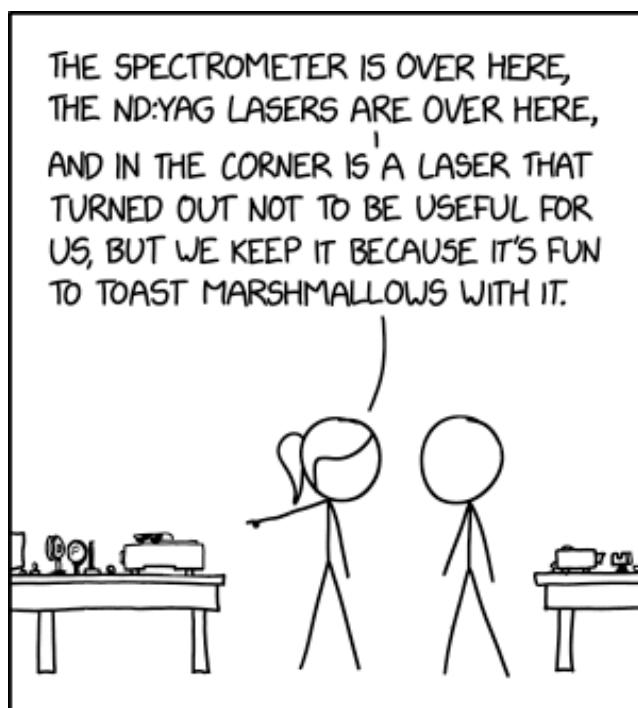


# CH2200 Spectroscopy Theory and Practice

## Part A

James Pickering



*Everything that living things do  
can be understood in terms of the  
jigglings and wigglings of atoms.*

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Richard P. Feynman

# Recommended Reading + Resources

## Textbooks

- **Modern Spectroscopy**, J M Hollas. *A classic textbook. Despite the title, a little dated now but the fundamentals haven't changed. If you want more physical insight than I give in the lectures this is a good place to start.*
- **Molecular Quantum Mechanics**, P Atkins. *Good for the quantum mechanical basis. If you find yourself wanting more mathematics, then this is the first place to look.*
- **Molecular Symmetry and Group Theory**, A Vincent. *Formatted as a step-by-step workbook, starting with real basics. Every chemistry undergraduate should have a copy.*
- The Oxford Primers on **Molecular Spectroscopy** and **Atomic Spectroscopy**.

## Non-Textbook Reading

- **QED - The Strange Theory of Light and Matter**, R P Feynman. *More physics than you need for this course, but a very nice introduction to thinking about light-matter interaction at a deep fundamental level. You'll end up understanding Feynman diagrams.*
- **In Search of Schrödinger's Cat**, J Gribbin. *If you're interested in the history of quantum chemistry and early spectroscopy, a nice read.*

## Websites

- <http://symmetry.jacobs-university.de/>. *A very useful site where you can find group theory tables, lots of example molecules, and calculators for reduction formulae.*
- <https://chem.libretexts.org/>. *Generally a decent resource, but beware that there are some errors and oversimplifications in it.*
- **Unit converters** are not cheating, and are useful for checking answers. However, you will **not** have access to these in an exam (so don't rely on them):
  - <https://halas.rice.edu/unit-conversions>. *Everyone's favourite.*
  - <https://www.weizmann.ac.il/oc/martin/tools/hartree.html>. *Arguably nicer, it calculates Boltzmann population ratios for you, and includes molar units.*
  - <https://toolbox.lightcon.com/>. *Mostly beyond what you'll need, but 'converters' is nice.*

# Lecture 1

## Why Spectroscopy?

### Lecture Aims

- To recap some basics from CH1200.
- To start to understand links between molecular structure and spectra.
- To appreciate how spectroscopy underpins everything we do in science.

It might seem odd that we have dedicated an entire lecture course to spectroscopy, which you may feel is only a small part of ‘chemistry’ as a whole. As a pure discipline, that’s true. However, ultimately every chemist (and almost every scientist) uses spectroscopy on a day-to-day basis to get their work done – even if they would not necessarily call themselves a ‘spectroscopist’. **Everything we know about molecular structure, we know because of spectroscopy.**

Today we are going to recap some of the basic things about spectroscopy that we learnt in CH1200, and then start to see how we will go deeper in this course. Throughout, I’ll try to emphasise areas where this stuff is actually used – **this is not an abstract, theoretical thing we are teaching you.** Every chemist uses spectroscopy to some extent, so it’s critical that that you understand how it works.

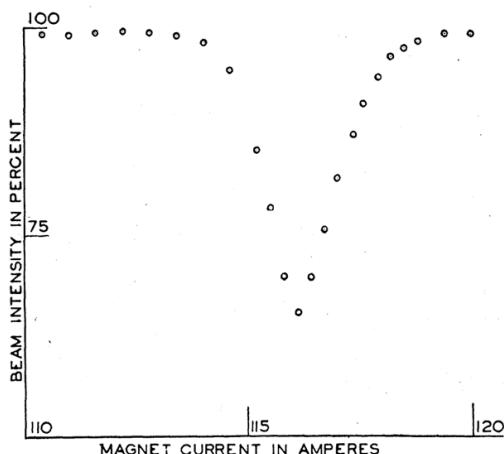
### 1.1 Spectroscopy in Science

It is impossible to overstate how fundamental spectroscopy is to modern science. Spectroscopy is used in some form in every scientific discipline, and in many it is *the* fundamental technique used to learn about the world around us. I went through and counted 38 Nobel Prizes which have been awarded since about 1910 that are largely based around the development of spectroscopic techniques, or are in the novel application of spectroscopy to a problem.

We can’t cover everything in this lecture course, but we can make a solid start. We are going to start by thinking about what spectroscopy *is*, and recap some of what we learnt last year (with a few new bits). Then we’ll move on and think very generally about what happens when light interacts with matter. Fundamentally, that is what spectroscopy is:

*Spectroscopy is the study of the interaction of light with matter.*

The range of different possible kinds of light and matter results in a huge range of different flavours of spectroscopy, which all look at different things. Ultimately though, it’s all about understanding what happens when different kinds of light hit matter, and a lot of the fundamentals

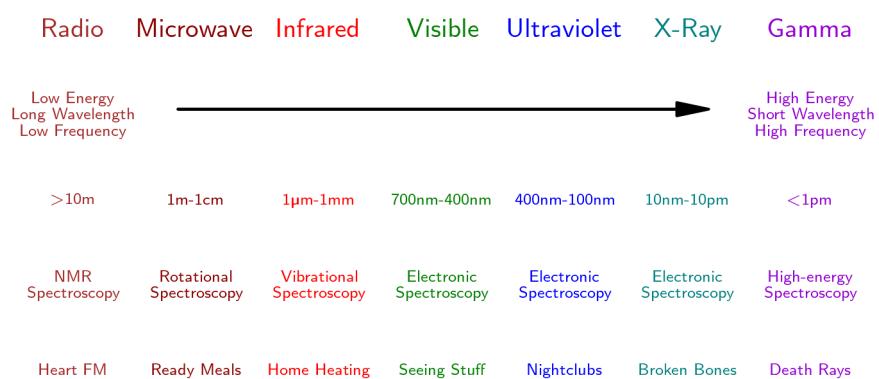


**Figure 1.1:** The first NMR spectrum, measured by Isidor Rabi in 1938. Humble beginnings!

are the same regardless of the specific kind of spectroscopy you are doing. Like humans, different spectroscopies have far more in common with each other than the things that divide them.

