Lecture 2 : Elementary Microwave Spectroscopy

Topics

- Introduction
- Rotational energy levels of a diatomic molecule
- Spectra of a diatomic molecule
- Moments of inertia for polyatomic molecules
- Polyatomic molecular rotational spectra
- Intensities of microwave spectra
- Sample Spectra
- Problems and quizzes
- Solutions

Topic 2

Rotational energy levels of diatomic molecules

- A molecule rotating about an axis with an angular velocity $\vec{\omega}$

  C=O (carbon monoxide) is an example.
  The rotational kinetic energy expression is given in classical mechanics as

  Rotational kinetic energy, $E_{rot} = \frac{1}{2}I\omega^2$

  I: moment of inertia $= \mu r^2$

  where $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ is the reduced mass, m_1 and m_2 are the masses of the two atoms and r is the bond length

- In terms of angular momentum $\vec{J}$, the rotational kinetic energy E_{rot} is

  $$\vec{J} = I\vec{\omega} \Rightarrow E_{rot} = \frac{J^2}{2I}$$

  This is the other form of classical expression.

- In quantum mechanics:

  Replace angular momentum $\vec{J}$ by the operator form and obtain the corresponding operator form for the Hamiltonian (which is only rotational kinetic energy). The form turns out to be

  $$\hat{H}_{rot} = -\frac{\hbar^2}{2I}\nabla^2$$

  where ∇^2 is the Laplanian operator, and $\hbar = \dfrac{h}{2\pi}$.

- You know the solution for ∇^2 operator from hydrogen atom.

  Assume a rigid diatomic molecule (bond lengths dont change.) The coordinate r is a constant, not required. We need to consider only the $\theta\phi$ equation. It is possible to derive formally the square of the total angular momentum operator using spherical polar coordinates and show that it has the same form as the differential operator for the $\theta\phi$ equation of the hydrogen atom. It wil not be done here but will be assumed.

- Hence the angular solutions of the hydrogen atom are the eigenfunctions of this Hamiltonian.

Solution:

$$\hat{H}_{rot}\psi = E_{rot}\psi$$

$$\psi = Y_J^K(\theta\varphi)$$

$$E_{rot} = \frac{\hbar^2 J(J+1)}{2I} \qquad J=0,1,2,\ldots\ldots; K = -J, -J+1, \ldots, J-1, J \text{ for each } J$$

■ For each J, there are (2J+1) K values namely K = -J, -J+!, ..., J-1, J. Hence the eigenfunctions are (2J+1)-fold degenerate for each J.

For example, for J = 1, K can have three values, K = -1, K = 0 and K = 1. For J = 2, K can have five values, K = -2, -1, 0, 1 and 2 and so on.

■ Rotational energy is thus quantized and is given in terms of the rotational quantum number J.

$$E_0 = 0$$

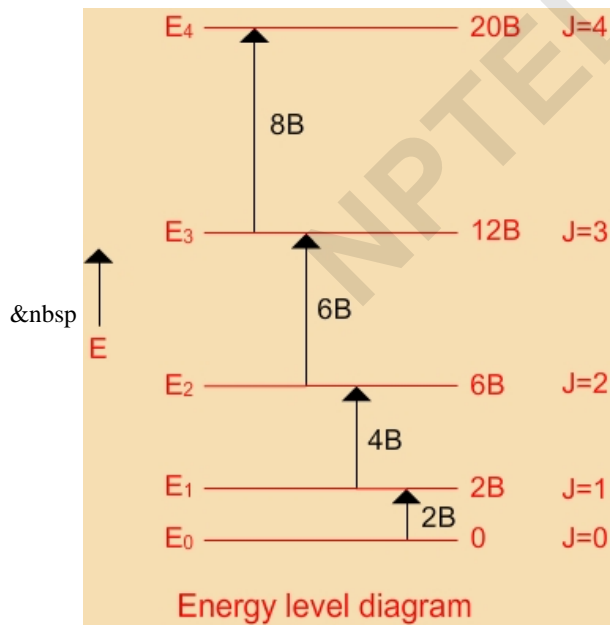$$E_1 = \frac{2h^2}{8\pi^2 I}$$

$$E_2 = \frac{6h^2}{8\pi^2 I}$$

$$E_3 = \frac{12h^2}{8\pi^2 I}$$

$$E = hc\bar{v}, \text{ or } \bar{v} = \frac{E}{hc}$$

$$\bar{v}_1 = \frac{E_1}{hc} = 2B \quad \text{where,} \quad B = \frac{h}{8\pi^2 Ic}$$

