

Chemistry 3P51 – Fall 2013

Quantum Chemistry

Lecture No. 19

Oct 25th, 2013

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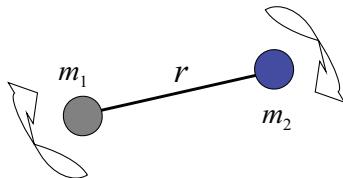
Objectives

- To introduce the rigid rotor as a model for rotational motion of diatomic molecules.
- To present the solutions of the Schrödinger equation for the rigid rotor.
- To show the energy level diagram for the rigid rotor.
- To present the selection rules for the rigid rotor.

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The rigid rotor and rotational spectroscopy

Consider a system in which two point masses (m_1 and m_2) are held together by a weightless non-extendable rod of length r



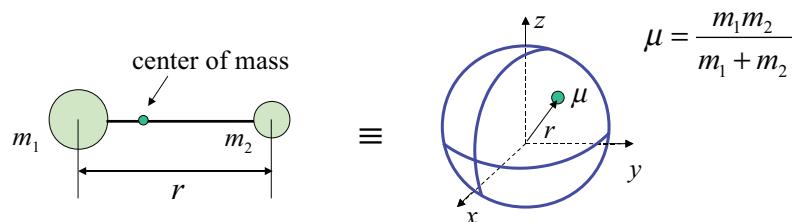
This system is called a **rigid rotor**; it serves as a realistic model for studying rotational motion of diatomic molecules.

The rigid rotor is an idealization because the internuclear distance in real molecules varies in time (reason: nuclear vibration). However, the smaller the vibrations, the better approximation this model provides.

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The Hamiltonian for the rigid rotor

It can be shown that the kinetic energy of a rigid system of two masses separated by distance r is identical to the kinetic energy of a single particle of reduced mass μ moving on the surface of a sphere of radius r :



If we also assume that the potential energy of the particle on a sphere is constant (say, $V=0$) then the Hamiltonian can be written as

$$\hat{H} = \hat{T} = \frac{\hat{L}^2}{2I} = \frac{\hat{L}^2}{2\mu r^2}$$

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The Schrödinger equation for the rigid rotor

Because the radial coordinate r of the particle is constant, the wave function will be a function of θ and φ only.

The Schrödinger equation for a rigid rotor (or a particle on a sphere) is:

$$\hat{H}\psi(\theta, \varphi) = E\psi(\theta, \varphi)$$

where

$$\hat{H} = \hat{T} = \frac{\hat{L}^2}{2\mu r^2}$$

Recall that the eigenvalues of \hat{L}^2 are

$$\hbar^2 l(l+1) \quad l = 0, 1, 2, \dots \\ (2l+1)\text{-fold degenerate}$$

Therefore, the eigenvalues of \hat{H} must be

$$E_{lm} = \frac{\hbar^2}{2\mu r^2} l(l+1) \quad l = 0, 1, 2, \dots \\ m = 0, \pm 1, \pm 2, \dots, \pm l$$

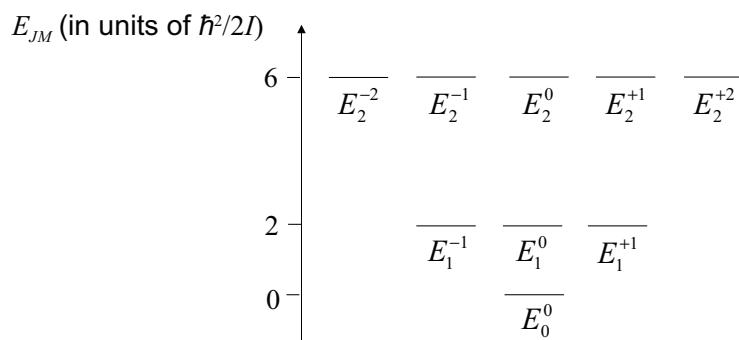
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Energy levels of the rigid rotor

In rotational spectroscopy, the quantum number l is denoted by J , while m is denoted by M .

The allowed energy levels of a diatomic molecule can then be written as

$$E_{JM} = \frac{\hbar^2}{2I} J(J+1), \quad J = 0, 1, 2, \dots \\ M = 0, \pm 1, \pm 2, \dots, \pm J$$



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Selection rules for the rigid rotor

The intensity of a transition between states (J, M) and (J', M') is proportional to the transition dipole moment:

$$I_{JM \rightarrow J'M'} \propto |\mu_{JM \rightarrow J'M'}|^2, \quad \text{where}$$

$$\mu_{JM \rightarrow J'M'} = \begin{pmatrix} \mu_x \\ \mu_y \\ \mu_z \end{pmatrix} \equiv \int [Y_{J'}^{M'}(\theta, \varphi)]^* \begin{pmatrix} \sin \theta \cos \varphi \\ \sin \theta \sin \varphi \\ \cos \theta \end{pmatrix} Y_J^M(\theta, \varphi) \sin \theta d\theta d\varphi$$

One can show by that the transition dipole moment between states Y_J^M and $Y_{J'}^{M'}$ vanishes unless

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

In addition, the rotator must have a permanent dipole moment.