## 1.2 What is Spectroscopy?

Spectroscopy is fundamentally the study of the interaction of **light** with **matter**. As chemists, the ‘matter’ is atoms and molecules. ‘Light’ doesn’t necessarily mean visible light, and in this context is just a slang term for **electromagnetic radiation**. This radiation could take the form of radio waves (in NMR spectroscopy), infrared light (in vibrational spectroscopy), microwaves (in rotational spectroscopy), or visible/ultraviolet light (in electronic spectroscopy), among others. The EM spectrum that we will become intimately familiar with is below.



**Figure 1.2:** The EM spectrum. Our best friend.

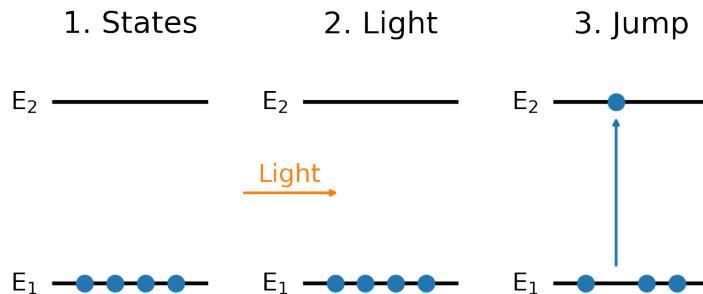
Last year, we learnt a simple ‘**states, light, jump**’ model of spectroscopy, shown in Figure 1.3. This model is a good way to think about what happens. You shoot a photon of light at a molecule, the photon is absorbed, and the molecule jumps up to a higher energy state. By recording the energy of the photon of light that made this jump happen, we can learn the energy gap between the two states. This energy gap links to a huge range of different molecular properties, and we will see this in much more detail as we go through the course. The fundamental idea is that

measuring this gap allows us to measure molecular properties (either directly or indirectly) – which is why spectroscopy is so useful.

Recall a few key things that arise from this model:

1. The energy of the photon has to exactly match the energy gap between the two states to cause the jump to happen, due to energy conservation.
2. We are **always** looking at the **energy gap** between two states, and not the energy of the individual states themselves.
3. There needs to be **population** in the state we are jumping *from*, and some kind of available space in the state we are jumping *to*.

Each of these points leads us to something we need to recap.



**Figure 1.3:** Simple model of spectroscopy. A photon of light causes a molecule to jump from one quantum state to another.

### 1.2.1 Energy Units

Point (1) above written mathematically says:

$$E_p = E_2 - E_1$$

Where  $E_p$  is the energy of the photon, and  $E_2$  and  $E_1$  are the energies the upper and lower state respectively. However, we know from CH1200 that usually we don't talk about the energy of photons in units of Joules, because the numbers get very small and unwieldy. We normally talk about the energy of photons in other units, such as:

- Wavelength ( $\lambda$ ) in **nanometres** (nm – for visible and UV light).
- Wavenumber ( $\bar{\nu}$ ) in **wavenumbers** ( $\text{cm}^{-1}$  – for infrared light).
- Frequency ( $\nu$ ) in **Hertz** ( $\text{s}^{-1}$  – for microwaves and radiowaves).
- Electronvolts ( $E(\text{eV})$ ) **electronvolts** (eV – for deep UV and X-rays).

Note the standard notation, which I'll try and stick to, however these are rules of thumb<sup>1</sup>. When we are doing calculations in spectroscopy, it is important that you pay attention to the units, as you can easily get tripped up. If you are adding or subtracting two energies, they need to be

<sup>1</sup>Rotational spectroscopists use both Hertz and wavenumbers, depending on their mood.

in the same units, and so you need to be able to convert between the different kinds of energy units.

To do these conversions, we use some fundamental constants, and looking at the units of those constants helps us work out what to do:

- The *Planck constant*,  $h$ , which has a value of  $6.626 \times 10^{-34} \text{ Js}$  (units of **Joule seconds**).
- The speed of light in vacuum,  $c$ , which has a value of  $2.997 \times 10^8 \text{ m s}^{-1}$  (units of **metres per second**).
- The electronvolt is defined such that  $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$  (i.e there are  $1.602 \times 10^{-19}$  **Joules per electronvolt**).

For example, if I have a radio tuned to a frequency of 198 kHz, then I can multiply this number by  $h$  to find the energy ( $E$ ) of the radio photons in Joules:

$$\begin{aligned} 198 \text{ kHz} &= 198 \times 10^3 \text{ Hz} = 198 \times 10^3 \text{ s}^{-1} \\ E &= 198 \times 10^3 \text{ s}^{-1} \times 6.626 \times 10^{-34} \text{ Js} \\ E &= 1.312 \times 10^{-28} \text{ J} \end{aligned}$$

Similarly, if I have an infrared laser emitting light at  $6000 \text{ cm}^{-1}$ , then I can multiply this number by  $c$  to get the frequency in Hertz, and then multiply this by  $h$  to get the energy in Joules:

$$\begin{aligned} 6000 \text{ cm}^{-1} &= 6000 \times 10^2 \text{ m}^{-1} \\ \nu &= 6000 \times 10^2 \text{ m}^{-1} \times 2.997 \times 10^8 \text{ m s}^{-1} \\ \nu &= 1.798 \times 10^{14} \text{ s}^{-1} \\ E &= 1.798 \times 10^{14} \text{ s}^{-1} \times 6.626 \times 10^{-34} \text{ Js} \\ E &= 1.191 \times 10^{-19} \text{ J} \end{aligned}$$

Finally, I might have an X-ray source emitting X-rays with an energy of 1400 eV. Here I can easily convert to Joules using the definition of the electronvolt:

$$\begin{aligned} E &= 1400 \text{ eV} \times 1.602 \times 10^{-19} \text{ JeV}^{-1} \\ E &= 2.243 \times 10^{-16} \text{ J} \end{aligned}$$

Note that the infrared photon is about 9 orders of magnitude (i.e. 1 billion times) more energetic than the radio photon, and the X-ray is a thousand times more energetic than that. This is the huge range of energies we deal with in spectroscopy, and why we use different units for things! Doing this process of looking at units will help you work out how to do energy conversions, without having to learn tedious formulae<sup>2</sup>. However, seeing these summarised as formulae can also be helpful, so:

$$E = \frac{hc}{\lambda} = h\nu = 100 \times hc\bar{\nu}$$

Another useful method might be to know some standard conversions like:

- $1 \text{ eV} = 8065.54 \text{ cm}^{-1}$
- $1 \text{ cm}^{-1} = 1 \times 10^7 \text{ nm}$

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<sup>2</sup>The units help you see where the formulae come from, much more valuable knowledge to have.

