

Molecular Spectroscopy

For molecules (e.g. diatomic), the total energy of molecule is a contribution of the following:

- 1- (Translation kinetic energy, E_{trans}) **FOR THE CENTER OF MASS**
- 2- (Excitation energy, E_{excit}) for the electrons in the molecule $\Delta E_{excit} \approx 1 \text{ eV} \approx 10^4 \text{ K}$.
- 3- (Vibrational energy, E_{vib}) for the electrons in the $\Delta E_{vib} \approx 10^{-3} \text{ eV}$ to 10^{-1} eV
- 4- (Rotational energy, E_{rot}) around the center of mass of the molecule $\Delta E_{rot} \approx 10^{-4} \text{ eV}$.

Potential Energy Curve between Bonding Atoms

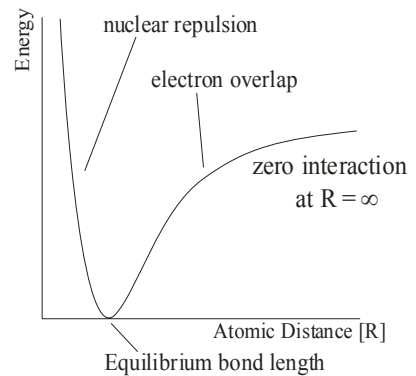
Notes about the potential energy curve

The equilibrium bond length is the distance where the electron overlap balances the nuclear repulsion.

At $R = \infty$, the energy of the system is the energy of the atoms themselves.

- The bonding of the atoms causes the system's energy to decrease.

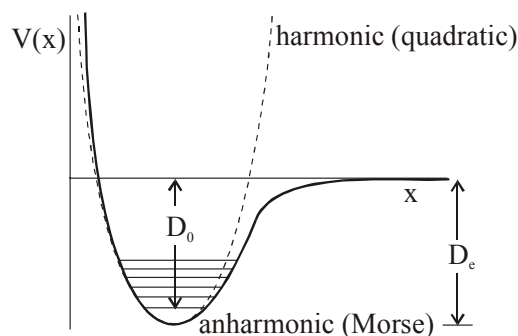
Once atoms are pushed closer than equilibrium bond length, nuclear repulsion causes potential energy of the system to increase.



Morse Potential

An excellent approximation of an actual potential energy curve is the **Morse potential**.

$$V(x) = D_e (1 - e^{-ax})^2 \quad \text{where } a = \left(\frac{\mu\omega^2}{2D_e} \right)^{\frac{1}{2}} \text{ and } D_e \text{ is the potential well depth.}$$



D_0 – dissociation energy

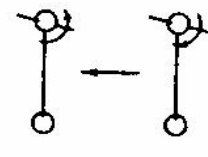
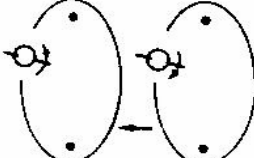

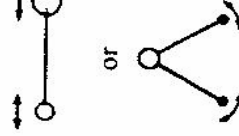
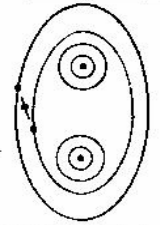
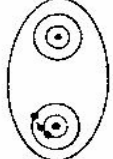

$$D_e - D_0 = \frac{1}{2} \hbar\omega - \text{zero point energy}$$

THE ELECTROMAGNETIC SPECTRUM

Acronym	Classification	Frequency Range, f	Wavelength
THF	Tremendously High Freq.	300–3000 GHz	1 mm – 100 μm
EHF	Extremely High Freq. (Millimetric waves/Microwaves)	30 – 300 GHz	1 cm – 1 mm
SHF	Super High Freq. (Centimetric waves/Microwaves)	3 – 30 GHz	10 – 1 cm
UHF	Ultra High Freq. (Radio frequency) (Decimetric wave)	300 – 3000 MHz	1 m – 10 cm
VHF	Very High Freq. (Metric waves)	30 – 300 MHz	10 – 1 m
HF	High Freq. (Decametric waves)	3 – 30 MHz	100 – 10 m
MF	Medium Freq. (Hectometric waves)	300 – 3000 kHz	1 km – 100 m
LF	Low Freq. (Kilometric waves)	30 – 300 kHz	10 km – 1 km
VLF	Very Low Freq. (Myriametric waves)	3 – 30 kHz	100 – 10 km
ULF	Ultra Low Freq.	300 – 3000 Hz	10^3 – 10^2 km
SLF	Super Low Freq.	30 – 300 Hz	10^4 – 10^3 km
ELF	Extremely Low Frequency	3 – 30 Hz	10^5 – 10^4 km
TLF	Tremendously Low Freq.	< 3 Hz	10^6 – 10^5 km

Region of the electromagnetic spectrum

region	Frequency Range, f (Hz)	Wavelength	
γ -ray	$3 \times 10^{18} \rightarrow 3 \times 10^{20}$?	Energy changes involve the rearrangement of nuclear configuration.
x -ray	$3 \times 10^{16} \rightarrow 3 \times 10^{18}$?	Energy changes involving the inner electrons of an atom or molecule.
Visible and ultra-violet	$3 \times 10^{14} \rightarrow 3 \times 10^{16}$?	To study electronic spectroscopy.
Infra-red	$3 \times 10^{12} \rightarrow 3 \times 10^{14}$?	To study the vibrations of molecules and yield information concerning the stiffness or rigidity of chemical bond.
Microwaves	$3 \times 10^{10} \rightarrow 3 \times 10^{12}$?	Investigation the rotation of molecules and yields moment of inertia and bond length,
Radio frequency	$3 \times 10^6 \rightarrow 3 \times 10^{10}$	1 cm \rightarrow 10 m	The energy change involved is that arising from the reversal of spin of a nucleus or electron.

Change of Spin		Change of Orientation		Change of Configuration		Change of Electron Distribution		Change of Nuclear Configuration	
n.m.r.	e.s.r.	Microwave	Infra-red	Visible and ultra-violet	X-ray	γ -ray			
									
10^{-2}	1	100	10^4	10^6	wavenumber 10^8				
10 m	100 cm	1 cm	100 μ m	1 μ m	10 nm	wavelength 100 pm			
3×10^6	3×10^8	3×10^{10}	3×10^{12}	3×10^{14}	Hz	frequency 3×10^{16}			
10^{-3}	10^{-1}	10	10^3	10^5	joules/mole	10^7	energy	10^9	

The Harmonic Oscillator

1. Classical description.

A particle of mass m is subject to a restoring force F_x , which is proportional to its displacement from the origin (Hooke's Law).

$$-\frac{dV(x)}{dx} = F_x = -kx$$

where k is the force constant. If we take the zero of the potential energy V to be at the origin $x = 0$ and integrate,

$$V(x) = \int_0^x dV = -k \int_0^x x dx = \frac{1}{2} kx^2$$

Note that this potential energy function differs from that in the particle-in-the-box problem in that the walls do not rise steeply to infinity at some particular point in space ($x = 0$ and $x = L$), but instead approach infinity much more slowly.

From Newton's second law,

$$F = ma = m \frac{d^2x}{dt^2} = -kx$$

thus,

$$\frac{d^2x}{dt^2} = -\frac{k}{m}x = -\omega^2 x, \quad \omega = \sqrt{\frac{k}{m}}$$

This second-order differential equation is just like that for the free particle, so solutions must be of the form

$$x(t) = A \sin[\omega t] + B \cos[\omega t]$$

where A and B are constants of integration. If we assume that $x = 0$ at $t = 0$, then $B = 0$ and

$$x(t) = x_0 \sin[\omega t]$$

where $x_0 = A$ is the maximum displacement amplitude.

