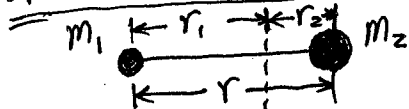# Chapter 9. Rotational Spectroscopy

Transitions between rotational states within the same electronic state and the same vibrational state give photons in the microwave frequency range.

The rotation motion of a diatomic molecule can be modeled as a rigid rotator in the first order approximation, and then further modeled as a non rigid rotator to make corrections to the rigid model results. Finally, a vibrating rotator is introduced.

§9.1. The Rigid Rotator

Dumbell Model of a Diatomic Molecule

[Rigid rotator]

We begin with the simplest model of a rotating molecule — the dumbell model.

Consider the two atoms of masses m_1 and m_2 to be point-like and fastened at a distance r apart to the ends of a weightless rigid rod.

In classical mechanics the energy of rotation E of a rigid body is given by

$$E = \frac{1}{2} I \omega^2, \qquad (1)$$

where I is the moment of inertia of the system about the axis of rotation, and ω is the angular velocity of the rotation: $\omega = 2\pi \nu_{rot}$.

$$I = \sum_i m_i r_i^2 \qquad \text{— the moment of inertia} \qquad (2)$$

$$P_J = I\omega \qquad \text{— the angular momentum} \qquad (3)$$

$$E = \frac{P_J^2}{2I} \quad - \text{ the energy of the rigid rotator.} \quad (4)$$

For the dumbell model,

$$I = m_1 r_1^2 + m_2 r_2^2 \quad (5) \quad \text{where} \quad r_1 = \frac{m_2}{m_1 + m_2} r \quad (6)$$

$$r_2 = \frac{m_1}{m_1 + m_2} r . \quad (7)$$

r_1 and r_2 are the distances of the masses m_1 and m_2 from the center of gravity C, and r is the distance of the two mass points from each other.

$$\therefore \quad I = \frac{m_1 m_2}{m_1 + m_2} r^2 = \mu r^2 \quad (8)$$

i.e., the moment of inertia is the same as that of a mass point with $\mu = \frac{m_1 m_2}{m_1 + m_2}$ (9) — reduced mass of the molecule.

at a distance r from the axis.

Thus, instead of considering the rotation of the dumbbell, we can equally well consider the rotation of a single mass point with mass μ at a fixed distance r from the axis of rotation. — a Simple Rigid Rotator.

Energy levels : In order to determine the possible energy state of such a rigid rotator, we should solve the time-independent Schrödinger equation, i.e., the eigenvalue equation of $\hat{H}$:

where $\hat{H} = \dfrac{\hat{P}^2}{2\mu} + V = \dfrac{\hat{P}^2}{2\mu}$ $\qquad$ (11)

potential energy $V=0$. $\qquad$ ($\hat{P}$ is momentum operator)

$$\boxed{\hat{H}\,\psi = E\,\psi \qquad (10)}$$

$\because \hat{P} = i\hbar\vec{\nabla}$ $\quad \therefore \hat{H} = \dfrac{-\hbar^2\nabla^2}{2\mu} = -\dfrac{h^2}{8\pi^2\mu}\nabla^2$ (12)

Eq. (10) becomes :

$$= -\dfrac{h^2}{8\pi^2\mu}\left(\dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2}\right)$$

$$\dfrac{\partial^2\psi}{\partial x^2} + \dfrac{\partial^2\psi}{\partial y^2} + \dfrac{\partial^2\psi}{\partial z^2} + \dfrac{8\pi^2\mu}{h^2}E\psi = 0 \qquad (13).$$

where $x^2 + y^2 + z^2 = r^2$ is a constant.

The solution of Eq. (13) is that ψ are single-valued, finite, and continuous, occur only for certain values of E, i.e., the eigenvalues :

$$E = \dfrac{h^2}{8\pi^2\mu r^2}J(J+1) = \dfrac{h^2}{8\pi^2 I}J(J+1) \qquad (14).$$

where the rotational quantum number $J = 0, 1, 2, 3, \cdots$.

Thus, we have a series of discrete energy levels whose energy increases quadratically with increasing J.