- $1 \text{ THz} = 33.36 \text{ cm}^{-1}$

Of course, there are lots of online calculators for these things, such as <https://halas.rice.edu/unit-conversions>. However, these don't help you a) in the exam, or b) when you are trying to have a conversation with someone about spectroscopy, so it's good to know how to do the conversions in your head (at least roughly).

#### Unit Conversions Practice

1. Convert  $266 \text{ nm}$  to eV.
2. Convert  $8 \text{ cm}^{-1}$  to GHz.
3. Convert  $100 \text{ kJ mol}^{-1}$  to  $\text{cm}^{-1}$ .

### 1.2.2 Energy Gaps - Lines and Levels

We will come back to this again and again, but point (2) in our list earlier is critical. In spectroscopy, we are always measuring the **difference in energy** between two energy states or energy levels. We call the thing we measure a **line**, because historically spectra looked like a series of lines that would be imaged on paper (see Figure 1.4). We are not going to go deeply into the underlying quantum mechanics in this course<sup>3</sup>, but it's useful to have an idea of what we mean by a **state**, which is really a shorthand for **quantum state**.

Spectroscopy is all about making atoms and molecules do stuff in response to being hit by light, and that 'stuff' involves electrons and/or nuclei moving around. However, we know from CH1200 that all motion at a molecular level is **quantised** – think about electrons in atoms, and how they occupy specific orbitals with well-defined energies. Each of these orbitals is a *state* that the electron exists in, and each state has a well-defined energy. There are quantised energy states that relate to every kind of molecular motion: vibrational states, rotational states, and electronic states, for example. Think of a state as a kind of condition that the molecule or atom can be in, which has a well-defined energy<sup>4</sup>. We normally represent states pictorially by drawing horizontal lines on paper, and jumping between these states is what we do in spectroscopy.

Later on, we will see that quantum mechanics allows us to relate the energies of specific **states** to molecular properties, which is where the power of spectroscopy comes from. Just remember that what you measure in a spectrum is always the *difference* between two energy levels or energy states (we'll get to the difference between levels and states shortly).



**Figure 1.4:** The visible-region spectrum of a hydrogen atom, with lines showing where the hydrogen atom emits light. Early spectroscopy mostly focussed on emission spectra from atoms.

<sup>3</sup>In fact, if you can draw two horizontal lines on some paper, that's about as much quantum mechanics as you need to understand 90% of the spectroscopy you'll encounter.

<sup>4</sup>Formally, the state refers to the wavefunction that describes the atom or molecule with a given energy. You can find them out by solving the Schrödinger equation, which is a story for another time.

**Lines and Levels Practice**

A molecule absorbs UV light with a wavelength of 353 nm and jumps from the ground to excited state. The energy of the ground state is 1.3 eV, what is the energy of the excited state?

**1.2.3 Populations and Degeneracy**

Finally, point (3) in our earlier list talks about the population of a given state. If a state is **populated** it means that there are some molecules in that state. You can find out the population in a given state relative to another at a given temperature using the **Boltzmann Distribution**, as we've seen last year.

$$\frac{n_i}{n_j} = \frac{g_i}{g_j} \exp\left(-\frac{\Delta E}{k_B T}\right) \text{ where } \Delta E = E_i - E_j$$

Where  $n_i$  is the number of molecules with energy  $E_i$ , and  $g_i$  is the **degeneracy** of the level with energy  $E_i$ . You've probably heard the word **degenerate** in a chemistry context before, and may know that:

*Two or more states with the same energy are known as degenerate states.*

For example, you've probably heard that the three p-orbitals in an atom are all degenerate. We can make this definition a little more robust now, and say that:

**Degeneracy**

An **energy level** that is **n-fold degenerate** consists of **n states** which all have the same energy.

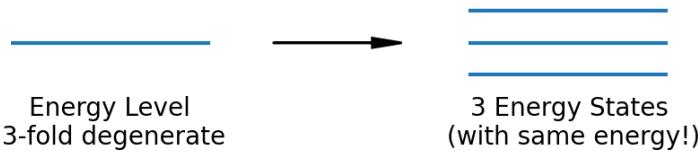
For example, in an atom, we might have the energy level corresponding to  $n = 2$  and  $l = 1$  (2p level). This level is **3-fold degenerate**, as we have 3 states, corresponding to our three p-orbitals ( $m_l = -1, 0, 1$ ). In fact, an atomic energy level with angular momentum quantum number  $l$  is  $2l + 1$ -fold degenerate. Can you explain why there are 5 d-orbitals, and 7 f-orbitals?

We've stumbled across the difference between a **level** and a **state** now too. A **level** refers to a state or set of states that have the same energy, whereas a **state** refers to a specific quantum mechanical energy state (i.e. a single solution to the Schrödinger equation). You can't break a state down into anything more granular, and a good way to think of them is as **the smallest place where you can put population**. To give some examples:

- The  $n = 3, l = 2$  level in an atom consists of 5 degenerate states (5 d-orbitals)<sup>5</sup>.
- In a hydrogenic atom, the  $n = 2$  level consists of 4 degenerate states (1 s-orbital and 3 p-orbitals).

Anyway, the bottom line is that now when we use the Boltzmann distribution, we account for degeneracy using this factor  $g$ . If the level with energy  $E_i$  is two-fold degenerate, then  $g_i = 2$ , if it is three-fold degenerate, then  $g_i = 3$  (illustrated in Figure 1.5) and so on. We will see later on how to know the degeneracies of different kinds of quantum states.

<sup>5</sup>Astute readers may note that each orbital holds two electrons, and so must be two-fold degenerate, making the overall level 10-fold degenerate. This is true, if we account for *spin degeneracy*, but in chemistry we often implicitly ignore this as we are used to putting two electrons in each state.



**Figure 1.5:** Degeneracy. An energy level that is 3-fold degenerate consists of 3 states with equal energy.

#### Boltzmann Distribution

A given molecule can exist in two states, and the lower state has a degeneracy of 1, and the upper has a degeneracy of 3.

1. A sample of the molecules is held at 200 K. If the energy gap between the states is  $300 \text{ cm}^{-1}$ , what is the population ratio?
2. If the measured population ratio is 1.48, what is the temperature of the sample of molecules?

#### 1.2.4 Absorption and Emission

Finally, recall than when light hits matter, there are essentially three things that can happen:

- **Absorption** – the light is absorbed and the molecule jumps to a higher energy state.
- **Spontaneous Emission** – the molecule randomly falls to a lower energy state and emits a photon.
- **Stimulated Emission** – a photon hits a molecule and causes it to fall to a lower energy state, so it emits another photon of the same energy.

Energy conservation is the basis for all of these processes. Whenever light hits a molecule all of these processes happen and the relative rates of them determine the finer points of the behaviour. The mathematics behind this is described by the **Einstein coefficients**, which is beyond the scope of what we'll do in this course (but worth looking at if you find this interesting<sup>6</sup>).

#### 1.2.5 Wave-Particle Duality

Finally, let us remind ourselves that we have two pictures for how we think about 'light'. One way think of it is as a **photon**, which is a discrete little package of energy. Another way is to think of the light as a **wave**, and specifically you can think about the wave as an **oscillating electric field**.