Since this can also be written as

$$x(t) = x_0 \sin(\omega t) = x_0 \sin(2\pi\nu t),$$

we see that the position of the particle oscillates in a sinusoidal manner with frequency

$$\nu = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad \Rightarrow \quad k = 4\pi^2 m \nu^2.$$

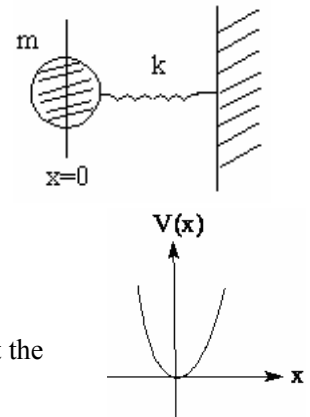
The energy of the classical oscillator is

$$E = T + V = \frac{1}{2} m v^2 + \frac{1}{2} k x^2$$

$$\therefore v(t) = \frac{dx}{dt} = \omega x_0 \cos[\omega t]$$

$$\therefore E = \frac{1}{2} m \omega^2 x_0^2 \cos^2[\omega t] + \frac{1}{2} k x_0^2 \sin^2[\omega t] = \frac{1}{2} k x_0^2,$$

and is not quantized.



Quantum mechanical description.

Following our prescription, we begin by writing down the classical energy expression for the oscillator

$$E = T + V = \frac{1}{2}mv^2 + \frac{1}{2}kx^2 = \frac{p_x^2}{2m} + \frac{1}{2}kx^2$$

and then convert this to the quantum mechanical analog, the Hamiltonian operator \hat{H} , by replacing each of the dynamical variables (p_x and x) by their operator equivalents,

$$p_x \rightarrow \hat{p}_x = -i\hbar \frac{\partial}{\partial x}, \quad x \rightarrow \hat{x} = x$$

This yields

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2$$

We then use this form of \hat{H} in the time-independent Schrödinger equation

$$\hat{H}\psi = E\psi$$

not zero. New feature.

yielding

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) + \frac{1}{2}kx^2 \psi(x) = E\psi(x). \quad (A)$$

Eigenvalues

The energies (eigenvalues) of the one-dimensional harmonic has the from:

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega = \left(n + \frac{1}{2}\right) h\nu, \quad n = 0, 1, 2, \dots$$

Here n is the vibrational quantum number. Converting to the spectroscopic units, m^{-1} , we have,

$$\tilde{E}_n = \frac{E_n}{hc} = \left(n + \frac{1}{2}\right) \tilde{\nu}$$

Here n is called term value.. $\tilde{\nu}$ is the vibrational frequency of the oscillator in wavenumbers, so its units is m^{-1} . Zero-point energy in $m^{-1} = \frac{1}{2} \tilde{\nu}$. The selection rule for the harmonic oscillator under going vibrational changes is $\Delta n = \pm 1$.

Vibrational energy changes will only give rise to an observable spectrum if the vibration can interact with radiation, i.e., if the vibration involves a change in the dipole moment of the molecule. Thus, vibrational spectra will be observable only in heteronuclear diatomic molecules (like HF, HCl, HBr) since homonuclear molecules (like H_2 , N_2 and O_2) have no dipole moment.

Example: Show that the vibrational absorption spectrum of a diatomic molecule in the harmonic oscillator approximation consists of just one line whose frequency is given by Eq. $\nu = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$.

Solution: From the Eq.:

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega = \left(n + \frac{1}{2}\right) h\nu, \quad n = 0, 1, 2, \dots$$

According to the selection rule, $\Delta n = +1$ for absorption, the vibrational energy change for absorption is

$$\Delta E = E_{n+1} - E_n = \left(n + 1 + \frac{1}{2}\right) h\nu - \left(n + \frac{1}{2}\right) h\nu = h\nu = \frac{h}{2\pi} \sqrt{\frac{k}{m}}$$

Thus, the spectrum consists of a single line whose frequency is

$$\nu_{obs} = \frac{\Delta E}{h} = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

Using the last equation, the observed infrared frequency can yield the force constant k , which is a direct measure of the stiffness of the bond. $\Rightarrow \Delta \tilde{E} = \tilde{\nu}$

It means that all the vibrational lines obtained from harmonic oscillator are of the same frequency. The allowed vibrational energy levels and transitions between them for a diatomic molecule undergoing simple harmonic motion are shown in Fig. 23.8.

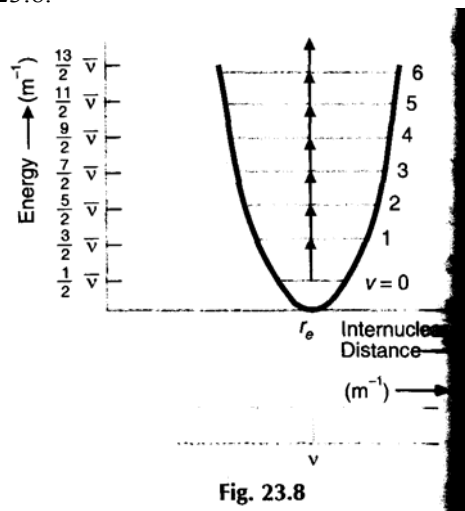


Fig. 23.8

Pure vibrational spectra are observed only in liquids. This is because interactions between neighboring molecules prevent their rotational motion.

Example. in the near infra-red spectrum of HCl molecule there is single intense band at 2885.9 cm^{-1} . Assuming that it is due to the transition between vibrational levels, show that the force constant k is 480 Nm^{-1} . (Given : $M_H = 1.68 \times 10^{-27} \text{ kg}$).

Solution. $\bar{\nu} = 2885.9 \text{ cm}^{-1} = 288590 \text{ m}^{-1}$.

Now, $\bar{\nu} = 1/\lambda = \nu/c$.

Frequency of vibration is

$$\nu = \bar{\nu}c = 288590 \times (3 \times 10^8) = 8.6577 \times 10^{13} \text{ Hz.}$$

Now, $\nu = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$ where k is the force constant and μ is the reduced mass of the molecule.

Therefore,

$$k = 4\pi^2 \mu \nu^2.$$

The reduced mass of $H^1 Cl^{35}$ is given by

$$\mu = \frac{M_H M_{Cl}}{M_H + M_{Cl}} = \frac{1 \times 35}{1 + 35} M_H = \frac{35}{36} \times (1.68 \times 10^{-27} \text{ kg}) = 1.63 \times 10^{-27} \text{ kg}$$

$$\therefore k = 4 \times (3.14)^2 \times (1.63 \times 10^{-27}) (8.6577 \times 10^{13})^2 = 482.3 \text{ Nm}^{-1}.$$

Example. The force constant of the bond in CO molecule is 187 Nm^{-1} . Calculate the frequency of vibration of the molecule and the spacing between its vibrational energy level in eV. Given that reduced mass of CO = $1.14 \times 10^{-26} \text{ kg}$, $h = 6.6 \times 10^{-34} \text{ Js}$ and $1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$.

