Chemistry 331

Lecture 5

Rotational Spectroscopy

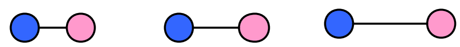
NC State University

The Dipole Moment Expansion

The permanent dipole moment of a molecule oscillates about an equilibrium value as the molecule vibrates. Thus, the dipole moment depends on the nuclear coordinate Q.

$$\mu(Q) = \mu_0 + \left(\frac{\partial \mu}{\partial Q}\right) Q + \ldots$$

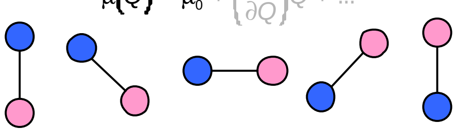
where μ is the dipole operator.



Rotational Transitions

Rotational transitions arise from the rotation of the permanent dipole moment that can interact with an electromagnetic field in the microwave region of the spectrum.

$$\mu(Q) = \mu_0 + \left(\frac{\partial \mu}{\partial Q}\right) Q + \ldots$$



The total wave function

The total wave function can be factored into an electronic, a vibrational and a rotational wave function.

$$Y = \psi_{el} \chi_v Y_{JM}$$

$$M_{rot} = \int \chi_{v'}^* Y_{J'M'} \left(\int \psi_{el}^* \mu \, \psi_{el} d\tau_{el} \right) \chi_v Y_{JM} d\tau_{nuc}$$

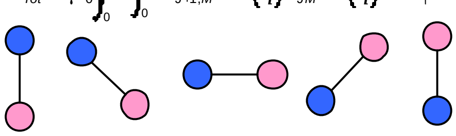
$$= \int \chi_{v'}^* \chi_v dQ \int \int \chi_{v'}^* Y_{J'M'} \mu_0 \chi_v Y_{JM} \sin\theta \, d\theta d\phi$$

$$= \int \int \chi_{v'}^* Y_{J'M'} \mu_0 \chi_v Y_{JM} \sin\theta \, d\theta d\phi$$

Interaction with radiation

An oscillating electromagnetic field enters as $E_0\cos(\omega t)$ such that the angular frequency $h\omega$ is equal to a vibrational energy level difference and the transition moment is

$$M_{rot} = \mu_0 \int_0^{2\pi} \int_0^{\pi} Y_{J+1,M}^* \cos(q) Y_{JM} \sin(q) d\theta d\phi$$



Interaction with radiation

The choice of $\cos(\theta)$ means that we consider z-polarized microwave light. In general we could consider x- or y-polarized as well.

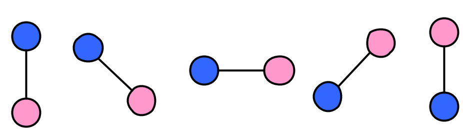
x $\sin(\theta)\cos(\phi)$

y $\sin(\theta)\sin(\phi)$

z $\cos(\theta)$

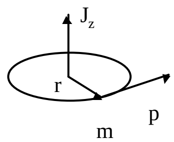
$$\mu_0 = \mu_X i + \mu_Y j + \mu_Z k$$

$$\mu_0 = \mu_0 \left\{ \sin\theta\cos\phi i + \sin\theta\sin\phi j + \cos\theta k \right\}$$



Rotation in two dimensions

The angular momentum is J_z = pr.

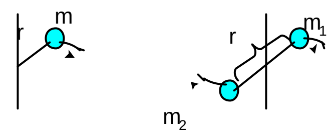


Using the deBroglie relation p = h/λ we also have a condition for quantization of angular motion J_z = hr/λ.

Classical Rotation

In a circular trajectory J_z = pr and E = $J_z^2/2I$.
I is the moment of inertia.

Mass in a circle I = mr^2. Diatomic I = μr^2



Reduced mass $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$

The 2-D rotational hamiltonian

- The wavelength must be a whole number fraction of the circumference for the ends to match after each circuit.
- The condition 2πr/m = λ combined with the deBroglie relation leads to a quantized expression, $J_z = m\hbar$.
- The hamiltonian is: $-\dfrac{\hbar^2}{2I}\dfrac{\partial^2 F}{\partial \phi^2} = EF$

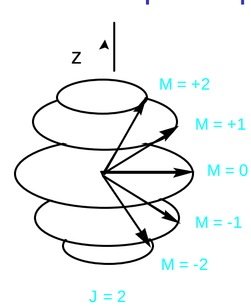
The 2-D rotational hamiltonian

- Solutions of the 2-D rotational hamiltonian are sine and cosine functions just like the particle in a box.
- Here the boundary condition is imposed by the circle and the fact that the wavefunction must not interfere with itself.
- The 2-D model is similar to condition in the Bohr model of the atom.