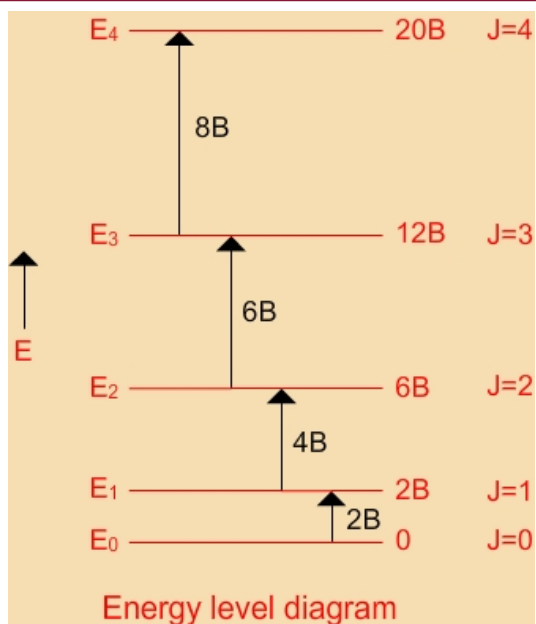$$\bar{v}_2 = 6B, \bar{v}_3 = 12B, \bar{v}_4 = 20B \text{ etc.,}$$

The energies are given in the figure below.

Energy level diagram

Topic 3

Spectra of diatomic molecules

■ Quantum mechanics predicts that transitions between states Y_J^K and $Y_{J'}^{K'}$ are possible only if J' = J±1, K' = K for a diatomic molecule. The figure below indicates allowed transitions for the first few levels.

Energy level diagram

- Rigid rotor energy levels are not equally spaced.

- Rigid rotor spectrum consists of equally spaced lines. (Please be very clear to distinguish these two statements.) The following animation will help you clarify this, I think.

click the play button to view the animation

- The only molecules that can have microwave transitions are those which have a permanent dipole moment.

■ Both of these results are from quantum mechanics and are experimentally verified.

■ Study one simple example below: Examine the dimensions first:

$$I = \mu r^2 \qquad\qquad mL^2$$

$$B \sim \frac{h}{8\pi^2 Ic} \qquad \frac{mL^2 T^{-1}}{mL^2 LT^{-1}} = \frac{1}{L} = L^{-1}$$

  ■ Rotational angular momentum is $\hbar \vec{J}$

  ■ the magnitude of which is also quantized. There are (2J+1) eigen functions (K=-J to +J) for any J, all having the same energy. Therefore rotational energy levels for a given J are (2J+1) fold degenerate

  ■   Example problem: for carbon monoxide you are given
     B=1.92118 cm^{-1}
     Mass of carbon atom = 19.92168x10^{-27}Kg
     Mass of oxygen atom = 26.56136x10^{-27}Kg

     Calculate the bond distance r.

$$I_{co} = \frac{h}{8\pi^2 cB} = 14.5695 \times 10^{-47} \, Kg.m^2$$

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

     $\Rightarrow$ r$_{co}$= 0.1131 nm or 1.131 Å

     Similar manipulations can be made for other diatomic molecules. The value of B is usually obtained from the pure microwave spectra of molecules in the gas phase. Rotations are restricted in the liquid phase and are arrested in the solid phase. Hence pure microwave spectra cannot be obtained by other means. If the spectrum is regular, then the spacing between two successive lines is 2B from which we can calculate the bond distances.

Topic 4
Moments of inertia for polyatomic molecules

■ Diatomic rotational energies areassociated with rotations about an axis perpendicular to the molecular axis since, moments of inertia about these axes are nonzero. The moment of inertia is the same for all axes in the plane perpendicular to the bond axis and passing through the centre of mass of the molecule..

■ Under the assumption of point masses, the moment of inertia about the bond axis is zero. In a three dimensional world, there are however, only two mutually perpendicular axex in the plane perpendicular to the bond axis.

■ Thus, if you denote the bond axis as z and the two perpendicular axes as x and y, then $I_x = I_y = I, \quad I_z = 0$

■ In a polyatomic system there are in principle 9 components of moments of inertia of which some components are equal to one another: The nine components are $I_{\alpha\beta}$, $\quad \alpha = x,y,z$ and $\beta = x,y,z$ .It is a symmetric, second rank tensor, $I_{\alpha\beta} = I_{\beta\alpha}$ Hence there are a total of six independent components.

    However, for any molecule an axis system may be found in which , I_{xx}, I_{yy}, I_{zz} are not zero, but all other components like I_{xy}, I_{xz} and I_{yz} are zero. Such an axis system is called the principal axis system. The moments of inertia in the pricipal axis system are called principal moments of inertia.