Solution: The frequency of vibration of the molecule is

$$\nu_{osc} = \frac{1}{2\pi} \sqrt{\left(\frac{k}{\mu}\right)} = \frac{1}{2 \times 3.14} \sqrt{\left(\frac{187 \text{ Nm}^{-1}}{1.14 \times 10^{-26} \text{ kg}}\right)} = 2.04 \times 10^{13} \text{ Hz}$$

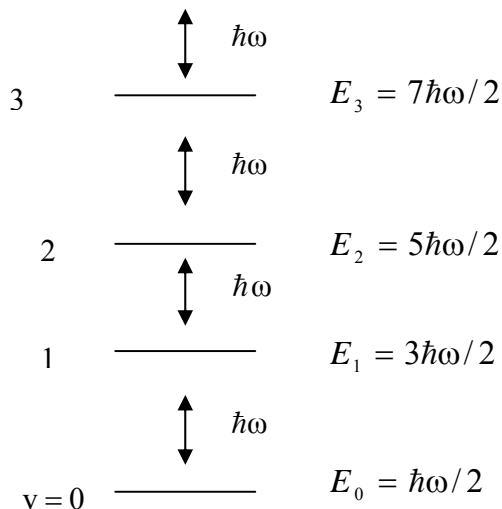
The vibrational energy of a diatomic molecule is

$$E_v = h\nu \left(v + \frac{1}{2}\right), v = 0, 1, 2 \dots$$

The separation between two successive vibrational energy levels is

$$\begin{aligned} \Delta E = E_{v+1} - E_v &= h\nu \left(v + \frac{3}{2}\right) - h\nu \left(v + \frac{1}{2}\right) = h\nu \\ &= (6.63 \times 10^{-34}) \times (2.04 \times 10^{13}) \text{ J} = 8.44 \times 10^{-2} \text{ eV}. \end{aligned}$$

Unlike the corresponding classical result, we find that the quantum mechanical energy is quantized, in units of $\hbar\omega$, where ω is the classical frequency $\omega^2 = k/m$. We also find that the lowest state, with $n = 0$, does not have zero energy but instead has $E = \hbar\omega/2$, the so-called zero point energy. We can summarize these results in the form of an energy level diagram



Boltzmann Distribution

As the numbers of molecules (or atoms) get larger, that is 10^{23} , the most probable distribution for a given amount of macroscopic energy among microscopic energy states is given by the Boltzmann distribution.

$$\frac{n_i}{N} = \frac{e^{-\frac{E_i}{kT}}}{\sum_j e^{-\frac{E_j}{kT}}}$$

n_i – number of molecules in the i^{th} energy state.
 N – total number of molecules.
 E_i – energy of the i^{th} energy state.
 k – Boltzmann's constant: 1.38×10^{-23} J/K

$$\text{Note: } R = kN_A$$

Let us examine how the energy of 10^6 HCl -molecules is distributed among the different vibrational states at $T = 298$ K, where $\tilde{\nu} = 2991 \text{ cm}^{-1}$.

$$E_n = hc\tilde{\nu}\left(n + \frac{1}{2}\right) = (6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.997 \times 10^{10} \text{ cm/s})(2991 \text{ cm}^{-1})\left(n + \frac{1}{2}\right)$$

$$= (5.617 \times 10^{-20} \text{ J})\left(n + \frac{1}{2}\right)$$

$$kT = (1.381 \times 10^{-23} \text{ J/K})(298 \text{ K}) = 4.118 \times 10^{-21} \text{ J}$$

n	E_n	$\frac{E_n}{kT}$	$e^{-\frac{E_n}{kT}}$
0	$2.802 \times 10^{-20} \text{ J}$	6.82	1.09×10^{-3}
1	$8.425 \times 10^{-20} \text{ J}$	20.46	1.31×10^{-9}
2	$1.404 \times 10^{-19} \text{ J}$	34.10	1.55×10^{-15}
3	$1.966 \times 10^{-19} \text{ J}$	47.74	1.85×10^{-21}
4	$2.528 \times 10^{-19} \text{ J}$	61.38	2.20×10^{-27}

$$\frac{n_0}{N} = \frac{n_0}{10^6} = \frac{e^{-6.82}}{e^{-6.82} + e^{-20.46} + e^{-34.10} + e^{-47.74} + e^{-61.38}} = \frac{1.09 \times 10^{-3}}{1.09 \times 10^{-3}} = 1 \Rightarrow n_0 = 10^6 \cdot 1 = 10^6$$

$$\frac{n_1}{N} = \frac{n_1}{10^6} = \frac{e^{-20.46}}{e^{-6.82} + e^{-20.46} + e^{-34.10} + e^{-47.74} + e^{-61.38}} = \frac{1.31 \times 10^{-9}}{1.09 \times 10^{-3}} = 1.21 \times 10^{-6} \Rightarrow n_1 = 10^6 \cdot 1.21 \times 10^{-6} = 1$$

The vibrational energy is large compared to the thermal energy; therefore, approximately 999,999 molecules out of a million are in the ground vibrational state at 298 K and 1 molecule is in the first excited state.

Let us consider what happens to the energy distribution at a higher temperature such as 2000 K?

$$kT = (1.381 \times 10^{-23} \text{ J/K})(2000 \text{ K}) = 2.762 \times 10^{-20} \text{ J}$$

n	$\frac{E_n}{kT}$	$n_n = 10^6 \frac{e^{-\frac{E_n}{kT}}}{\sum_v e^{-\frac{E_v}{kT}}}$
0	1.02	868998
1	3.04	113843
2	5.08	14911
3	7.11	1950
4	9.15	260
5	11.17	34
6	13.21	4

Conclusion: Most diatomic molecules are in the ground vibrational state ($n = 0$) at room temperature.

Role of Degeneracy in the Boltzmann Distribution

The Boltzmann distribution includes all degenerate states as equally probable as well. Therefore the more precise formulation of the Boltzmann distribution is

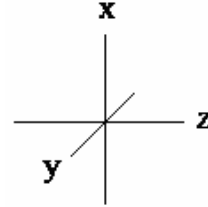
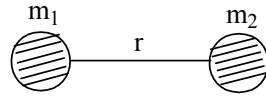
$$\frac{n_i}{N} = \frac{g_i e^{-\frac{E_i}{kT}}}{\sum_j g_j e^{-\frac{E_j}{kT}}},$$

g_i – degeneracy of the i^{th} energy state.

Rotational motion of rigid linear molecules

Classical description.

A rigid rotor is a dumbbell-shaped object consisting of two masses, m_1 and m_2 , separated by a fixed distance r .



In general, the rotational energy of any three-dimensional object can be written as

$$E_{rot} = \frac{1}{2} I_x \omega_x^2 + \frac{1}{2} I_y \omega_y^2 + \frac{1}{2} I_z \omega_z^2$$

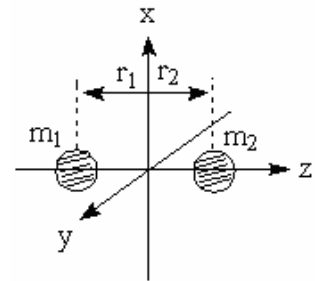
Here, ω_x , etc., are the angular velocities of rotation and I_x , etc., are the moments of inertia, each referred to the principal axes of rotation.

For our dumbbell, if we assume that m_1 and m_2 are point masses, then

$$\omega_x = \omega_y = \omega, \quad \omega_z = 0$$

$$I_x = I_y = I, \quad I_z = 0$$

$$I_x = m_1 r_1^2 + m_2 r_2^2$$



If the origin of the coordinate system is located at the center of mass (CM), use the relations: $m_1 r_1 = m_2 r_2$, $r = r_1 + r_2$, we can write:

$$r_1 = \left(\frac{m_2}{m_1 + m_2} \right) r, \quad r_2 = \left(\frac{m_1}{m_1 + m_2} \right) r$$

$$I = \left(\frac{m_1 m_2}{m_1 + m_2} \right) r^2 = \mu r^2, \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \quad (\text{reduced mass})$$

From this we see that the rotational motion of our “dumbbell” can also be described as the rotational motion of a mass μ , which is located at a distance R_0 from the center of a spherical polar coordinate system. So

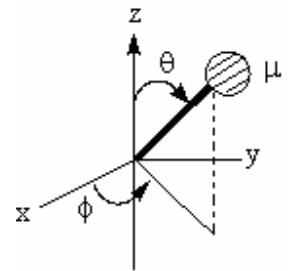
$$E_{rot} = \frac{1}{2} I_x \omega_x^2 + \frac{1}{2} I_y \omega_y^2 = I \omega^2 = (m_1 r_1^2 + m_2 r_2^2) \omega^2$$

$$= \left[m_1 \left(\frac{m_2}{m_1 + m_2} \right)^2 + m_2 \left(\frac{m_1}{m_1 + m_2} \right)^2 \right] R_0^2 \omega^2 = \frac{1}{2} \mu R_0^2 \omega^2 = \frac{1}{2} I \omega^2$$

\Rightarrow particle on a ring, on a sphere.

