

## Rotational Spectroscopy

Molecules have quantized energy levels for rotation. Individual molecules in a vacuum, (or gas phase molecules at low pressures) can be considered as *free rotors*, uninfluenced by interactions from neighboring molecules. Of course, isolated atoms rotate as well, but there is no change in angular momentum observable, so we concern ourselves only with molecules here.

Molecules in condensed phases reorient, even at low temperatures, but their rotations are strongly hindered by interactions with their neighbors.

Our discussions will focus on understanding gas-phase rotations of molecules.

Differences between rotational energy levels in small to medium size molecules occur in the *microwave* region of the electromagnetic spectrum. Microwave wavelengths are typically a few millimeters, hence the historical term *millimeter wave spectroscopy*.

To study molecular rotations, we begin with angular momentum, and use the rigid rotor solutions as a model for diatomic molecules.

The *rigid rotor* is an excellent model for diatomic molecules, because their vibrational displacements are typically only about 1% of the equilibrium bond length. The Hamiltonian for the *rigid rotor* model is given by

$$\hat{H} = \frac{\mathbf{J}^2}{2I}$$

where  $\mathbf{J}$  is the angular momentum operator and  $I$  is the moment of inertia.

It is helpful to recall the classical definition of angular momentum,  $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ , which can be most easily defined by the determinant relation

$$L = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = (yp_z - zp_y)\hat{i} + (zp_x - xp_z)\hat{j} + (xp_y - yp_x)\hat{k}$$

Converting the classical observables of position and momentum to their quantum equivalent Hermitian operators, we substitute

$$p_x = -i\hbar \frac{\partial}{\partial x}; p_y = -i\hbar \frac{\partial}{\partial y}; \text{ and } p_z = -i\hbar \frac{\partial}{\partial z}$$

to obtain the quantum angular momentum operator

$$J = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ -i\hbar \frac{\partial}{\partial x} & -i\hbar \frac{\partial}{\partial y} & -i\hbar \frac{\partial}{\partial z} \end{vmatrix} = -i\hbar \left[ \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \hat{i} + \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \hat{j} + \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \hat{k} \right]$$

The **rigid rotor** model has solutions for the energy eigenvalues of the Schrödinger equation given by

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

where  $I = \mu r^2$  is the moment of inertia, with  $\mu$  the reduced mass, and  $r$  the equilibrium bond length; and  $J$  is the rotational quantum number. The difference between adjacent energy levels is the transition energy since  $\Delta J = \pm 1$  (*see selection rules, below*). This energy difference is given by

$$\Delta E = E_{J+1} - E_J = \frac{\hbar^2}{I} (J+1) = \frac{h^2}{4\pi^2 I} (J+1)$$

The key property for understanding molecular rotations is the **moment of inertia**. The **moment of inertia** is defined by

$$I = \sum_i m_i R_i^2$$

where  $m_i$  is the atomic mass, and  $R_i$  is the distance of the atom from the molecular *center of mass*. It is clear that the moment of inertia depends strongly on the shape of the molecule.

### **Generalizing the moment of inertia from Rigid Rotator to Polyatomic Molecules**

It is helpful to consider the molecular moment of inertia projected on each of the three Cartesian (xyz) axes. Written in this way, we see that the moment of inertia is actually a two-dimensional vector, called a *tensor*, or the **inertia tensor**

$$\mathbf{I} = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{pmatrix}$$

where the individual elements are defined as

$$\begin{aligned}
 I_{xx} &= \sum_{j=1}^N m_j [(y_j - y_{cm})^2 + (z_j - z_{cm})^2] \\
 I_{yy} &= \sum_{j=1}^N m_j [(x_j - x_{cm})^2 + (z_j - z_{cm})^2] \\
 I_{zz} &= \sum_{j=1}^N m_j [(y_j - y_{cm})^2 + (x_j - x_{cm})^2], \text{ and} \\
 I_{xy} &= - \sum_{j=1}^N m_j [(x_j - x_{cm})(y_j - y_{cm})], \dots \text{ with} \\
 & \quad I_{xy} = I_{yx}, \dots
 \end{aligned}$$

with the subscript  $cm$  representing the center of mass positions for the molecule.

