

## ROTATIONAL SPECTROSCOPY

### SUMMARY:

Linear molecules:  $E(J) = BJ(J+1) - DJ^2(J+1)^2$

The centrifugal term is needed only for high precision.

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

K is the angular momentum quantum number for rotation about the symmetry axis.

Molecules include e.g. CH<sub>3</sub>Cl, benzene.

### Selection Rules:

For microwave and far IR spectra:

1. the molecule must have a permanent dipole moment.
2.  $\Delta J = \pm 1$  (+1 in absorption).

For rotational Raman spectra:

1. the molecule must have anisotropic polarisability (this is all molecules except spherical).
2.  $\Delta J = \pm 2$  ( $\Delta J = 0$  is the Rayleigh line).

But in Raman spectra of symmetric tops when  $\Delta K \neq 0$ ,  $\Delta J = \pm 1, \pm 2$ ,  $\Delta K = 0$ .

### Line positions in microwave and far IR –

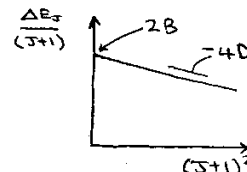
Combining the energy levels and IR or microwave selection rule for linear molecules in the line position  $\nu$  is:  $\nu$  (same units as B and D) =  $2B(J+1) - 4D(J+1)^3$

This comes from:  $\nu_J = F(J+1) - F(J) = B_0[(J+1)(J+2) - J(J+1)] - D_0[(J+1)^2(J+2)^2 - J^2(J+1)^2]$

Adjacent lines are separated by approximately  $2B$ .

D represents the centrifugal distortion, as bond length increases as rotational energy increases. Thus, the effective value of B decreases with J (proportional to  $1/\langle r^2 \rangle$ ).

To analyse a microwave or far IR rotation spectrum, use the line spacing to get a rough value of B. Then use B to find the J values for each line. Finally use the full formula for line positions to get precise B and D values by plotting a graph of  $\nu/(J+1)$  against  $(J+1)^2$ , where intercept =  $2B$ , slope =  $-4D$ .



Note though that for the equilibrium bond length to be calculated, extrapolation is required (i.e.  $B_e$  does not equal  $B_0, B_1$ , etc). The more data that can be obtained, the more accurate the extrapolation will be.

### Line positions in Rotational Raman Spectra –

Displacement from the Rayleigh line  $\Delta\nu$  is  $2B(2J+3)$ . Line spacing is  $4B$ . The line positions are never so precise as to need a centrifugal term.

### Level populations and line intensities –

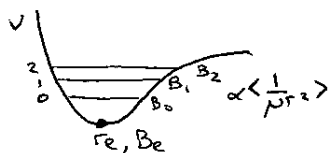
The number of molecules in energy level  $E_j$  is:

$$N_j = N_0 g_j \exp(-E_j/k_B T), \text{ where } g_j \text{ is the degeneracy.}$$

Line intensities are proportional to  $N_j$ . In the simplest case (unsymmetrical diatomic or linear molecule), the degeneracy is  $(2J+1)$ . By differentiating you can show that in this case maximum population is at  $J_{\max}$  given by:

$$J_{\max} = (k_B T / 2B)^{1/2} - 1/2$$

This comes from differentiating  $N_j$  by  $J$ . ( $k_B T$  and  $B$  must be in the same units! -  $\text{cm}^{-1}$  or Joules)



In spectra of symmetrical linear molecules nuclear spin must be included in the degeneracy – there is alternation of intensity if the nuclear spin of equivalent nuclei is non-zero ( $H_2, N_2, F_2$  etc). If the nuclear spin is zero, half the lines are missing and the line spacing is 4 or 8B (e.g.  $O_2, CO_2$ ). For nuclear spin I, intensity ratio approaches  $(I+1)/I$  at high J.

