

# Energy, Spectroscopy and Solid State Chemistry

## §1 SPECTROSCOPY

### §1.1 INTRODUCTION

28/10/20 — WEEK 1

#### §1.1.1 The Born-Oppenheimer Approximation

The assumption that the electronic motion and the nuclear motion in molecules can be separated, due to the difference in mass between the electron and the nuclei.

$$\Psi_{tot} = \psi_{el}\psi_{nuc}$$

Where the resulting total energy is a simple sum.

$$E_{tot} = E_{el} + E_{nuc}$$

It is very convinient, although slightly less rigorous, to factorise  $\Psi_{nuc}$  into vibrational and rotational parts. Translational energy is unquantised and so useless for spectroscopy.

$$\Psi_{tot} = \psi_{el}\psi_{vib}\psi_{rot}$$

$$E_{tot} = E_{el} + E_{vib} + E_{rot}$$

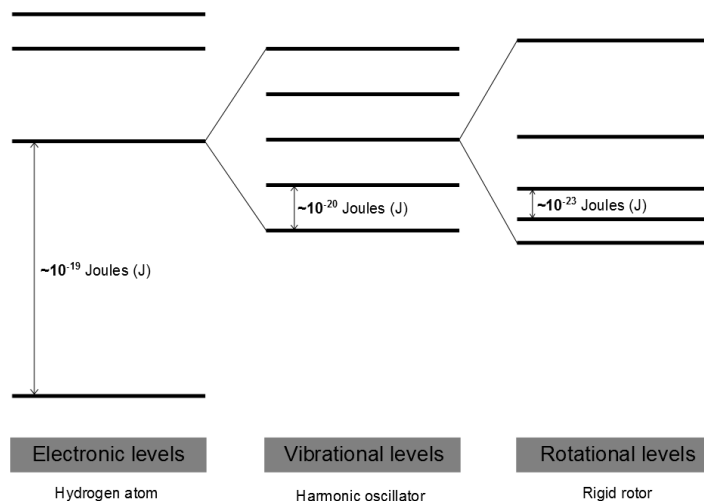


Figure 1: Transitions of different energy levels

$\Delta E \approx$	$10^4 - 10^5 \text{ cm}^{-1}$	$10^2 - 10^3 \text{ cm}^{-1}$	$0.1 - 10 \text{ cm}^{-1}$
Transitions at $\Delta \lambda \approx$	$500 - 100 \text{ nm}$	$100 - 2 \mu\text{m}$	$10 \text{ cm} - 1 \text{ mm}$
Light range	Vis-UV	Infrared	Microwave

Every electronic energy level contains multiple vibrational levels which contains multiple rotational levels. More on this to come.

### §1.1.2 The Boltzmann Law

At thermal equilibrium the relative population of the  $i^{\text{th}}$  energy level is given by:

$$\frac{n_i}{n_0} = \frac{g_i}{g_0} e^{-\frac{\Delta E_i}{k_B T}}$$

- $g_i$  is the degeneracy of the  $i^{\text{th}}$  level (the number of states with the same energy)
- $\Delta E_i$  is the energy difference between the lowest (ground) and  $i^{\text{th}}$  levels
- $k_B$  is the Boltzmann constant
- $T$  is the temperature (in Kelvin, obviously)

☞ Degeneracy is when there are multiple energy levels with the same energy. Think back to a Hydrogen atom, only  $n$  determines its energy, yet it has different states which are determined by  $l$  and  $m_l$ , thus it has degenerate states. When  $n = 2$  and  $l = 0, 1$  there are  $(2l + 1)$  states for  $m_l$ , each with the same energy. Thus the degeneracy of the  $n = 2$  energy level is  $(2(0)+1)+(2(1)+1) = 4$ .

Example: Find the relative populations of the lowest two energy levels for each in a CO molecule at 298K if

1. The two lowest rotational levels are  $3.382 \text{ cm}^{-1}$  apart with  $g_1 = 3$  and  $g_0 = 1$
2. The two lowest vibrational levels are  $1743 \text{ cm}^{-1}$  apart each with a degeneracy of 1
3. The two lowest electronic levels are  $48690 \text{ cm}^{-1}$  apart with  $g_1 = 6$  and  $g_0 = 1$

Since we are given the energy spacings in  $\text{cm}^{-1}$  we should convert our  $k_B T$  to  $\text{cm}^{-1}$  by using  $\frac{E}{hc} = \nu$  so  $k_B T = 207 \text{ cm}^{-1}$ . From here the calculations are relatively simple.

1.  $\frac{3}{1} e^{-\frac{3.382}{207}} = 2.95$
2.  $\frac{1}{1} e^{-\frac{1743}{207}} = 2.24 \times 10^{-4}$
3.  $\frac{6}{1} e^{-\frac{48690}{207}} = 4.2 \times 10^{-102}$  so small it might as well be 0

What does this tell us? At normal temperatures there is enough energy to promote to higher rotational energy levels. Since  $k_B T = 207 \text{ cm}^{-1}$  and rotational levels are separated by only  $10 \text{ cm}^{-1}$  this should be obvious. It is also clear that there is nowhere near enough energy at normal temperatures for there to be much vibrational transition, and not enough energy for there to be any electronic transitions at all.

## §2 ATOMIC WAVEFUNCTIONS ET AL.

WEEK 2

For a one electron atom or ion, X, the energy only depends on the principal quantum number.

$$E = -\frac{Z^2 R_x}{n^2}$$

$Z$  = nuclear charge,  $R_x$  is the Rydberg constant for that atom or ion.

