Combination Differences

In high resolution spectroscopy, it possible to resolve rotational fine structure along with vibrational transitions. To understand this, first note that any vibrational state will have it's own set of rotational states that are 'nested' inside the vibrational state. These have energies given by $F(J) = B_v J(J+1)$[1], where $F(J)$ is the energy (in wavenumbers) of the J^{th} level, and B_v is the **rotational constant** associated with this specific vibrational state. The rotational constant is just a proportionality constant between F_J and $J(J+1)$. We know that:

$$B_v = \frac{h}{8\pi^2 cI} = \frac{h}{8\pi^2 c\mu R^2} \tag{1}$$

Where I is the moment of inertia of the rotor, which is given by $I = \mu R^2$ in the case of a diatomic molecule. All other symbols have their usual meanings. Note here that B_v is given in wavenumbers.

From this, we see clearly that the rotational constant is inversely proportional to R^2, where R is the bond length of our diatomic. When we excite a **vibration** in our molecule, this bond will start to stretch and vibrate - it should, therefore, make intuitive sense that the rotational constant will be **slightly different in each different vibrational state**.

These differences are quite small, and actually for low levels of excitation saying that $B_1 = B_0 = B$ isn't an awful approximation. But with high resolution spectroscopy we don't need to assume this, we can use **combination differences** to find out different rotational constants, and then extrapolate to an *equilibrium* bond length of the molecule.

Now let us consider what happens when a molecule undergoes ro-vibrational excitation[2]. Quite simply, we excite the vibration (say, from $v = 0 \to 1$), and then can excite rotations alongside it. If the rotations we excite correspond to an *increase* in J, (i.e $\Delta J = +1$), this produces an 'R-Branch' in the spectrum. Conversely, if the rotations correspond to a *decrease* in J ($\Delta J = -1$), then this produces a 'P-Branch'[3]. We can write expressions for a particular ro-vibrational state, if we assume the vibrations behave as a harmonic oscillator, and the rotations as a rigid rotor, then:

$$S(v,J) = G(v) + F(J) = (v + \frac{1}{2})\hbar\omega + B_v J(J+1) \tag{2}$$

Simply the sum of a vibrational level and rotational level! All symbols have their usual meanings. Let us now imagine we do an arbitrary excitation from v to $v+1$, and from J to J' - the energy of the *spectral line*, E, would be:

$$E = S(v+1, J') - S(v,J) = \left[(v + \frac{3}{2})\hbar\omega + B_{v+1}J'(J'+1)\right] - \left[(v + \frac{1}{2})\hbar\omega + B_v J(J+1)\right] \tag{3}$$

Which simplifies down to:

$$E = \hbar\omega + B_{v+1}J'(J'+1) - B_v J(J+1) \tag{4}$$

Which is an expression for a generic rovibrational line, under the harmonic oscillator and rigid rotor approximations. We haven't decided if our rotational transition will be in the R or P branch, so let's do that now.

First taking the R-branch, where $J' = J+1$. To help us keep track of all the different J's, let's call the J value for the initial state in the R-branch J_R, such that our transition is from $J = J_R$ to $J' = J_R + 1$. The energy of an R-Branch line, E_R, is therefore:

$$E_R = \hbar\omega + B_{v+1}(J_R^2 + 3J_R + 2) - B_v(J_R^2 + J_R) \tag{5}$$

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[1] Within the rigid rotor approximation.

[2] The excitation of rotations and vibrations simultaneously

[3] The 'R' and 'P' designations actually come from the French: 'Riches' and 'Pauvres'. However, they could just as easily come from English 'Rich' and 'Poor', so presumably in post-Brexit Britain this particular nugget of spectroscopic history will be whitewashed.

And similarly, a P-branch line, E_P, from $J = J_P$ to $J' = J_P - 1$, is:

$$E_P = \hbar\omega + B_{v+1}(J_P^2 - J_P) - B_v(J_P^2 + J_P) \tag{6}$$

Convince yourself that these are correct by writing it out in full!

Now we have expressions for a generic R and P branch line, we are well on the way to extracting useful information from our spectrum, so let's take stock and remember what our aim actually is. We want to find out the rotational constants B_v and B_{v+1}, so that we can extrapolate to find the equilibrium rotational constant B_e, and therefore the equilibrium bond length. This is **not** the same B_0, because there is a vibrational zero-point energy - we want the bond length at the **bottom of the harmonic well**, not at the zero-point level. An obvious question, therefore, is 'How are B_e and B_v linked?'. The answer is:

$$B_e = B_v + \alpha(v + \frac{1}{2}) \tag{7}$$

Where α is a parameter we need to determine. So we have two unknowns, B_e and α, so it makes sense that we need to have two equations (two different B_v values) to find them both. Therefore, our mission is to **find two values of** B_v that we can use.

Let's now turn back to our expressions for an R and a P branch line. Let's also now assume that our vibrational excitation was from $v = 0$ to $v = 1$, so we can write them:

$$E_R = \hbar\omega + B_1(J_R^2 + 3J_R + 2) - B_0(J_R^2 + J_R) \tag{8}$$

$$E_P = \hbar\omega + B_1(J_P^2 - J_P) - B_0(J_P^2 + J_P) \tag{9}$$

So, quite simply, we need to eliminate B_1 or B_0 from these equations by taking the difference of the two lines, and in general the way we can do that is as follows. To eliminate B_0 by taking a difference, we require that:

$$J_R^2 + J_R = J_P^2 + J_P \tag{10}$$

Such that:

$$E_R - E_P = B_1(J_R^2 + 3J_R + 2 - J_P^2 + J_P) \tag{11}$$

Now, when is equation (10) satisfied? Clearly only when $J_R = J_P = J$ - i.e. when both the R and the P branch line have a **common initial state** such that:

$$E_R - E_P = B_1(4J + 2) \tag{12}$$

Where J is the quantum number for the common initial state. Often, you will be given examples where two lines originate from $J = 1$, and then clearly the difference between two lines is equal to $6B_1$.

Alternatively, we could try to eliminate B_1. This would require that:

$$J_R^2 + 3J_R + 2 = J_P^2 - J_P \tag{13}$$

This condition is true when $J_P = J_R + 2$. This is tricker to conceptualise, but means the the initial state of the P-branch line is two quantum numbers higher than the initial state of the R-branch line. This, my friends, means that the **final state** of the R-branch line is $J_R + 1$ (as J_R was the initial state), and the final state of the P-branch line is $J_P - 1 = J_R + 2 - 1 = J_R + 1$. Therefore, we can eliminate B_1 by taking the difference of two lines with a **common final state**. We could follow the same process again, and would find that if the common final state is given by $J_R + 1 = 1$, then the difference of the two lines is $6B_0$, in an analogous way to before.

So, having done this, we will have found values for B_0 and B_1, which we can bang into equation (7) to find B_e and α. A good check for when you've done this is to note that at higher vibrational excitations, the B constant will decrease as R increases - so you should find B_e is bigger than both B_0 and B_1.