

### 3.9: Spectra of Gases - Rovibronic Transitions

IR spectroscopy of gases is special in that rotational fine structure contributes to the spectral lineshapes and can often be resolved – providing another layer of information to be obtained from the spectra about structure of the molecule. Rotational structure is not obtained in liquid and solids, because the molecules are not allowed to freely rotate by the intermolecular interactions (librations are hindered rotations in condensed phases) of the neighbors.

Just as the [Born-Oppenheimer approximation](#) allows us to separate electronic and nuclear motions, because electrons move so much more rapidly than nuclear, the [nuclear vibrations](#) can be separated from [molecular rotations](#), because their timescale is shorter. The Hamiltonian can be separated into two contributions:

$$H_{\text{tot}} = H_{\text{elect}} + H_{\text{rot}} + H_{\text{vib}}$$

Resulting in the nuclear energy being written as the sum of two contributions.

$$\varepsilon_{mc} = \varepsilon_{\text{elect}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}}$$

Let's consider only a diatomic for this discussion and ignoring electronic transitions (i.e.,  $\varepsilon_{\text{elect}} = 0$ ), so there is only one degree of vibrational freedom (a stretch) with a frequency of  $\nu_0$ , thus the

$$\varepsilon_{\text{vib}} = \left(v + \frac{1}{2}\right) h\nu_0$$

with  $v = 0, 1, 2, 3, \dots$

Now,  $\varepsilon_{\text{rot}}$  can be obtained by considering that the diatomic is a pair of masses held together by a rigid bond (the rigid rotor approximation). The bond is not actually rigid, the atoms are vibrating naturally (with at least zero point motion), but because vibrations are fast, we can think of an “average” bond length. Solving the quantum mechanics for this system gives the following energy level manifold:

$$\varepsilon_{\text{rot}} = hBJ(J+1)$$

with  $J = 0, 1, 2, \dots$

where  $J$  is the rotational quantum number and  $B$  is the **rotational constant**, which depends on the moment of inertia,  $I$ .

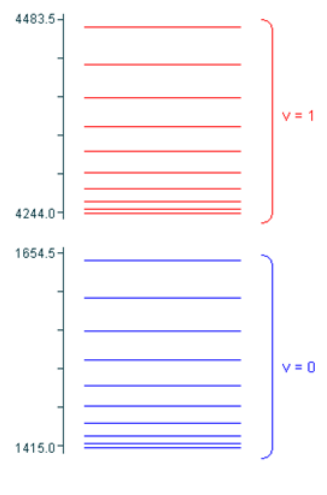
$$B = \frac{h}{8\pi^2 I}$$

with

$$I = \mu \langle R^2 \rangle$$

$\mu$  is the reduced mass and  $\langle R^2 \rangle$  is the mean square displacement of the bond length. Thus the total nuclear energy is

$$\varepsilon_{mc} = (v + 1/2)h\nu_0 + hBJ(J+1)$$



## Occupations

The vibrational transitions from ground state vibration eigenstate to the next higher eigenstate is ( $v = 0 \rightarrow v' = 1$ ), but the various rotational eigenstates are population thermally (far less than  $kT$  of  $200 \text{ cm}^{-1}$ ), hence many different  $J$  state are initially populated in the sample. Now, a point of importance since we are going to do a little statistics. The eigenstates calculated from the harmonic oscillator are non-degenerate, meaning that each eigenstate corresponds to a signal energy and each energy (allowed) has only one eigenstate. For the rotation rigid rotor, the eigenstates have a degeneracy of  $(2J + 1)$ . So while the ground rotational level has only one eigenstate (one vibrational and one rotation), the next higher energy ( $V = 0, J = 1$ ) has three eigenstates associated with it.

### ✓ Example 3.9.1: Thermal population of rotational levels, a skirmish with statistical mechanics and the Boltzmann Distribution

A typical diatomic molecule might have  $B \approx 2 \times 10^{10} \text{ Hz}$ . What are the relative number of molecules in the  $J = 5$  state?