Recall in CH1200 we learnt that neither of these two pictures provided us a complete description of how light behaves, and this is also true in spectroscopy. There are two pictures of how light

<sup>6</sup>For example, either in the first couple of chapters of Hollas, or [https://en.wikipedia.org/wiki/Einstein\\_coefficients](https://en.wikipedia.org/wiki/Einstein_coefficients) is actually OK.

interacts with matter: the ‘photon’ picture and the ‘wave picture’. Or, as I have christened them, the **jumping molecule** picture and the **jiggling molecule** picture. We’ll start thinking about jiggling molecules more thoroughly next time.

#### Take Home Messages

- Spectroscopy is all around you – and is fundamental to all of science.
- Spectroscopy is about measuring energy gaps between quantised energy states, which leads to information about molecular structure and properties.
- Revise energy unit conversion and the Boltzmann distribution from last year if you are rusty!

## Lecture 2

# Light and Matter I

### Lecture Aims

- To understand what light is at a deeper level.
- To understand how the two models of light lead to two models of light interacting with matter.
- To start to understand the wave picture of how light interacts with matter.

We ended last time by briefly recapping wave-particle duality. Some of you might recall how last year we talked about Richard Feynman's famous thought experiment, involving shooting bullets, waves, and electrons at a screen, and thinking about what happens. In that experiment, we found that electrons behaved like bullets *and* waves:

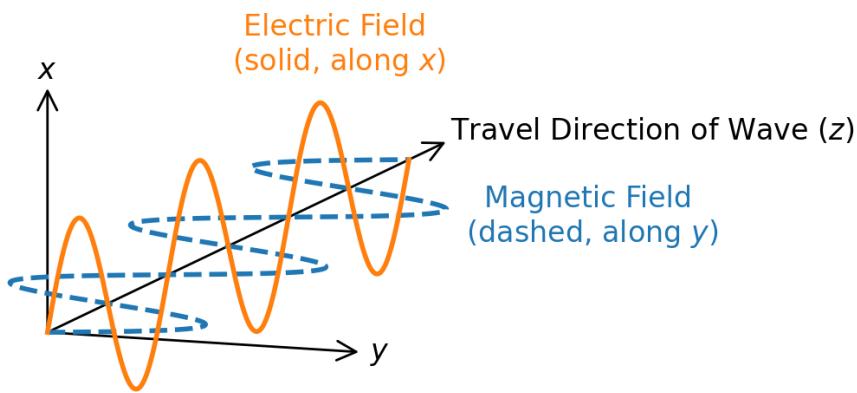
- Electrons are detected as 'lumps' - we never detect half an electron, or a third of an electron. So they are like bullets (particles).
- Electrons can diffract through an aperture, and interfere with each other. So they are like waves.

We concluded that *electrons are weird*. In reality, however, everything can behave in this way due to something called **wave-particle duality**. That is, we need both a **wave** (interfer-y, diffract-y, oscillate-y) picture and a **particle** (ball-of-energy, lump-y, packet-of-stuff) picture to describe the behaviour of electrons, and therefore to describe the behaviour of atoms and molecules. Neither picture is correct on its own, but sometimes one is more useful than another – the pictures are *complementary*. Light is also something that can be thought about as a wave or as a particle, which leads us nicely to be able to think about two ways in which light and matter interact.

### 2.1 Photons and Waves

#### 2.1.1 Wave Picture of Light

Recall that when we say 'light', we really mean 'electromagnetic radiation'. We call it this because it consists of both an **electric field** and a **magnetic field** that travel together in a certain direction. These fields are **oscillating fields**, and so can be drawn as waves travelling in a given direction, as shown in Figure 2.1. The wave travels in a given direction (here  $z$ ), and the two fields oscillate perpendicular to this direction of travel. Here I have drawn the electric



**Figure 2.1:** Electromagnetic radiation (a light wave) consists of an electric field (orange, solid line) and a magnetic field (blue, dashed line) that propagate together. In this drawing, the light wave is travelling along the  $z$  direction, with the electric field polarised along  $x$ , and the magnetic field polarised along  $y$ .

field oscillating along  $x$  and the magnetic field oscillating along  $y$  – the electric and magnetic fields are always perpendicular to each other.

This might seem like a lot of physics but it's important, as the direction with which the wave oscillates has important consequences for spectroscopy. The direction is known as the **polarisation state** of the wave. In the example in Figure 2.1, the electric field is polarised along  $x$ , and the magnetic field is polarised along  $y$ . Normally we talk about these directions as relative to some fixed axis, so if we defined the  $x$  axis as 'vertical', then in the case shown in Figure 2.1 the electric field is *vertically polarised*, and the magnetic field is *horizontally polarised*<sup>1</sup>.

Pretty much all the time in spectroscopy we only care about one component of the light at a time, and normally it's the *electric* component we care about, because we're interacting with *electrically charged* particles like electrons (the magnetic component becomes important in *magnetic resonance spectroscopy* later). So, we don't need to worry about thinking in 3D all the time. From now on, when I talk about light, I want you to have this picture in your head in addition to the photon picture – a sinusoidal wave that oscillates with a given frequency. We describe this wave either by how it oscillates as a function of time, or as a function of distance, using quantities summarised in Table 2.1 (from CH1200). Remembering how to convert between these is vital!

Concept	Time Picture	Distance Picture
One Cycle	Time Period	Wavelength
Cycles Per Unit	Frequency	Wavenumber

**Table 2.1:** Describing waves: all of these quantities can be used to describe an EM wave, and all are commonly used in spectroscopy – revise how to convert between them!

This picture is good for explaining a lot of things, and we will come back to it later, but it doesn't intuitively provide us with an explanation of how much *energy* the light carries. To get a feel for this, we have to move to the **photon picture** of light.

<sup>1</sup>Other things can happen too, like it being *circularly polarised* or *elliptically polarised*, and hardcore physicists would get annoyed at the 'horizontal' and 'vertical' nomenclature, but who cares what they think.

### 2.1.2 Photon Picture of Light

As an alternative to the wave picture, we can think of the light as a stream of particles, and we call each particle a **photon**. Think of a photon as like little packet of energy, or as a ‘ball of light’, that can hit something and impart energy to it. When you stand in the sun on a hot day, you feel warm because you are being pounded by trillions upon trillions upon trillions of photons every split second, and all that energy adds up to making you feel hot (or giving you sunburn).

#### Photons

The solar flux that hits the surface of the Earth on a sunny day is about  $1.36 \text{ kW m}^{-2}$ . If the average photon of sunlight has a wavelength of 700 nm, how many photons hit each square metre of earth every second?

In thinking about this, we have stumbled across another question:

Why does some sunlight just make us warm, and other sunlight give us sunburn?

We don’t get sunburn from a radiator, or feel warm if we stand in front of an LED light, so what’s going on here?

The answer is that the sunlight is affecting the molecules that make up our bodies, but in different ways. Sunlight consists of many different wavelengths of light, and so photons of many different energies. These photons of different energies interact differently with different molecules in our bodies, to create all the different effects we experience. Ultimately, it’s all about the different interactions of light with matter, which is what spectroscopy is all about studying.

