

### 308(4): Splittings of a Pure Rotational Spectrum

The wavenumber of the pure rotational spectrum is:

$$\bar{\nu} = (E_{l+1} - E_l) / (hc) = 2B(l+1), \quad l=0, 1, 2 \quad - (1)$$

and the transition dipole moments are:

$$\langle \mu_z \rangle = \int \psi_{l'm'}^* \mu_z \psi_{lm} d\tau \quad - (2)$$

$l=0$  The transition wavenumber is  $\bar{\nu} = 2B$ , i.e.:

$$\bar{\nu} = 2B = (E_1 - E_0) / (hc) \quad - (3)$$

with selection rule:

$$\Delta l = 1 \quad - (4)$$

The  $m$  quantum number does not enter into the definition of the transition frequency, which is the same for all  $m$ . The number of  $m$  quantum numbers is  $-l, \dots, l$  so there are  $(2l+1)$  in total. The absorption line occurs at the transition wavenumber and is said to be  $(2l+1)$  fold degenerate. This is the usual description, but the number of possible transition dipole moments is given by:

$$\gamma_{00} \rightarrow \gamma_{11}, \quad \gamma_{00} \rightarrow \gamma_{10}, \quad \gamma_{00} \rightarrow \gamma_{1-1} \quad - (5)$$

The selection rule for  $\Delta m$  is:

$$\begin{aligned} \Delta m &= 1 && \text{(left circularly polarized probe)} \\ \Delta m &= 0 && \text{(linearly polarized probe)} \\ \Delta m &= -1 && \text{(right circularly polarized probe)} \end{aligned}$$

- (6)

Therefore:

$$d) \left. \begin{array}{l} Y_{00} \rightarrow Y_{11} \text{ (left CP)} \\ Y_{00} \rightarrow Y_{10} \text{ (linear)} \\ Y_{00} \rightarrow Y_{1-1} \text{ (right CP)} \end{array} \right\} - (7)$$

Therefore there is one transition dipole moment possible in each case.

$$\underline{l = 1}$$

The transition wave number is :

$$\bar{\nu} = 4B = (E_2 - E_1) / (hc) - (8)$$

The number of possible transition dipole moments is given by :

$$Y_{11}, Y_{10}, Y_{1-1} \rightarrow Y_{22}, Y_{21}, Y_{20}, Y_{2-1}, Y_{2-2} - (9)$$

Therefore :

$$\left. \begin{array}{l} Y_{11} \rightarrow Y_{22} \\ Y_{10} \rightarrow Y_{21} \\ Y_{1-1} \rightarrow Y_{20} \end{array} \right\} \text{ (left CP), } \Delta l = 1, \Delta n = 1 - (10)$$

Similarly

$$\left. \begin{array}{l} Y_{11} \rightarrow Y_{21} \\ Y_{10} \rightarrow Y_{20} \\ Y_{1-1} \rightarrow Y_{2-1} \end{array} \right\} \text{ (linear), } \Delta l = 1, \Delta n = 0 - (11)$$

and

$$\left. \begin{array}{l} Y_{11} \rightarrow Y_{20} \\ Y_{10} \rightarrow Y_{2-1} \\ Y_{1-1} \rightarrow Y_{2-2} \end{array} \right\} \text{ (right CP), } \Delta l = 1, \Delta n = -1 - (12)$$

Therefore there are three transition dipole moments possible in each case.

Continuing in this way gives the following table:

$l$	$\bar{\omega}$	$N_{l,k}$
0	2B	1
1	4B	3
2	6B	5
3	8B	7
4	10B	9
5	12B	11
6	14B	13
7	16B	15

$$N = 2l + 1 \quad - (13)$$

So where  $N$  is the number of red shifted frequencies energies from a sample path length  $Z$ . It is seen that the number of red shifted frequencies is the same as the energy degeneracy of each line.

The equation governing this effect is:

$$\omega = \omega_0 \exp\left(-\frac{AZ}{2}\right) \quad - (14)$$

where

$$A = \left(\frac{N_0}{V}\right) \frac{|\mu_{if}|^2}{6\epsilon_0 \hbar} \quad - (15)$$

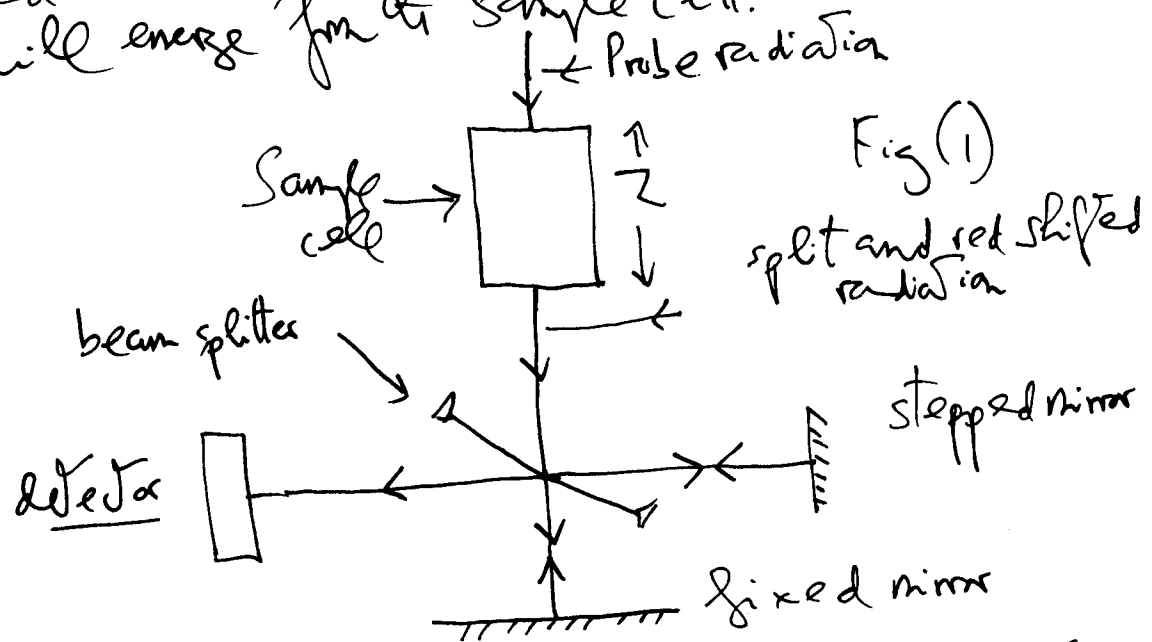
where  $\omega_0$  is the initial angular frequency,  $N_0$  the number of molecules in a sample volume  $V$ ,

4)  $\omega$  the frequency shifted angular frequency,  $\mu$  is the transition dipole moment,  $z$  the sample path length,  $\epsilon_0$  the vacuum permittivity,  $c$  the speed of light and  $h$  the reduced Planck constant.

The initial angular frequency  $\omega_0$  is

$$\omega_0 = 2\pi \bar{\nu} c \quad (16)$$

given by:  $\omega_0$  is in radians per second, where  $\bar{\nu}$  is the wavenumber in the table. For example, if the initial probe frequency is tuned to  $\bar{\nu} = 4B$ , three red shifted frequencies will emerge from the sample cell. If it is tuned to 16B, fifteen red shifted frequencies will emerge from the sample cell.



These split and red shifted frequencies can be observed by the interferometric set up of Fig. (1)