Compare Eq. (4) with Eq. (14), we obtain the angular momentum

$$P_J^2 = \frac{h^2}{4\pi^2} [J(J+1)]$$

$$\Rightarrow P_J = \frac{h}{2\pi} \sqrt{J(J+1)} \qquad (15)$$

$$= \hbar \sqrt{J(J+1)}$$

The rotational quantum number J thus gives approximately the angular momentum in units $\hbar$. Thus, $\vec{J}$ means an angular momentum vector of magnitude $\sqrt{J(J+1)}\,\hbar$.

$$\therefore \text{ rotational quantum number } J \longrightarrow \text{ angular momentum.}$$

Since only certain discrete energy values and angular momenta of the rigid rotator are possible, it follows that only certain rotational frequencies are possible. Recall Eq. (3), we have the angular frequency (velocity)

$$\omega = \frac{\hbar}{I} \sqrt{J(J+1)} \qquad (16)$$

$$\therefore \text{ rotational frequency is}$$

$$\nu_{rot} = \frac{\omega}{2\pi} = \frac{\hbar}{2\pi I} \sqrt{J(J+1)} \qquad (17)$$

i.e., the rotational frequency increases approximately linearly with J: $\nu_{rot} \approx \frac{\hbar}{2\pi I} J$.

Spectrum : Only when permanent dipole moment is non zero, can a rigid rotator emits or absorbs radiations. During the rotation the component of the dipole in a fixed direction changes periodically with a frequency equal to the rotational frequency. Thus, classically, light with frequency ν_{rot} should be emitted.

For molecules consisting of two like atoms, no dipole moment arises and therefore no light is emitted. Conversely, only if a permanent dipole moment is present, can an infrared frequency be absorbed and thereby a rotation of the system be produced, or a rotation already present be increased. According to classical theory, the absorbed or emitted spectrum of the rotator is continuous, since ν_{rotal} can take any value.

According to quantum theory, the emission of photon takes place as a result of a transition of the rotator from a higher to a lower energy level, while the absorption of photon with proper frequency produces a transition from a lower level to a higher level. The wave number of the transition line is

$$\tilde{\nu} = (E_k - E_i)/hc$$

E_k } upper and lower
E_i } energy levels.

$$E_J = \frac{\hbar^2}{2I} J(J+1) = \frac{h^2}{8\pi^2 I} J(J+1) = hc\, B\, J(J+1), \quad (18)$$

where $B = \dfrac{h}{8\pi^2 c\, I}$ is called the rotational constant. (19)

$\therefore$ Transition lines' Wave number is given by

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{(E_k - E_i)}{hc} = B\left[J_k(J_k+1) - J_i(J_i+1) \right] \quad (20)$$

Selection rules: $\Delta J = \pm 1$. $\Delta M = 0, \pm 1$ (22)

$$J_k > J_i , \quad \therefore J_k = J_i + 1$$

$$\Rightarrow \tilde{\nu} = 2B(J+1), \quad J = 0, 1, 2, \cdots \quad (23)$$

$$\boxed{P_{J,z} = M_J \hbar, \quad M_J = 0, \pm 1, \pm 2, \cdots, \pm J} \quad (21)$$

Thus, the spectrum of the simple rigid rotator consists of a series of equidistant lines.

Rotational frequency
$$\nu_{rot} = c \cdot 2B\sqrt{J(J+1)} \quad (24)$$

$\therefore$ the rotational frequency in any given state of the rotator is approximately equal to the frequency of the spectral line that has this state as upper state.
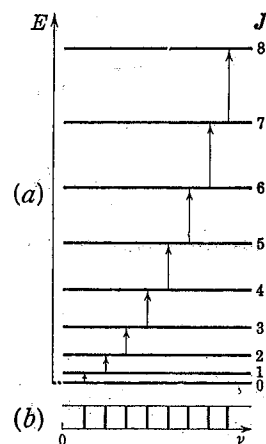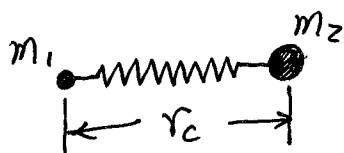

FIG. Energy Levels and Infrared Transitions of a Rigid Rotator. (a) The energy level diagram. (b) The resulting spectrum (schematic).