The mathematics of classical rigid bodies tells us that the **inertia tensor** for molecules can always be diagonalized so that the off-diagonal elements (*e.g.*,  $I_{xy}$ ) are zero. The convention is that the resulting **diagonalized inertia tensor** has the diagonal elements relabeled as  $I_{xx} = I_A$ ,  $I_{yy} = I_B$ , and  $I_{zz} = I_C$ , or

$$\mathbf{I} = \begin{pmatrix} I_A & & \\ & I_B & \\ & & I_C \end{pmatrix}$$

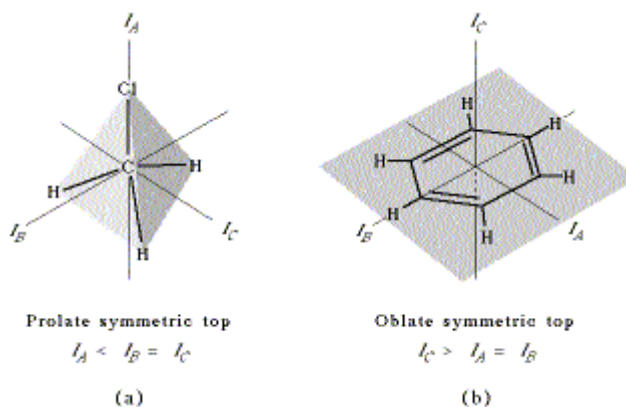
Thus, to represent molecular rotations for even the most asymmetric molecules, we need consider only the three axes  $A$ ,  $B$ , and  $C$  that are mutually orthogonal along the  $x$ ,  $y$ , and  $z$  directions. Another convention is that for molecules, we always define the  $A$  axis to have the smallest moment of inertia, and hence the highest rotation frequency, as  $I_A \leq I_B \leq I_C$ .

**Spherical rotors**, (or **spherical tops**) are molecules for which  $I_A = I_B = I_C$ . Examples of **spherical top** molecules are methane ( $\text{CH}_4$ ), sulfur hexafluoride ( $\text{SF}_6$ ), and carbon tetrachloride ( $\text{CCl}_4$ ).

Linear molecules have  $I_A = I_B$ , and  $I_C = 0$ . Examples of linear rotors are all of the diatomic molecules, plus carbon dioxide ( $\text{CO}_2$ ).

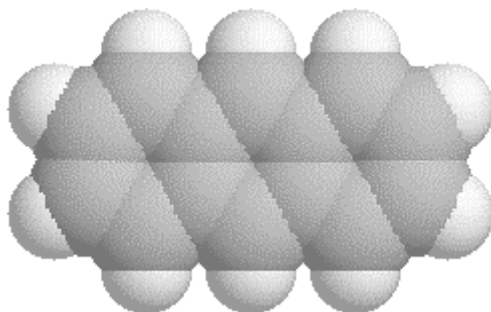
When the molecule has some high degree of symmetry, often two of the moments of inertia are the same, where  $I_A = I_B \neq I_C$  or  $I_A \neq I_B = I_C$ . These cases are referred to a **symmetric rotors**, *a.k.a.* in the spectroscopic literature as **symmetric tops**.

A **symmetric top** with  $I_A < I_B = I_C$  is called a *prolate symmetric top*; when  $I_C > I_A = I_B$ , then the molecule is classified an *oblate symmetric top*. Examples of *symmetric top* molecules are chloroform ( $\text{CHCl}_3$ , prolate), and benzene ( $\text{C}_6\text{H}_6$ , oblate).



