

CHEM 3420: Physical Chemistry II — Spring 2009

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Lecture 25: Let's go for a spin: Rotations

References

1. Levine, *Physical Chemistry*, Chapter 20.3, 17.14
2. Molecular Spectroscopy Handouts

Key Concepts

- Some interesting results of modeling pure vibrational spectroscopy:
 1. The vibrational energy levels are no longer equally spaced. As v increases the anharmonic correction term increases in magnitude resulting in levels that are more closely spaced.
 2. The selection rules become relaxed resulting in observable transitions for $\Delta v = \pm 1, \pm 2, \pm 3, \dots$. The fundamental transition, $\Delta v = \pm 1$ is still the strongest, while the overtones ($\Delta v = \pm 2, \pm 3, \dots$) are much weaker. The overtones allow for the characterization of the anharmonicity of the bonding curve.
 3. The observed spectroscopic bond energy (D_o) is actually less than the electronic bond energy (D_e , calculated from the minimum of the bonding curve). This is a result of the $v = 0$ vibrational state being the zero point energy and therefore the ground state does not lie at the minimum of the bonding curve but at a slightly higher energy:

$$D_e = D_o + \frac{1}{2}h\nu_e - \frac{1}{4}h\nu_e x_e$$

4. The isotope effect impacts vibrational spectrum through changes in the reduced mass. Isotopes differ in mass and not electronic configuration, so the chemical properties of isotopes are similar. This leads to a different μ and the same force constant k .

$$\bar{\nu}_{obs} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

A heavier mass will shift vibrational transitions to lower frequency (and energy).

- Other models exist for the anharmonic oscillator that are used frequently to model the asymmetry of the potential energy curve:
 1. Lennard-Jones potential (LJ or 6-12): this model uses an empirical approach to capture the repulsive and attractive interaction between two atoms:

$$E(R) = 4D_e \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right]$$

where σ is a constant. The repulsive term (to the left of the minimum in the curve) is short-ranged and rises steeply and is therefore modeled to the power 12. The attractive part is longer range and rises more slowly, and is therefore the term with the power 6.

2. Morse potential: another model of the anharmonic shape, less conceptual insight, but functional form works well

$$E(R) = D_e \left(1 - e^{-\alpha(R-R_e)} \right)^2$$

where α is a parameter that describes the width of the potential:

$$\alpha = \sqrt{\frac{k}{2D_e}}$$

- As we saw with the high-resolution vibrational spectrum of HCl, there are many more peaks than we expect and no peak where we predict their ought to be one. This is an indication of the need to consider rotational states and transitions.
- Rotational transitions are lower in energy as compared to vibrational and electronic transitions. They typically occur in the microwave region of the spectrum.
- Just like for vibrations, we will consider a diatomic molecule first. The simplest model of a rotating body consisting of two atoms is the rigid rotor. This model fixes the distance between the two bodies (atoms). This is a bit of a simplification since we know from our discussion of vibration that the atoms are not fixed, but this model is a good place to start.
- For a rotating body, an important parameter is the moment of inertia, I , which for two masses (m_1 and m_2) is given as:

$$I = m_1 r_1^2 + m_2 r_2^2 = \mu R_e^2$$

where r_1 and r_2 is the distance between the center of mass of the body and masses 1 and 2, respectively. It is useful to compact this a little and express it in terms of the reduced mass and the fixed interatomic distance, R_e . The expression for moment of inertia is dependent on the molecular geometry.

- Using the moment of inertia along with the expression for the kinetic energy of a rigid rotor, you can solve the Schrödinger Equation for the rigid rotor to obtain wave functions and permitted energy states. We have already seen the wave functions (although you didn't know it at the time): they are the angular parts of the hydrogen atom orbitals.
- At this point, the permitted energies is what we are after:

$$E_J = \frac{\hbar^2}{2I} J(J+1) = hB_e J(J+1) \quad J = 0, 1, 2, 3, \dots$$

where J is the rotational quantum number, and the parameter $B_e = \frac{h}{8\pi^2 I}$.

- The absolute energy levels aren't as interesting as the change in energy between them.

$$\Delta E_J = 2hB_e(J+1)$$

where the energy is in Joules. It is also convenient to write the expression in terms of wave number (cm^{-1}) since that is what is usually measured spectroscopically.

$$\bar{\nu}_{obs} = 2\bar{B}_e(J+1) \quad \bar{B}_e = \frac{B_e}{c}$$

For the rigid rotor, the selection rules for allowed transitions is $J = \pm 1$.