Since $\vec{L} = I \vec{\omega}$, where \vec{L} is the angular momentum of the object, we can also write

$$E_{rot} = \frac{|\vec{L}|^2}{2\mu r^2} = \frac{|\vec{L}|^2}{2I}$$



Quantum mechanical description.

To describe the system by QM, we need the operator equivalent of $|\underline{L}|^2$. This is, in polar coordinates

$$\hat{L}^2 = -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \frac{\cos \theta}{\sin \theta} \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right)$$

So, $\hat{H} = \hat{L}^2 / 2\mu r^2$ is the QM analog of the classical energy.

$$\hat{L}^2 Y_{J,m} = \hbar^2 J(J+1) Y_{J,m}, \quad J = 0, 1, 2$$

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

With the degeneracy $g_J = 2J + 1$

When we consider both rotations and vibrations simultaneously, we take advantage of the fact that these transitions occur on different timescales. Typically, a molecular vibration takes on the order of 10^{-14} s. A molecular rotation is normally much slower, taking on the order of 10^{-9} s or 10^{-10} s. Hence, as a molecule rotates one revolution, it vibrates many, many times. Since the vibrational energies are large compared with the rotational energies, the appropriate energy level diagram is:

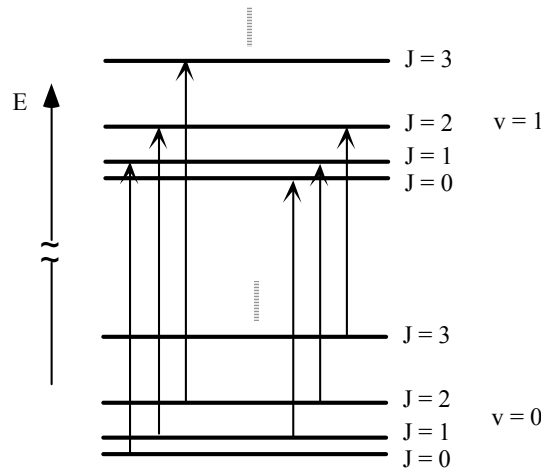


Figure 4

In wave-numbers, the energy, $\tilde{\nu}(J)$, and the rotational constant, \tilde{B} , are related by the equation:

$$\tilde{\nu}(J) = \tilde{B} J(J+1) \text{ cm}^{-1} \quad \text{and} \quad \tilde{B} = \frac{h}{8\pi^2 c I} \text{ cm}^{-1}$$

Proof: $E_J = \frac{\hbar^2}{2I} J(J+1)$, but $E = h\nu = h \frac{c}{\lambda} = hc\tilde{\nu}$

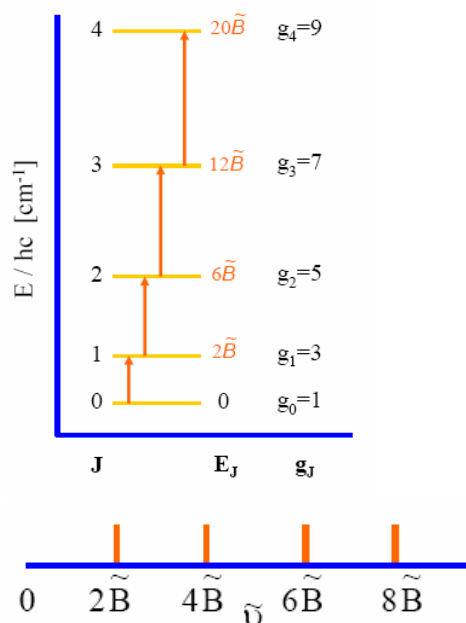
$$E_J = hc\tilde{\nu} \Rightarrow \tilde{\nu} = \frac{E_J}{hc} = \frac{1}{hc} \frac{\hbar^2}{2I} J(J+1) = \frac{h}{8\pi^2 c I} J(J+1) = \tilde{B} J(J+1)$$

\tilde{B} for diatomic molecules are in the order 1 cm^{-1} .

Rotational spectra are always obtained in absorption. Hence for a transition from some initial state of quantum number J to the next higher state of quantum number J + 1, the wave number of the absorbed photon is:

$$\tilde{\nu}_{J \rightarrow J+1} = \tilde{B} (J+1)(J+2) - \tilde{B} J(J+1) = 2\tilde{B} (J+1)$$

The energy level diagram is



Notice that:

- 1- the levels are *not* equally spaced, and that the lowest level has *zero* energy (unlike HO). By calculating \tilde{B} , we can calculate I , and then the distance R_o between the nuclei can be calculated. This gives the length of the chemical bond between the atoms..
- 2- Rotational transitions occur only in those molecules which possess a permanent electric dipole moment. For this reason nonpolar diatomic molecules such as H_2 and symmetric polyatomic molecules such as CO_2 and CH_4 do not exhibit rotational spectra.
- 3- The selection rule for rotational transitions is $\Delta J = \pm 1$.

Example. The lines in the pure rotational spectrum of HCl are spaced as $20.8 \times 10^2 \text{ m}^{-1}$. Calculate the moment of inertia and the internuclear distance. Mass of proton = $1.67 \times 10^{-27} \text{ kg}$; mass of chlorine = $58.5 \times 10^{-27} \text{ kg}$.

Sol. The reduced mass is defined as

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(1.67 \times 10^{-27})(58.5 \times 10^{-27})}{(1.67 + 58.5) \times 10^{-27}} = 1.62 \times 10^{-27} \text{ kg}$$

$$\text{Here, } \Delta \bar{\nu} = \frac{\hbar}{2\pi I c} = 20.8 \times 10^2 \text{ m}^{-1}$$

$$\therefore I = \frac{\hbar}{2\pi c \Delta \bar{\nu}} = \frac{1.054 \times 10^{-34}}{2\pi(3 \times 10^8)(20.8 \times 10^2)} = 2.689 \times 10^{-47} \text{ kg m}^2$$

$$\therefore R_o = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{2.689 \times 10^{-47}}{1.62 \times 10^{-27}}} = 1.286 \times 10^{-10} \text{ m.}$$

Example: In the CO molecule the wavenumber difference between the successive absorption lines in the pure rotational spectrum is 384 m^{-1} . Calculate the moment of inertia of the molecule and the equilibrium bond length of the molecule. Masses of the C^{12} and O^{16} atoms are respectively $1.99 \times 10^{-26} \text{ kg}$ and $2.66 \times 10^{-26} \text{ kg}$.