■ The rotational kinetic energy of a rigid polyatomic molecule can always be expressed using the principal moments of inertia , I_{xx} , I_{yy} and I_{zz} as,

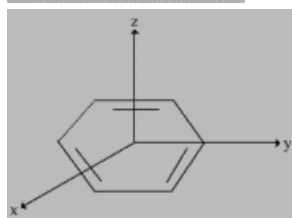$$E_{rot} = \frac{J_x^2}{2I_{xx}} + \frac{J_y^2}{2I_{yy}} + \frac{J_z^2}{2I_{zz}}$$

where, $\vec{J}$ is the angular momentum vector with components along the principal axes as above.

■ Examples of different moments of inertia for polyatomic molecules: The principal axis systems are indicated.
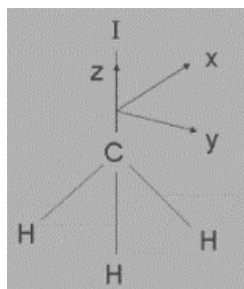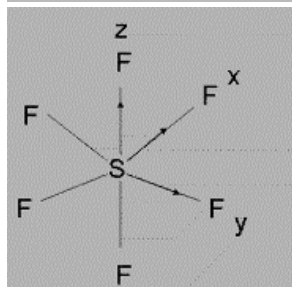

■ Two moments of inertia are equal and are not equal to the third. $I_{xx} = I_{yy} \neq I_{zz}$
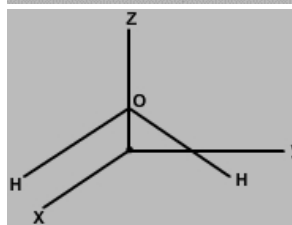
Such molecules are called symmetric top molecules

■ Two moments of inertia are equal, and are different from the third, $I_{xx} = I_{yy} \neq I_{zz}$

■ All the three moments of inertia are equal. $I_{xx} = I_{yy} = I_{zz}$. Such molecules are called spherical tops.

All the three moments of inertia are unequal. Such molecules are called asymmetric tops.

Topic 5
Polyatomic molecular rotational spectra

■ Rotational kinetic energy of polyatomic molecule is expressed as, $E_{rot} = \frac{J_x^2}{2I_{xx}} + \frac{J_y^2}{2I_{yy}} + \frac{J_z^2}{2I_{zz}}$

■ Spherical top: All the three moments of inertia are identical. Examples: CH_4 , SF_6

$$E_{rot} = \frac{1}{2I}(J_x^2 + J_y^2 + J_z^2)$$

$$= \frac{J^2}{2I}$$

- Quantum mechanically,

$$\hat{H}_{rot} = \frac{\hat{J}^2}{2I}$$

Energy levels have the same value as in a diatomic molecule

$$.E_{rot} = hcBJ(J+1) \qquad J = 0, 1, 2 .....$$

Energy levels are (2J+1)-fold degenerate.

- Symmetric top: Two moments of inertia are equal but not equal to the third.

$$I_{xx} = I_{yy} \neq I_{zz}$$

$$\hat{H}_{rot} = \frac{1}{2I_{xx}}(\hat{J}_x^2 + J_y^2) + \frac{1}{2I_{zz}}J_z^2 .$$

$$= \frac{1}{2I_{xx}}(\hat{J}^2 - \hat{J}_z^2) + \frac{1}{2I_{zz}}J_z^2$$

- Recall:

$$\hat{J}^2 Y_J^K(\theta\phi) = \hbar^2 J(J+1) Y_J^K(\theta\phi)$$

$$\hat{J}_z Y_J^K(\theta\phi) = \hbar K Y_J^K(\theta\phi)$$

$$K = 0, \pm 1, \pm 2 .... \pm J$$

are possible values for k

$$E_{rot} = \frac{\hbar^2}{2I_{xx}}\left[J(J+1) - K^2\right] + \frac{\hbar^2}{2I_{zz}}K^2$$

$$hc \, \overline{\nu}_{rot} = E_{rot}$$

$$\overline{\nu}_{rot} = \frac{E_{rot}}{hc} = \frac{h}{8\pi^2 I_{xx}c}\left[J(J+1) - K^2\right] + \frac{h}{8\pi^2 I_{zz}}K^2$$

Denote, $B = \dfrac{h}{8\pi^2 I_{zz}c} \qquad A = \dfrac{h}{8\pi^2 I_{xx}c}$

$$\Rightarrow \overline{\nu}_{rot} = BJ(J+1) + (A-B)k^2$$

Energy levels are not (2J+1) degenerate but doubly degenerate for (K and -K) and non-degenerate for K =0

Click to see the movie for drawing energy levels of a symmetric top

- The selection rule for a transition between levels labeled by J", K" (by convention these are assumed to be lower energy states) and J', K ' (higher energy states) is **D**J = J' – J" = ± 1, **D**K = K' –K" = 0

- Hence the microwave spectrum of a symmetric top is identical to that of a diatomic spectrum earlier. The energy level diagram is very different, but the spectrum that results from the two different energy level diagrams are identical.