§9.2. The Nonrigid Rotator

A better model for representing the rotation of the molecule is given by the nonrigid rotator — a rotating system consisting of two mass points which are not connected by a massless rigid bar but by a massless spring.

m_1 ⌇⌇⌇⌇⌇ m_2

$\longleftarrow r_c \longrightarrow$

$\left(\mu = \dfrac{m_1 m_2}{m_1 + m_2} \right)$

In such a system, as a result of the action of centrifugal force, the inter-nuclear distance, and consequently the moment of inertia, increases with increasing rotation.

$I_c = \mu r_c^2$, recall rigid rotator energy $E = \dfrac{h^2}{8\pi^2 I} J(J+1)$

increasing rotation $(J \uparrow) \Rightarrow r_c \uparrow \Rightarrow I \uparrow$

$\Rightarrow$ factor $\dfrac{h^2}{8\pi^2 I} \downarrow \Rightarrow E \downarrow$ with increasing J

In the rotating molecule, the internuclear distance assumes such a value r_c, that the centrifugal force is just balanced by the restoring force $k(r_c - r_e)$ that arises on account of the small displacement $r_c - r_e$ from the equilibrium position r_e. The centrifugal force F_c is given by

$$F_c = \mu \omega^2 r_c = \dfrac{P_J^2}{\mu r_c^3} \qquad (25)$$

where ω is the angular velocity (angular frequency) and

$P = I\omega = \mu r_c^2 \omega$ is the angular momentum.

$\because F_c = k (r_c - r_e)$, where k is restoring force constant,

$\therefore r_c - r_e = \dfrac{P_J^2}{\mu r_c^3 k}$ $\qquad\qquad$ (26)

The kinetic energy of rotation is $E_k = \dfrac{P_J^2}{2 I_c}$. $\qquad$ (27)

In addition, for the nonrigid rotator there is potential energy

$$E_v = \tfrac{1}{2} k (r_c - r_e)^2 \qquad\qquad (28)$$

$\left(\text{Note: rigid rotator has no potential energy.}\right)$

Therefore, the total energy of rotation is

$$E = \dfrac{P_J^2}{2 I_c} + \tfrac{1}{2} k (r_c - r_e)^2 \qquad (29)$$

$\because I_c = \mu r_c^2 \qquad\qquad$ (k is the force constant of
$\qquad\qquad\qquad\qquad\qquad\qquad$ the chemical bond)

$\therefore \qquad E = \dfrac{P_J^2}{2 \mu r_c^2} + \tfrac{1}{2} k (r_c - r_e)^2 \qquad (30)$

$$= \dfrac{P_J^2}{2 \mu r_c^2} + \dfrac{P_J^4}{2 \mu^2 r_c^6 k} \qquad (31)$$

$$\dfrac{1}{r_c^2} = \dfrac{1}{(r_e + r_c - r_e)^2} = \dfrac{1}{r_e^2} \cdot \dfrac{1}{\left(1 + \frac{r_c - r_e}{r_e}\right)^2} \qquad (32)$$

$\because r_c - r_e \ll r_e \qquad \therefore \dfrac{r_c - r_e}{r_e} \ll 1$

Using $\dfrac{1}{(1+x)^2} \approx 1 - 2x + \cdots$, we have Eq. (32) as

$$\dfrac{1}{r_c^2} \approx \dfrac{1}{r_e^2} \left(1 - 2 \cdot \dfrac{r_c - r_e}{r_e}\right) \qquad\qquad (33)$$

Substitute Eq. (33) into Eq. (31), We obtain

$$E \approx \frac{P_J^2}{2\mu r_e^2} \left(1 - 2 \cdot \frac{r_c - r_e}{r_e}\right) + \frac{P_J^4}{2\mu^2 r_c^6 k}$$

$$= \frac{P_J^2}{2\mu r_e^2} - 2 \cdot \frac{P_J^2}{2\mu r_e^3}(r_c - r_e) + \frac{P_J^4}{2\mu^2 r_c^6 k} \qquad (34)$$