Example: calculate the energy of an electron in the 2s orbital of Hydrogen, where  $R_H = 109678.7717 \text{ cm}^{-1}$ . This will give the answer in  $\text{cm}^{-1}$  since  $R_H$  is in  $\text{cm}^{-1}$ , that is really the wavenumber instead of the energy.  $\tilde{\nu} \text{ cm}^{-1} = -\frac{Z^2 R_x (\text{cm}^{-1})}{n^2}$ , however in spectroscopy we can say that the energy is in  $\text{cm}^{-1}$ . We can also multiply  $R_H$  by  $hc$  to convert it to J.

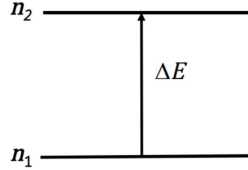
So carrying on with the example  $E (\text{cm}^{-1}) = -\frac{1^2 \cdot 109678.7717}{2^2} = -27,419.69 \text{ cm}^{-1}$

## §2.1 RYDBERG CONSTANT

$$R_X(\text{cm}^{-1}) = \frac{\mu e^4}{8h^3 \tilde{c} \epsilon_0^2} \quad \tilde{c} \text{ is } c \text{ in } \text{cm s}^{-1}$$

$$\mu = \frac{m_e m_N}{m_e + m_N}$$

Where  $\mu$  is the reduced mass,  $m_e$  is the mass of an electron and  $m_N$  is the mass of the nucleus.



The change in energy of an electron when changing level is

$$\Delta E = Z^2 R_X \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

When changing energy we can change  $n$  however we like, however  $l$  is restricted to only  $\pm l$ . So we can go from 1s to 3p, however not to 2s or 3d etc.

How do we calculate the ionisation energy (IE) of a Hydrogen atom ( $Z = 1$ )? An atom is ionised when  $n \rightarrow \infty$ , so

$$IE = \Delta E = 1^2 R_H \left( \frac{1}{1^2} - \frac{1}{\infty^2} \right) = R_H$$

## §2.2 ANGULAR MOMENTA

For a spectra of atoms/ions with more than one electron each electron will have its own set of  $n, l, m_l, s$  and  $m_s$ . The angular momenta ( $l$ ) of different electrons can couple together in different ways which will have different energies. Since they determine the energy levels they determine spectroscopy i.e. lines we see on a spectrum. Considering different spins and angular momenta is called Russel-Saunders coupling.

### §2.2.1 Coupling Spin

Consider two electrons, 1 and 2, each has  $s_1 = s_2 = \frac{1}{2}$  and  $m_s = +\frac{1}{2}$  or  $-\frac{1}{2}$ . If  $S$  is the overall spin of the two electron system then the allowed values from the Clebsch-Gordan series:

$$S = s_1 + s_2, (s_1 + s_2) - 1 \dots |s_1 - s_2|$$

So the allowed values of  $S$  are  $\frac{1}{2} + \frac{1}{2} = 1$  and  $\frac{1}{2} - \frac{1}{2} = 0$

### §2.2.2 Coupling Orbital Angular Momenta

Again, consider two electrons, they will have orbital angular momenta of  $l_1$  and  $l_2$ . The value of these could be any real positive integer, 0, 1, 2... If  $L$  is the total orbital angular momenta of the combined system then the allowed values again come from the Clebsch-Gordan series:

$$L = l_1 + l_2, (l_1 + l_2) - 1, (l_1 + l_2) - 2, / \dots |l_1 - l_2|$$

So if  $l_1 = 2$  and  $l_2 = 3$  then we have a highest value of  $2 + 3 = 5$  and a lowest value of  $|2 - 3| = 1$ . So  $L$  has a range of values of  $L = 5, 4, 3, 2, 1$

### §2.2.3 Coupling Spin and Orbital Angular Momenta

We have  $S$  and  $L$  for a two-electron atom, we can combine these to get the allowed values of the spin-orbit angular momentum,  $J$ . Unsurprisingly we use a Clebsch-Gordan series:

$$J = L + S, L + S - 1, \dots |L - S|$$

So if both  $L$  and  $S$  are 1, then the allowed values of  $J$  are 2, 1 and 0

### §2.2.4 Many electron atom

For any electron in a many-electron atom it will have its own values of  $l, m_l, s, m_s, j$ . However the system as a whole (the entire atom) will have its own values of  $L, M_L, S, M_S, J$ .

$$M_L = L, L - 1, \dots -L$$

$$M_S = S, S - 1, \dots -S$$

$$M_L = \sum m_l$$

$$M_S = \sum m_s$$

## §2.3 ATOMIC TERM SYMBOLS AND TRANSITIONS

$$^{2S+1}L_J \quad \text{e.g.} \quad {}^2P_{\frac{3}{2}}$$

- $2S + 1$  is the "spin multiplicity,  $S$  is the total spin quantum number for the atom
- $L$  is the total orbital angular momentum quantum number for the atom

In the same vein of s, p, d and f orbitals the same applies to  $L$

$$S : L = 0$$

$$P : L = 1$$

$$D : L = 2$$

$$F : L = 3$$

- $J$  is the total angular momentum quantum number for the atom, i.e. how  $L$  and  $S$  are coupled

A p-orbital has  $l = 1$ , thus  $m_l = +1, 0, -1$ , instead of using  $p_x, p_y, p_z$  we will use the  $m_l$  numbers instead.

$$\begin{array}{ccc} \boxed{1} & \boxed{1} & \boxed{1} \\ m_l = +1 & m_l = 0 & m_l = -1 \end{array}$$

Electron spin is represented with up ( $m_s = +\frac{1}{2}$ ) and down ( $m_s = -\frac{1}{2}$ ) arrows  $\boxed{\uparrow\downarrow}$

### §2.3.1 Closed-shell atoms

A closed (sub)shell atom is any atom for which all of the electrons are paired.

$$\boxed{\uparrow\downarrow} \\ m_l = 0$$

$$M_s = \sum m_s = S, S - 1, \dots -S$$

Well we know for He that we have two electrons, where  $m_s = \pm \frac{1}{2}$  so  $M_S = 0$ . This is the only value we could have for He so  $S = 0$  as well. This is true for every closed shell atom (like the Noble gasses).

$$M_L = \sum m_l = L, L-1, \dots -L$$

For an s orbital  $l = 0$  and so  $m_l = 0$  as well, thus  $M_L = 0$ , this also means that  $L = 0$  for helium, and as such  $J = 0$  too, we know this from the equations above. This is true for all closed shell atoms. So our term symbol for He is thus  $^1S_0$ , this is read as “singlet S 0”, this is the same for all closed shell atoms, e.g. Ne,  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ , we call these singlet states.