Answer: Here

$$\Delta \tilde{\nu} = \frac{\hbar}{2\pi I c} = 384 \text{ m}^{-1}$$

$$\therefore I = \frac{\hbar}{2\pi c \Delta \tilde{\nu}} = \frac{1.054 \times 10^{-34}}{2\pi \times (3 \times 10^8) \times 384} = 1.456 \times 10^{-46} \text{ kg m}^2$$

The reduced mass μ of the CO molecule is

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \left[\frac{1.99 \times 2.66}{1.99 + 2.66} \right] \times 10^{-26} \text{ kg} = 1.138 \times 10^{-26} \text{ kg}.$$

$$\therefore \text{Bond length} = R_0 = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{1.456 \times 10^{-46}}{1.138 \times 10^{-26}}} = 0.1131 \text{ nm}.$$

Intensity of Rotational Transitions

Degeneracy is important when partitioning the rotational energy of sample of molecules. Remember that each rotational state J can have an M value that ranges from $J, \dots, -J$. Thus each rotational state J has $2J + 1$ M values; thus the degeneracy for rotational energy levels is $2J + 1$. The intensity of a transition in the absorption (microwave) or Rotational Raman spectrum is proportional to the number of molecules in the initial state (J'); i.e. $\text{Int.} \propto N_J$

Boltzmann Distribution:

$$N_J \propto g_J e^{-\frac{E_J}{kT}} \Rightarrow N_J \propto (2J + 1) e^{-\frac{hc\tilde{B}J(J+1)}{kT}}$$

EXAMPLE 1: Calculate ΔE for radiation of wave number, $\bar{\nu} = 1.00 \text{ cm}^{-1}$. To what type of molecular process will this radiation correspond?

Solution: Recall that wave number is given by reciprocal wavelength or that

$$\bar{\nu} = \frac{1}{\lambda}$$

Therefore, ΔE is related to $\bar{\nu}$ by

$$\Delta E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$$

and so

$$\begin{aligned} \Delta E = hc\bar{\nu} &= (6.626 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m}\cdot\text{s}^{-1})(100 \text{ m}^{-1}) \\ &= 1.99 \times 10^{-23} \text{ J} \end{aligned}$$

According to table (1), this value of energy corresponds to rotational transition.

EXAMPLE 2: Show that the rotational absorption predicted by the rigid rotator model consists of a series of equally spaced lines in the microwave region.

Solution: The energy levels are given by Eq.

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

According to the selection rule for rotational transitions, $\Delta J = 1$ for absorption. The energy change for a rotational transition is:

$$\Delta E = E_{J+1} - E_J = \frac{\hbar^2}{2I} \left\{ (J+1)(J+2) - \frac{\hbar^2}{2I} J(J+1) \right\} = \frac{\hbar^2}{I} (J+1)$$

and

$$\nu = \frac{\Delta E}{h} = \frac{h}{4\pi^2 I} (J+1), \quad J = 0, 1, 2, \dots$$

The spectrum consists of a series of equally spaced lines whose frequencies are integral multiples of $h/4\pi^2 I$. Using an atomic mass of 40×10^{-27} kg and a bond length of 200 pm, we find

$$\begin{aligned} I &= \mu R_0^2 = \left(\frac{m_1 m_2}{m_1 + m_2} \right) R_0^2 = \frac{(40 \times 10^{-27} \text{ kg})^2}{(40 + 40) \times 10^{-27} \text{ kg}} (2 \times 10^{-10} \text{ m})^2 \\ &= 8 \times 10^{-46} \text{ kg} \cdot \text{m}^2 \end{aligned}$$

The corresponding frequencies, then, are integral multiples of $h/4\pi^2 I$, or

$$\begin{aligned} \nu &= \frac{h}{4\pi^2 I} (J+1) = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})}{4\pi^2 (8 \times 10^{-46} \text{ kg} \cdot \text{m}^2)} (J+1) \\ &= 2.1 \times 10^{10} (J+1) \text{ Hz} \quad J = 0, 1, 2, \dots \end{aligned}$$

According table (1), these lines occur in the microwave region.

$h = 6.63 \times 10^{-34} \text{ J} \cdot \text{s}$ $c = 3.00 \times 10^8 \text{ m/s}$ $c = 3.00 \times 10^{10} \text{ cm/s}$ $NA = 6.02 \times 10^{23} \text{ mol}^{-1}$ $k = 1.38 \times 10^{-23} \text{ J/K}$ $1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$

Example 3: The HCl bond length is 0.127 nm. Calculate the spacing between lines in the rotational absorption spectrum of HCl, in cm^{-1} .

Answer:

$$\mu = \frac{m_H m_{Cl}}{m_H + m_{Cl}} = \frac{(1 \text{ amu})(35 \text{ amu})}{1 \text{ amu} + 35 \text{ amu}} = 0.972 \text{ amu} = 0.972 \text{ amu} \cdot \frac{1.66 \times 10^{-27} \text{ kg}}{1 \text{ amu}} = 1.61 \times 10^{-27} \text{ kg}$$

$$I = \mu r^2 = (1.61 \times 10^{-27} \text{ kg})(0.127 \times 10^{-9} \text{ m})^2 = 2.60 \times 10^{-47} \text{ kg} \cdot \text{m}^2$$

$$\tilde{B} = \frac{h}{8\pi^2 I c} = \frac{6.63 \times 10^{-34} \text{ J} \cdot \text{s}}{8(3.14)^2 (2.60 \times 10^{-47} \text{ kg} \cdot \text{m}^2)(3.00 \times 10^{10} \text{ cm/s})} = 10.78 \text{ cm}^{-1} \approx 10.8 \text{ cm}^{-1}$$

As discussed above, microwave absorption lines occur at 2B, 4B, 6B, ... Therefore, the spacing is 2B

$$\text{Spacing} = 2\tilde{B} = 2 \times 10.8 = 21.6 \text{ cm}^{-1}$$

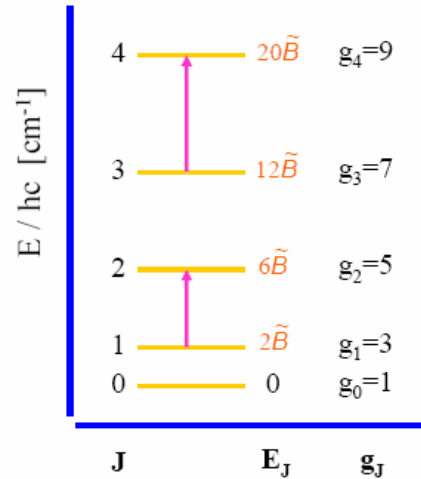
Example 4: calculate the ratio of intensities $\frac{I_{3 \rightarrow 4}}{I_{1 \rightarrow 2}}$ in the above example at 25° C, where

$$\tilde{B} = 10.8 \text{ cm}^{-1}$$

Answer:

$$\frac{I_{3 \rightarrow 4}}{I_{1 \rightarrow 2}} = \frac{N_3}{N_1} = \frac{g_3 e^{-E_3/kT}}{g_1 e^{-E_1/kT}} = \frac{7 e^{-12hc\tilde{B}/kT}}{3 e^{-2hc\tilde{B}/kT}} = \frac{7}{3} e^{-10hc\tilde{B}/kT}$$

$$\frac{I_{3 \rightarrow 4}}{I_{1 \rightarrow 2}} = \frac{7}{3} e^{-0.52} \approx 1.4$$



$$\frac{10hc\tilde{B}}{kT} = \frac{10(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^{10} \text{ cm/s})(10.8 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})} = 0.52$$

Summary

The Harmonic Oscillator

$$\frac{d^2x}{dt^2} = -\frac{k}{m}x = -\omega^2 x, \quad \omega = \sqrt{\frac{k}{m}}$$

$$v = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \Rightarrow k = 4\pi^2 m v^2.$$