To understand how light with different energies cause molecules to move and react in different ways, we need to build up an intuitive picture for *how* light can interact and make a molecule move around. The most intuitive picture of this comes from the wave picture of light, so we start there.

### 2.2 Jiggling Molecules

We have two models that allow us to describe light (photon and wave), so it makes sense that there are then two models that describe how light interacts with matter. I call these models the **jumping molecule** model (which uses the photon picture), and the **jiggling molecule** model (which uses the wave picture)<sup>2</sup>.

Fundamentally, spectroscopy is about light interacting with matter, and making the matter (a molecule) to do something. Different kinds of spectroscopy make the matter do different things:

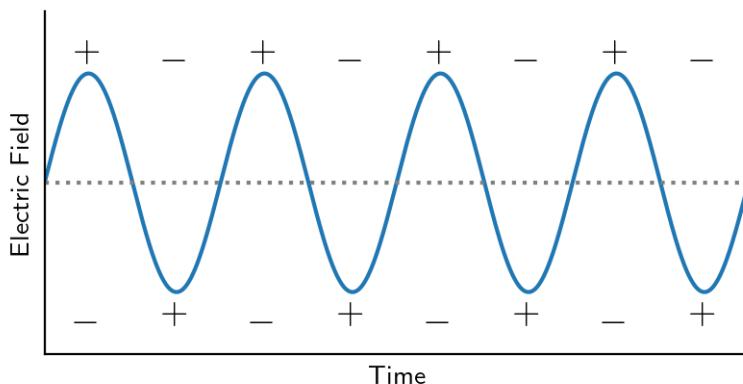
- **Rotational** spectroscopy: light makes molecules **rotate**.
- **Vibrational** spectroscopy: light makes molecules **vibrate**.
- **Electronic** spectroscopy: light makes **electrons** in molecules (or atoms) jump around.
- **Nuclear Magnetic Resonance (NMR)** spectroscopy: light make the **nuclei** in molecule jump between spin states (via a **magnetic** interaction).

We are now going to start to understand how exactly light can make a molecule do these things.

<sup>2</sup>You probably won’t find these names in textbooks, as as far as I know nobody else teaches it like this – you are experiencing cutting-edge spectroscopy tuition (and are the guinea pigs, apologies).

### 2.2.1 Electric Fields

To think about what an oscillating electric field actually is, imagine it as a wave where the peaks are positively charged, but because the peaks move up and down, the positive bit moves up and down – as shown in Figure 2.2. What would happen if you put a charged particle (say, an electron), in this field?

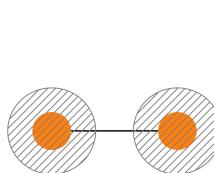


**Figure 2.2:** The electric field of light can be thought of as a wave where the peaks/troughs are positively charged, and change direction over the course of a cycle. An electron in this field would oscillate (following the blue curve).

You can maybe imagine that the electron would follow the field as it is attracted to the positive part, which keeps on changing direction. So as the wave oscillates up and down, the electron would also oscillate up and down<sup>3</sup>. It would be attracted to the positive bits and repelled from the negative bits. *Remember that the field is oscillating in time*, once the electron starts being attracted to the positive bit, the direction flips and it gets pulled in the other direction.

### 2.2.2 Jiggling Electrons

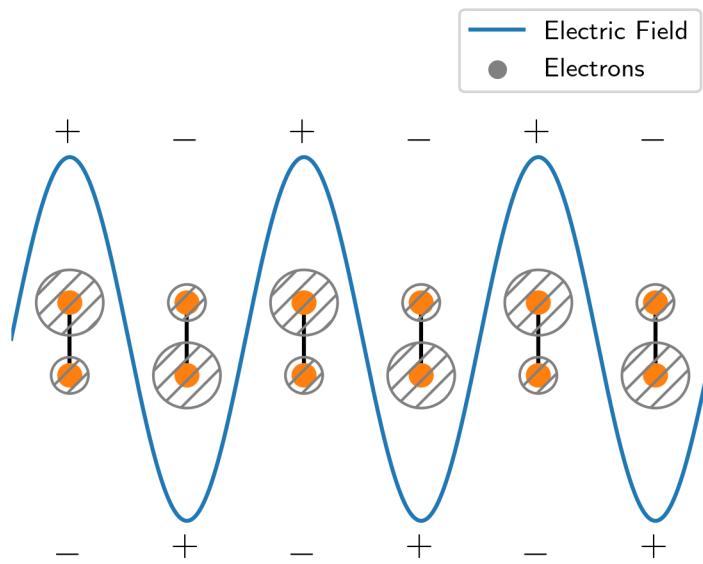
Ok, so that's a free electron, but free electrons are boring. What happens if we do this to molecule, which contains electrons, but electrons that are already tightly held in molecular orbitals that are attracted to the positive nuclei? Firstly, let's meet our molecule, which is a homonuclear diatomic (something like O<sub>2</sub>), so has a symmetrical distribution of electrons around it (shown in grey on Figure 2.3).



**Figure 2.3:** Our example molecule. Nuclei are orange, and the electrons are the grey shading.

What would happen if you put this molecule into the electric field from Figure 2.2? Something like what is shown in Figure 2.4.

<sup>3</sup>Researchers in Lund, Sweden, who I used to drink beer Ribena with, actually filmed this for the first time in about 2008: <https://www.youtube.com/watch?v=ofp-OHIq6Wo>.



**Figure 2.4:** Putting the molecule in an oscillating electric field makes the electrons jiggle up and down. The molecule is polarised now due to the unequal charge distribution, and this oscillation is called an oscillating polarisation.

So, in the presence of a light wave, the electrons in the molecule have started jiggling around and moving. **This is how spectroscopy works.** We have assumed that the electric field of the light is not strong enough to rip the electrons off the molecule (this can happen and is called *photoionisation*). The electrons will just move around whilst still being attached to the molecule, and we say that the molecule has become **polarised** by the field<sup>4</sup>. We say this because at each peak in our wave (see drawing in Figure 2.4), the molecule that was previously non-polar has become polar, there are more electrons on one side than the other. You might have heard of the *polarisability* of a molecule in the context of hard and soft acids and bases, a polarisable atom or molecule is simply one where the electrons are not held very tightly by the nuclei and so it's easy for the electric field of the light to 'push' them about<sup>5</sup>.