### §2.3.2 Alkali Metal Atoms

We know they have a single unpaired electron in an s orbital  $\boxed{1}$

So for Potassium, which has an electronic config of  $[\text{Ar}] 4s^1$ , up until the  $4s^1$  shell it is a closed shell atom, and so overall it will have values  $S = 0$  and  $L = 0$ . So we can consider it as a single unpaired electron,  $m_s = \frac{1}{2}$  and so  $s = \frac{1}{2}$  thus  $S = \frac{1}{2}$ . The electron is in an s orbital, so  $l = 0$ ,  $m_l = 0$  hence  $L = 0$ .

$$J = L + S, L + S - 1 \dots |L - S| = 0 + \frac{1}{2}, |0 - \frac{1}{2}| = \frac{1}{2}$$

$$^2S_{\frac{1}{2}}$$

This term symbol is the same for all Alkali metal atoms, since the only difference between them is the size of the closed shell, which always gives 0. The same applies to other elements with a closed shell before a  $ns^1$  electronic config, like Copper.  $[\text{Ar}] 3d^{10} 4s^1$

What happens if we excite an alkali metal atom so that the outermost s orbital electron is moved up into a p orbital? For potassium that would give a configuration of  $[\text{Ar}] 4p^1$

$$\begin{array}{ccc} \boxed{1} & \boxed{\phantom{1}} & \boxed{\phantom{1}} \\ m_l = +1 & m_l = 0 & m_l = -1 \end{array}$$

We can forget about  $[\text{Ar}]$  since they only give 0, and so  $s = \frac{1}{2}$ ,  $m_s = \frac{1}{2}$ ,  $S = \frac{1}{2}$ . But now the electron is in a p orbital so  $l = 1$ ,  $L = 1$ .

$$J = L + S, L + S - 1 \dots |L - S| = \frac{3}{2}, \frac{1}{2}$$

So now we have two term symbols, these are two different electronic states that will have different energies. This will give us two different states in spectroscopy. Since  $2S + 1 = 2$  we call these states “doublet” states.

$$^2P_{\frac{3}{2}} \quad \text{and} \quad ^2P_{\frac{1}{2}}$$

### §2.3.3 What do we see in the spectrum?

We have selection rules,  $\Delta J = 0, \pm 1$ , we can leave J unchanged (but not going from 0 to 0), but we have to change our orbital, i.e. l has to change, this is due to photons having an angular momentum.  $\Delta S = 0$ , since photons have no spin.

So when we promote, say, a Sodium atom, from  $3s$  to  $3p$  the term symbol goes from  $^2S_{\frac{1}{2}}$  to either  $^2P_{\frac{3}{2}}$  or  $^2P_{\frac{1}{2}}$ , these two final states are slightly different in energy. We can confirm our that changes are valid,  $S = \frac{1}{2}$  does not change on the transition to/from the s/p orbital. However  $J$  does change, but only for  $\Delta J = 0, 1$ , so it is valid.

The intensity of the transition is determined by the relative degeneracy of the upper levels, which is  $2J + 1$ . So we have a ratio of 2:1 for our transitions of Sodium. The 3 in front of the term symbols is the energy level i.e. 3

$$3^2P_{\frac{3}{2}} \rightarrow 3^2P_{\frac{1}{2}} \quad 2 \cdot \frac{3}{2} = 4$$

$$3^2P_{\frac{1}{2}} \rightarrow 3^2P_{\frac{1}{2}} \quad 2 \cdot \frac{1}{2} = 2$$

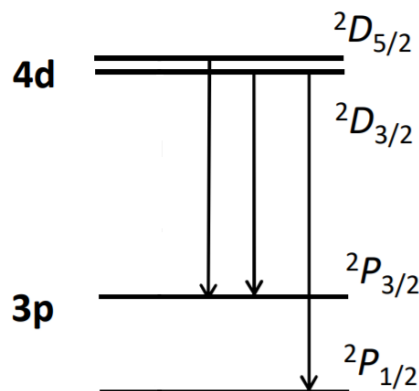
What happens if we transition Sodium to a  $4d^1$  orbital? This will give an electronic config of  $[\text{Ne}] 4d^1$

$$s = \frac{1}{2}, \quad S = \frac{1}{2}$$

$$l = 2, \quad L = 2$$

$$J = L + S, \dots |L - S| = \frac{5}{2}, \frac{3}{2}$$

We cannot have a transition from  $^2D_{\frac{5}{2}}$  to  $^2P_{\frac{1}{2}}$  as  $\Delta J = 2$  which breaks our selection rules.  $^2D_{\frac{5}{2}}$  and  $^2D_{\frac{3}{2}}$  are very close in energy and so if the resolution of our equipment isn't low enough we may see only 2 peaks for the transitions from d to p, this is always something to consider.