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} kx^2$$

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega = \left(n + \frac{1}{2}\right) h\nu, \quad n = 0, 1, 2, \dots \quad \Delta n = \pm 1$$

$$\Delta E = E_{n+1} - E_n = \left(n + 1 + \frac{1}{2}\right) h\nu - \left(n + \frac{1}{2}\right) h\nu = h\nu = \frac{h}{2\pi} \sqrt{\frac{k}{m}}$$

$$v_{obs} = \frac{\Delta E}{h} = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \Rightarrow \Delta \tilde{E} = \tilde{\nu}$$

Boltzmann Distribution:

$$\frac{n_i}{N} = \frac{g_i e^{-\frac{E_i}{kT}}}{\sum_j g_j e^{-\frac{E_j}{kT}}}, \quad g_i - \text{degeneracy of the } i^{\text{th}} \text{ energy state, } kT = (1.381 \times 10^{-23} \text{ J/K})(T \text{ K})$$

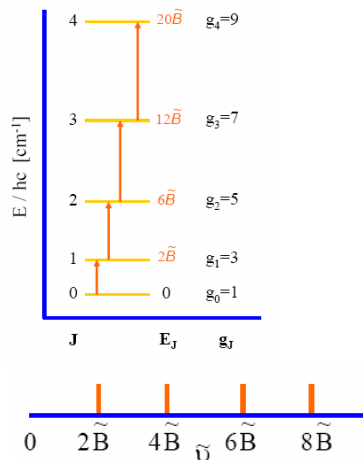
Rotational motion of rigid linear molecules

$$E_{rot} = \frac{1}{2} \mu R_0^2 \omega^2 = \frac{1}{2} I \omega^2, \quad E_{rot} = \frac{|\vec{L}|^2}{2\mu r^2} = \frac{|\vec{L}|^2}{2I}, \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \quad (\text{reduced mass})$$

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

$$\tilde{\nu}(J) = \tilde{B} J(J+1) \text{ cm}^{-1} \quad \text{and} \quad \tilde{B} = \frac{h}{8\pi^2 c I} \text{ cm}^{-1}$$

$$\tilde{\nu}_{J \rightarrow J+1} = \tilde{B} (J+1)(J+2) - \tilde{B} J(J+1) = 2\tilde{B} (J+1)$$



Rotational Transitions Accompany Vibrational Transitions

Within the rigid rotator-harmonic oscillator approximation, the rotational and vibrational energy of a diatomic molecule is:

$$E_{vib,rot} = \left(n + \frac{1}{2}\right)h\nu_o + hc\tilde{B}J(J+1) \quad \begin{array}{l} n = 0,1,2,\dots \\ J = 0,1,2,\dots \end{array}$$

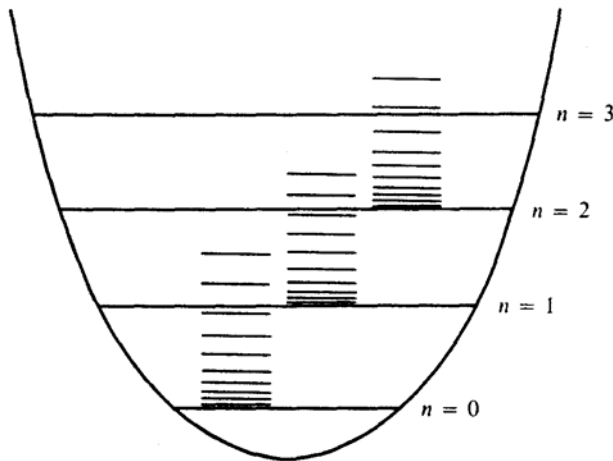


Figure 10-2. An energy diagram showing the rotational levels associated with each vibrational state for a diatomic molecule. The lower rotational levels are too closely spaced to be shown.

where the rotational constant $\tilde{B} = \frac{\hbar}{4\pi Ic}$. Typical values of the spacing between rotational levels are around 10^{-23} J molecule⁻¹ (cf. Table 10-1) and of those of vibrational levels are around 10^{-21} J molecule⁻¹ (cf. Table 10-1). This result is shown schematically in Figure 10-2. When a molecule absorbs infrared radiation, the vibrational transition is accompanied by a rotational transition. The selection rules for absorption of infrared radiation are:

$$\begin{array}{l} \Delta n = +1 \\ \Delta J = \pm 1 \end{array}$$

The frequency associated with the absorption is:

$$\nu_{obs} = \nu_o + c\tilde{B} [J'(J'+1) - J(J+1)]$$

Where J' can be either $(J+1)$ or $(J-1)$. If $J' = J+1$, then

$$\nu_{obs} (\Delta J = +1) = \nu_o + 2c\tilde{B}(J+1), \quad J = 0,1,2,\dots \quad \text{R - branch (A)}$$

If $J' = J-1$

$$\nu_{obs} (\Delta J = -1) = \nu_o - 2c\tilde{B}J, \quad J = 1,2,3,\dots \quad \text{P - branch (B)}$$

In both Eqs. (A) and (B), J is the initial rotational quantum number. Typically, $\tilde{B} \approx 10^{11}$ Hz and $\nu_o \approx 10^{13}$ Hz, and so the spectrum predicted by Eqs. (A) and (B) typically contains lines at 10^{13} Hz \pm integral multiples of 10^{11} Hz. Notice that there is no line at ν_o . The rotational-vibrational spectrum of HBr(g) is shown in Figure 10-3. The gap centered around 2560 cm⁻¹

corresponds to the missing line at ν_o . On each side of the gap is a series of lines whose spacing is about 10 cm^{-1} . The series toward the high-frequency side is called the **R** branch and is due to rotational transitions with $\Delta J = +1$. The series toward the low frequencies is called the **P** branch and is due to rotational transitions with $\Delta J = -1$.

, or $2c\tilde{B} = 3.82 \text{ cm}^{-1}$ (cf. Figure 10-3 for HBr).

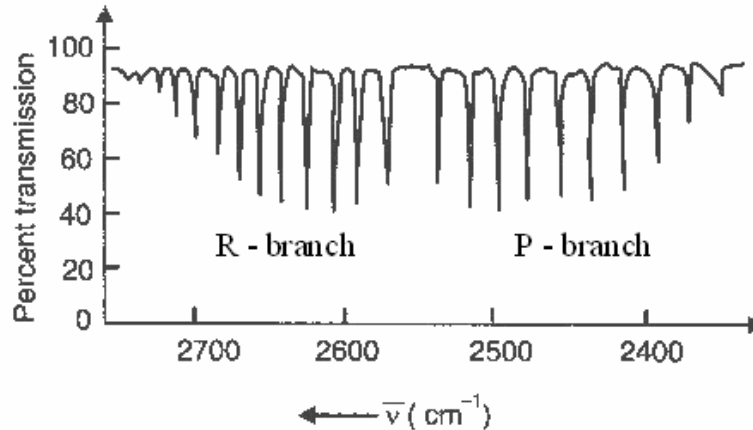


Figure 10-3: The vibration-rotation spectrum of the $0 \rightarrow 1$ vibrational transition of HBr. The R- and P- branches are indicated in the figure.

EXAMPLE 10-6

The bond length in $\text{C}^{12}\text{N}^{14}$ is 117 pm and its force constant is $1630 \text{ N}\cdot\text{m}^{-1}$. Predict the vibration-rotation spectrum of $\text{C}^{12}\text{N}^{14}$.