**Energy Levels**

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

$$B = \frac{h^2}{8\pi^2 \mu r^2}$$

Considering centrifugal distortion (bond stretches) –

$$E_J = BJ(J+1) - DJ^2(J+1)^2$$

***Diatomic –***

$m_1$  and  $m_2$  point masses.

Rigid rotor length  $r$ .

$$E_{rot} = \frac{1}{2} I \omega^2$$

$$I = m_1(z_1 - z)^2 + m_2(z_2 - z)^2, \text{ i.e.}$$

$$I = \mu r^2$$

$$E_{rot} = \frac{1}{2} (p^2/I), \quad p = I\omega$$

Hence,

$$H_{rot} = \left( \frac{h^2}{2I} \right) J^2$$

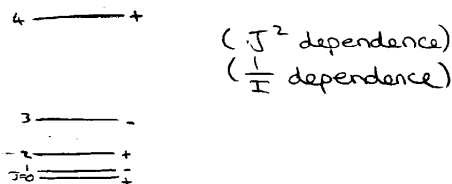
Find eigenfunctions and values.

$$\rightarrow J^2 \psi_{JM} = J(J+1) \psi_{JM}$$

Therefore,

$$E_{rot} = \left( \frac{h^2}{2I} \right) J(J+1), \quad J = 0, 1, 2, \dots$$

Implies:



$B = h^2/2I$ , rotational constant (Joules).

$B = h^2/2hl$  (Hz)

$B = h^2/2hcl$  ( $\text{cm}^{-1}$ )

$\psi_{JM}$  – spherical harmonics. Rotational coordinates  $\theta, \phi$ . Quantum numbers  $J$  and  $M \rightarrow J_z \psi = M_J \psi$ ,  $M_J = -J \dots +J$

Note that  $E = BJ(J+1)$  implies independent of  $M_J$  (in the absence of external electric / magnetic fields).

Each rotational level  $J$  is  $(2J+1)$  fold degenerate.

Note also parity labels on  $J$ :

$J$  odd  $\rightarrow$  negative

$J$  even  $\rightarrow$  positive

***Selection Rules –***

$$\Delta J = 0, \pm 1$$

$$\Delta \Lambda = 0$$

parity  $\leftrightarrow$

All imply: must possess electric dipole moment (heteronuclear)

$\Delta J = +1$  most relevant to closed shell diatomic, as  $^1\Sigma^+$  is a given (parity).

Allowed transitions for  $E = BJ(J+1)$  are thus:

$$h\nu = B [J(J+1)(J+2) - J(J+1)] = 2B(J+1)$$

Spectrum consists of equally spaced lines starting as  $\nu = 2B/h$  and separated by  $2B/h$ . Rotational transitions occur from microwave up to far-infrared.

Populations:

$$(N'' - N') = N''(1 - e^{-h\nu/kT})$$

$h\nu \ll kT$  (for rotational region), therefore population of upper M state involved in the transition is not negligible compared with lower. Absorption intensity is a measure of population difference.

Expand,

$$(N'' - N') = N''(1 - 1 + h\nu/kT - \dots)$$

- linear with  $\nu$ .

$$N'' = N_0 e^{-BJ(J+1)/kT}$$

in terms of  $J = 0$  level.

Centrifugal Distortion

Not exactly  $2B/h$  spacing, but get slightly closer as increase  $J$ .

This is because bond is not infinitely stiff. Faster rotation  $\rightarrow$  masses move apart,  $I$  increase and  $B$  decreases. Use Hooke's Law,  $F = -k(r - r_e) = -\mu r \omega^2$

Stretching bond contributes to rotational energy as Kinetic and Potential. Summing these for total centrifugal contribution:

$$E_{cd} = -\frac{1}{2} \frac{\mu P^4}{I_e^3 k} \Rightarrow -\frac{1}{2} \left[ \frac{h^4}{I_e^3 k} \right] J^2(J+1)^2$$

Hence,

$$E_{rot} = BJ(J+1) - DJ^2(J+1)^2, \text{ where } D = \frac{1}{2} \frac{h^4}{I_e^3 \left(\frac{k}{\mu}\right)}$$

Hence, a  $J+1 \leftarrow J$  transition has frequency  $\nu = 2B(J+1) - 4D(J+1)^3$

$$\nu/(J+1) = 2B - 4D(J+1)^2$$

- plot  $\nu/(J+1)$  against  $(J+1)^2$  gives intercept  $2B$  and slope  $-4D$ .