#### Solution

This is just the application for the Boltzmann equations discussed before in class:

$$N_J = g_J e^{-\epsilon_J/kT}$$

where  $g$  is the degeneracy for the  $J^{\text{th}}$  energy state and  $\epsilon$  is the energy of that eigenstate. We can construct a ratio to answer this question

$$\frac{N_J}{N_{J=0}} = \frac{g_J e^{-\epsilon_J/kT}}{g_{J=0} e^{-\epsilon_{J=0}/kT}}$$

or

$$\frac{N_J}{N_{J=0}} = \frac{g_J}{g_{J=0}} e^{-(\epsilon_J - \epsilon_{J=0})/kT}$$

The energy for the  $J = 5$  eigenstate is

$$\epsilon_{\text{rot}} = hBJ(J+1) = hB5(5+1) = 30hB$$

For the  $J = 0$ , the energy is zero (note: there is no such thing as a zero point rotational energy)

So the different in energy between the two eigenstates is  $30hB = 4 \times 10^{22} \text{ J/molecule}$  or  $240 \text{ J/mole}$ . Now let's look at the degeneracy

$$g_{J=0} = 2J + 1 = 1$$

$$g_{J=5} = 2J + 1 = 11$$

So the relative population of the  $J = 5$  level vs. the  $J = 0$  level is

$$\frac{N_J}{N_{J=0}} = \frac{11}{1} e^{-(240)/8.34T} = \frac{11}{1} (0.9) = 10$$

So many rotational states are populated at room temperature, more so than non-rotating molecules.

## Spectra

Three major types of transitions can be observed in this case (with a corresponding change in  $v$ ):

1.  $\Delta J = 0$ . The photon initiates no change in the rotational quantum number. Transitions of this type are called **Q-branch** transitions
2.  $\Delta J = +1$ . The photon initiates an increase in the rotational quantum number. Transitions of this type are called **R-branch** transitions
3.  $\Delta J = -1$ . The photon initiates a decrease in the rotational quantum number. Transitions of this type are called **P-branch** transitions

These are the three major components of a vibrational transition of a molecule that has rotational levels in the vibrational transition (mostly gases).

### Initial Approximation

$B$  is the same for  $v = 0$  and  $v = 1$  (i.e., no change in the moment of inertia, hence average bond distance squared). What do the branches look like in this case?

**Q-branch:**  $J' = J$  Same Rotational Quantum number in the ground and vib. Excited state

$$\begin{aligned}\Delta\varepsilon_{mc} &= hv_0 + hB[J(J+1) - J'(J'+1)] \\ &= hv_0\end{aligned}$$

So all transitions will have same frequency regardless of initially population  $J$  levels!

**R-branch:**  $J' = J + 1$  One more Rotational Quantum number in the vib. Excited state vs. the Ground state

$$\begin{aligned}\Delta\varepsilon_{mc} &= hv_0 + hB[J(J+1) - J'(J'+1)] \\ &= hv_0 + hB[(J+1)(J+2) - J(J+1)] \\ &= hv_0 + 2hB(J+1)\end{aligned}$$

**P-branch:**  $J' = J - 1$  One less Rotational Quantum number in the vib. Excited state vs. the Ground state

$$\begin{aligned}\Delta\varepsilon_{mc} &= hv_0 + hB[J(J+1) - J'(J'+1)] \\ &= hv_0 + hB[J(J-1) - J(J+1)] \\ &= hv_0 - 2hBJ\end{aligned}$$

As seen in Figure 1, the lines of the P-branch (represented by purple arrows) and R-branch (represented by red arrows) are separated by specific multiples of  $B$  ( $2B$ ), thus the bond length can be deduced without the need for pure [rotational spectroscopy](#).

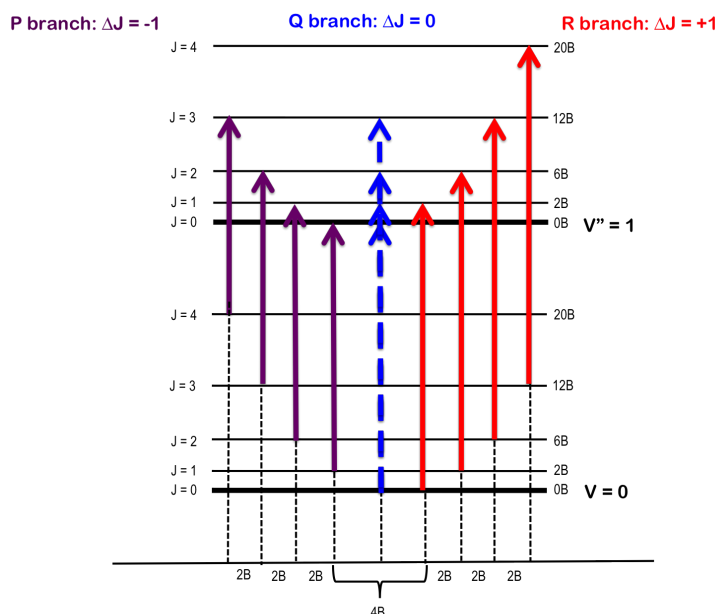


Figure 1: Cartoon depiction of rotational energy levels,  $J$ , imposed on vibrational energy levels,  $v$ . The transitions between levels that would result in the P- and R-branches are depicted in purple and red, respectively, in addition to the theoretical Q-branch line in blue.