## §2.4 MORE ATOMIC TERM SYMBOLS

Consider a Carbon atom in its ground state  $[\text{Be}] 2p^2$ , so we have  $s_1 = s_2 = \frac{1}{2}$  thus  $S = 0, 1$

$$s_1 = s_2 = \frac{1}{2} \quad \text{thus} \quad S = 0, 1$$

$$l_1 = l_2 = 1 \quad \text{thus} \quad l = 0, 1, 2$$

$$^1S, ^3S, ^1P, ^3P, ^1D, ^3D \text{ Different "states"}$$

Lets look closer at the  $^3D$  term,  $L = 2$  and so it must have an  $M_L = 2$  component, so we must have an  $m_l = 1$  for each electron as  $\sum m_l = M_L$ , and we have two electrons. For the triplet D state ( $^3D$ ) it must have  $S = 1$  as  $3 = 2S + 1$ , so it must have an  $M_S = 1$  component which means that  $m_s = \frac{1}{2}$  for each electron.

$$\begin{array}{ccc} \uparrow\uparrow & \text{---} & \text{---} \\ m_l = +1 & m_l = 0 & m_l = -1 \end{array}$$

This would mean that there would be two up ( $m_s = \frac{1}{2}$ ) spin electrons with the same  $m_l$ , they have the same quantum numbers, this violates the pauli exclusion principle.

### §2.4.1 Hund's Rules

Within Russell-Saunders coupling, for a given configuration, in its **ground state**:

1. The term with the largest  $S$  is lowest in energy
2. For a given  $S$  the term with the largest  $L$  is lowest in energy
3. For a term with several levels:
  - if the sub-shell is less than half full then the lowest  $J$  level is the lowest in energy
  - if the sub-shell is more than **or** half full then the highest  $J$  level is lowest in energy

To find the ground state of a Carbon atom we work through these rules.

1. Largest  $S$  (and so largest  $M_S$ ), so parallel spins ( $m_s$  are the same)
  - $S = \frac{1}{2} + \frac{1}{2}, \frac{1}{2} - \frac{1}{2}, = 1, 0$
  - $M_S = \frac{1}{2} + \frac{1}{2} = 1$
2. For a given  $S$ , largest  $L$  (and so largest  $M_L$ ), so the two highest  $m_l$  are needed
  - $m_l = 1, 0$
  - $M_L = 1 + 0 = 1 = L$
3.  $J = L + S, L + S - 1, \dots |L - S| = 2, 1, 0$ 
  - Since our orbital is less than half filled then  $J$  must take the lowest value, so  $J = 0$

$$\begin{array}{ccc} \boxed{1} & \boxed{1} & \boxed{\phantom{1}} \\ m_l = +1 & m_l = 0 & m_l = -1 \end{array}$$

Putting this all together gets the ground state of Carbon to be  $^3P_0$

This is similar to Carbon. We have two extra electrons, obeying Hund's rules we add it to  $m_l = -1$  with the same spin as the other two, and then with the one left over it has to have the opposite spin but go with the highest  $m_l$ . Our orbital is now more than half full and so we must go with the highest  $J$  value.  $^3P_2$

$$\begin{array}{ccc} \boxed{\uparrow\downarrow} & \boxed{\uparrow} & \boxed{\uparrow} \\ m_l = +1 & m_l = 0 & m_l = -1 \end{array}$$

Now let us consider a Nitrogen atom,  $[\text{Be}] 2p^3$ . Obeying the first rule we know they should all have parallel spins so  $m_s = +\frac{1}{2}$  for each electron. Obviously they all need different  $m_l$  values.  $M_S = 3\frac{1}{2} = \frac{3}{2}$  and  $M_L = 1 + 0 - 1 = 0$ . So we take the highest  $S$  value,  $\frac{3}{2}$  and the highest  $L$  value, 0, which means that  $J = \frac{3}{2} + 0$ , we take the highest  $J$  value since our shell is only half full.  $^4S_{\frac{3}{2}}$

$$\begin{array}{ccc} \boxed{1} & \boxed{1} & \boxed{1} \\ m_l = +1 & m_l = 0 & m_l = -1 \end{array}$$

Consider a Fluorine atom now, this is symmetrically similar to Boron.

$$\begin{array}{ccc}
 \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow} & \boxed{\uparrow} \\
 m_l = +1 & m_l = 0 & m_l = -1 \\
 \\ 
 \boxed{\uparrow} & \boxed{\phantom{\uparrow\downarrow}} & \boxed{\phantom{\uparrow\downarrow}} \\
 m_l = +1 & m_l = 0 & m_l = -1
 \end{array}$$

For Fluorine we have

- $M_S = 3\frac{1}{2} - 2\frac{1}{2} = \frac{1}{2} = S$
- $M_L = 1 + 0 - 1 + 1 + 0 = 1 = L$
- $J = \frac{3}{2}, \frac{1}{2}$

Since this has one unpaired electron we will get the same term ( $^2P$ ) as a single unpaired electron. And now we just need to consider if the subshell is half full or half empty for our J value.

- $M_S = \frac{1}{2} = S$
- $M_L = 1 = L$
- $J = \frac{3}{2}, \frac{1}{2}$

For Boron  $^2P_{\frac{1}{2}}$  and for Fluorine  $^2P_{\frac{3}{2}}$ , this is a very useful symmetry, that would also apply for two unpaired electrons.

#### §2.4.2 Examples

Term symbols for Arsenic, Phosphorus and Selenium<sup>+</sup>. Notice how they all have the same electronic configuration after the closed shells,  $p^3$ . This means they're isoelectric and so will have the same term symbol.

