

CHEM 3420: Physical Chemistry II — Spring 2009

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Lecture 26: Combining vibrations and rotations

References

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

Key Concepts

- The quantized energy levels of a rigid rotor are given as:

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

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

- The ground energy state ($J = 0$) for the rigid rotor has $E_0 = 0$.
- The energy states of the rigid rotor have a degeneracy (g_J) given by:

$$g_J = 2J + 1$$

- 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}) by dividing both sides of the above expression by hc . This is a helpful way to write this expression 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 $J = \pm 1$.

- Changes between rotational energy states is what we observe in a microwave spectrum, so we can use the above expression to predict what the microwave spectrum would look like. So using the rigid rotor model, we find that the spacing between the **observed peaks** in the spectrum is $2\bar{B}_e$ (in cm^{-1}) or $2hB_e$ (in Joules). Using this spacing, we can determine B_e , which gives us I . which in turn leads to R_e for a simple diatomic molecule.
- Reality Check: are vibrational and rotational transitions independent, like we initially assume? Well, the answer is no. Remember, the harmonic (and anharmonic) predicts an IR spectrum with a single peak at ν_e (the fundamental peak). However, a real IR spectrum has a set of closely spaced peaks centered around the fundamental frequency, but there is no peak at the fundamental frequency!
- So for a better description of our diatomic molecule and its associate IR spectrum we need to consider both vibrational and rotational energy states. Multiple transitions are possible between different vibrational-rotational states. There are also interactions/coupling between rotations and vibrations which impact the energies of the transitions.
- At room temperature, the system will be in the vibrational ground state of $v = 0$ but can exist in any number of rotational states, $J = 0, 1, 2, 3, \dots$. This is due to the spacing between the states: for vibrational levels, the $\Delta E_v(v = 0 \rightarrow v = 1) > k_b T$ (thermal energy), so everything starts in the ground state. However, the spacing of rotational states is much smaller, $\Delta E_J(J = 0 \rightarrow J = 1) \ll k_b T$, which means there is a possibility to be in any number of excited rotational states.

- For example, the following absorption transitions are possible:

$$\begin{aligned}
 v = 0, J = 0 &\rightarrow v = 1, J = 1 \\
 v = 0, J = 1 &\rightarrow v = 1, J = 0 \\
 v = 0, J = 1 &\rightarrow v = 1, J = 2 \\
 v = 0, J = 2 &\rightarrow v = 1, J = 1 \\
 v = 0, J = 5 &\rightarrow v = 1, J = 6
 \end{aligned}$$

While $v = 0, J = 0 \rightarrow v = 1, J = 0$ is NOT permitted since $\Delta J = 0$. This transition corresponds to the fundamental frequency and is a forbidden transition that is not observed in a vibrational-rotational spectrum.

- 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 ν_e is the fundamental frequency and B_e is the rotational constant, both for a specific molecule.