Chapter 11: Molecular rotation and vibration

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Hydrogen bonding (finishing the survey)

Molecules can be bound by a hydrogen atom that is part of one of the molecules—the proton make a positive charge center on the molecule that can be attracted to areas of enhanced negative charge on another polar molecule.

H bonding is relatively weak, but extremely important in biological systems.

Rotation and Vibration

In gas phase, a molecule has

electronic energy due to interaction between electrons and nucleus;

translation energy due to motion of CM through space;

rotational energy due to motion about the CM; and

vibrational energy due to vibration of constituent atoms.

$$E = E_{el} + E_{trans} + E_{rot} + E_{vib}$$

Rotation Consider a diatomic ("dumbell") atom. Has 2 rotational degrees of freedom. See figure 11.6.

The angular momentum is

$$L = (m_1 r_1^2 + m_2 r_2^2)\omega = I\omega$$

and the rotation energy is

$$E_{rot} = \frac{1}{2}I\omega^2$$

eliminate ω

$$E_{rot} = \frac{L^2}{2I}.$$

Note the similarity to translational KE of a particle:

$$T = \frac{p^2}{2m}.$$

Reduced mass

I depends on the rotation axis. If we use the CM as the axis, then

$$I_{CM} = \left(\frac{m_1 m_2}{m_1 + m_2} \right) R_0^2 \equiv \mu R_0^2$$

where R_0 is the interatomic separation and μ is the *reduced mass:*

$$\mu = \frac{m_1 m_2}{m_1 + m_2}.$$

This same form of reduced mass is also used in gravitational orbit problems in celestial mechanics.

Quantize angular momentum

L is dynamical, so L^2 becomes quantized. The rule is

$$L^2 = \ell(\ell+1)\hbar^2 \quad \ell = 0, 1, 2 \ldots$$

This restricts rotational energy:

$$E_{rot} = \frac{\hbar^2}{2I_{CM}}\ell(\ell+1)$$

Putting in the integers you get

$$\frac{\hbar^2}{2I_{CM}} \cdot \{0, 2, 6, 12, 20, 30, 42, \ldots\}$$

as rotational energy levels.

The spacing between levels is

$$\Delta E_{rot} = \frac{\hbar^2}{I_{CM}} \ell$$

where ℓ is the *highest* of the adjacent levels.

The same procedure can be applied to more complex molecules by using an appropriate I_{CM}.

It is interesting to note that microwave ovens act by exciting the rotational levels of water molecules, and then this energy is transferred to vibrational modes as thermal energy.

Molecular Vibration

Consider a molecule as a pair of masses joined by an effective spring of constant K. If ξ_1, ξ_2 are displacements from equilibrium of the masses, the elastic energy is

$$U = \frac{1}{2}K(\xi_1 - \xi_2)^2.$$

Note that $\xi_1 - \xi_2$ will be the total stretch. If we go to CM coordinates and use the reduced mass μ, then $p_2 = -p_1$ and

$$KE_{vib} = \frac{p_1^2}{2\mu}.$$

This all describes a 1–D oscillator with vibration coordinate $\xi = \xi_1 - \xi_2$.

This gives us the Schrödinger equation

$$-\frac{\hbar^2}{2\mu}\frac{d^2}{d\xi^2}\psi + \frac{1}{2}K\xi^2\psi(\xi) = E_{\text{vib}}\psi(\xi)$$

which is the one for a 1-d quantum oscillator. Using the known solution, we get

$$E_{\text{vib}} = (v + \frac{1}{2})\hbar\omega; \quad v = 0, 1, 2, \ldots$$

This gives a set of energy levels

$$\{\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \ldots\}\hbar\omega.$$

Also

$$K = \mu\omega^2$$

if we need to find the effective force constant.

More realistic models

More complete treatment of molecular rotations and vibrations would involve

- 3–D quantum mechanics of multiparticle systems. Calculations difficult so approxations necessary.

- More realistic (anharmonic) potential functions, such as the Morse oscillator (see p. 384).

Problems

For next week (by Friday) do 11.1, 11.2 and 11.5. We will discuss these and some of the in-text examples in class next week.

Also take a look at the file in the course area whose filenames start with `1985xxWeisskopf`, which give interesting order-of-magnitude essays on these topics.