Rotational and Vibrational Transitions

After having tackled electronic transitions in molecules last time, we'll look at rotation and vibration in more detail now. As always, the real deal is fully quantum mechanical, but we'll first look at a semiclassical model to gain some physical intuition.

As before, let's consider first a rigid rotator: imagine two heavy point particles (nuclei) of masses M_1 and M_2 connected by a rod of fixed length r_0. **Ask class:** given the quantization of angular momentum, what are the rotational energy levels? As before, we would expect $L = n\hbar$, and with $E = L^2/2I$ the energies will be $E = n^2\hbar^2/2I$, where I is the moment of inertia. For a two-particle system like this one, the moment of inertia is μr_0^2, where $\mu = M_1M_2/(M_1+M_2)$ is the reduced mass. Therefore, the energies increase in a strictly quadratic sequence.

Now suppose that the two particles are connected instead by a massless spring whose rest length is r_0. This is more realistic, since it simulates the interatomic potential. **Ask class:** qualitatively, what difference will this make to the energy levels in our classical model? If two particles connected by a spring are spun around, centrifugal force will stretch the spring. This increases the separation, and hence increases the moment of inertia. Therefore, for a fixed angular momentum, the energy is less than it would have been at fixed separation, so that the energy levels are slightly closer together than they would have been.

Ask class: how do we set this up quantum mechanically? In order to include the effects of rotation, we need an addition to the Hamiltonian that represents rotational energy. To do this, we need an operator for $H_{\rm rot}$, which is $H_{\rm rot} = \mathbf{K}^2/(2\mu r^2)$, where $\mathbf{K}$ is the angular momentum operator. The energy eigenvalues for the rotation Hamiltonian are $E_K = \frac{\hbar^2}{2\mu r^2}K(K+1)$ for quantum number K. Inserting into the Schrödinger equation and doing a little manipulation we find (in spherical coordinates)

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) + \frac{2\mu}{\hbar^2}\left[E - V_n(r) - \frac{\hbar^2 K(K+1)}{2\mu r^2}\right]\psi = 0\ . \tag{1}$$

Here $V_n(r)$ is the electronic potential of the nuclei in state n, and r is the separation of the nuclei.

As is discussed in some more detail in the book, one can get an idea of the resulting energy levels by expanding the potential $V_n(r)$ in a Taylor series around its minimum point r_0:

$$V_n(r) = V_{n0} + \frac{1}{2}k_n(r-r_0)^2 + \ldots \tag{2}$$

Here the coefficient k_n acts as a spring constant. Further manipulation gives rotational energy levels of

$$E_{nk} \approx V_{n0} + \frac{\hbar^2 K(K+1)}{2\mu r_0^2}\left[1 - \frac{2\hbar^2 K(K+1)}{k_n \mu r_0^4}\right] . \tag{3}$$

The emission frequencies for rotational transitions are therefore

$$\omega_K = \frac{\hbar(K+1)}{\mu r_0^2}\left[1 - \frac{4\hbar^2 (K+1)^2}{k_n \mu r_0^4}\right] . \tag{4}$$

Ask class: qualitatively, what does this tell us? The lowest order rotational term is more or less quadratic; the $K(K+1)$ instead of K^2 is an indication of quantum effects. The next order term indicates that the energy doesn't increase strictly in accordance with the $K(K+1)$ law, but more slowly. This is the quantum term that corresponds to the "stretching of the spring" classical analogy we used earlier.

What about selection rules? Let's consider dipole radiation. From an analogy to classical radiation, we expect that the only way we can get dipole radiation is if the dipole moment changes. Now, if the molecule is rotating, this means that the permanent dipole moment of the molecule must be nonzero, otherwise rotation doesn't change that dipole moment and hence there is no radiation. The permanent dipole moment contains contributions from the nuclei and from the electrons:

$$d \equiv Z_1 e r_1 + Z_2 e r_2 + d_e , \tag{5}$$

where the last term is the electronic one. Here r_1 and r_2 are measured with respect to the center of mass of the system. **Ask class:** for an H_2 molecule, what is d? It's zero! If the masses and charges of the nuclei are the same, the symmetry of the molecule means that $r_1 = -r_2$, and thus $Zer_1 + Zer_2 = 0$. This means that homopolar molecules (H_2, O_2, N_2, etc.) don't have dipolar rotational transitions. Higher-order rotational transitions are required. Another transition rule for dipolar transitions is similar to what we had for atoms: $\Delta K = \pm 1$. To summarize, for dipolar transitions:

$$\begin{aligned} d &\neq 0 \\ \Delta K &= -1 \quad \text{(emission)} \\ &= +1 \quad \text{(absorption)} \end{aligned} \tag{6}$$

Now let's consider modes that include vibration. As we found in the last class, vibrational modes have much higher energies than rotational modes do, so it's difficult to excite a vibrational mode without also exciting a rotational mode. However, we can treat the rotational effects as perturbations.