Topic 7
**Intensities of microwave spectra and sample spectra**

- Intensity of a microwave transition line is proportional to the number of molecule undergoing that transition

- The number of molecules in the level J is proportional to $(2J+1)e^{-BJ(J+1)hc/k_B T}$ where, (2J+1) is the degeneracy factor and $e^{-BJ(J+1)hc/k_B T} = e^{-E_J/k_B T}$ is the Boltzmann factor. (k_B - Boltzmann constant and T - temperature of the sample)

- If N_0 is the total number of molecules, then the ratio is ,

$$P_J = \frac{N_J}{N_0} = \frac{(2J+1)e^{-BJ(J+1)hc/k_B T}}{\displaystyle\sum_{\substack{\text{all possible} \\ \text{energy} \\ \text{levels J}}} (2J+1)e^{-BJ(J+1)hc/k_B T}}$$
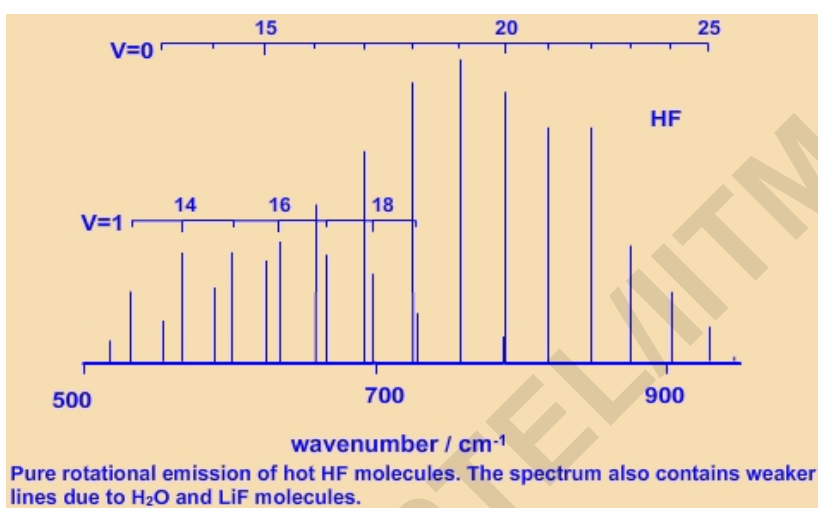
In particular the number ratio of upper level to lower level,

$$\frac{N_{J+1}}{N_J} = \frac{(2J+3)e^{-hcB(J+1)(J+2)/k_B T}}{(2J+1)e^{-hcBJ(J+1)/k_B T}} = \frac{(2J+3)e^{-2hcB(J+1)/k_B T}}{(2J+1)}$$

