

CHEM 3420: Physical Chemistry II — Spring 2009

March 30, 2009

Lecture 27: Vibrational-rotational spectroscopy

### References

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

### Key Concepts

- Combining the expression for the energy levels of the harmonic oscillator (vibrations) and the rigid rotor (rotations) we get an expression for the total energy of the system (both vibrational AND rotational energies):

$$E_{v,J} = \nu_e h \left( v + \frac{1}{2} \right) + B_e h J(J+1)$$

where  $\nu_e$  is the fundamental frequency and  $B_e$  is the rotational constant, both for a specific molecule.

- It is often easier to write the energy in units of  $\text{cm}^{-1}$ , or so-called “terms”. The vibrational “term” becomes:

$$G(v) = \bar{\nu}_e \left( v + \frac{1}{2} \right)$$

and the rotational “term” is:

$$F(J) = \bar{B}_e J(J+1)$$

This gives us an expression for the total energy as the sum of the two terms:

$$E_{v,J} (\text{cm}^{-1}) = G(v) + F(J) = \bar{\nu}_e \left( v + \frac{1}{2} \right) + \bar{B}_e J(J+1)$$

- The fundamental frequency is typically on the order of  $10^3 \text{ cm}^{-1}$  and the rotational constant is on the order of  $1 \text{ cm}^{-1}$ .
- An IR spectra will show peaks where there is a permitted transition between one vibrational-rotational state to another. The selection rules are still  $\Delta v = \pm 1$  and  $\Delta J = \pm 1$ . However, since all molecules will start in the vibrational ground state ( $v = 0$ ) we only need to consider the vibrational transition from  $v = 0$  to  $v = 1$  along with rotational transitions of  $\Delta J = \pm 1$ .
- For  $\Delta J = +1$  we can write out an expression for  $\Delta E$  or  $\bar{\nu}_{obs}$  using our “terms” from above, with  $J$  being the initial rotational state and  $J+1$  being the final state:

$$\Delta E (\text{cm}^{-1}) = E_{1,J+1} - E_{0,J} = \bar{\nu}_e \left( 1 + \frac{1}{2} \right) + \bar{B}_e (J+1)(J+2) - \left[ \bar{\nu}_e \left( 0 + \frac{1}{2} \right) + \bar{B}_e J(J+1) \right]$$

$$\Delta E (\text{cm}^{-1}) = \bar{\nu}_{obs} = \bar{\nu}_e + 2\bar{B}_e(J+1) \quad J = 0, 1, 2, 3, \dots$$

This indicates that we would observe peaks shifted to the right from the fundamental frequency ( $\bar{\nu}_e$ ) by an integral multiple of  $2\bar{B}_e$ . This is called the *R-branch* of the spectrum.

- A similar expression is obtained for looking at transitions where  $\Delta J = -1$ :

$$\Delta E (\text{cm}^{-1}) = \bar{\nu}_e - 2\bar{B}_e J \quad J = 1, 2, 3, \dots$$

In the spectrum, this would lead to peaks shifted to lower energies (to the left) away from the fundamental frequency by an integral multiple of  $2\bar{B}_e$ . This is called the *P-branch* of the spectrum.

- In a real high-resolution IR spectrum, we observed the multiple lines but we also saw that the spacing between the lines was not 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.

### **Related Exercises in Levine**

Exercises 20.25, 20.26