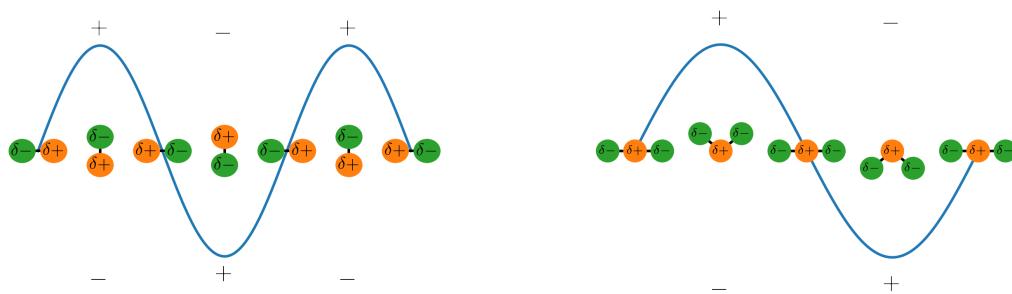
The electrons jiggle up and down at the same frequency as the driving light wave, so we could work out how fast they move if we wanted to. Crucially, the frequency of the driving light wave affects this interaction significantly. If the frequency is too high, the field might move so fast that the electrons cannot 'catch up' and follow it (so no interaction happens). Conversely, it could be so slow that the electrons don't move with much energy and so nothing really happens either. A good way to picture this is to imagine you are the electron and are trying to run alongside the light wave

- If the light wave was an F1 car travelling at  $300 \text{ km h}^{-1}$ , then no matter how fast you tried to run, you couldn't keep up.

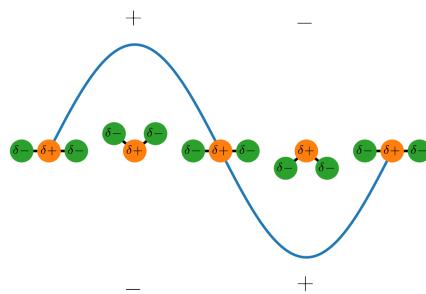
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<sup>4</sup>This is a different kind of polarisation from the one discussed earlier in the context of light waves – apologies, it's just the terminology everyone uses.

<sup>5</sup>Something like iodine, big and floppy, is polarisable. Something like hydrogen, small and hard, is not.



**Figure 2.5:** A polar molecule in an electric field can start to rotate.



**Figure 2.6:**  $\text{CO}_2$  in an electric field, it starts to bend and vibrate.

- If the light wave was a snail, then no matter how slowly you tried to run, you couldn't 'run' and still remain alongside it.
- If the light wave was another human runner, then you could keep up and could follow it.

The idea of a molecule being able to 'follow' the light field is an important one. The electrons in the molecule will have some kind of intrinsic frequency at which they want to jiggle around, and when the frequency of the oscillating field of the light matches intrinsic frequency, the jiggling of the electrons is as strong as it can be. When this happens, we say that the light is **resonant** with this intrinsic frequency. This is the same kind of resonance that you get when a microphone produces feedback, or someone scrapes their fingers down a blackboard.

### Jigging Electrons

A molecule is irradiated with UV light ( $\lambda = 266 \text{ nm}$ ). If we assume that the electrons in the molecule move along the bond length ( $1 \text{ \AA}$ ) as they jiggle, how fast must the electrons be moving?

### 2.2.3 Jigging Molecules

There's a beautifully large amount of extra complexity that goes with the picture we have just learnt, but we will worry about that later. For now, I want to give you an intuitive feel for how two very important kinds of spectroscopy work: **rotational spectroscopy** and **vibrational spectroscopy**. Or, to put it another way, I want you to have feel for how exposure to different wavelengths of light can make molecules start to rotate and vibrate.

#### Rotating Molecules

Imagine we now have a different molecule, that is a polar diatomic molecule, so it has an asymmetric electron distribution (i.e. a dipole moment). If we put this molecule in our field, what might happen?

If the field goes positive first, then the negative part of the molecule is pulled towards it, and the positive part is pushed away from it: **the molecule is rotating!** Then when the field changes direction, the negative part is pulled in the other direction and the molecule keeps on rotating. This is illustrated in Figure 2.5. It's a bit like putting your hands on a car steering wheel and pulling harder with one hand than another – if the unbalanced forces will make the wheel rotate.

There's a lot of wonderful complexity to get into here, which involves thinking about quantum mechanical rotation and other things. We'll get into this later on. For now, all I want is for

you to see that it doesn't seem *insane* that exposing a molecule to light could make it start to rotate, right?

### Rotation

A molecule absorbs radiation with a wavelength of 3 mm and starts to rotate. What is the rotational period of this rotation (i.e. the time taken for one complete rotation)?

Would a non-polar molecule rotate when exposed to EM radiation?

### Vibrating Molecules

As a final example, let's imagine a molecule like CO<sub>2</sub>. This molecule is non-polar, so it won't rotate in the oscillating field. Looking at the polarity, can you see what will happen?

As the field oscillates, the negative parts of the dipoles are pushed and pulled up and down. The bond angle opens and closes, and the molecule is **vibrating**. This kind of vibration is called a **bend** for obvious reasons. As before, the frequency of the light affects the frequency of the vibration, because the molecule 'follows' the field of the light.

### Vibration

A ketone absorbs light with a wavenumber of 1715 cm<sup>-1</sup> and starts to vibrate. How many times does the ketone vibrate per second?

Again, lots of complexity here we have skimmed over, but hopefully you can see there is a reason for molecules moving and doing stuff in response to being hit by light beyond 'because that's what the textbook says' – it actually makes some intuitive sense when you think about the charges in the molecules and how they're affected in this oscillating electric field. Later on, we will take these pictures again and reconcile them with a more quantum-mechanical picture of molecular motion, and discover things like **selection rules**. Next time, we are going to look at quantum mechanics, and answer the question:

Can *any* wavelength of light make a molecule vibrate/rotate/become electronically excited?

### Take Home Messages

- We need two pictures (photon and wave) to describe how light behaves, and so there are two corresponding pictures of spectroscopy.
- Light consists of oscillating electric and magnetic fields, and we mostly care about the electric one (unless doing NMR).
- We can understand how molecules respond to being hit by light by thinking about how the charges in them will move as a response to an external field.

## Lecture 3

# Light and Matter II

### Lecture Aims

- To understand that all motion at the atomic scale is quantised.
- To go deeper into photon picture of the interaction of light and matter.
- To start to understand selection rules.

Last time we ended by looking at the wave picture of light, and saw how we can intuitively explain how light makes molecules move around. Specifically, we looked at electrons moving (which results in electronic spectroscopy) and then molecules rotating and vibrating (which result in rotational and vibrational spectroscopy respectively). The real key here is that **the incoming light made the molecules move in some way**. We're going to think about this motion today.

### 3.1 Quantised Molecular Motion

#### 3.1.1 Particle in a Box

At the atomic scale, we already know that things behave differently to how they behave at the macroscopic scale. We've seen last year how the motion of an electron becomes quantised if you trap it in a box, or into a molecule, and you'll explore this in much more depth in CH2203 next semester. Recall that for the particle in a box system, when we had a free particle, the energy of the particle was also totally free and unconstrained. However, when we trapped the particle into a box, we found out that the energy of the particle was **quantised** as a result of needing to fit the wavefunction of the particle into the box. In fact, we wrote an expression for energy of the particle moving around in the box,  $E_n$ :

$$E_n = \frac{n^2 h^2}{8mL^2}$$

Where  $h$  was Planck's constant,  $m$  was the mass of the particle,  $L$  was the length of the box, and  $n$  was a **quantum number** that told us how excited the particle was. If  $n = 1$ , then the particle was in its *ground state*, and if  $n = 2$  it is in the *first excited state*, if  $n = 3$  it is in the *second excited state*, and so on. There are two important things to understand from this picture:

- The energies of the particle **explicitly depend on physical properties of the system**. Here, those properties are the mass of the particle  $m$ , and the length of the box,  $L$ .