- $M_S = 3\frac{1}{2} = \frac{3}{2} = S$
- $M_L = 1 + 0 - 1 = 0 = L$
- $J = \frac{3}{2}$
- $^4P_{\frac{3}{2}}$

Another example for Cl, Cl<sup>-</sup>, Cl<sup>+</sup>. They are no isoelectric and so will have different term symbols, not to worry. For Cl  $3p^5$ , we can treat it like a single electron atom.

- $M_S = \frac{1}{2}$
- $M_L = 1$
- $J = \frac{3}{2}, \frac{1}{2}$
- Since the subshell is more than half full we use the highest J value
- $^2P_{\frac{3}{2}}$

Cl<sup>-</sup> has one more electron, thus making it a closed shell ion, so it will be  $^1S_0$ . Cl<sup>+</sup> has a config of  $3p^4$ , we can treat this as a two unpaired electron atom.

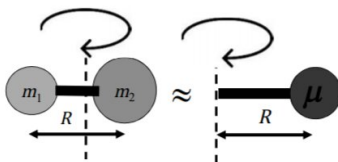
- $M_S = 1$
- $M_L = 1$
- $J = 2, 1, 0$
- Since the subshell is more than half full we use the highest J value
- $^3P_2$



### §3 ROTATIONAL SPECTROSCOPY

WEEK 3

For a diatomic molecule, the masses of the two nuclei are  $m_1$  and  $m_2$ . We can instead model this as a single atom of mass  $\mu$  rotating a distance  $R$  away from its axis.  $I = \mu R^2$ ,  $I$  is the moment of inertia, it is the rotational equivalent to mass.



If we solve the Schrödinger equation for rotational motion and find the eigenvalues (energies). We get an expression, where  $F(J)$ , or  $E_J$ , is the rotational energy,  $J$  is the rotational quantum number, where  $J = 0, 1, 2, 3, \dots$  and  $B$  is the rotational constant given by  $B = \frac{\hbar^2}{2I}$ , it depends on the molecule.

$$F(J) = E_J = BJ(J+1)$$

For molecules with Hydrogen we get values in the  $10 - 100 \text{ cm}^{-1}$  range, but without Hydrogen they are single digit. There is obviously no energy when there is no rotation,  $F(0) = 0$ . With each increasing  $J$  the energy levels space out more because of the  $J^2$  term in  $F(J)$

#### §3.1 THE ROTATIONAL CONSTANT $B$

Although  $B$  should be given in Joules, in microwave (rotational) spectroscopy we use Hertz.

$$\begin{aligned} B(\text{J}) &= \frac{\hbar^2}{2I} = \frac{h^2}{8\pi^2 I} & \text{since } E &= hf \\ B(\text{Hz}) &= \frac{h}{8\pi^2 I} & \text{since } E &= \frac{hc}{\lambda} \\ B(\text{cm}^{-1}) &= \frac{h}{8\pi^2 I \tilde{c}} & \tilde{c} & \text{is } c \text{ in } \text{cm s}^{-1} \end{aligned}$$

#### §3.2 ROTATIONAL SELECTION RULES

A molecule must have a permanent dipole moment for it to exhibit a pure rotational (microwave) spectrum. It cannot be linear e.g.  $\text{CO}_2$ , however it can be linear and asymmetric, e.g.  $\text{N}_2\text{O}$  which is N-N-O. Transitions can only change by 1, i.e.  $\Delta J = \pm 1$

$$\begin{aligned} F(J) &= BJ(J+1) \\ \Delta F(J) &= \tilde{\nu}(J) = F(J+1) - F(J) \\ &= B(J+1)(J+2) - BJ(J+1) \\ &= 2B(J+1) \end{aligned}$$

So the transitions that we see on a microwave spectrum will be equally spaced by  $2B$ . We do not see any transitions from rotations about the axis that goes *through* the molecule. Rotations from the other two axes are indistinguishable from each other, they are degenerate.

$B \propto \frac{1}{I} = \frac{1}{\mu R^2}$  Thus we can get an accurate value for bond length through microwave spectroscopy.  $B$  is isotope dependent, so so two isotopes will have different spacings. In the absence of any external fields, for each  $J$  level there are  $2J+1$  levels with the same energy (degenerate) for each  $J$  level, this comes from the  $M_J$  projection quantum number, we will assume there is no external field.

### §3.3 POPULATIONS OF THE ROTATIONAL LEVELS

From the Boltzmann distribution

$$n_J \propto g_J \exp\left(-\frac{F(J)}{k_B T}\right) = (2J+1) \exp\left(-\frac{BJ(J+1)}{k_B T}\right)$$

We saw earlier that the degeneracy for each  $J$  is  $g_J = (2J+1)$  and  $F(J) = BJ(J+1)$

The most populated level occurs at the turning point of the function, so  $dn_J/dJ = 0$

$$\frac{dn_J}{dJ} = \left(2 - (2J+1)^2 \frac{B}{k_B T}\right) \exp\left(-\frac{BJ(J+1)}{k_B T}\right) = 0$$

Since an exponential cannot be zero except for at negative infinity the term that must go to zero is its coefficient.

$$2 - (2J_{\max} + 1)^2 \frac{B}{k_B T} = 0$$

$$J_{\max} = \sqrt{\frac{k_B T}{2B}} - \frac{1}{2}$$

### §3.4 CENTRIFUGAL DISTORTION

Are molecules rigid? Unfortunately, no. As the molecule is rotated the atoms move further apart, so  $I$  will change with  $J$ . However this is small enough that we can account for it in a clever way.

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

$D$  is the centrifugal distortion constant, in  $\text{cm}^{-1}$ .  $D$  is very small, ( $10^{-5} - 10^{-3}$ ). As  $J$  increases the *centrifugal distortion* caused by the non-rigidity will get bigger and bigger and bring down  $F(J)$  more, causing it to deviate the higher  $J$  gets.