Eq. (26) can be approximated as

$$r_c - r_e = \frac{P_J^2}{\mu r_c^3 k} \approx \frac{P_J^2}{\mu r_e^3 k} \qquad (35)$$

Substitute Eq. (35) into Eq. (34) and replace r_c^6 with r_e^6 in the third term, We obtain

$$E = \frac{P_J^2}{2\mu r_e^2} - \frac{P_J^4}{\mu^2 r_e^6 k} + \frac{P_J^4}{2\mu^2 r_e^6 k}$$

$$= \frac{P_J^2}{2\mu r_e^2} - \frac{P_J^4}{2\mu^2 r_e^6 k} \qquad (36)$$

From quantum mechanics, We know $P_J = \sqrt{J(J+1)}\, \hbar$,

$$\therefore E(J) = \frac{J(J+1)}{2\mu r_e^2} \hbar^2 - \frac{J^2(J+1)^2}{2k\mu^2 r_e^6} \hbar^4$$

$$= \frac{J(J+1)}{2 I_e} \hbar^2 - \frac{J^2(J+1)^2}{2K I_e^2 r_e^2} \hbar^4 \qquad \left(I_e = \mu r_e^2\right) \qquad (38)$$

$$= hc\, B_e\, J(J+1) - hc\, D_e\, J^2(J+1)^2 \qquad (37)$$

where $B_e = \dfrac{h}{8\pi^2 I_e c}$ (m^{-1}) $\qquad (39) \qquad$ — rotational constant

$$D_e = \frac{1}{hc} \cdot \frac{\hbar^4}{2K I_e^2 r_e^2} \quad (m^{-1}) \ (40) \qquad \text{— rotational constant}$$

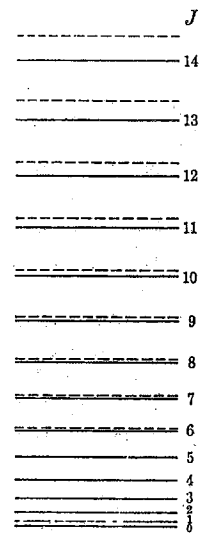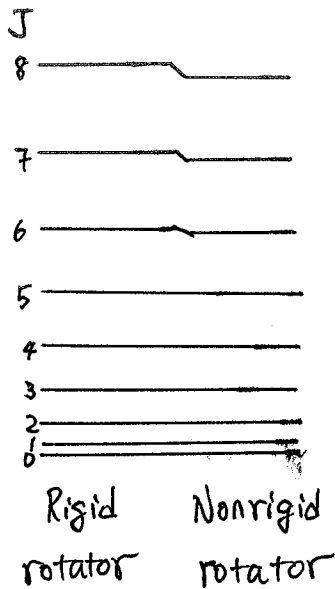Figure ( ) shows the Comparison of energy levels for the rigid rotator and the nonrigid rotator.

FIG. Energy Levels of the Non-rigid Rotator. For comparison, the energy levels of the corresponding rigid rotator are indicated by broken lines (for $J < 6$, they cannot be drawn separately).

Let us take a look at the rotational constant B_e and D_e.

$$B_e = \frac{h}{8\pi^2 I_e c} = \frac{h}{8\pi^2 \mu^2 r_e^2 c} \qquad (41)$$

B_e has a dimension/unit of m^{-1}:

$$\frac{J \cdot S}{kg \cdot m^2 \cdot m/s} = \frac{J \cdot S}{J \cdot S \cdot m}$$

$$= m^{-1} \qquad (43)$$

$$\boxed{\begin{array}{l} E = W = F \cdot S = ma^2 \cdot S \\ \therefore \ J = kg \cdot m/s^2 \cdot m \end{array}} \quad (42)$$

$h = 6.626 \times 10^{-34} \ J \cdot S$

$\mu = $ some number $\times 1.67 \times 10^{-27} kg$

$r_e = $ some number $\times 10^{-10} m$

$c = 3 \times 10^8 \ m/s$

$\Rightarrow$ We can calculate B_e once r_e is known.