- The quantum number  $n$  can only take integer values, so the energy can only take on certain well-defined values. Thus, the energy is **quantised**, and the number  $n$  gives us an index that tells us how energetic the particle is.

### Particle in a Box

What is the energy in eV of the lowest 3 states of an electron trapped inside a box of length 1 Å?

This kind of picture doesn't just apply to a particle moving around in a 1-dimensional box, but actually applies to **every kind of motion at the atomic scale**. Thus, we can find expressions for the energies of electrons in atoms and molecules, the energies of rotating molecules, or the energies of vibrating molecules. All of these different kinds of motion are quantised, just like the energies of the particle in our box.

### 3.1.2 An Example: Quantised Rotation

What I am really saying here sounds weird, that a rotating molecule can only rotate with specific, well defined energies. This is quite weird, but it's the quantum mechanical reality. A rotating molecule can only rotate at certain speeds that are defined by the physical properties of the molecule and a rotational quantum number, which has the symbol  $J$ . Similarly, a vibrating molecule can only vibrate at certain frequencies, defined by the physical properties of the molecule and a vibrational quantum number,  $v$ . It's just the same idea as how electrons in atoms only exist with certain, well-defined energies - in 1s, 2s, 2p, etc.. orbitals, which all have well defined energies. This seems bizarre, but it's real, and we know it is real from looking at spectra. In a few lectures we will see these spectra and see for yourself, and you'll do more of the maths behind this in CH2203 and CH3203 later on. For now, I hope now that you can just trust me as we go forward.

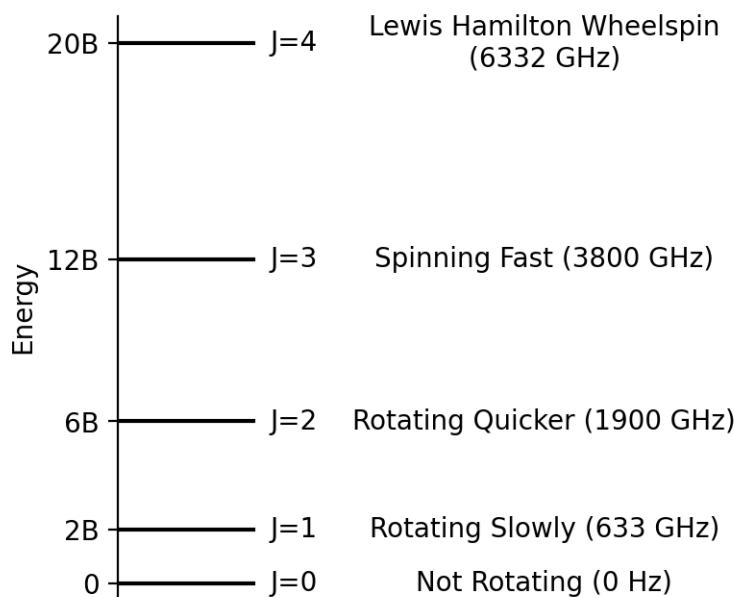
To give you a concrete example of what I mean, let's think about rotating molecules. It turns out<sup>1</sup> that we can describe the quantised rotational motion of a rigid diatomic molecule (where the bond length doesn't change on rotation) with the following expression for the quantised rotational energy levels  $E_J$ :

$$E_J = BJ(J + 1) \text{ where } J = 0, 1, 2 \dots \quad (3.1)$$

Here  $B$  is called the **rotational constant** and  $J$  is the quantum number that keeps track of how excited the molecule is.  $J$  can take any value from zero to infinity, and so we have an infinite number of **accessible states**, even though for any real molecule only the first few will be populated at any normal temperature. The rotational constant  $B$  depends on molecular properties like the mass of the molecule and the bond length, which we will come back to later. You can think of  $B$  as the proportionality constant that links the quantum numbers to the energy. We can calculate the first few energies and see that we have a lot of different levels in Figure 3.1. Higher values of  $J$  correspond to higher rotational excitation.

A good way to try and reconcile this quantum mechanical picture with a classical picture of a simple spinning molecule is to think that when  $J = 0$ , the molecule is not rotating. Then as  $J$  increases we 'step' the rotational speed up higher and higher – the higher the value of  $J$ , the more rotational energy the molecule has, and the faster it rotates. Similar analogies apply to vibration too, but don't panic about understanding all of this right now, as we will see it again much more slowly – this is just to give you a flavour.

<sup>1</sup>See Chapter 1 of Hollas' *Modern Spectroscopy*, or look up 'Diatom Rigid Rotor Model' on Libretexts for a derivation – be warned it gets mathematical!



**Figure 3.1:** Rotational energy levels, with the rotational speeds of HCl annotated for info (1 GHz is 1 billion rotations per second – molecules spin fast!).

It's important to understand this quantisation because it lies at the heart of spectroscopy. Recall the last lecture, where we showed that molecules could start to rotate and vibrate in response to being hit by some light. Now, we hopefully accept that this motion is quantised, so molecules can only rotate and vibrate with specific, well-defined energies. This must mean that **only specific, well-defined energies of light can cause this motion to happen**. So, the question we must now answer is:

*Which energies of light make the different kinds of molecular motion happen?*

To answer this we will go back to our old *states-light-jump* picture.

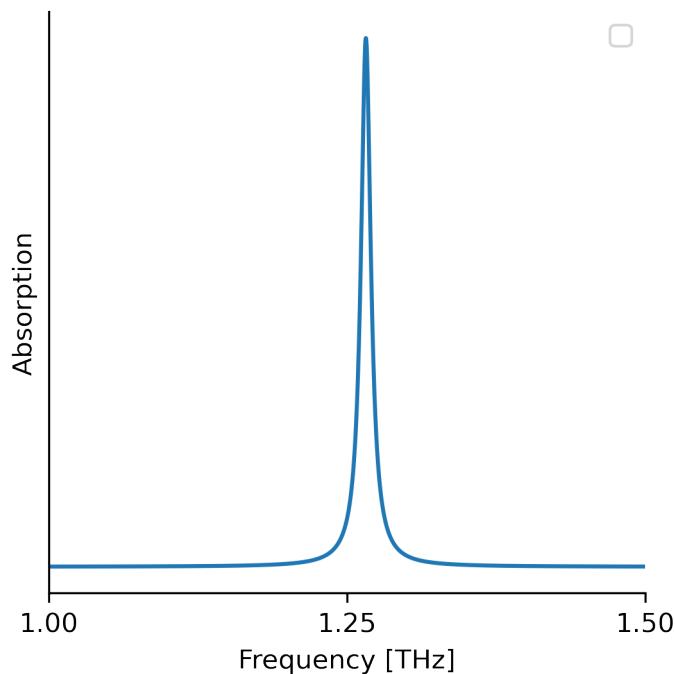
### 3.1.3 Photon Picture Revisited

Recall our old friend, the ‘photon’ picture of spectroscopy where a molecule jumps between two states. We need to think about what these two states actually are in a real atom or molecule. We’ve just seen that molecular motion at the atomic scale is quantised, so any kind of molecular motion is quantised into discrete energy states. **These states are what we are jumping between in the photon picture of spectroscopy.**

Recall that due to energy conservation, the energy of the photon that causes the jump has to exactly match the energy gap between the lower and the upper state:

$$E_{\text{photon}} = E_{\text{upper}} - E_{\text{lower}}$$

Given that we know that the lower and upper state energies are discrete and well-defined due to the quantisation of motion, the energy of the photon that causes the jump must also be specific and well-defined. **Thus, only certain energies of light can make a molecule move.** If we can measure the energy of the light that caused the jump, we can work out a whole host of molecular properties from the definitions of the states.