The transitions (spacing between the levels, wavenumber) when accounting for centrifugal distortion

$$\begin{aligned} \Delta F(J) &= \tilde{\nu}(J) = F(J+1) - F(J) \\ &= 2B(J+1) - 4D(J+1)^3 \\ \frac{\tilde{\nu}(J)}{J+1} &= 2B - 4D(J+1)^2 \end{aligned}$$

From this we can form a plot, where  $y = \frac{\tilde{\nu}(J)}{J+1}$ ,  $x = (J+1)^2$ , the y-intercept is  $2B$  and the *gradient* is  $-4D$

### §3.5 VIBRATIONAL FREQUENCY

Since the molecule stretches slightly when rotating, we can deduce something about the strength of the bond. This is called the vibrational frequency,  $\omega_e$ , it can be shown (but we won't) that

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

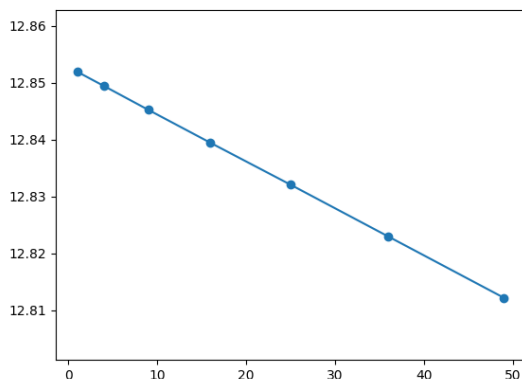
#### §3.5.1 Example

The pure rotational spectrum for HI has been measured and has lowest observed line positions as follows.

$\frac{\Delta F(J)}{J+1}/\text{cm}^{-1}$
12.8519
25.6877
38.5358
51.3580
64.1602
76.9376
89.6852

So we need to plot  $\frac{\Delta F(J)}{J+1}$  against  $(J+1)^2$ , where  $2B$  will be the intercept and  $-4D$  the slope.

$\frac{\Delta F(J)}{J+1}$	$(J+1)^2$
12.8519	1
12.8494	4
12.8452	9
12.8494	16
12.8320	25
12.8229	36
12.8121	49



From this plot we can derive our gradient and intercept and get  $B = 6.4265\text{cm}^{-1}$  and  $D = 2.069 \times 10^{-4}\text{cm}^{-1}$  so  $\omega_e = 2265\text{cm}^{-1}$

#### §3.5.2 Practice

- $\text{H}_2$  has no rotational spectra because it does not have a dipole moment.
- $\text{HBR}$  has a rotational spectra because it has a dipole moment.
- $\text{CO}_2$  has no rotational spectra because it is linear.
- $\text{H}_2\text{O}$  has a rotational spectra because it is not linear.
- $\text{N}_2\text{O}$  has a rotational spectra because despite being linear, it is asymmetric,  $\text{N}-\text{N}-\text{O}$

- Cis-dichloromethane has a spectra because the chlorines are on one end, so the mass is unbalanced.
- Trans-dichloromethane has no spectra because the chlorines are on either end, so the mass is balanced.
- A symmetric molecule like  $\text{BF}_3$  will not have a spectra because the mass is balanced, all the fluorides cancel out.

## §4 HARMONIC AND ANHARMONIC VIBRATIONS

WEEK 4

Some confusing preliminary knowledge:

- $\omega_e \text{ cm}^{-1}$  is the vibrational wavenumber (the vibrational frequency in  $\text{cm}^{-1}$ ), we saw in the previous section
- $\omega$  is the angular frequency
- $\nu$  (NOT  $\nu$ ) or  $\nu_{\text{vib}}$  is the vibrational frequency
- $\omega = 2\pi\nu$
- $\hbar\omega = h\nu$
- $\omega_e$  has units  $\text{cm}^{-1}$  whilst  $h\nu$  has units J, we can sub one in for the other, to change the units, so if the energy is given in  $\text{cm}^{-1}$  we use  $\omega_e$
- To get  $\omega_e$  in J we do  $\hbar\tilde{\omega}_e = h\nu$ , since they are both in Joules, so  $\omega_e = \frac{\nu}{\tilde{c}}$

We can assume that molecules obey Hooke's Law,  $F = -k_F x$ ,  $V = -\int F dx$ , so that *classical* harmonic frequency of oscillation is  $\nu_{\text{vib}} = \frac{1}{2\pi} \sqrt{\frac{k_F}{\mu}}$ , where  $\nu_{\text{vib}}$  is the vibrational frequency. If we solve the Schrödinger equation for harmonic motion, we can find the vibrational wavenumber,  $\omega_e \text{ cm}^{-1}$  and vibrational frequency  $h\nu_{\text{vib}}$  J

$$\omega_e = \frac{\nu_{\text{vib}}}{\tilde{c}} = \frac{1}{2\pi\tilde{c}} \sqrt{\frac{k_F}{\mu}} \text{ cm}^{-1}$$

So the energy levels that arise (similar to  $F(J)$ ), where  $v$  (NOT  $\nu$ ) is the vibrational quantum number,  $v = 0, 1, 2, \dots$

$$G(v) = \left(v + \frac{1}{2}\right) \omega_e$$

Remember how for  $F(J)$  when  $J = 0$  then  $F(0) = 0$ , however for vibrational motion this is not the case.  $G(0) = \frac{1}{2}\omega_e \neq 0$ . So the energy levels start at  $\frac{1}{2}\omega_e$  and are spaced evenly from there e.g.  $G(1) = \frac{3}{2}\omega_e$ , the gap between each is  $\hbar\omega$  or  $h\nu$  is measured in Joules.

