

### 3.8: Rotation of Polyatomic Molecules

For a non-linear polyatomic molecule, again with the centrifugal couplings to the vibrations evaluated at the equilibrium geometry, the following terms form the rotational part of the nuclear-motion kinetic energy:

$$T_{rot} = \sum_{i=a,b,c} \left( \frac{J_i^2}{2I_i} \right).$$

Here,  $I_i$  is the eigenvalue of the moment of inertia tensor:

$$I_{x,x} = \sum_a m_a [(R_a - R_{CofM})^2 - (x_a - x_{CofM})^2]$$

$$I_{x,y} = \sum_a m_a [(x_a - x_{CofM})(y_a - y_{CofM})]$$

expressed originally in terms of the cartesian coordinates of the nuclei (a) and of the center of mass in an arbitrary molecule-fixed coordinate system (and similarly for  $I_{z,z}$ ,  $I_{y,y}$ ,  $I_{x,z}$  and  $I_{y,z}$ ). The operator  $J_i$  corresponds to the component of the total rotational angular momentum  $\mathbf{J}$  along the direction belonging to the  $i^{\text{th}}$  eigenvector of the moment of inertia tensor.

Molecules for which all three principal moments of inertia (the  $I_i$ 's) are equal are called 'spherical tops'. For these species, the rotational Hamiltonian can be expressed in terms of the square of the total rotational angular momentum  $J^2$  :

$$T_{rot} = \frac{J^2}{2I},$$

as a consequence of which the rotational energies once again become

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

However, the  $Y_{J,M}$  are not the corresponding eigenfunctions because the operator  $J^2$  now contains contributions from rotations about three (no longer two) axes (i.e., the three principal axes). The proper rotational eigenfunctions are the  $D_{M,K}^J(\alpha, \beta, \gamma)$  functions known as 'rotation matrices' (see Sections 3.5 and 3.6 of Zare's book on angular momentum) these functions depend on three angles (the three Euler angles needed to describe the orientation of the molecule in space) and three quantum numbers- J, M, and K. The quantum number M labels the projection of the total angular momentum (as  $M\hbar$ ) along the laboratory-fixed z-axis;  $K\hbar$  is the projection along one of the internal principal axes ( in a spherical top molecule, all three axes are equivalent, so it does not matter which axis is chosen).

The energy levels of spherical top molecules are  $(2J+1)^2$  -fold degenerate. Both the M and K quantum numbers run from -J, in steps of unity, to J; because the energy is independent of M and of K, the degeneracy is  $(2J+1)^2$  .

Molecules for which two of the three principal moments of inertia are equal are called symmetric top molecules. Prolate symmetric tops have  $I_a < I_b = I_c$  ; oblate symmetric tops have  $I_a = I_b < I_c$  ( it is convention to order the moments of inertia as  $I_a \leq I_b \leq I_c$ ). The rotational Hamiltonian can now be written in terms of  $J^2$  and the component of  $\mathbf{J}$  along the unique moment of inertia's axis as:

$$T_{rot} = J_a^2 \left( \frac{1}{2I_a} - \frac{1}{2I_b} \right) + \frac{J^2}{2I_b}$$

for prolate tops, and

$$T_{rot} = J_c^2 \left( \frac{1}{2I_c} - \frac{1}{2I_b} \right) + \frac{J^2}{2I_b}$$

for oblate tops. Again, the  $D_{M,K}^J(\alpha, \beta, \gamma)$  are the eigenfunctions, where the quantum number K describes the component of the rotational angular momentum  $\mathbf{J}$  along the unique molecule-fixed axis (i.e., the axis of the unique moment of inertia). The energy levels are now given in terms of J and K as follows:

$$E_{J,K} \hbar^2 \frac{J(J+1)}{2I_b} + \hbar^2 K^2 \left( \frac{1}{2I_a} - \frac{1}{2I_b} \right)$$

for prolate tops, and

$$E_{J,K} = \hbar^2 \frac{J(J+1)}{2I_b} + \hbar^2 K^2 \left( \frac{1}{2I_c} - \frac{1}{2I_b} \right)$$

for oblate tops.

Because the rotational energies now depend on K (as well as on J), the degeneracies are lower than for spherical tops. In particular, because the energies do not depend on M and depend on the square of K, the degeneracies are (2J+1) for states with K=0 and 2(2J+1) for states with |K| > 0; the extra factor of 2 arises for |K| > 0 states because pairs of states with K = |K| and K = -|K| are degenerate.

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