Determining Bond Lengths -

Can relate  $B$  to  $I$  and so obtain  $r$ .

Note though that there is a weak vibrational dependence as:

$$B_v = B_e - \alpha_e (v + 1/2) + \dots$$

where  $\alpha_e$  is a vibrational coefficient (harmonic and anharmonic contributions).

$B_v$  gets slightly smaller as  $v$  increases.

$$B_e \propto \mu^{-1}$$

$$\alpha_e \propto \mu^{-3/2}$$

Simplest way is to measure  $B_0$  and  $D_0$  for diatomic in its zero point level.  $B_0$  gives  $r_0$ , and  $r_0$  is averaged over the  $v = 0$  wavefunction.

More accurate - measure several vibrational levels and extrapolate back to  $B_e$  (equilibrium rotational constant), which gives  $r_e$ .

Stark Effect -

The effect of an external electric field on the spectrum.

$$W_{stark} = -\mu \cdot E \quad [\text{negative as energy lowest when dipole and E-field parallel}]$$

Difference to electric dipole transition is that apply a static, time-independent field.

When field is large, there is extensive mixing and  $J$ -values cannot be assigned.

$J$  and parity no longer good quantum numbers.

$M$  remains good. E-field causes the molecule to rotate "cock-eyed" about the field direction rather than having rotational angular momentum vector point in a fixed direction.

There are 1<sup>st</sup> order and 2<sup>nd</sup> order Stark effects. 1<sup>st</sup> order is very rare - requires vibration/electronic degeneracy in rotational energy levels. One diatomic example is NO ( $^2\Pi$  electronic ground state).

2<sup>nd</sup> order  $\rightarrow$  closed-shell electronic and rotational level has only  $(2J+1)$  degeneracy.

**Summary:**

$$F(J) = E_J/hc = BJ(J+1) - DJ^2(J+1)^2, J = 0, 1, 2, \dots$$

- B – rotational constant =  $h/8\pi^2 Ic$  (cm<sup>-1</sup>)
- I – moment of inertia =  $\mu R^2$  (kg m<sup>2</sup>)
- R – internuclear distance (m)
- $\mu$  - reduced mass (kg)
- D – centrifugal distortion constant =  $4B^3c^2/v^2$  (cm<sup>-1</sup>)
- $\nu$  – vibrational frequency =  $(1/2\pi)(k/\mu)^{1/2}$  (Hz)

Degeneracy 2J+1

$$N_J = N_0(2J+1) \exp(-BhcJ(J+1)/kT)$$

(N<sub>J</sub> = number in level J)

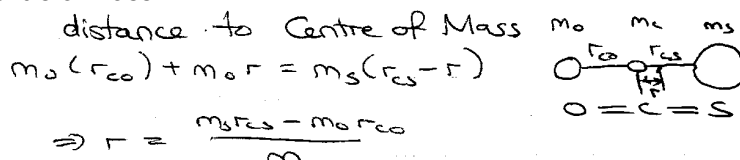
Maximum population:  $dN_J/dJ = 0 \rightarrow J_{max} = (kT/2hcB)^{1/2} - 1/2$

**Isotope Effects in Linear Polyatomics –**

Spectra for polyatomics same form as diatomics.  
B depends on more than one bond length.

$$I = \sum_i m_i r_i^2 \text{ for a linear polyatomic.}$$

r<sub>i</sub> – distance to centre of mass.



