EPS 237 Lesson 8: Vibration-rotation absorption lines and bands

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1 Overview

To understand line locations, strengths and shapes quantitatively, we must delve into quantum mechanics. In the classical world, molecules can have precisely defined properties like position and momentum simultaneously, but in quantum mechanics this no longer holds true in general. Instead, we use the wavefunction Ψ to determine the probability of finding a molecule in a given state. The evolution of the wavefunction is governed by Schrödinger's equation

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi. \tag{1}$$

Here $i = \sqrt{-1}$, $\hbar = h/2\pi$ and h is Planck's constant. $\hat{H}$ is the hamiltonian operator, which often takes the form

$$\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + V(\mathbf{r}, t) \tag{2}$$

with m particle mass, ∇ the spatial gradient operator, V a general potential term and $\mathbf{r}$ the position vector. The wavefunction is complex-valued and cannot be measured directly, but the square of its absolute value $|\Psi|^2 = \Psi^*\Psi$ gives the probability that a molecule will be found in a given state.

We can break the hamiltonian operator into space- and time-dependent terms

$$\hat{H} = \hat{H}_0(\mathbf{r}) + \hat{H}_1(\mathbf{r}, t). \tag{3}$$

Because the Schrödinger equation is linear, we can also separate the wavefunction into space- and time-dependent parts

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\phi(t) \tag{4}$$

In this lesson we focus on the *time-independent* part of the hamiltonian, which is the part that tells us about atomic/molecular energy levels (and hence spectral line locations). In the next lesson we consider the *time-dependent* part, which governs how and when transitions occur.

The stationary states are given by the equation

$$\hat{H}_0\psi = E\psi \tag{5}$$

which is analogous to the classic eigenvalue equation from linear algebra

$$\mathbf{A}\mathbf{x} = \lambda\mathbf{x}. \tag{6}$$

Solving it allows us to determine the discrete eigenvalues E_n and eigenfunctions ψ_n that define a molecule's energy levels. Transitions *between* energy levels due to photon emission or absorption is what gives rise to spectral lines.

2 Vibrational transitions

In one dimension the time-independent hamiltonian becomes

$$\hat{H}_0 = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x). \tag{7}$$

We can Taylor expand the potential about a mean separation x_0

$$V(x) \approx V(x_0) + xV'(x)|_{x_0} + \frac{1}{2}x^2V''(x)|_{x_0}. \tag{8}$$

If x_0 occurs where $V(x)$ is minimum, $V'(x)|_{x_0} = 0$. We can also set $V(x_0) = 0$ without loss of generality. Then we can write

$$\hat{H}_0 \approx \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2. \tag{9}$$

where $k = V''(x)|_{x_0}$ is a constant with units of N/m. k can be understood as the *molecular bond stiffness*. This is the quantum hamiltonian for simple harmonic motion[1].

We can solve this as a standard ordinary differential equation by doing separation of variables for the wavefunction. It turns out that the eigenfunctions (quantum states) are expressed in terms of Hermite polynomials. More important for us here are the eigenvalues (energy levels). It turns out that for this system they are

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega. \tag{10}$$

Note that $\omega = \sqrt{k/m}$. Also, remember that $\hbar\omega = h\nu = 100hc\tilde{\nu}$, with $\tilde{\nu}$ in cm^{-1} units. In the context of molecules, m should be taken to be the reduced mass, $m = m_r = m_1m_2/(m_1 + m_2)$. Important: the energy of a given level does not tell us where the absorption line appears — it's the *difference* between energy levels that counts. For a pure vibrational transition $n \to n + 1$,

$$\Delta E_{n\to n+1} = E_{n+1} - E_n = h\nu. \tag{11}$$

3 Rotational transitions

Classically, angular momentum is $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, where $\mathbf{r}$ is location and $\mathbf{p}$ is momentum. In quantum mechanics, $\mathbf{L} \to \hat{L}$, an operator. The individual components of $\hat{L}$ in 3D do not commute, so we cannot simultaneously know all their values. The square of angular momentum operator $\hat{L}^2$ *does* commute with each component of $\hat{L}$ individually, however. $\hat{L}^2$ has eigenvalues

$$\hat{L}^2\psi = \hbar^2 J(J+1)\psi \tag{12}$$

where J is an integer. Similarly, the allowed values of angular momentum along some axis are

$$\hat{L}_z\psi = \hbar K\psi, \tag{13}$$

where $|K| \leq J$. We can visualize this by thinking about a top that can only spin at given angles to the measurement angle. These results can be derived by use of ladder operators or (more directly) by expressing the angular momentum operator as $\hat{L} = (\hbar/i)(\mathbf{r} \times \nabla)$ in spherical coordinates.

[1] In the classical simple harmonic oscillator, the hamiltonian would be $H_0 = p^2/2m + \frac{1}{2}kx^2$, where p is momentum.

To link angular momentum to energy and hence to the location of spectral lines, we also need to know moment of inertia. For any molecule, three moments of inertia can be defined about three principal axes: I_a, I_b, I_c. By convention $I_a \leq I_b \leq I_c$. The definition of moment of inertia for a collection of point masses is

$$I = \sum_i m_i r_i^2. \tag{14}$$

For a diatomic molecule,

$$I = m_r r^2 \tag{15}$$

where m_r is the reduced mass.