## Spectra

Ramp over all initially populated  $J$  rotational levels and exclude  $J = 0$  (since that is the ground rotational state).

For frequencies divide by  $h$  to get:

- **P-branch:**

$$\begin{aligned}\frac{\Delta\epsilon_{mc}}{h} &= \nu^P \\ &= \nu_0 - 2BJ\end{aligned}$$

w/  $J = 1, 2, 3 \dots$

- **Q-Branch:**

$$\begin{aligned}\frac{\Delta\epsilon_{mc}}{h} &= \nu^Q \\ &= \nu_0\end{aligned}$$

for all  $J$  values

- **R-Branch:**

$$\begin{aligned}\frac{\Delta\epsilon_{mc}}{h} &= \nu^R \\ &= \nu_0 + 2BJ\end{aligned}$$

w/  $J = 0, 1, 2, 3 \dots$

The Q-branch is a single frequency at  $\nu_0$  and P-branch is a set of lines equally spaces ( $2B$ ) to lower frequencies. R-branch is a set of lines equally spaces to higher frequencies. (<https://scilearn.sydney.edu.au/spect...ce.php?res=low>)

The spectrum we expect, based on the conditions described above, consists of lines equidistant in energy from one another, separated by a value of  $2B$ . The *relative* intensity of the lines is a function of the rotational populations of the ground states, i.e. the intensity is proportional to the number of molecules that have made the transition. The *overall* intensity of the lines depends on the vibrational transition dipole moment.

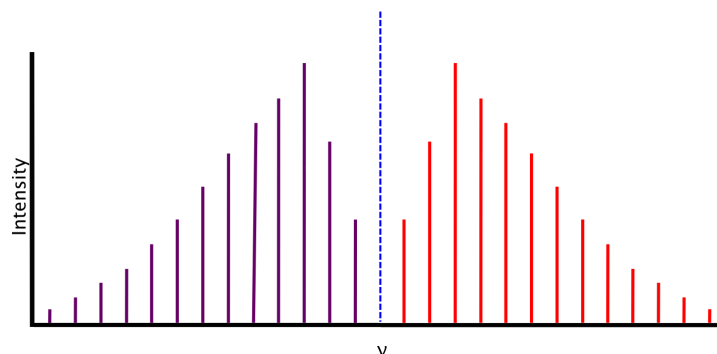


Figure 2: A cartoon depiction of an ideal rovibrational spectrum of a diatomic. Note the absence of the q-branch

### Missing Q-branches

A diatomic molecule does not exhibit a Q-branch, in general, and only P and R branches. The diatomic molecules must have electronic angular momentum about the internuclear axis in order to exhibit  $\Delta J=0$  transition. NO, a  $^2\Pi$  molecule has  $\Lambda=1$  and shows a Q-branch.  $\Sigma$  states (most ground state diatomics) do not.

Between  $P(1)$  and  $R(0)$  lies the zero gap, where the first lines of both the P- and R-branch are separated by  $4B$ , assuming that the rotational constant  $B$  is equal for both energy levels. The zero gap is also where we would expect the Q-branch, depicted as the dotted line, if it is allowed.

We find that real spectra do not exactly fit the expectations from above.

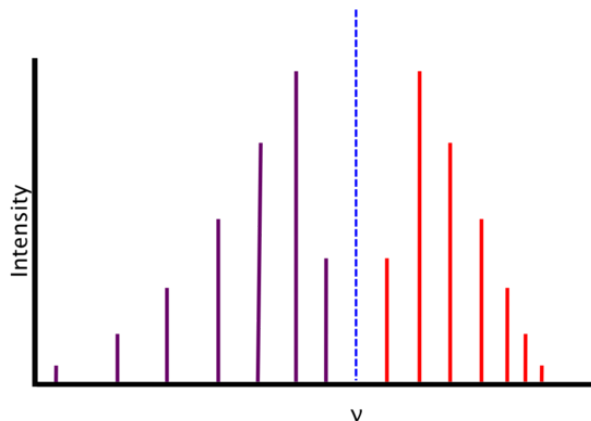


Figure 3: A cartoon depiction of a real rovibrational spectrum.

