

CHEM 3420: Physical Chemistry II — Spring 2009

April 1, 2009

Lecture 28: Vibrational-rotational spectroscopy: improving our model

**References**

1. Levine, *Physical Chemistry*, Section 20.4
2. Molecular Spectroscopy Handouts

**Key Concepts**

- In a real high-resolution IR spectrum, we observed the multiple lines but we also saw that the spacing between the lines was no uniform. In the R-branch the spacing decreases as you move to higher energies while in the P-branch the peaks move further apart as you go to lower energies.
- The discrepancy between our basic model and the experimental observations can be attributed to coupling between rotational and vibrational energies. Therefore our simple model of the harmonic oscillator and rigid rotor will not cut it.
- One improvement would be to use an anharmonic oscillator to model the vibrations, leading to a vibrational term of:

$$G(v) = \underbrace{\bar{\nu}_e \left( v + \frac{1}{2} \right)}_{\text{harmonic part}} - \underbrace{\bar{\nu}_e x_e \left( v + \frac{1}{2} \right)^2}_{\text{anharmonic correction}}$$

- We can also include the impact of vibrations on the rotation of a molecule through a coupling constant. This constant characterizes the impact of being in a certain vibrational state on the rotational constant of a molecule.

$$E_{rot} (cm^{-1}) = \underbrace{\bar{B}_e J(J+1)}_{\text{rigid rotor}} - \underbrace{\bar{\alpha}_e \left( v + \frac{1}{2} \right) J(J+1)}_{\text{correction for vib-rot coupling}}$$

where  $\bar{\alpha}_e$  is the vibration-rotation coupling constant.

- An additional correction includes the change in rotational energy due to centrifugal forces. As the molecules is rotating, the forces of circular motion distort the bond and lead to changes in the rotational energy. This distortion is characterized by  $D$ , the centrifugal distortion constant.

$$E_{rot} (cm^{-1}) = \underbrace{\bar{B}_e J(J+1)}_{\text{rigid rotor}} - \underbrace{\bar{\alpha}_e \left( v + \frac{1}{2} \right) J(J+1)}_{\text{correction for vib-rot coupling}} - \underbrace{\bar{D} J^2 (J+1)^2}_{\text{centrifugal distortion}}$$

Often  $D$  is quite small and can be neglected.

- Using these correction, the total vibrational-rotational energy is:

$$E_{v,J} (cm^{-1}) = \underbrace{\bar{\nu}_e \left( v + \frac{1}{2} \right)}_{\text{harmonic part}} - \underbrace{\bar{\nu}_e x_e \left( v + \frac{1}{2} \right)^2}_{\text{anharmonic correction}} + \underbrace{\bar{B}_e J(J+1)}_{\text{rigid rotor}} - \underbrace{\bar{\alpha}_e \left( v + \frac{1}{2} \right) J(J+1)}_{\text{correction for vib-rot coupling}} - \underbrace{\bar{D} J^2 (J+1)^2}_{\text{centrifugal distortion}}$$

- Applying this expression we see that it correctly predicts the shifts seen in the experimental IR spectrum.

**Related Exercises in Levine**

Exercises 20.25, 20.26