Solution: First we must calculate the fundamental frequency ν_o (Eq. 10-21) and the rotational constant \tilde{B} (Eq. 10-16). Both quantities require the reduced mass, which is

$$\mu = \frac{(12.0 \text{ amu})(14.0 \text{ amu})}{(12.0 + 14.0) \text{ amu}} (1.66 \times 10^{-27} \text{ kg}\cdot\text{amu}^{-1}) = 1.07 \times 10^{-26} \text{ kg}$$

Using Eq. 10-21 for ν_o ,

$$\begin{aligned} \nu_o &= \frac{1}{2\pi} \left(\frac{k}{\mu} \right)^{1/2} = \frac{1}{2\pi} \left(\frac{1630 \text{ N}\cdot\text{m}^{-1}}{1.07 \times 10^{-26} \text{ kg}} \right)^{1/2} \\ &= 6.20 \times 10^{13} \text{ s}^{-1} = 2.07 \times 10^3 \text{ cm}^{-1} \end{aligned}$$

Using Eq. 10-16 for \tilde{B} ,

$$\begin{aligned} \tilde{B} &= \frac{h}{8\pi^2 c l} = \frac{h}{8\pi^2 c \mu R_0^2} \\ &= \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})}{8\pi^2 (3.00 \times 10^8 \text{ m}\cdot\text{s}^{-1})(1.07 \times 10^{-26} \text{ kg})(117 \times 10^{-12} \text{ m})^2} \\ &= 1.91 \text{ cm}^{-1} = 5.73 \times 10^{10} \text{ s}^{-1} \end{aligned}$$

The vibration-rotation spectrum will consist of lines at:

$$\nu_o \pm 2c j \tilde{B}, \quad j = 1, 2, 3, \dots$$

There will be no line at ν_o and the separation of the lines in the P and R branches will be $2c\tilde{B} = 1.15 \times 10^{11} \text{ s}^{-1}$ or $2\tilde{B} = 3.82 \text{ cm}^{-1}$ (See the above figure).

If we compare the results of Example 10-6 to experimental data, or look closely at Figure 10-3, we see that there are several features in the vibration-rotation spectrum that we are not able to explain. For examples:

- 1- The **intensities**, or **heights**, of the lines in the P and R branches show a definite pattern and the spacing of the lines is not equal.
- 2- The lines in the R branch are more closely spaced with increasing frequency and that the lines of the P branch become further apart with decreasing frequency, i.e. the **spacing** between the lines is not equal.

Comments: Using Boltzmann distribution one can explain the following:

- 1- most diatomic molecules are in the $n = 0$ vibrational state at room temperature.
- 2- the intensities of the lines in the P and R branches in a vibration-rotation spectrum.

The Intensities of the Lines in the P and R Branches in a Vibration-Rotation Spectrum Are Explained By a Rotational Boltzmann Distribution

If we assume that the intensities of the rotational lines in a vibration-rotation spectrum are proportional to the fraction of molecules in the rotational level from which the transition occurs, then we can use the Boltzmann distribution of rotational energies to explain the observed intensities. We cannot use Eq. 10-22 directly because the rotational energy levels are $(2J + 1)$ -fold

degenerate. If the i th level has a degeneracy g_i , then Eq. 10-22 becomes

$$N_i = c g_i e^{-E_i/k_B T}$$

For rotational energies, we have

$$N_J = c(2J + 1) \exp\left[\frac{-\bar{B}J(J + 1)}{k_B T}\right] \quad (10-32)$$

Instead of evaluating the proportionality constant by summing over J as we did in the case of a harmonic oscillator, it is easier in this case to evaluate c in Eq. 10-32 by letting $J = 0$ to obtain

$$N_0 = c$$

Thus, Eq. 10-32 can be written in the form

$$\frac{N_J}{N_0} = (2J + 1) \exp\left[\frac{-\bar{B}J(J + 1)}{k_B T}\right] \quad (10-33)$$

Note that N_J/N_0 is *not* the fraction of molecules in the J th energy level, but it is the number in the J th level relative to the number in the ground state. Equation 10-33 is plotted in Figure 10-4 for HCl ($\bar{B} = 10.6 \text{ cm}^{-1}$) at 300 K. Note that the envelope of the lines in Figure 10-4 is similar to the envelope of the lines of the P and R branches in Figure 10-3. Thus we see that the shape of the P and R branches reflects the population of the rotational energy levels.

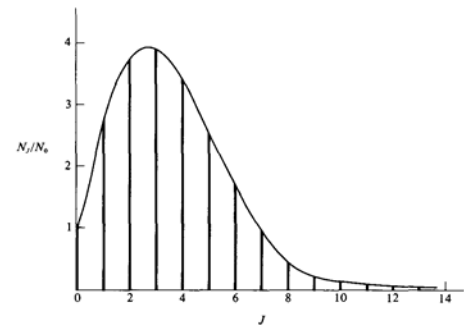


Figure 10-4. The relative populations of the rotational levels of HCl(g) at 300 K.

Non-Rigid Rotator

On the wavenumber scale, the frequency difference between two successive lines in the pure rotational spectrum of a diatomic molecule is given by:

$$\Delta \tilde{\nu} = \frac{\hbar}{2\pi I c}$$

The rotational spectrum can be recorded. The absorption lines are equi-spaced. The separation between the adjacent lines is identified as $2\tilde{B}$.

$$\Delta \tilde{\nu} = \frac{\hbar}{2\pi I c} = 2\tilde{B} \Rightarrow \tilde{B} = \frac{\hbar}{4\pi I c}$$

By measuring $\Delta \tilde{\nu}$, the rotational constant \tilde{B} can be calculated. From this, the moment of inertia of the molecule I can be calculated. Knowing I , one can calculate the reduced mass μ of the molecule and R_o the bond length.

The following table lists some of the observed lines in the rotational spectrum H^{35}Cl . The differences listed in the third column clearly show that the lines are not exactly equally spaced as the rigid rotator approximation predicts.

The Rotational Absorption Spectrum of H^{35}Cl

Transition	$\bar{\nu}_{\text{obs}}/\text{cm}^{-1}$	$\Delta\bar{\nu}_{\text{obs}}/\text{cm}^{-1}$	$\bar{\nu}_{\text{calc}} = 2\tilde{B}(J+1)$ $\tilde{B} = 10.34 \text{ cm}^{-1}$	$\bar{\nu}_{\text{calc}} = 2\tilde{B}(J+1) - 4\tilde{D}(J+1)^3$ $\tilde{B} = 10.395 \text{ cm}^{-1}$ $\tilde{D} = 0.0004 \text{ cm}^{-1}$
3 → 4	83.03	21.07	82.72	83.06
4 → 5	104.10	20.20	103.40	103.75
5 → 6	124.30	20.73	124.08	124.39
6 → 7	145.03	20.48	144.76	144.98
7 → 8	165.51	20.35	165.44	165.50
8 → 9	185.86	20.52	186.12	185.94
9 → 10	206.38	20.12	206.80	206.30
10 → 11	226.50		227.48	226.56

Experimental investigations have shown that the successive lines in the far infra-red spectrum are not evenly spaced, but the frequency separation decrease slightly with increasing the value of J (Larger speed of rotation). It shows that the bond length R_o increases with J . Therefore, our assumption that the molecule is a rigid rotator is false. In fact, all bonds are elastic to some extent. The more quickly a diatomic molecule rotates, the greater is the centrifugal force tending to move the atoms apart.

Now we discuss the consequences of the change in bond length with J .

- I- When a bond is elastic, it will stretch and compress periodically with a certain functional frequency dependent upon the masses of the atoms and the elasticity (or force constant k) of the bond. This means that the molecule may have vibrational energy. If the vibrational motion is simple harmonic, the force constant k is given by:

$$k = 4\pi^2 \omega^2 c^2 \mu \quad (1)$$

Here, ω is the vibration frequency (in m^{-1}). μ is the reduced mass of the molecule. The variation of B with J is determined by the force constant, i.e., the weaker the bond, more readily will it distort under centrifugal forces.

II- The second consequence of elasticity is that the quantities r and B vary during a vibration.

