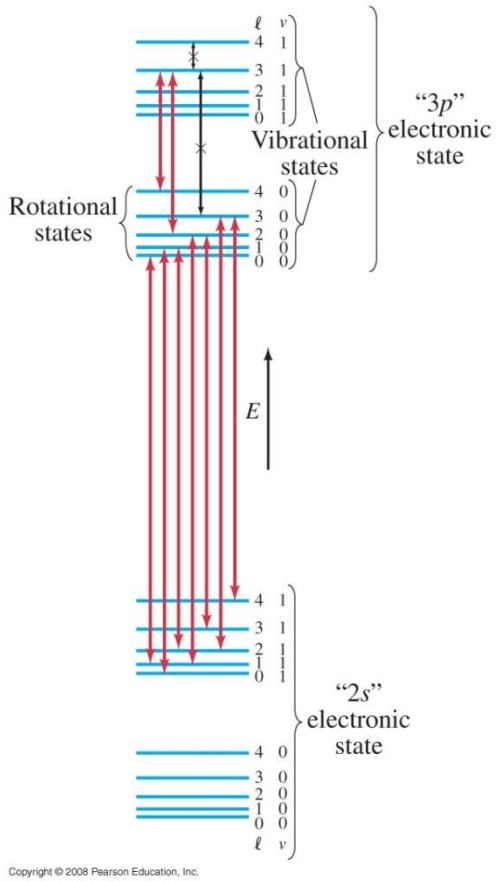
The overlap of orbits alters energy levels in molecules. Also, more types of energy levels are possible, due to rotations and vibrations. The result is a band of closely spaced energy levels:

Molecular band spectra (electronic transitions, with vibration and rotation superimposed); → Selection rules



Molecular Spectra

electronic transitions, with vibration and rotation superimposed)



→Selection rules

Franck-Condon principle

P, Q, R transitions