- A plot of P_J vs J
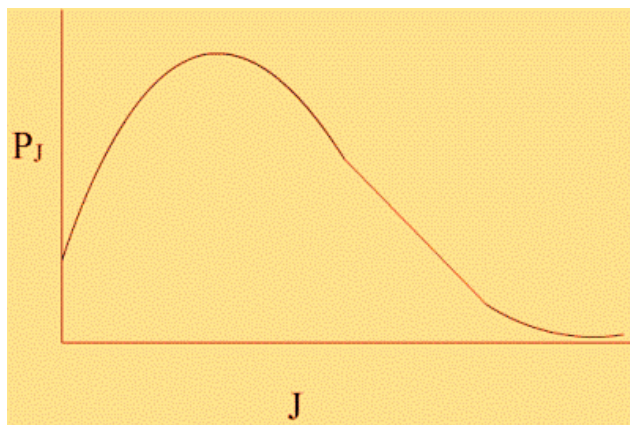
- A few samples of microwave spectra of simple molecules are given below. More beautiful microwave spectra may be obtained from two excellent monographs by Professor Kroto (Molecular rotation spectra, H. W. Kroto, Dover Publications, Inc. New York, 1992) and Professor Peter Bernath (Spectra of Atoms and Molecules, Petre F. Bernath, Oxford University, Oxford, 1995). Also you can find more details about microwave spectra of semirigid and nonrigid molcules in these two books.
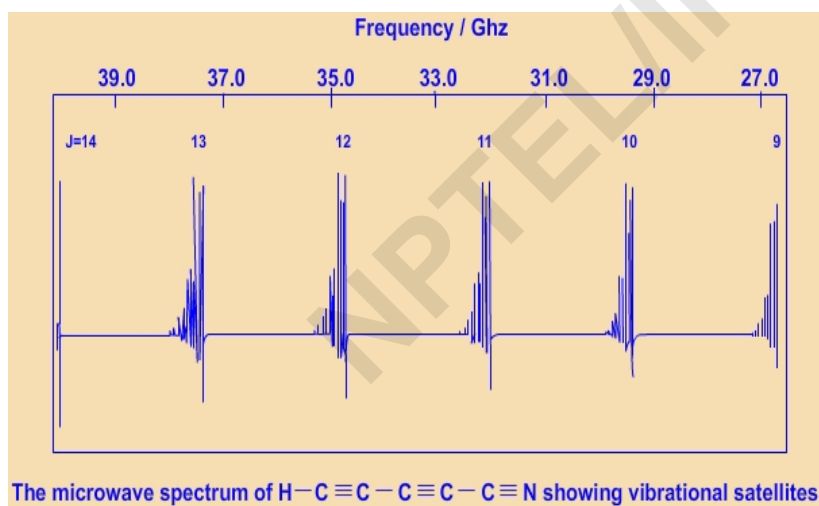

Pure rotational emission of hot HF molecules. The spectrum also contains weaker lines due to H_2O and LiF molecules.

Both the equal line spacing and the Boltzmann distribution of intensities are observed in the experimental spectrum of HF shown above.

Far-infrared absorption spectrum of CO showing J = 4 ← 3 at 15.38 cm⁻¹ to J = 10 ← 9 at 38.41 cm⁻¹.
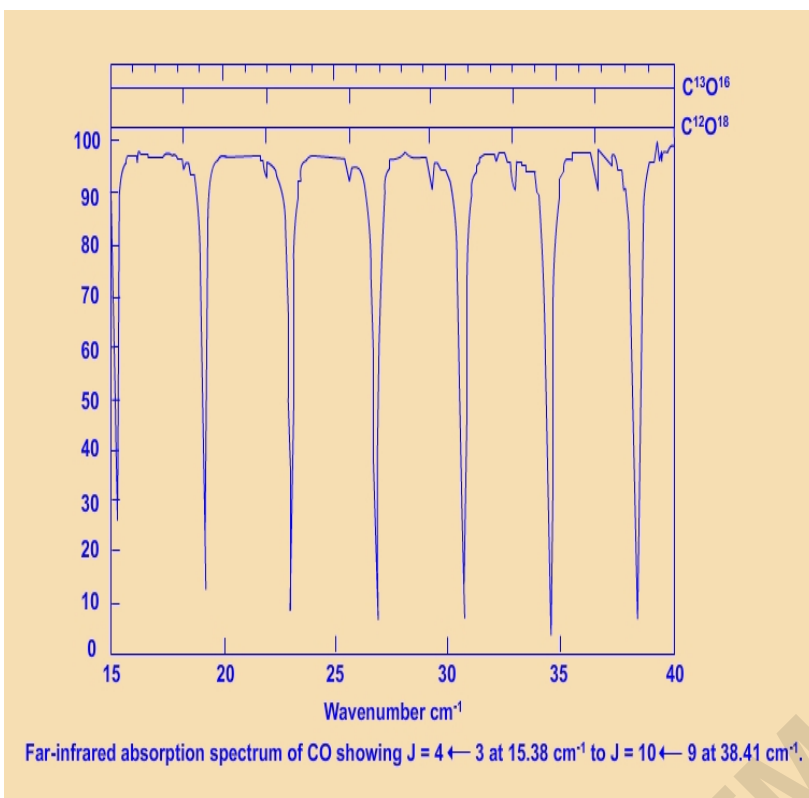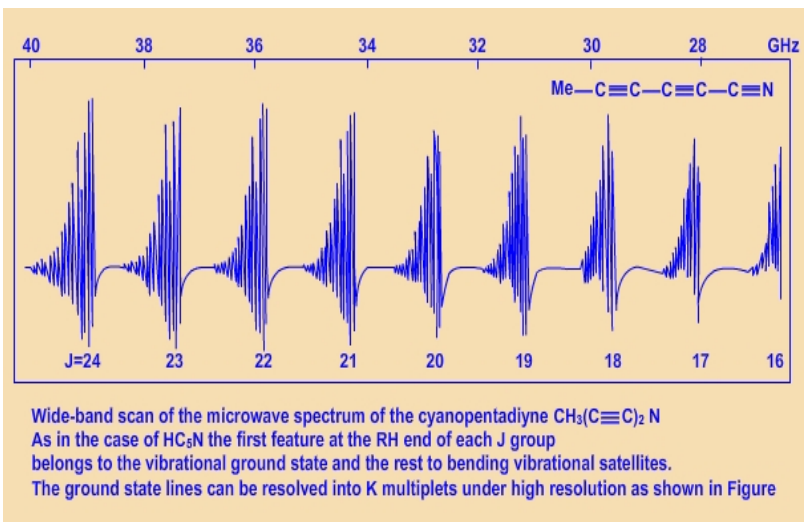
The slight shift in the frequencies due to the very low abundant carbon-13 substitiuted CO spectrum gives the small intensities shown in the picture.