Molecules can be classified according to their momentum of inertia values. The three most important categories for planetary climate are:

- Linear rotors (e.g. CO_2, C_2H_2, all diatomics), which have $I_a = 0$, $I_b = I_c = I$.
- Spherical tops (e.g. CH_4, GeH_4), which have $I_a = I_b = I_c$.
- Asymmetric rotors, which have $I_a \neq I_b \neq I_c$. Examples include H_2O, O_3 or H_2S.

Classical rotational energy is defined as

$$E = \frac{1}{2}\left(\frac{L_a^2}{I_a} + \frac{L_b^2}{I_b} + \frac{L_c^2}{I_c}\right). \tag{16}$$

Because $L^2 = L_a^2 + L_b^2 + L_c^2$, linear rotors and spherical tops have simply:

$$E = \frac{1}{2}\frac{L^2}{I}. \tag{17}$$

Subbing $L^2 \rightarrow \hat{L}^2$ and using (12) we have

$$E = \frac{\hbar^2 J(J+1)}{2I}. \tag{18}$$

For other rotors, things are more complex, but we won't explore that further here.

Now in spectroscopist's cm^{-1} notation we can write

$$F(J) = \frac{E}{hc} = BJ(J+1) \tag{19}$$

B is the *rotational constant* (units cm^{-1}):

$$B = \frac{h}{8\pi^2 cI}. \tag{20}$$

It should not be confused with the Planck spectral irradiance we defined earlier! We can write the spectral position of rotational lines as

$$\tilde{\nu}_{J+1,J} = F(J+1) - F(J) = 2B(J+1). \tag{21}$$

In spectroscopist's units of cm^{-1}, $\tilde{\nu}_{J+1,J}$ is exactly equivalent to $\Delta E_{J+1,J}$.

Rotational bands

The strength of spectral lines depends on several factors. But for rotational bands, occupancy of the lowest state is key. This is given by the Boltzmann relation

$$N_J = \frac{N}{Z_r} g_J e^{-E_J/k_B T} \tag{22}$$

Here Z_r is the rotational partition function, g_J is the degeneracy of state J, N is the total number density and N_J is the density of state J. For a linear rotor such as HCl, degeneracy is $g_J = 2J + 1$ (see figure in the slides) and energy is $E_J = \hbar^2 J(J+1)/2I$. Hence

$$N_J = \frac{N}{Z_r}(2J+1) e^{-\frac{\hbar^2 J(J+1)}{2I}/k_B T}. \tag{23}$$

This gives rise to a well-defined band that peaks and then decreases again, as seen in the slides for HCl.

Centrifugal Distortion

At high rotational energy levels, a centrifugal term becomes important and $F(J)$ becomes

$$F(J) = BJ(J+1) - DJ^2(J+1)^2. \tag{24}$$

D is a small constant, the *centrifugal distortion constant*. It can also be written as

$$D = \frac{4B_e^3}{\omega_e^2}. \tag{25}$$

where B_e is the equilibrium rotational constant and ω_e is the equilibrium vibration frequency. This modifies the line position to

$$\tilde{\nu}_{J+1,J} = 2B(J+1) - 4D(J+1)^3. \tag{26}$$

Slight deviations from even spacing can be seen in the rotational bands of many simple species like HCl, HBr and CO.

4 Vibrational-rotational bands

To first order, vibrational and rotational degrees of freedom are independent, so there are rotational level changes that appear around frequencies where vibrational transitions are excited. But why do simple molecules like HCl have no strong line at the center of their first vibrational transitions? The answer is selection rules. Selection rules originate from the properties of the transition dipole matrix (see next lecture).

The vibrational selection rule is

$$\Delta n = \pm 1. \tag{27}$$

Alone, this doesn't explain why symmetric linear molecules like HCl have no central line. But we also must think about rotational selection rules. It turns out that for HCl, we also have

$$\Delta J = \pm 1. \tag{28}$$

Rotational transitions give rise to the *P-branch* for lower frequencies and the *R-branch* for higher frequencies. The two branches are almost mirror images of each other, with slight differences. The frequencies of lines in wavenumber units are given by

$$\tilde{\nu} = \tilde{\nu}_n \pm 2B(J+1) \tag{29}$$

If $n = 0$, only positive values are allowed, which corresponds to the pure rotational band seen at low frequencies. But for higher values, both positive and negative branches are allowed, as is seen in the first vibrational-rotational band for HCl.

The Q-branch

You may have noticed that the spectra of more complex molecules like CO_2 *do* contain a central peak in their vibrational-rotational bands. This is called the *Q-branch*. The Q-branch is complex, but it emerges due to a combination of non-rigid-rotor effects, including centrifugal and Coriolis interactions between vibrational and rotational levels, which allow the simple selection rules described here to be broken. The CO_2 Q-branch is very important to planetary climate. There's something rather wonderful about the fact that the Coriolis effect is important to Earth's climate both on the scale of the entire planet, and on the scale of a single CO_2 molecule!