As energy increases, the R-branch lines become increasingly similar in energy (i.e., the lines move closer together) and as energy decreases, the P-branch lines become increasingly dissimilar in energy (i.e. the lines move farther apart). This is attributable to two phenomena:

1. **rotational-vibrational coupling** and
2. **centrifugal distortion**.

### Rotational-Vibrational Coupling

As a diatomic molecule vibrates, its bond length changes. Since the moment of inertia is dependent on the bond length, it too changes and, in turn, changes the rotational constant  $B$ . We assumed above that  $B$  of  $R(0)$  and  $B$  of  $P(1)$  were equal, however they differ because of this phenomenon and  $B$  is given by

$$B_e = \left( -\alpha_e \nu + \frac{1}{2} \right)$$

Where  $B_e$  is the rotational constant for a rigid rotor and  $\alpha_e$  is the **rotational-vibrational coupling constant**. The information in the band can be used to determine  $B_0$  and  $B_1$  of the two different energy states as well as the rotational-vibrational coupling constant, which can be found by the method of combination differences.

## Centrifugal Distortion

Similarly to rotational-vibrational coupling, centrifugal distortion is related to the changing bond length of a molecule. A real molecule does not behave as a rigid rotor that has a rigid rod for a chemical bond, but rather acts as if it has a spring for a chemical bond. As the rotational velocity of a molecule increases, its bond length increases and its moment of inertia increases. As the moment of inertia increases, the rotational constant  $B$  decreases.

$$F(J) = BJ(J+1) - DJ^2(J+1)^2$$

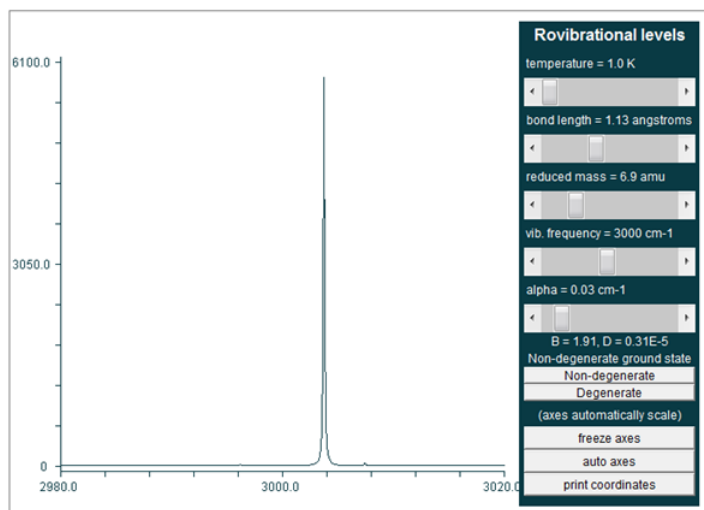
Where  $D$  is the **centrifugal distortion constant** and is related to the vibration wavenumber,  $\omega$

$$D = \frac{4B^3}{\omega^2}$$

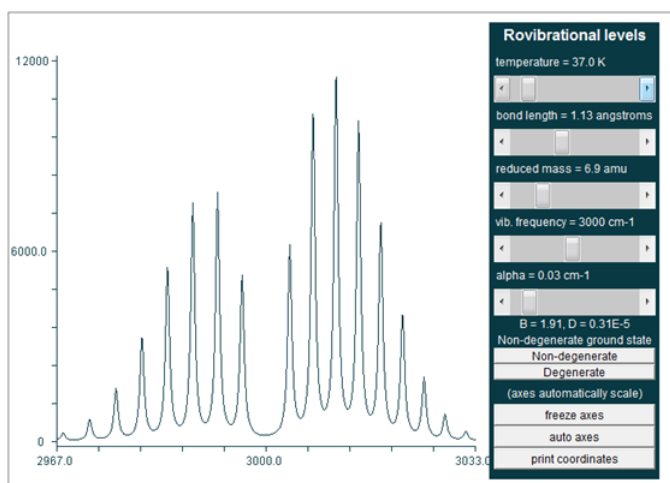
When the above factors are accounted for, the actual energy of a rovibrational state is

$$S(v, J) = \left(v + \frac{1}{2}\right) \nu_0 + B_e J(J+1) - \alpha_e \left(v + \frac{1}{2}\right) J(J+1) - D_e [J(J+1)]^2$$