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An example of selection rules for the rigid rotor

The dipole moment is a vector. This means that a transition between two rigid rotor states can occur due to its either x or y or z component.

For instance, a transition with $J' = 1, M' = 0, J = 0, M = 0$ is allowed:

$$\begin{aligned} \mu_x^{0,0 \rightarrow 1,0} &\sim \int_{\theta=0}^{\pi} \int_{\varphi=0}^{2\pi} (Y_1^0(\theta, \varphi))^* [\sin \theta \cos \varphi] (Y_0^0(\theta, \varphi))^* \sin \theta d\theta d\varphi \\ &\sim \frac{\sqrt{3}}{4\pi} \int_{\theta=0}^{\pi} \int_{\varphi=0}^{2\pi} \sin^2 \theta \cos \theta \sin \varphi d\theta d\varphi = 0 \\ \mu_y^{0,0 \rightarrow 1,0} &\sim \int_{\theta=0}^{\pi} \int_{\varphi=0}^{2\pi} (Y_1^0(\theta, \varphi))^* [\sin \theta \sin \varphi] (Y_0^0(\theta, \varphi))^* \sin \theta d\theta d\varphi \\ &\sim \frac{\sqrt{3}}{4\pi} \int_{\theta=0}^{\pi} \int_{\varphi=0}^{2\pi} \sin^2 \theta \cos \theta \sin \varphi d\theta d\varphi = 0 \\ \mu_z^{0,0 \rightarrow 1,0} &\sim \int_{\theta=0}^{\pi} \int_{\varphi=0}^{2\pi} (Y_1^0(\theta, \varphi))^* [\cos \theta] (Y_0^0(\theta, \varphi))^* \sin \theta d\theta d\varphi \\ &\sim \frac{\sqrt{3}}{4\pi} \int_{\theta=0}^{\pi} \int_{\varphi=0}^{2\pi} \cos^2 \theta \sin \theta d\theta d\varphi = \frac{1}{\sqrt{3}} \neq 0 \end{aligned}$$

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In microwave (rotational) spectroscopy, it is customary to express rotational energy levels in terms of frequencies:

$$\nu_J = \frac{E_J}{h} = \frac{1}{h} \frac{\hbar^2}{2\mu r^2} J(J+1) = \frac{\hbar}{8\pi^2 \mu r^2} J(J+1) = BJ(J+1),$$

The quantity B is called the **rotational constant**:

$$B \equiv \frac{h}{8\pi^2 \mu r^2} \quad [\text{in Hz}]$$

In terms of wavenumbers,

$$\tilde{B} \equiv \frac{B}{c} = \frac{h}{8\pi^2 c \mu r^2} \quad [\text{in wavenumbers}]$$

The frequency of a rotational transition $J \rightarrow J+1$ in Hz is

$$\nu_{J \rightarrow J+1} = \nu_{J+1} - \nu_J = B(J+1)(J+2) - BJ(J+1) = 2B(J+1)$$

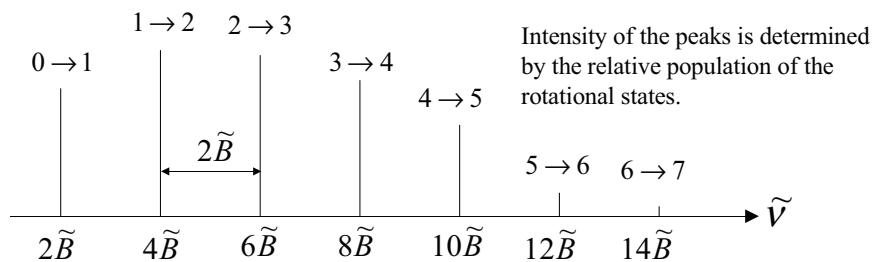
In terms of wavenumbers, $\tilde{\nu}_{J \rightarrow J+1} = 2\tilde{B}(J+1)$

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Transition, $J \rightarrow J+1$	Wavenumber $\tilde{\nu}$
$0 \rightarrow 1$	$2\tilde{B}$
$1 \rightarrow 2$	$4\tilde{B}$
$2 \rightarrow 3$	$6\tilde{B}$
$3 \rightarrow 4$	$8\tilde{B}$