Energy Levels

Consider a single particle of mass μ rotating about a fixed point with an angular velocity, ω . Let the particle be at a distance R_o from the fixed point when there is no rotation. Let this length increase to R , when the particle rotates.

$$\text{Centrifugal force during rotation} = \mu R \omega^2 .$$

$$\text{Restoring force due to bond stretching (Hook's law)} = k (R - R_o)$$

The above two forces balance each other at any instant of rotation.

$$\mu R \omega^2 = k (R - R_o) \Rightarrow R = \frac{k R_o}{(k - \mu \omega^2)}$$

This gives the distorted bond length.

Total energy of the rotating system = K. E. + P. E

$$\Rightarrow E = \frac{1}{2} I \omega^2 + \frac{1}{2} k (R - R_o)^2 = \frac{1}{2} I \omega^2 + \frac{1}{2} \frac{\mu^2 R^2 \omega^4}{k} = \frac{L^2}{2I} + \frac{L^4}{2I^2 k R^2} .$$

Where we used: $L = I \omega = \mu R^2 \omega$. The quantum restriction that the angular momentum $I \omega$ be

quantized according to $\hbar \sqrt{J(J+1)}$ will convert this classical result to a quantum-mechanical result:

$L = \hbar \sqrt{J(J+1)}$. The correct allowed energies are,

$$E_J = \frac{\hbar^2}{2I} J(J+1) + \frac{\hbar^4}{2I^2 k R^2} J^2(J+1)^2$$

Using:

$$\text{Important note: } R = \frac{k R_o}{(k - \mu \omega^2)} \Rightarrow \frac{1}{R^2} = \frac{[1 - (\mu \omega^2 / k)]^2}{R_o^2} = \frac{1}{R_o^2} \left[1 - \frac{2\mu \omega^2}{k} + \frac{\mu \omega^2}{k} \right] = \frac{1}{R_o^2} \left[1 - \frac{2L^2}{\mu k R_o^4} + \frac{L^4}{\mu^2 k^2 R_o^8} \right]$$

Then

$$E_J = \frac{\hbar^2}{2I_o} J(J+1) - \frac{\hbar^4}{2k I_o^2 R_o^2} J^2(J+1)^2 + \dots, \quad I_o = \mu R_o$$

$$\tilde{E}_J = \frac{E_J}{hc} = \tilde{B} J(J+1) - \tilde{D} J^2(J+1)^2$$

In the last Eq., the first term is of major importance. The second is a minor term. The quantity \tilde{D} is called the centrifugal distortion constant, $\tilde{D} \ll \tilde{B}$.

$$\text{H.W. Show that } \tilde{D} = \frac{4\tilde{B}}{\tilde{\nu}^2}, \quad \tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} .$$

H.W. Check the following:

$$\begin{aligned} \bar{\nu}_{J+1} - \bar{\nu}_J &= \Delta\bar{\nu} = B[(J+1)(J+2) - J(J+1)] \\ &\quad - D[(J+1)^2(J+2)^2 - J^2(J+1)^2] \\ &= 2B(J+1) - 4D(J+1)^3 \text{ m}^{-1} \dots(8) \end{aligned}$$

Fig. 23.5 shows the lowering of rotational levels when passing from the rigid to the non-rigid diatomic molecule. The difference between the energy levels increases with increasing value of J. The rotational absorption spectrum is produced due to molecular transition from the state J to the state (J+ 1). The selection rule is $\Delta J = +1$.

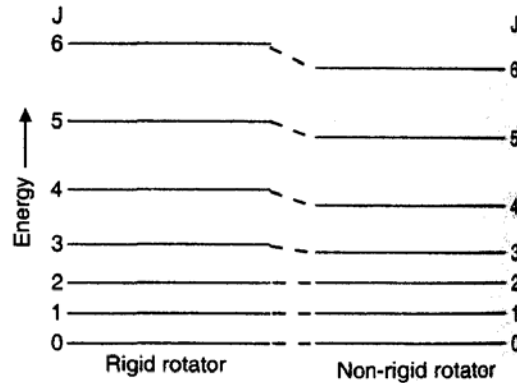


Fig. 23.5

Thus, we see that the spectrum of a non-rigid diatomic molecule is similar to that of the rigid molecule except that each line is displaced slightly to low frequency (Fig. 23.6). We note from Eq. (8) that the lines are no longer exactly equidistant but their separation decreases slightly with increasing J. The effect, however, is small owing to the smallness of D as compared to B.

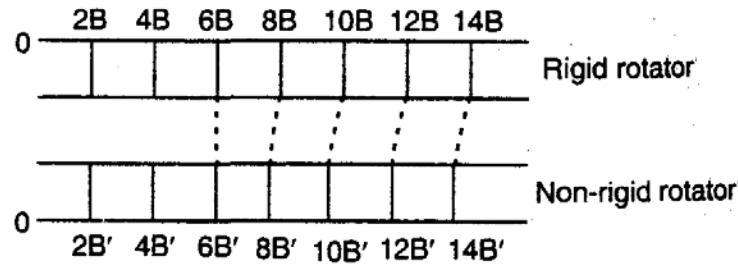


Fig. 23.6

MOLECULAR SPECTRA

Determination of Force Constant from Rotational Spectrum

By making observations on a number of lines in the rotation spectrum of a molecule, and by curve fitting method, the values of B and D are found out. Once D is known, the J values of lines in the observed spectrum can be determined. Further, knowing B and D, the angular frequency of vibration of the rotating molecule can be calculated using the relation

$$\omega^2 = \frac{4B^3}{D}$$

For hydrogen fluoride, $\omega = 405000 \text{ m}^{-1}$.

The reduced mass of the molecule m is known.

The force constant k is calculated using the equation

$$k = 4\pi^2 c^2 \omega^2 m.$$

For hydrogen fluoride, the force constant is 960 Nm^{-1} which indicates that H-F is a relatively strong bond.

Example: HCl molecule has a rotational constant B value of 1059.3 m^{-1} and a centrifugal constant D of $5.3 \times 10^{-2} \text{ m}^{-1}$. Estimate the vibrational frequency and force constant of the molecule.

Sol. $\omega^2 = \frac{4B^3}{D}$. Here, ω is the vibrational frequency in wave number unit.

$$\omega = \sqrt{\frac{4B^3}{D}} = \sqrt{\frac{4 \times (1059.3)^3}{5.3 \times 10^{-2}}} = 299516.3 \text{ m}^{-1}.$$

Force constant $k = 4\pi^2 c^2 \omega^2 m$.

$$m = \frac{m_1 m_2}{m_1 + m_2} = \frac{(1.008)(35.46)}{(1.008 + 35.46)} \frac{1}{6.023 \times 10^{26}} = 1.627 \times 10^{-27} \text{ kg}.$$

$$k = 4\pi^2 \times (3 \times 10^8)^2 \times (299516.3)^2 \times 1.627 \times 10^{-27} = 518.6 \text{ Nm}^{-1}.$$

$$E_J = \frac{\hbar^2}{2I} J(J+1) \Rightarrow \bar{\nu} = \frac{E_J}{hc} = \bar{B}J(J+1), \quad \bar{B} = \frac{h}{8\pi^2 cI}$$

$$E_n = (n + \frac{1}{2})h\nu \Rightarrow \Delta E = E_{n+1} - E_n = h\nu = \hbar\sqrt{\frac{k}{m}} \Rightarrow \nu_{obs} = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

The rotational and vibrational energy of a diatomic molecule is given by:

$$E_{vib,rot} = (n + \frac{1}{2})h\nu_o + hc\bar{B}J(J+1) \quad \begin{matrix} n = 0,1,2,\dots \\ J = 0,1,2,\dots \end{matrix}$$