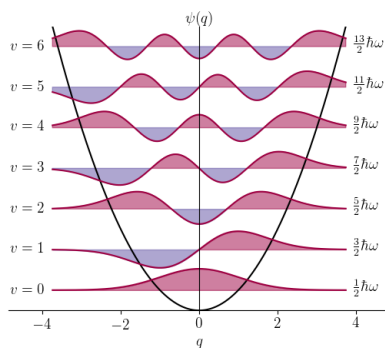
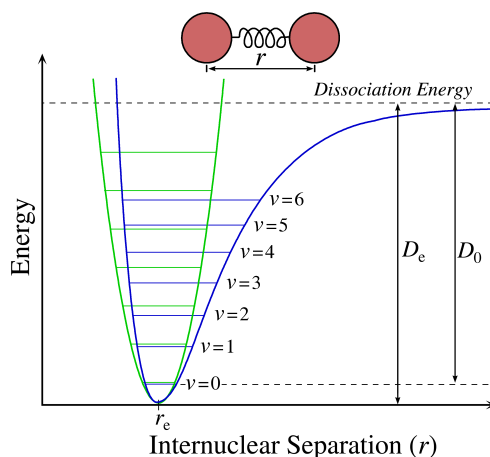


Figure 2: Harmonic oscillator wavefunctions

## §4.1 ANHARMONICITY

Molecular bonds are not harmonic oscillators, we can not increase the frequency indefinitely, as the bond stretches and gets longer it will eventually reach dissociation energy and fall apart. So for HCl it will split into H and Cl *atoms*



We describe the *anharmonic* oscillations using the morse potential (the blue on the above diagram).

$$V(R) = D_e (1 - \exp(-\beta(R - R_e)))^2$$

$D_e$  is the dissociation energy, however since the molecule always vibrates we can't measure this (remember that  $G(0) \neq 0$ ), so instead we have to measure  $D_0 = D_e - G(0)$ .

### §4.1.1 Anharmonic oscillator transitions

$$G(v) \text{ or } E(v) \text{ or } \tilde{\nu} = (v + \frac{1}{2})\omega_e - (v + \frac{1}{2})^2\omega_e x_e$$

$x_e$  is the dimensionless anharmonicity constant, however we normally talk about this constant in the form of  $\omega_e x_e$ . We need a dipole moment during the vibration, so only heteronuclear diatomics will work.

- Harmonic oscillator  $\Delta v = \pm 1$
- Anharmonic oscillator  $\Delta v = \pm 1, 2, 3, \dots$

The transitions can be calculated by  $\tilde{\nu}(2) - \tilde{\nu}(0)$ .

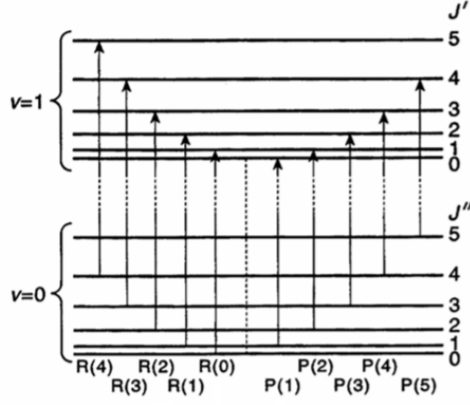
- fundamental ( $0 \rightarrow 1$ )  $\tilde{\nu} = \omega_e - 2\omega_e x_e \text{ cm}^{-1}$
- 1st overtone ( $0 \rightarrow 2$ )  $\tilde{\nu} = 2\omega_e - 6\omega_e x_e \text{ cm}^{-1}$

## §4.2 VIBRATION-ROTATION SPECTROSCOPY

As we saw in a graph at the beginning, each vibrational transition has many rotational transitions associated with it, however, they occur independently, and so we can add just add them together.  $E_{\text{tot}} = E_{\text{vib}} + E_{\text{rot}}$  We denote this energy by  $S(v, J) = G(v) + F(J)$

$$S(v, J) = \left(v + \frac{1}{2}\right)\omega_e - \left(v + \frac{1}{2}\right)^2\omega_e x_e + B_v J(J+1)$$

- All  $\Delta J = +1$  transitions give rise to an R-branch absorption, they have a higher wavenumber than  $\tilde{\nu}_0$
- All  $\Delta J = -1$  transitions give rise to a P-branch absorption, they have a lower wavenumber than  $\tilde{\nu}_0$



$$\tilde{\nu}_0 = \omega_e - 2\omega_e x_e \text{ i.e. } \tilde{\nu}_0 = S(1,0) - S(0,0)$$

We can see the different types of transitions (R on the left, P on the right). The energy associated with any vibrational transition ( $v$ ) is the same no matter the rotational transition ( $J$ ). For any transition we call the lower rotational energy  $J''$  and the higher level  $J'$ , so for some generic transition.

$$\Delta\tilde{\nu} = S(v', J') - S(v'', J'')$$

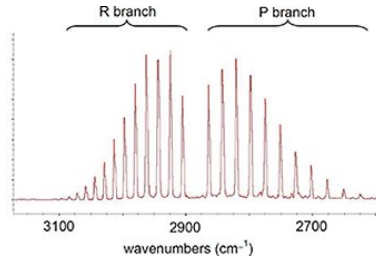
Take for example a vibrational transition in the fundamental vibrational band ( $0 \rightarrow 1$ ), for any  $J$  values the vibrational energy is always  $\omega_e - 2\omega_e x_e$ , so we only have to worry about the rotational transition. Calculating for some generic  $\tilde{\nu}$  in the fundamental vibrational band i.e.  $J$  goes from  $J''$  to  $J'$ . For  $\tilde{\nu}_R$  transitions we can say that  $J' = J'' + 1$  (look at the above graph).