The 3-D rotational hamiltonian

- There are two quantum numbers J is the total angular momentum quantum number M is the z-component of the angular momentum
- The spherical harmonics called Y_{JM} are functions whose probability $|Y_{JM}|^2$ has the well known shape of the s, p and d orbitals etc.
- J = 0 is s , M = 0
- J = 1 is p , M = -1, 0 , 1
- J = 2 is d , M = -2 , -1, 0 , 1, 2

Space quantization in 3D

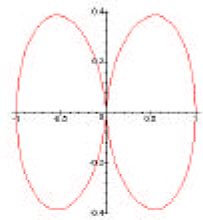


- Solutions of the rotational Schrödinger equation have energies $E = \hbar^2 J(J+1)/2I$
- Specification of the azimuthal quantum number m_z implies that the angular momentum about the z-axis is $J_z = \hbar m_z$.
- This implies a fixed orientation between the total angular momentum and the z component.
- The x and y components cannot be known due to the Uncertainty principle.

Spherical harmonic for $P_0(\cos\theta)$

- Plot in polar coordinates represents $|Y_0^0|^2$ where $Y_0^0=(1/4\pi)^{1/2}$.
- Solution corresponds to rotational quantum numbers J = 0,
- M or $J_z = 0$.
- Polynomial is valid for n≥1 quantum numbers of hydrogen wavefunctions

Spherical harmonic for $P_1(\cos\theta)$

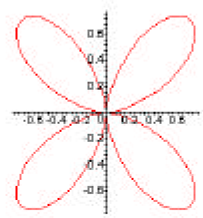


- Plot in polar coordinates represents $|Y_1^1|^2$ where $Y_1^1=(1/2)(3/2\pi)^{1/2}\sin\theta e^{i\phi}$.
- Solution corresponds to rotational quantum numbers J = 1, $J_z = \pm1$.
- Polynomial is valid for n≥2 quantum numbers of hydrogen wavefunctions

Spherical harmonic for $P_1(\cos\theta)$

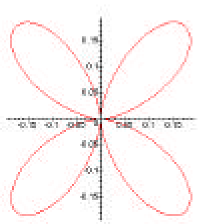
- Plot in polar coordinates represents $|Y_1^0|^2$ where $Y_1^0=(1/2)(3/\pi)^{1/2}\cos\theta$ with normalization.
- Solution corresponds to rotational quantum numbers J = 1, $J_z = 0$.
- Polynomial is valid for n≥2 quantum numbers of hydrogen wavefunctions.

Spherical harmonic for $P_2(\cos\theta)$



- Plot in polar coordinates of $|Y_2^2|^2$ where $Y_2^2=1/4(15/2\pi)^{1/2}\cos^2\theta e^{2i\phi}$
- Solution corresponds to rotational quantum numbers J = 2, $J_z = \pm 2$
- Polynomial is valid for n≥3 quantum numbers of hydrogen wavefunctions

Spherical harmonic for $P_2(\cos\theta)$



- Plot in polar coordinates of $|Y_2^1|^2$ where $Y_2^1=(15/8\pi)^{1/2}\sin\theta\cos\theta e^{i\phi}$
- Solution corresponds to rotational quantum numbers J = 2, $J_z = \pm 1$
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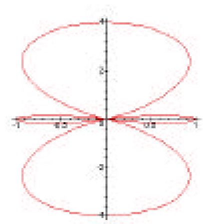
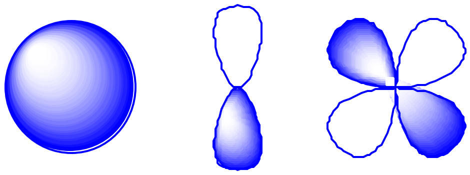
Spherical harmonic for $P_2(\cos\theta)$



- Plot in polar coordinates of $|Y_2^0|^2$ where $Y_2^0=1/4(5/\pi)^{1/2}(3\cos^2\theta-1)$
- Solution corresponds to rotational quantum numbers J = 1, $J_z = 0$.
- Polynomial is valid for n≥3 quantum numbers of hydrogen wavefunctions

Rotational Wavefunctions

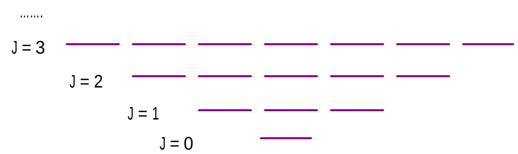


J = 0 J = 1 J = 2

These are the spherical harmonics Y_{JM}, which are solutions of the angular Schrodinger equation.

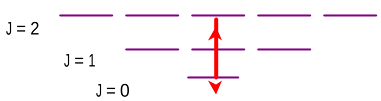
The degeneracy of the solutions

- The solutions form a set of 2J + 1 functions at each energy (the energies are $E = \hbar^2 J(J+1)/2I$).
- A set of levels that are equal in energy is called a degenerate set.



Rotational Transitions

- Electromagnetic radiation can interact with a molecule to change the rotational state.
- Typical rotational transitions occur in the microwave region of the electromagnetic spectrum.
- There is a selection rule that states that the quantum number can change only by + or - 1 for an allowed rotational transition ($\Delta J = \pm 1$).