To lowest order, the vibrational modes proceed as a harmonic oscillator, around the minimum in the electronic potential:

$$\begin{aligned} E_{nv} &= \hbar\omega_{nK}(v + 1/2) \\ \omega_{nK} &= \mu^{-1/2}(k_n + \ldots) \end{aligned} \tag{7}$$

where the "…" includes rotational contributions. Stated another way, the effective potential of the system has a minimum, and we can Taylor expand around that minimum. To lowest order (above), we have a pure harmonic oscillator from the quadratic terms, but cubic, quartic, etc. terms will add complications. One approach is to try a relatively simple but representative functional form that captures much of the structure. A commonly used form is the *Morse potential*

$$U_n(r) = U_{n0} + B_n \left\{1 - \exp[-\beta_n(r - r_0)]\right\}^2 \tag{8}$$

where B_n, β_n, and r_0 are parameters to be fit to the curve. This has the advantage that the energy eigenvalues relative to the minimum U_{n0} may be determined exactly:

$$E_{nv} = \hbar\omega_{n0}(v + 1/2) - \frac{\hbar^2\omega_0^2}{4B_n}(v + 1/2)^2 \tag{9}$$

where

$$\omega_{n0} = \beta_n(2B_n/\mu)^{1/2} \; . \tag{10}$$

There are of course selection rules for vibration-rotation transitions. Some are familiar: $d \neq 0$ (nonzero dipole moment), d must change during a vibrational transition, $\delta v = \pm 1$. The last one is more complicated, and involves the component Λ of the electronic orbital angular momentum along the axis between the two nuclei. These electronic states are $\Lambda = 0, 1, 2, 3, \ldots$. The final transition rule is $K = \pm 1$ for $\Lambda = 0$, but $K = \pm 1, 0$ for $\Lambda > 0$. That's because when there is no electronic orbital angular momentum ($\Lambda = 0$), the entire change in angular momentum comes from the rotational component, so the selection rules are the same as before. However, when there is orbital angular momentum, there are different projections of that angular momentum (positive or negative), so a transition between those states can occur even if the rotational angular momentum K remains constant. Note that since most of the energy of transition is vibrational, either $\Delta K = +1$ or $\Delta K = -1$ is allowed for either emission or absorption. This has the effect of producing "fine structure" on top of the vibrational transitions.

When we consider electronic transitions in molecules, then again we must think about vibrational and rotational transitions, since these are much lower energies. **Ask class:** what do they expect the qualitative features of the spectrum to be? Vibration and rotation give successive levels of fine structure on top of the electronic transitions. The selection rules for electronic dipole transitions of a molecule are

$$\begin{aligned}
\Delta\Lambda &= -1, 0, +1 \\
\Delta J &= -1, 0, +1 \\
&\quad J = 0 \rightarrow J = 0 \qquad \text{not allowed} \\
&\quad \Delta J \neq 0 \text{ if } \Lambda = 0 \rightarrow \Lambda = 0 \\
\Delta v &= \text{any integer.}
\end{aligned} \tag{11}$$

Here $\mathbf{J} = \mathbf{K} + \mathbf{L}$ is the total angular momentum and again Λ is the component of the electronic angular momentum along the axis between the two nuclei. Most of the qualitative features of these selection rules can be understood from the principle that a photon carries angular momentum, so the total angular momentum of the system must change in a dipolar transition.

Let's wrap up by looking at a couple of applications. First, we'll follow Shu in thinking about molecular clouds. In molecular clouds (typical temperatures 10–100 K), H_2 is by far the most common molecule. However, CO is the most common tracer of molecular gas. **Ask class:** can they think of why? First, the temperatures of molecular clouds are low enough that primarily rotational transitions will be excited, rather than vibrational or electronic. However, since H_2 is a homopolar molecule, it doesn't undergo dipolar rotational transitions. At this point you might be willing to give up on H_2, but remember that there are higher-order transitions that can take place, e.g., $2 \rightarrow 0$. Given the overwhelming abundance advantage of H_2, you might think it could overcome the weaker transition. But there's another factor. **Ask class:** in clouds of this temperature, what might be a problem for the $2 \rightarrow 0$ rotational transition? The other difficulty is that H_2 is rather light, meaning that it has a high excitation energy; for H_2, the temperature equivalent of the $2 \rightarrow 0$ transition is $\Delta E_{20}/k = 510$ K, so in most molecular clouds the temperature isn't high enough to excite it. Thus, a comparatively uncommon molecule such as CO gives a stronger signal. In fact, CO has other advantages. It is composed of abundant elements, and is a robust molecule (it is seen in the spectra of sunspots). In addition, C and O have a strong affinity for each other, and CO doesn't tend to get locked up in interstellar dust.

Now consider cooling of gas in the very early universe, before metals (elements more massive than helium) have had a chance to form in quantity. The formation of the first generation of stars depends on the cooling of gas, for fragmentation; the cooler the gas can become, the smaller the fragmentation scale is, so whether the gas gets to 500 K or 100 K makes a big difference to whether the first generation of stars (population III stars) are a few solar masses, tens of solar masses, or hundreds of solar masses. If only H_2 cooling is involved, the temperature only gets down to a few hundred Kelvin. **Ask class:** what happens if one considers HD? This is not a homopolar molecule, so it *can* undergo dipolar rotational transitions. This increases the strength of the transition and lowers the required temperature. The spontaneous transition probability for $2 \rightarrow 0$ in H_2 is $A_{20} = 3 \times 10^{-11}\ \mathrm{s}^{-1}$, and that of $1 \rightarrow 0$ in HD is $A_{10} = 5 \times 10^{-8}\ \mathrm{s}^{-1}$. Moreover, the excitation energy of the first rotational level in HD is only 128 K. Therefore, if the temperature can be brought down to a few hundred Kelvin by H_2, it can be brought down to less than 100 K by HD. People are currently debating whether this plays an important role.