For example, HCl molecule, the internuclear distance

$$r_e = 0.12746 nm = 1.2746 \times 10^{-10} m.$$

Molecular Weight $H = 1$, $Cl = 35.47$

$$\therefore \mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{35.47}{36.47} \times 1.67 \times 10^{-27} kg$$

$$\therefore B_e (HCl) = \frac{h}{8\pi^2 \mu r_e^2 c}$$

$$= \frac{6.626 \times 10^{-34}}{8\pi^2 \times \frac{35.47}{36.47} \times 1.67 \times 10^{-27} \times \left(1.2746 \times 10^{-10}\right)^2 \times 3 \times 10^8}$$

$$= 1060 \ m^{-1} \qquad\qquad (44)$$

$$= 10.6 \ cm^{-1}$$

$$D_e (HCl) = \frac{1}{hc} \cdot \frac{\hbar^4}{2K\mu^2 r_e^6}$$

$$\left(K = 516.3 \ N/m\right) \searrow \frac{h^3}{(2\pi)^4 \times 2K\mu r_e^6 c}$$

$$= \frac{(6.626 \times 10^{-34})^3}{(2\pi)^4 \times 2 \times 516.3 \times \left(\frac{35.47}{36.47} \times 1.67 \times 10^{-27}\right)^2 \left(1.2746 \times 10^{-10}\right)^6} \left(\times 3 \times 10^8\right)$$

$$= 0.053 \ m^{-1}$$

$$= 5.3 \times 10^{-4} \ cm^{-1} \qquad\qquad (45)$$

$$\therefore \text{Generally,} \quad D_e < 10^{-4} - 10^{-5} \ B_e.$$

Only when J is large enough ($J \geqslant 6$), the energy difference

between the rigid rotator and nonrigid rotator is distinguishible.

Spectrum. Selection rules for the rotational spectrum (real transitions) are $\begin{cases} \Delta J = \pm 1 \\ \Delta M = 0, \pm 1 \end{cases}$. They are valid regardless the rotator is rigid or not.

The wave number of the transition lines is given by

$$\tilde{\nu} = \frac{E(J+1) - E(J)}{hc}$$

$$= 2B_e(J+1) - 4D_e(J+1)^3. \qquad (46)$$

Therefore, the lines are no longer exactly equal-spaced, as for a rigid rotator, but their separation decreases slightly with increasing J. However, this effect is small because $D_e \ll B_e$.

Thus, we see that the model of the nonrigid rotator allows us to explain the observed far infrared and microwave spectrum in all details. From the observed spectrum we obtain not only the rotational constant B_e, the moment of inertia I_e, and internuclear distance r_e in the molecule, but also the rotational constant D_e, which gives a measure of the influence of centrifugal force.

§9.3. The Vibrating Rotator

So far we have regarded the rotation and the vibration of the molecule quite separately. However, it seems natural to assume that rotation and vibration can take place simultaneously, and, in fact, the observed fine structure of the rotation bands suggested very strongly that such a simultaneous rotation and vibration occurs. For this reason, we shall now consider a model — the vibrating rotator (or rotating oscillator) in which simultaneous rotation and vibration take place.

This vibrating rotator model must take into consideration the fact that during the vibration, the internuclear distance and consequently the moment of inertia and the rotational constant B are changing.

Since the period of vibration is very small compared to the period of rotation, we use a mean B value for the rotational constant in the vibrational state considered, i.e.,

$$B_v = \frac{h}{8\pi^2 c \mu}\overline{\left(\frac{1}{r^2}\right)} = \frac{h}{8\pi^2 c \mu}\langle \psi_v | \frac{1}{r^2} | \psi_v \rangle. \quad (47)$$

where $\overline{\left(1/r^2\right)} = \langle \psi_v | \frac{1}{r^2} | \psi_v \rangle$ is the mean value of $\frac{1}{r^2}$ during the vibration (v represents the vibrational quantum number).

It is expected that the rotational constant B_v is somewhat smaller than B_e, — B_e corresponds to the equilibrium separation r_e that is the internuclear distance corresponding to the minimum

of the Vibrational potential curve.