Orthogonality of wavefunctions

- The rotational wavefunctions can be represented as the product of sines and cosines.
- Ignoring normalization we have:
- s 1
- p $\cos\theta$ $\sin\theta\cos\phi$ $\sin\theta\sin\phi$
- d $1/2(3\cos^2\theta - 1)$, $\cos^2\theta\cos2\phi$, $\cos^2\theta\sin2\phi$, $\cos\theta\sin\theta\cos\phi$, $\cos\theta\sin\theta\sin\phi$
- The differential angular element is $\sin\theta d\theta d\phi/4\pi$ over
- the limits $\theta = 0$ to π and $\phi = 0$ to 2π.

The angular wavefunctions are orthogonal.

Orthogonality of wavefunctions

- For the theta integrals we can use the substitution
- $x = \cos\theta$ and $dx = \sin\theta d\theta$
- For example, for s and p-type rotational wave functions we have

$$< s | p > \propto \int_0^\pi \cos\theta \sin\theta \, d\theta = \int_1^{-1} x \, dx = \frac{x^2}{2}\Big|_1^{-1} = \frac{1}{2} - \frac{1}{2} = 0$$

Question

Which of the following statements is true:

A. The number of z-projection of the quantum numbers is 2J+1.

B. The spacing between rotational energy levels increases as 2(J+1).

C. Rotational energy levels have a degeneracy of 2J+1.

D. All of the above.

Question

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B. The spacing between rotational energy levels increases as 2(J+1).

C. Rotational energy levels have a degeneracy of 2J+1.

D. All of the above.

$$DE \sim (J+2)(J+1) - J(J+1) = 2(J+1)$$

Question

The fact that rotational wave functions are orthogonal means that

A. They have no overlap

B. They are normalized

C. They are linear functions

D. None of the above

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The moment of inertia

The kinetic energy of a rotating body is $1/2I\omega^2$.
The moment of inertia is given by:

$$I = \sum_{i=1}^{\infty} m_i r_i^2$$

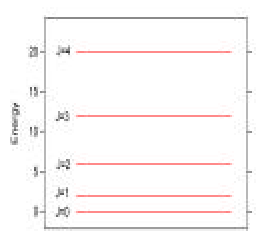
The rigid rotor approximation assumes that molecules do not distort under rotation. The types or rotor are (with moments I_a, I_b, I_c)

- Spherical: Three equal moments (CH_4, SF_6)
  (Note: No dipole moment)
- Symmetric: Two equal moments (NH_3, CH_3CN)
- Linear: One moment (CO_2, HCl, HCN)
  (Note: Dipole moment depends on asymmetry)
- Asymmetric: Three unequal moments (H_2O)

Pure rotational spectra

- A pure rotational spectrum is obtained by microwave absorption.
- The range in wavenumbers is from 0-200 cm^{-1}.
- Rotational selection rules dictate that the change in quantum number must be $\Delta J = \pm 1$ and $\Delta M_J = 0$.
- A molecule must possess a ground state dipole moment in order to have a pure rotational spectrum.

Energy level spacing



Energy levels

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

Energy Differences of $\Delta J = \pm 1$

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

The rotational constant

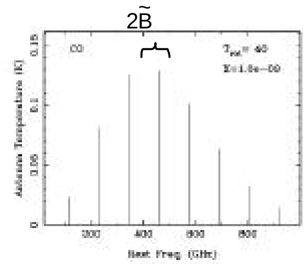
The spacing of rotational levels in spectra is given by $\Delta E = E_{J+1} - E_J$ according to the selection rule.

$$\Delta E = \frac{\hbar^2}{2I}\left[(J+1)(J+2) - J(J+1)\right] = \frac{\hbar^2}{2I}2(J+1)$$

The line spacing is thus proportional to the rotational constant

$$\frac{\hbar^2}{2I} = hc\tilde{B}\ ,\ \tilde{B} = \frac{\hbar}{4\pi cI} = \frac{h}{8\pi^2 cI} = \frac{h}{8\pi^2 c\mu R^2}$$

A pure rotational spectrum



A pure rotational spectrum is observed in the microwave range of electromagnetic spectrum.

Question

Which molecule found in the atmosphere has a pure rotational spectrum?

A. Diatomic oxygen
B. Diatomic nitrogen
C. Water
D. Carbon Dioxide

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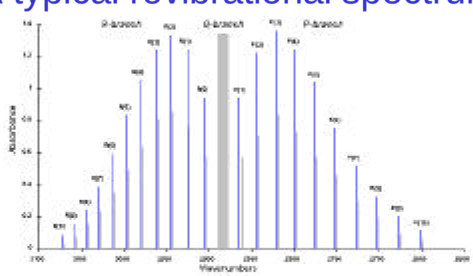
A typical rovibrational spectrum



Note that the rotational spectrum is centered a vibrational frequency