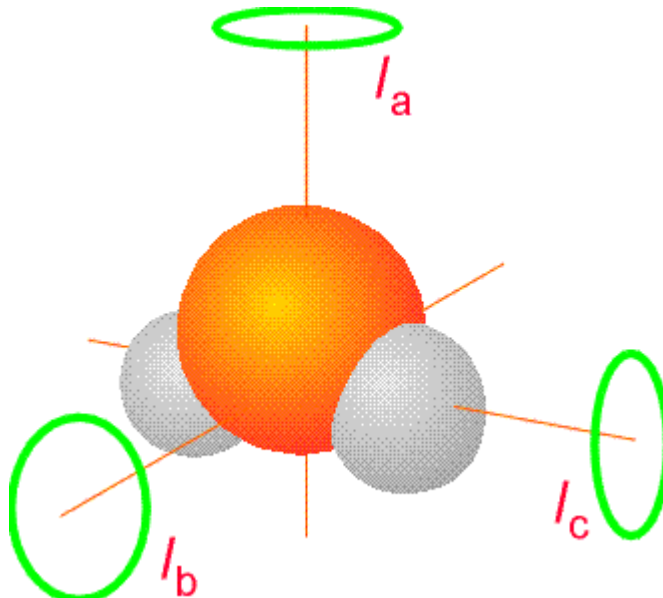
The general case where  $I_A \neq I_B \neq I_C$  is called the **asymmetric rotor**. Most all larger molecules are asymmetric rotors, even when they have a high degree of molecular symmetry.

Anthracene is an example of a highly symmetric molecule that despite its high symmetry is an **asymmetric rotor**, shown below.



Most biologically important molecules are *asymmetric rotors*, including all of the amino acids and nucleic acid bases.

As shown below, water is also an *asymmetric rotor*.



The generalization of the *rigid rotor* to the three-dimensional case for an *asymmetric rotor* requires that we consider the fact that the angular momentum squared operator  $\mathbf{J}$  is now represented as

$$J^2 = J_A^2 + J_B^2 + J_C^2$$

and consequently, the Hamiltonian operator for the *asymmetric rotor* is given by

$$\hat{H} = \frac{J_A^2}{2I_A} + \frac{J_B^2}{2I_B} + \frac{J_C^2}{2I_C}$$

There are in general three rotational energies, one for rotation about each of the three orthogonal axes  $A$ ,  $B$ , and  $C$ . Because of orthogonality, the rotational axes have separable rigid rotor solutions, leading to energy eigenvalues

$$E_A(J) = h^2/(8\pi^2 I_A) \times J(J+1), E_B(J) = h^2/(8\pi^2 I_B) \times J(J+1), \text{ and } E_C(J) = h^2/(8\pi^2 I_C) \times J(J+1).$$

It is *very important* to keep track of units in spectroscopy. In rotational spectroscopy, the energies may be reported in GHz ( $10^9 \text{ s}^{-1}$ ), or  $\text{cm}^{-1}$  ( $1 \text{ cm}^{-1} = 30 \text{ GHz}$ ). It is quite common to find the rotational energies written in terms of the three *rotational constants*  $A$ ,  $B$ , and  $C$ , given by

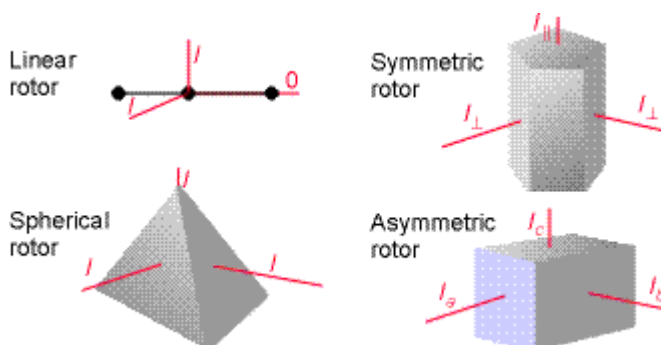
$$\tilde{A} = \frac{h}{8\pi^2 c I_A}; \tilde{B} = \frac{h}{8\pi^2 c I_B}; \text{ and } \tilde{C} = \frac{h}{8\pi^2 c I_C};$$

where the units are wavenumbers ( $\text{cm}^{-1}$ ).

For spherical rotors, the rotational constants are equal, so that  $A = B = C$ , and the three energy levels are degenerate.

Symmetric tops have two of the three inertial axes equal, so either  $A = B \neq C$  (oblate top) or  $A \neq B = C$  (prolate top).

The diagram below from Atkins summarizes the cases for *spherical*, *symmetric*, *asymmetric*, and *linear* rotors.