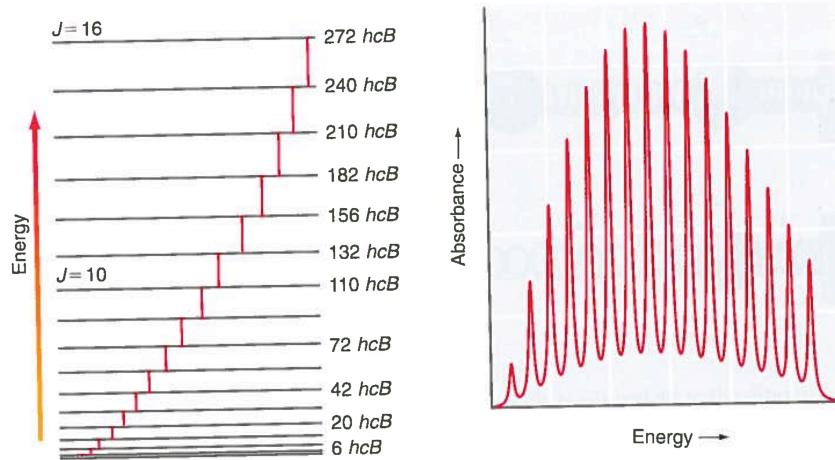
and so on

Thus, the spectrum of rigid rotator consists of equally spaced lines



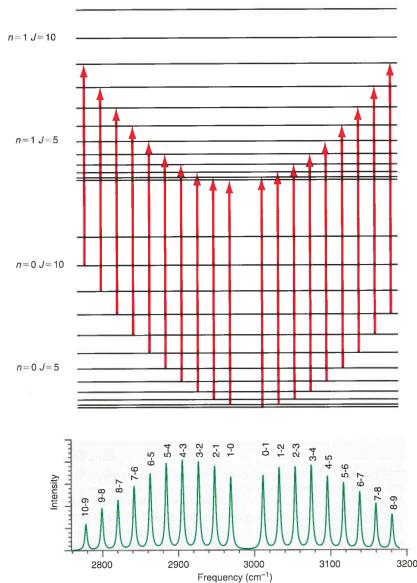
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Energy levels and spectrum for a rigid rotor



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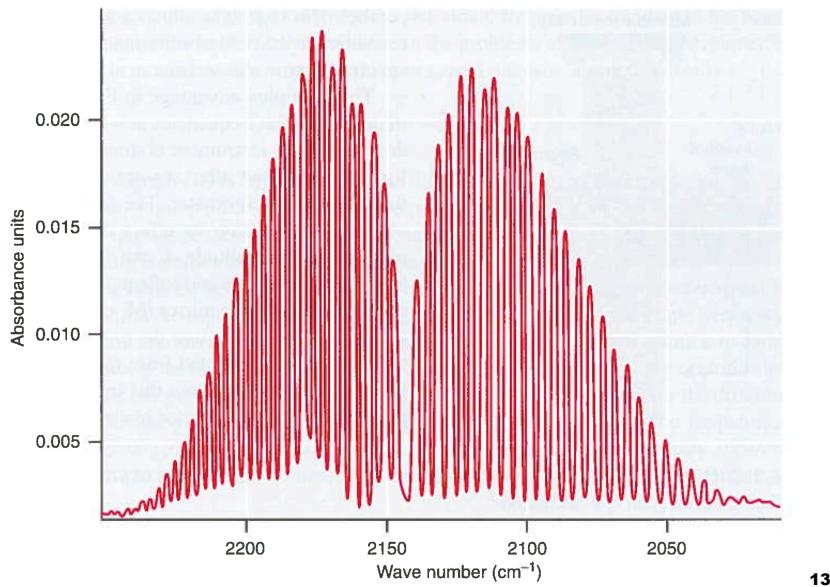
Simulated infrared absorption spectrum and energy diagram for HCl



- The two indices above the peak refer to the initial (first) and final (second) J values.
- The region of the spectrum with $J_{final} - J_{initial} = +1$ (higher frequency) is called the **R branch**.
- The region of the spectrum with $J_{final} - J_{initial} = -1$ (lower frequency) is called the **P branch**.

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A high resolution spectrum for CO with the R and P branches resolved



Examples of rotational spectroscopy problems

Problem. Pure rotational spectrum of H³⁵Cl consists of a series of lines separated by 20.9 cm⁻¹. Estimate the H–Cl bond length.

$$m(\text{H}) = 1.0078, m(\text{Cl}) = 34.96885$$

Answer: 1.28 Å

Unstable species can be detected spectroscopically by observing their rotational spectra. Also, rotational spectroscopy allows one to distinguish isotopomers of the same compound.

Problem. Compute the rotational spacings $2\tilde{B}$ for the ¹⁶OH radical ($r=0.970$ Å) and for the ¹⁶OD radical.

$$m(\text{H}) = 1.0078, m(\text{D}) = 2.0141, m(\text{O}) = 15.9949$$

$$\text{Answer: } 2\tilde{B}_{\text{OH}} = 37.8 \text{ cm}^{-1}; \quad 2\tilde{B}_{\text{OD}} = 20.0 \text{ cm}^{-1}$$

The rotational constant \tilde{B} is different for each isotopomer of a molecule.

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