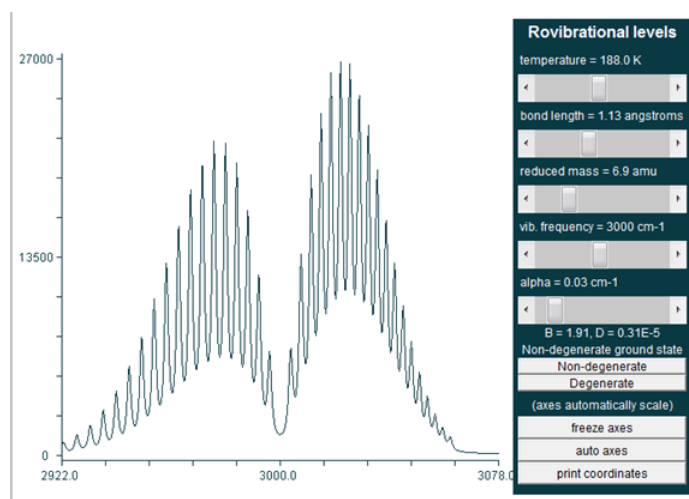
## Temperature Dependence



The rovibrational spectrum at 0K



The rovibrational spectrum at 37K



The rovibrational spectrum at 188K

Sometimes the individual rotational fine structure cannot be resolved and only the contour is observed. The relative intensities are controlled by the populations of the individual  $J$  rotational energy levels.

The ideal spectrum will NOT be observed because

1.  $B$  varies with  $v$  because of anharmonicity. It will increase as  $v$  increases, producing a decrease in  $B$  for  $v=1$  vs.  $v=0$ .
2. Centrifugal stretching in the higher  $J$  states. The bond stretches (not a rigid rotor) causing  $B$  to decrease with increasing  $J$ .
3. Selection rules. **Q-branch may not occur and usually does not occur in diatomic molecules.**

This type of vibrational spectrum is formed for any vibrational transition in a polyatomic molecule, except that the rotational analysis is not as simple as in a diatomic. Generally, P, Q, and R branches are seen.

### Linear Polyatomic Molecules (Not covered)

The shape of the rotational –vibrational transition depends on whether the vibration induces a dipole moment,  $\mu$ , along the bond axis of perpendicular to it. If  $\mu$  changes along the bond axis (as in a diatomic) we have a  $\parallel$  band with the same selection rules, e.g. no Q-branch. This is the case for the asymmetric stretch,  $\nu_3$ , of  $\text{CO}_2$ . So no Q-branch is observed in the high resolution rovibrational spectrum for this mode.

If  $\mu$  changes  $\perp$  to the bond axis, we have a  $\perp$  band. This will carry P, Q, and R branches. For example the  $\nu_2$  band (bends) of  $\text{CO}_2$ .

#### Key point!

Observation of pure rotational spectra ( $\Delta J = \pm 1$ ) in the microwave region requires that the molecule possesses a permanent dipole moment. But, rotational structure is observed in a rovibrational band from which the rotational constants can be deduced. No permanent dipole moment is required in this case. Hence rotational features in molecules like  $\text{CO}_2$ .

### Spin Statistics (Not covered)

In some molecules with equivalent sets of nuclear, certain rotational and vibrational states do not occur or occur with reduced statistical weights because of the fact that half integral spin nuclei obey Fermi statistics while 0 and integer spin nuclei obey Bose-Einstein statistics. We do not have the time here to discuss this aspect in more detail.

$$\hat{P}_{12}\Psi(1, 2) = +\Psi(1, 2)$$

Where the exchange operator switches the two equivalent nuclei (like in a rotation). This case the eigenvalue is positive and the wavefunction acts as a **Boson ( $I=\text{integral}$ )**

$$\hat{P}_{12}\Psi(1, 2) = -\Psi(1, 2)$$

Where the exchange operator switches the two equivalent nuclei (like in a rotation). This case the eigenvalue is negative and the wavefunction acts as a **Fermion ( $I=\text{half integral}$ )**

This has consequences on which rovibrational states occur and what their statistical weight is. This is only a consideration with molecules with equivalent nuclei.

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