Parallel Axis Theorem:

$$I_{COM} = I_c - m r^2$$

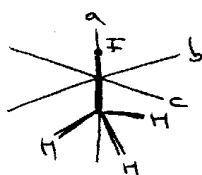
$$= m_o r_{co}^2 + m_s r_{cs}^2 - \left( \frac{m_s r_{cs} - m_o r_{co}}{m} \right)^2$$

Determine r<sub>co</sub>, r<sub>cs</sub> by isotopic substitution.

**Polyatomic Non-Linear Molecules –**

Define axes through Centre of Mass, such that one axis has largest possible I and one perpendicular has the smallest.

CH<sub>3</sub>l:



e.g.  $I_a = \sum_i m_i r_{i,a}^2$

c axis has largest I, while a axis has smallest.

$$E = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c}$$

Spherical Top –

e.g. SF<sub>6</sub>.

$$I_a = I_b = I_c, E = J^2/2I.$$

Quantum:  $\langle J^2 \rangle = J(J+1)\hbar^2$

$$E = hcBJ(J+1)$$

(B =  $h/8\pi^2 Ic$ )

Symmetric Top –

Any molecule with at least one n-fold axis of rotation.

e.g. NH<sub>3</sub>, benzene (n ≥ 3).

PROLATE: I<sub>b</sub> = I<sub>c</sub> > I<sub>a</sub> (CH<sub>3</sub>F)

OBLATE: I<sub>c</sub> > I<sub>a</sub> = I<sub>b</sub> (benzene)

**Prolate,**

$$E = \frac{J_a^2}{2I_a} + \frac{J_b^2 + J_c^2}{2I_b}$$

$$E = \frac{J_a^2}{2I_a} + \frac{J^2 - J_a^2}{2I_b}$$

J<sub>a</sub> is component of angular momentum along the molecule-fixed a axis.

By analogy,

$$\langle J_a \rangle = K\hbar.$$

K is a projection quantum number along a axis. K = 0, ±1, ... ±J.

$$\rightarrow E = \frac{\hbar^2}{2I_b} J(J+1) + \left( \frac{\hbar^2}{2I_a} - \frac{\hbar^2}{2I_b} \right) K^2$$

$$F(J,K) = BJ(J+1) + (A-B)K^2 \quad [ A > B ]$$

**Oblate,** same but:

$$F(J,K) = BJ(J+1) + (C-B)K^2 \quad [ C < B ]$$

If K = J – rotational motion is primarily about the top axis.

**Selection Rules:**

ΔJ = ±1, ΔK = 0 (dipole unchanged through rotation about symmetry axis).

$$F(J+1, K) - F(J, K) = \nu = 2B(J+1)$$

Taking into account centrifugal distortion,

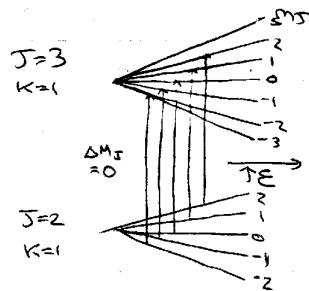
$$F(J,K) = BJ(J+1) + (A-B)K^2 - D_J J^2 (J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4$$

$$V = 2B(J+1) - 4D_J (J+1)^3 - 2D_{JK} (J+1)K^2$$

*Stark Effect* – lifts M degeneracy –

M<sub>J</sub> space-fixed projection quantum number.

$$F(J,K,M_J) = BJ(J+1) + (A-B)K^2 + \frac{\mu\epsilon KM_J}{J(J+1)hc}$$



E-field splits each energy level into 2J+1 components.

PARALLEL POLARISATION: ΔM<sub>J</sub> = 0  
 PERPENDICULAR POLARISATION: ΔM<sub>J</sub> = ±1

Asymmetric Tops –

I<sub>a</sub> ≠ I<sub>b</sub> ≠ I<sub>c</sub>.