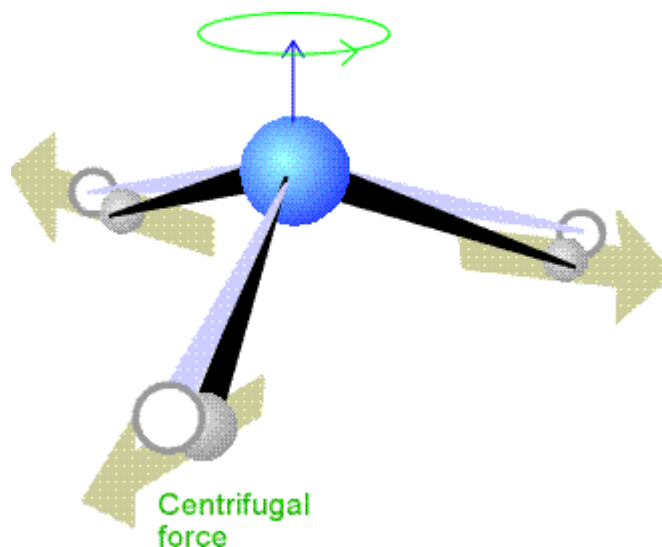


### [Beyond the Rigid Rotor Model ...](#)

Up to this point, we have been modeling molecular rotations assuming that the molecules are rigid, and that they are in the ground vibrational and electronic quantum states. Frequently, this is not the case.

As a gas phase molecule rotates at a very high level of rotational energy, the rigid rotor approximation is no longer valid. If we think of the chemical bond in a diatomic molecule as a spring holding the nuclei together, then for fast enough (or high enough energy) rotations, the nuclei will distort. This is called *centrifugal distortion*.

The picture below from Atkins illustrates how the ammonia molecule is distorted by rotations of high quantum numbers around its three-fold symmetry axis:



For very large rotational quantum numbers, the tetrahedral ammonia molecule is distorted towards a more planar geometry.

When *centrifugal distortion* is included in the Hamiltonian for a rotating diatomic molecule, a small correction term cubic in the quantum number is subtracted from the energy eigenvalue, to yield

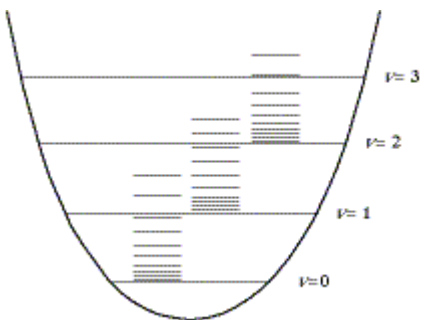
$$E_J = hc [BJ(J+1) - D_J J^2 (J+1)^2]$$

### Selection Rules for Rotational Transitions

In general, for absorption of light to stimulate a transition between energy levels, the transition dipole matrix element must be non-zero, *i.e.*,  $\langle f | \mu | i \rangle \neq 0$ . Since we already have worked out the solutions for the rigid rotor as being the same as the angular part of the hydrogen-like atom wavefunctions, we know that the permitted transitions must have  $\Delta J = \pm 1$ .  $\Delta J = +1$  corresponds to absorption of a photon, while  $\Delta J = -1$  corresponds to emission of microwave radiation from the molecule.

*Historical footnote:* The prediction and observation of stimulated emission from a population inversion in a gas sample undergoing rotational transitions permitted creation of the first *MASER* (microwave amplification by stimulated emission of radiation), which was the direct precursor of the *LASER*.

A gas phase molecule can be simultaneously vibrating and rotating. The rotational and vibrational energy levels combine to give a potential energy diagram like the one below, indicating all of the vibrational and rotational quantum numbers for a diatomic molecule for which the rigid rotor and harmonic oscillator approximations are valid. Usually, the simple rigid rotor and harmonic oscillator descriptions are no longer precisely valid, and we must introduce energy correction terms into the Hamiltonians to describe the interactions between the vibrations and rotations.



After a more detailed study of molecular vibrations, we will return to rotation-vibration coupling.