The microwave spectrum of H—C≡C—C≡C—C≡N showing vibrational satellites

(adopted from Bernath's book).

Wide-band scan of the microwave spectrum of the cyanopentadiyne $CH_3(C\equiv C)_2N$
As in the case of HC_5N the first feature at the RH end of each J group
belongs to the vibrational ground state and the rest to bending vibrational satellites.
The ground state lines can be resolved into K multiplets under high resolution as shown in Figure

(adopted from Kroto's book).

Topic 8
Quizzes and problems

- **Problem 1:**
The frequency of microwave transition from J=0 to J=1 for $^{12}C^{16}O$ is given as 3.845 cm^{-1}. Calculate the C=O bond distance using a rigid rotor model
$$\left(h = 6.627 * 10^{-34}\, J.s,\ c = 2.99 \times 10^8\, m.s^{-1},\ N_A = 6.023 \times 10^{23} \right)$$

- **Problem 2:**
Classify each of the following molecules as a spherical, symmetric or asymmetric top molecule.

  a) CH_4

  b) CH_3Cl

  c) CH_2Cl_2

  d) $CHCl_3$

  e) CCl_4

  f) SF_6

  g) H_2O

  h) C_2H_6

  i) Benzene

  j) NH_3

  k) O_3

- **Problem 3:**
The rotational constants B and A for the ground vibrational state of a symmetric top molecule are B=0.2502 cm^{-1} and A=5.1739 cm^{-1}. Calculate the frequencies for the transitions J=1 to J=2 and J=4 to J=5.

- **Problem 4:**
Determine the ratio of population in J′=2 and J″=1 states for $^{12}C^{16}O$ at room temperature given that the rotational constant for the molecule is 1.923 cm^{-1}
$$\left(k_B = 1.381 \times 10^{-23}\, J.K^{-1},\ h = 6.627 \times 10^{-34}\, J.s,\ c = 2.99 \times 10^8\, m.s^{-1} \right)$$

- **Problem 5:**
Calculate the components of principal moments of inertia for $^{17}F_2O$ given O-F bond length is 1.405Å and the FOF bond angle is 103°.

Topic 8
Solutions

■ **Problem 1:**

1. $\triangle E$ for the transition from J = 0 to 1 is equal to 2B where $B = \dfrac{h}{8\pi^2 Ic}$ is in wave number units.

2. $I = \mu\, r^2$ where μ is the reduced mass and r is the internuclear (bond) distance.

3. $2B = \dfrac{2h}{8\pi^2 \mu r^2 c} = 3.845\, cm^{-1} = 384.5\, m^{-1}$

(use SI units for calculations)

$$\therefore r = \sqrt{\dfrac{h}{8\pi^2 \mu c B}}$$

r will be in meters, if h is in joule-sec, μ is in kg, c in ms^{-1} and B is in m^{-1}.

Ans: $1.133\,\overset{..}{\text{Å}}$

$$\mu = \dfrac{16*12*0.001}{(16+12)*6.023*10^{23}}\, kg$$
$$= 1.138*10^{-26}\, kg$$

$$\dfrac{h}{8\pi^2 \mu c B} = \dfrac{6.626*10^{-34}\, J.s}{8*\pi^2*1.138*10^{-26}\, kg*2.99*10^8\, m.s^{-1}*192.25\, m^{-1}}$$
$$= 1.283*10^{-20}\, m^2$$

$$\sqrt{\dfrac{h}{8\pi^2 \mu c B}} = 1.133*10^{-10}\, m$$

$$= 1.133\,\overset{..}{\text{Å}}$$

■ **Problem 2:**

CH_4 - Spherical top

CH_3Cl - symmetric top

CH_2Cl_2 - asymmetric top

$CHCl_3$ - symmetric top

CCl_4 - spherical top

SF_6 - spherical top

H_2O - asymmetric top

C_2H_6 - symmetric top

Benzene - symmetric top

NH_3 - symmetric top

O_3 - asymmetric top

Convince yourself through molecular diagrams and principal axes passing through the centre of gravity of each molecule that the above is correct.