$$\begin{aligned} \tilde{\nu}_R(J'') &= S(1, J') - S(0, J'') = G(1) - G(0) + F(J') - F(J'') \\ &= \omega_e - 2\omega_e x_e + F(J') - F(J'') \\ \Delta F &= F(J') - F(J'') = B_1 J'(J' + 1) - B_0 J''(J'' + 1) \\ J' &= J'' + 1 \\ \Delta F &= B_1(J'' + 1)(J'' + 2) - B_0 J''(J'' + 1) \\ \tilde{\nu}_R &= \omega_e - 2\omega_e x_e + B_1(J'' + 1)(J'' + 2) - B_0 J''(J'' + 1) \end{aligned}$$

For  $\tilde{\nu}_P$  transitions in the fundamental vibrational band,  $J'' = J' + 1$ , so the maths is slightly different, but only for the  $\Delta F$  part.

$$\begin{aligned} \Delta F &= F(J') - F(J'') = B_1 J'(J' + 1) - B_0 J''(J'' + 1) \\ J'' &= J' + 1 \\ \Delta F &= B_1(J'' + 1)(J'' + 2) - B_0 J''(J'' + 1) \\ \tilde{\nu}_P &= \omega_e - 2\omega_e x_e + B_1(J'' - 1)(J'') - B_0 J''(J'' + 1) \end{aligned}$$

If we assume that  $B_1 = B_0 = B$  then we can say that the spacing between each branch is  $2B$  and the central gap is  $4B$



### §4.3 VIBRATIONAL DEPENDENCE OF ROTATIONAL CONSTANTS

But is  $B_1 = B_0$ ? For a harmonic oscillator, which has symmetric energies, yes, it is. However for an anharmonic oscillator where the distance changes this is not the case, the wavefunction skews up the well. We say  $B \propto \frac{1}{\mu R^2}$ , but  $R$  is changing with the vibration, so we need to consider  $\langle \frac{1}{R^2} \rangle$  for  $B$ .  $\langle R^2 \rangle$  increases with  $v$ , so  $\langle \frac{1}{R^2} \rangle$  decreases with  $v$ , so

$$B_0 > B_1 > B_{(v>1)}$$

The rotational constant gets small the higher  $v$  we go.

$$B_v = B_e - \alpha \left( v + \frac{1}{2} \right)$$

$B_e$  is the rotational constant for the bottom of the well, it needs to be calculated and can't be found experimentally.  $\alpha$  is the vibration-rotation interaction constant. This means that if we know  $B_v$  for any two energy levels then we derive  $B_e$  and  $\alpha$

We use transitions with common upper or lower levels to determine the rotational constants.

#### §4.3.1 From the same level

With two different transitions starting from the same  $J$  value,  $J''$ , at where  $v$  goes  $0 \rightarrow 1$ . Since both of them have the same  $v$  transition, when they are subtracted they will equal 0 so this simplifies the maths a lot. Since our transition equations are in the form of the initial  $J$  value we can say.

$$\nu_R(J) - \nu_P(J) = 2B_1(2J + 1)$$

And from this we can obtain our  $B_1$

#### §4.3.2 To the same level

It is very similar, but now our transitions end on the same level, since  $\nu_R$  goes up and  $\nu_P$  goes down in  $J$  value, they must start like this.

$$\nu_R(J - 1) - \nu_P(J + 1) = 2B_0(2J + 1)$$

What we can do for both of these is then plot a graph, where the slope is  $B$  and from there we can calculate  $B_e$  and  $\alpha$

### §4.4 EXAMPLE

HI molecule has its vibration-rotation spectrum measured, only four lines are given ( $\text{cm}^{-1}$ ).

$\tilde{\nu}$	Difference
2204.019	
	13.021
2217.040	
	25.030
2242.070	
	12.009
2254.079	

We can see from the differences that one is double the others, that means that 2242 will be the  $\tilde{\nu}_0$  line. The numbers lower than  $R(0)$  are  $P$  branches.

$\tilde{\nu}$	Branch
2204.019	P(2)
2217.040	P(1)
2242.070	R(0)
2254.079	R(1)

Remember from our equations, that  $\nu(J)$  uses the starting level, so to find  $B_1$  we need levels with the same  $J$  value.

$$\begin{aligned}\nu_R(J) - \nu_P(J) &= 2B_1(2J + 1) \\ R(1) - P(1) &= 2254.079 - 2217.040 = 37.039 \\ &= 2B_1(2J + 1) = 6B_1 \\ B_1 &= 6.1732\end{aligned}$$

For  $B_0$  we need equations which end on the same level, or start two levels apart, luckily we have those too

$$\begin{aligned}\nu_R(J) - \nu_P(J) &= 2B_0(2J + 1) \\ R(0) - P(2) &= 38.051 \\ B_0 &= 6.3418\end{aligned}$$

Now we can find  $B_e$  and  $\alpha$  from our equations from before

$$\begin{aligned}B_v &= B_e - \alpha \left( v + \frac{1}{2} \right) \\ B_0 &= B_e - \frac{1}{2}\alpha \\ B_1 &= B_e - \frac{3}{2}\alpha \\ B_0 - B_1 &= \alpha = 0.1686 \text{ cm}^{-1} \\ B_e &= B_0 + \frac{1}{2}\alpha = 6.4261 \text{ cm}^{-1}\end{aligned}$$

We can now calculate the equilibrium bond length,  $R_e$ , recall that

$$\begin{aligned}B_e \text{ cm}^{-1} &= \frac{h}{8\pi^2\mu R_e^2\tilde{c}} \\ R_e &= \sqrt{\frac{h}{8\pi^2\mu\tilde{c}B_e}} \text{ cm} \\ &= 1.62 \text{ \AA}\end{aligned}$$