The mean internuclear distance r_v in the Vibrational state v is greater than r_e, and also $r_0 < r_1 < r_2, \cdots$, i.e., the higher vibrational state ($v \uparrow$) has larger r_v.

Recall $\quad B_e = \dfrac{h}{8\pi^2 c \mu r_e^2} = \dfrac{h}{8\pi^2 c I_e} = \dfrac{27.9928 \times 10^{-40}}{I_e} \qquad (48)$

QM gives

$$B_v = B_e - \alpha_e \left(v + \tfrac{1}{2}\right) + \cdots \qquad (49)$$

Here, α_e is a constant which is small compared to B_e, since the change in internuclear distance by the vibration is small compared to the internuclear distance itself.

In a similar manner, a mean rotational constant D_v, representing the influence of centrifugal force, must be used for the vibrational state v:

$$D_v = D_e + \beta_e \left(v + \tfrac{1}{2}\right) + \cdots \qquad (50)$$

where β_e is small compared to

$$D_e = \frac{4 B_e^3}{\omega_e^2} \qquad (51)$$

ω_e is the vibrational frequency.

Thus, the rotational energy levels in a given vibrational level is

$$E_v(J) = hc\, B_v\, J(J+1) - hc\, D_v\, J^2 (J+1)^2 \qquad (52).$$

This is the rotational energy levels in the vibrating rotator model.

For the lowest vibrational state $(\mathcal{v}=0)$, the rotational constant B_0 should be used in Eq. (52). For the vibrational state $\mathcal{v}=1$, the rotational constant B_1 should be used in Eq. (52).

B_0 and B_1 are smaller than B_e, because r_0 and r_1 (the mean value of internuclear distance in the vibrational states $\mathcal{v}=0$ and $\mathcal{v}=1$) are greater than r_e.
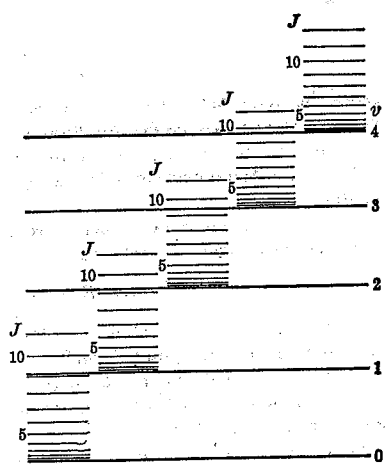

Fig.   Energy Levels of the Vibrating Rotator. For each of the first five vibrational levels, a number of rotational levels are drawn (short horizontal lines).
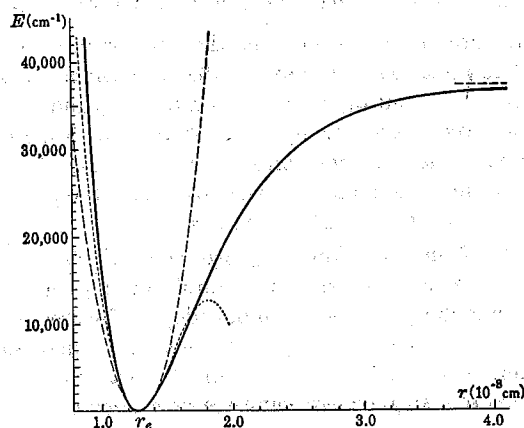

Fig.   Potential Curve of the Molecule (Anharmonic Oscillator). The full curve is drawn for the ground state of HCl. The broken-line and the dotted curves are the ordinary and the cubic parabola, respectively, that form the best approximation to the full curve at the minimum.

Spectrum . For pure rotational spectrum (within the same vibrational state $\mathcal{v}$), selection rules : $\Delta J = \pm 1$, $\Delta M = 0, \pm 1$. The wave number of the transition lines for the vibrating rotator is given by :

$$\tilde{\mathcal{v}} = \frac{E_{\mathcal{v}} (J+1) - E_{\mathcal{v}} (J)}{hc}$$

$$= 2 B_{\mathcal{v}} (J+1) - 4 D_{\mathcal{v}} (J+1)^3 \qquad (53)$$

The rotational spectrum (from the rigid rotator, nonrigid rotator, and the vibrating rotator) is usually in microwave and far IR region.