The rotational energy levels of a diatomic molecule in 3D space is given by the quantum mechanical solution to the rotating rigid rotor:

\[ E = J(J + 1) \frac{\hbar^2}{2I} \tag{5.8.30} \]

where

- \( J \) is a rotational quantum number ranging from \( J=0 \) to \( J=\infty \).
- \( I \) is the moment of inertia and is the rotational equivalent to mass in translation.

The moment of inertia of a molecule is very sensitive to the geometry to the the molecule (see below).

Values of rotational inertia for common shapes of objects.

In general, any three-dimension species (e.g., a molecule) will have three degrees of rotational energy since it can rotation in the \( \{x\} \), \( \{y\} \) and \( \{z\} \) axis (i.e., the angular momentum vector can lie in each axis). This energy spacing for rotation in each degree is given by Equation \( \text{(5.8.30)} \) and is shown geometrically below.
Energy spacing for a rigid rotor (in 3D) as a function of $J$ quantum number.

The lowest energy transition is the $J=0 \rightarrow J=1$ transition and corresponds to

$$E_{J=0 \rightarrow J=1} = \frac{\hbar^2}{2I}$$  \[EQ2\]

Most of the mass of the molecule is in the nuclei, so when calculating the moment of inertia $I$ we can ignore the electrons and just use the nuclei. But the size of the nuclei is around $10^{-5}$ times smaller than the bond length. This means the moment of inertia around an axis along the bond is going to be about $10^{10}$ smaller than the moment of inertia around an axis normal to the bond. Therefore the energy level spacings will be around $10^{10}$ times bigger along the bond than normal to it.

It is common to argue that linear molecules do not rotate perpendicular to the axis of symmetry and often justified in terms of symmetry of the molecule (see Group Theory). Therefore, out of three possible rotational degrees of freedom for a three dimensional object, only two are applicable to linear molecules and the third rotation is often ignored. This is capitalized in terms of justifying how many vibrational degrees of freedom a molecule has:

- **Non-linear** molecules have 3N degrees of freedom in total: 3 are translational and 3 are rotational (all are allowed for non-linear molecules) so the remaining 3N-6 are vibrational.
- In contrast, **linear** molecules have 3 translational and only 2 rotational, and to keep a total of 3N degrees of freedom, they have 3N-5 vibrational degrees.

These equations are justified since rotation around the axis along the bond of the molecule requires huge energies (Equation \ref{EQ2}) since $I$ due to the much smaller moment of inertia. To excited these rotations, gamma ray photons are required and is the topic of high energy physics. Moreover, the temperature at which energy levels above the ground level are important is extremely high (e.g., it can be higher than the temperature of dissociation of the molecule). Therefore, at temperatures of practical interest, rotation around the axis of the linear molecule is not important for thermodynamic properties.

Contributors

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