■ **Problem 3:**

1. The rotational energies of a symmetric top are dependent on two quantum numbers J and K and are doubly degenerate, except for K = 0, for each J.

$$E(J,K) = BJ(J+1) + (A-B)K^2$$

2. Given $B = 0.2502$ cm^{-1} and $A = 5.1739$ cm^{-1}.

$\triangle E$ for transition from J to J+1.
must not change K. i.e. $\Delta J = +1$, $\Delta K = 0$.

$\therefore$ For any J to J+1, there is only one transition frequency, and it is the same for all K.

3. The transition frequencies are

$$\triangle E(J=1 \to J=2)$$
$$= \left[6B + (A-B)K^2\right] - \left[2B + (A-B)K^2\right]$$
$$= 4B$$
$$\triangle E(J=4 \to J=5)$$
$$= \left[30B + (A-B)K^2\right] - \left[20B + (A-B)K^2\right]$$
$$= 10B$$

4. The answers are: 1.0008 cm^{-1} and 2.502 cm^{-1} and do not depend on A, which is given in the problem.

■ **Problem 4:**

1. $\dfrac{N_{J'}}{N_{J''}} = \dfrac{(2J'+1)e^{-BJ'(J'+1)/k_BT}}{(2J''+1)e^{-BJ''(J''+1)/k_BT}}$

$J' = 2, J'' = 2$

2. $k_BT = 1.381 \times 10^{-23} \, J.K^{-1} \times 300 \, K$

$\qquad = 4.143 \times 10^{-21} \, J$

$BJ'(J'+1) = 6B \Rightarrow$

$E = hc \times 6B$

$6.627 \times 10^{-34} J.s \times 2.99 \times 10^8 \, ms^{-1} \times 6 \times 192.3 m^{-1}$

$= 0.229 \times 10^{-21} \, J$

$BJ''(J''+1) = 6.627 \times 10^{-34} \, J \times 2.99 \times 10^8 \, ms^{-1} \times 2 \times 192.3 m^{-1}$

$= 0.762 \times 10^{-22} \, J$

$e^{-BJ'(J'+1)/k_BT} = e^{-0.055} \approx 0.946$

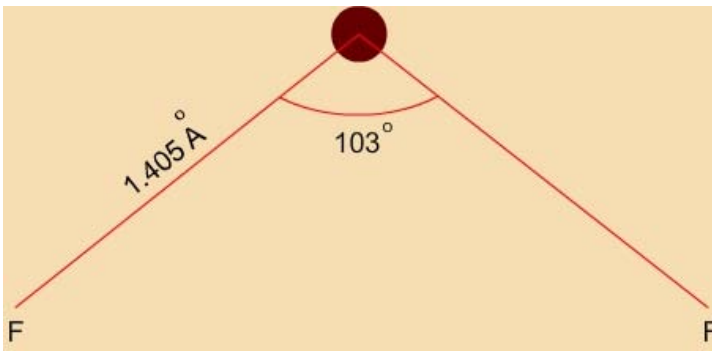$\left(k_B = 1.381 \times 10^{-23} \, J.K^{-1}, \ h = 6.627 \times 10^{-34} \, J.s, \ c = 2.99 \times 10^8 \, m.s^{-1}\right)$

Likewise for $e^{-BJ''(J''+1)} \approx 0.982$

$\therefore \dfrac{N_{J'}}{N_{J''}} \approx \dfrac{5}{3} \times \dfrac{0.946}{0.982} = 1.606$
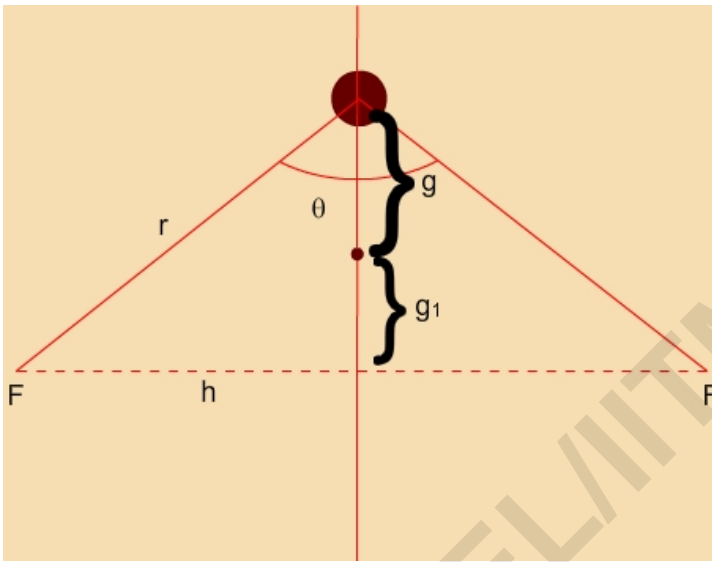
The higher energy state is more populated than the lower energy state. (Read the section on intensity if this is not clear).

