

Rotation-supplement

3D rotor selection rules

Assume that the molecular axis is in the z direction and that the dipole in the z direction is $\mu = \mu_z \cos \theta$

What are the selection rules for absorption of light?

We need to evaluate the integral

$$\mu_z \int Y_\ell^m(\theta, \phi)^* (\cos \theta) Y_{\ell'}^{m'} \sin \theta d\theta d\phi$$

One can separate the integral in integrals over Θ and ϕ

From the ϕ integral we have $m = m'$

From the Θ integral one has $\Delta \ell = 1$

Recall, that for $m = 0$, the relevant functions are $1, \cos \theta, 3\cos^2 \theta - 1$, etc.

Check the integral for the transition from $\ell = 0$ to $\ell = 1$

$$\int_0^\pi (\cos \theta)^2 \sin \theta d\theta = -\frac{\cos^3 \theta}{3} \Big|_0^\pi = 2/3$$

What about the ΔJ selection rule

Suppose we start in Y_0^0

Suppose we end in Y_0^0 Forbidden for radiation in x, y, z directions

Suppose we end in Y_1^0 Allowed for radiation in the z direction,
forbidden for radiation in x, y directions

Suppose we end in $Y_1^{\pm 1}$ Allowed for radiation in the x,y directions,
forbidden for radiation in z direction

Here we $z = r \cos \theta$
made use of $x = r \sin \theta \cos \phi$

Can show that no matter what level we start in the only allowed transitions are $\Delta J = \pm 1$

This conclusion can be reached by evaluating the integrals or from symmetry considerations

Rotational spectrum only observed if the molecule has a non-zero dipole moment

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

B_e often given in cm^{-1} (\tilde{B}_e)

Recall, $1 \text{ eV} = 8066 \text{ cm}^{-1}$

Rotational constants $\sim 1\text{-}10 \text{ cm}^{-1}$

Vibrational frequencies of $\sim 1000\text{-}3600 \text{ cm}^{-1}$

E		ΔE	
$J = 0$	0	$J = 0 \rightarrow 1$	$2 B_e$
$J = 1$	$2 B_e$	$J = 1 \rightarrow 2$	$4 B_e$
$J = 2$	$6 B_e$	$J = 2 \rightarrow 3$	$6 B_e$
$J = 3$	$12 B_e$	$J = 3 \rightarrow 4$	$8 B_e$

So the spectrum is a series of evenly spaced lines

Intensities depend on what levels are populated at the T of the experiment

At 300K kT in cm^{-1} units is $\sim 200 \text{ cm}^{-1}$ so several rotational levels are populated at room temperature.

Population
of level J

$$P_J = \frac{(2J+1)e^{-E_J/kT}}{\sum_{J=0} (2J+1)e^{-E_J/kT}}$$

exponential decreases with increasing T but degeneracy grows.

What value of J corresponds to the maximum in the intensity?

$$P_J = \frac{(2J+1)e^{-\beta J(J+1)B}}{\sum_J (2J+1)e^{-\beta J(J+1)B}}, \quad \beta = 1/kT$$

treat J as continuous

$$\frac{\partial P_J}{\partial J} = \frac{2 - (2J+1)\beta B(2J+1)}{D} = 0$$

$$2J+1 = \sqrt{\frac{2}{B\beta}}$$

$$J_{\max} \approx \frac{1}{2} \sqrt{\frac{2}{B\beta}} = \frac{1}{2} \sqrt{\frac{4IkT}{\hbar^2}}$$

Suppose $B_e = 2 \text{ cm}^{-1}$ and $kT \sim 200 \text{ cm}^{-1}$

$$J_{\text{max}} \sim \frac{1}{2} \sqrt{\frac{2(200)}{2}} \sim \frac{10}{2} \sqrt{2} \sim 7$$

Do we expect the levels to be evenly spaced in the rotational spectrum of a real molecule?