■ **Problem 5:**

1. The structure of $^{17}F_2O$ is that of the bent molecule. The principal axes all pass through the centre of gravity for this molecule.

2. Determine the centre of mass of the molecule as follows $\sum_i m_i \vec{r}_i = 0$
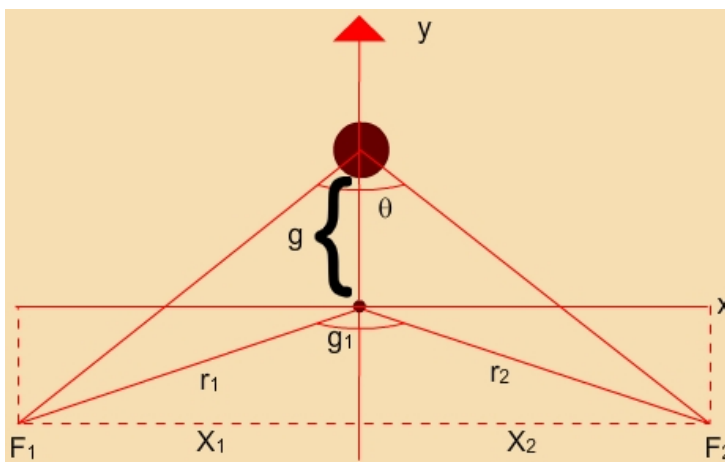

Determine g and h as follows:

$$\frac{h}{r} = \sin\frac{\theta}{2} \qquad \therefore h = r\sin\frac{\theta}{2}$$

$$= 1.405 * \sin(51.5) = 1.1\overset{\circ}{\text{Å}}$$

Let the vertical axis be the y axis.

About the y-axis: $\sum_i m_i \vec{r}_i = 0$ the y component of the vector equation is: $-m_F * g_1 - m_F * g_1 + m_O * g = 0$

$$\therefore \frac{g}{g_1} = 2.125$$

Also, $\dfrac{(g + g_1)}{r} = \cos\dfrac{\theta}{2}$

$\Rightarrow \quad \dfrac{3.125 g_1}{r} = \cos\dfrac{\theta}{2} \quad \text{or} \quad g_1 = \dfrac{1.405 \times \cos(51.5)}{3.125}$

$= 0.28 \overset{0}{A}; \quad g = 0.595 \overset{0}{A}$

Use SI units

$m_F = \dfrac{0.017}{6.023 \times 10^{23}} \text{kg} \qquad m_0 = \dfrac{0.016}{6.023 \times 10^{23}}$

$\qquad\qquad\qquad\qquad\qquad = 2.66 \times 10^{-26}\,\text{kg}$

$I_{yy} = \sum m_i y_i^2 = 2.82 \times 10^{-26}\,kg \times 1.1^2 \times 10^{-20}\,m^2 + 2.82 \times 10^{-26}\,kg \times 1.1^2 \times 10^{-20}\,m^2$

$= 6.82 * 10^{-46}\ \text{kgm}^2$

$I_{xx} = \left(2.82 * 10^{-26} * 0.28^2 * 10^{-20} + 2.82 * 10^{-26} * 0.28^2 * 10^{-20} + 2.66\ * 10^{-26} * 0.595^2 \times 10^{-20} \right) \text{kgm}^2$

$= 1.38 * 10^{-46}\ \text{kgm}^2$

$I_{zz} = \left[2.82 * 10^{-26} * \left(h^2 + g_1^2 \right) * 2 + 2.66 * 10^{-26} * g^2 \right] \text{kgm}^2$

$= \left(2.82 * 10^{-26} * \left(1.1^2 + 0.28^2 \right) * 10^{-20} * 2 + 2.66 * 10^{-26} * 0.595^2 * 10^{-20} \right) \text{kgm}^2$

$= 8.21 * 10^{-46}\,\text{kgm}^2$

All the three principal moments of inertia are different, indicating that F_2O is an asymmetric top.