**Figure 3.2:** The spectrum we would obtain if we shone light with frequencies from 1 to 1.5 THz at our HCl molecule and measured how much was absorbed. HCl absorbs light at 1.266 THz, leading to a peak in the absorption spectrum.

#### Rotational Excitation

A photon of light causes a molecule of HCl undergo a transition from a rotational state with energy  $21.18 \text{ cm}^{-1}$  to an excited state with energy  $63.54 \text{ cm}^{-1}$ . What is the wavelength and frequency of the photon?

## 3.2 Generating Spectra

We are now in a position to understand how we can generate a spectrum by shining light on a molecule. You should have found in the example above that the frequency of the photon was 1.266 THz. So, if we took a sample of HCl and shone some light on it, but we scanned the frequency of the light from 1 to 1.5 THz, then when the frequency of the light hits 1.266 THz, the HCl molecule will absorb the light and start rotating. If we measured how much of the light was absorbed as a function of frequency, we would see something like Figure 3.2, which is a part of the **rotational spectrum** of HCl.

From Figure 3.2 we can work out that the molecule absorbs light at a wavelength of 1.266 THz, and that this corresponds to the energy gap between two rotational states. We say that the light of wavelength 1.266 THz is **resonant** with this energy gap. Later we will see how we can use this to work out properties of the molecule being rotated, like its bond length, and we will explain why this looks like a 'peak' rather than just a straight line. For now, to recap:

- The position of the line in the spectrum corresponds to the energy *difference* between two states (rotational states in this case).
- Knowing this energy difference allows us to calculate various molecular properties.

- The spectrum is generated *because* a transition from a lower state to an upper state happens when light hits the molecule, and in this case it starts to rotate – if this didn't happen, then we wouldn't get a spectrum.

This final point leads us to discussion of an important topic, which is *which transitions can happen, and are all transitions allowed?* What would happen if we used a totally different energy of light to excite the molecule?

### 3.2.1 Selection Rules

Looking at our diagram for the possible rotational energy levels (Figure 3.1), it's clear that we have a very large number of different states, and so an even larger number of combinations of different states we could have transitions between. Are all of these transitions possible?

We have already seen an important rule which is that light can only cause a transition between two states if the photon energy of the light exactly matches the energy gap between the two states, or:

$$E_{\text{photon}} = E_{\text{upper}} - E_{\text{lower}}$$

This rule arises due to conservation of energy. However, this is not the only rule that governs transitions between states. There are other rules, known as **selection rules**, that also determine which transitions are allowed or forbidden. Sometimes a photon might have exactly the right energy to cause a jump between two states, but it is not able to due to another rule being violated.

Selection rules are all specific to different kinds of spectroscopy - the rotational selection rules are different to the vibrational selection rules, and so on. However, in all cases there are **gross selection rules** and **specific selection rules**:

- Gross selection rules determine which broad classes of molecules can produce a certain kind of spectrum.
- Specific selection rules determine which transitions between states are allowed or not.

Rather than talk about all the different possible selection rules here, we will talk about them later on when we spend more time thinking about specific kinds of spectroscopy. For now, let's understand the difference between gross and specific selection rules for rotational spectroscopy.

#### Gross Selection Rules

We've already met a gross selection rule without realising it, in our discussion of rotating molecules last time. Recall that we said a non-polar molecule would not rotate in an oscillating electric field. Now, thinking about the photon picture, we know that this means that absorbing light cannot induce any transitions between rotational states in a non-polar molecule. Thus, if we want to measure a *pure*<sup>2</sup> rotational spectrum of a molecule, the molecule needs to be polar. **This is the gross selection rule for rotational spectroscopy.** It's a gross selection rule, because it tells us a broad class of molecules that can produce a given spectrum – here, it tells us that anything polar can, in theory, produce a rotational spectrum if we shine light of the right wavelength on it.

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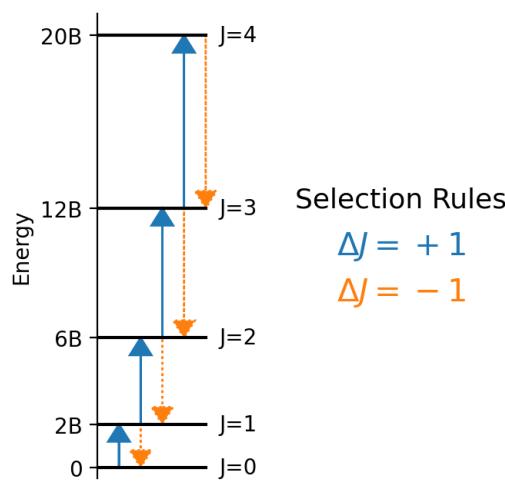
<sup>2</sup>'Pure' in this example means a rotational spectrum that is measured purely by absorbing photons of light. There are other ways to rotationally excite molecules that don't rely on absorption, such as rotational Raman scattering, that can rotationally excite non-polar molecules.

### Specific Selection Rules

Once we accept that our molecule can actually produce a spectrum based on the gross selection rule, then we can apply *specific selection rules* to work out which transitions between different states are actually possible. Specific selection rules are derived from quantum mechanics, and particularly from something called the **transition dipole moment**, which we will discuss later on. For now, recall that we already met some selection rules last year in atomic spectroscopy, where we had that  $\Delta l = \pm 1$ , and so on. For rotational spectroscopy, the selection rule is quite similar:

$$\Delta J = \pm 1$$

Which comes from the fact that the photon carries one ‘unit’ of angular momentum<sup>3</sup>, so can only change the angular momentum of the molecule by 1 each time it hits the molecule ( $\Delta J = +1$  for absorption and  $-1$  for emission). This means that the allowed transitions are as shown in Figure 3.3.



**Figure 3.3:** Allowed transitions in rotational spectroscopy. Absorptions ( $\Delta J = +1$ ) are shown in blue solid, and emissions ( $\Delta J = -1$ ) are shown in orange dashed.

We are now agonisingly close to being able to predict what a real rotational spectrum looks like, so let’s do it.

### 3.2.2 Real Rotational Spectra

To take stock, we know what the rotational energy levels are (from Equation 3.1 and Figure 3.1), and we know that an allowed transition will obey the rule that  $\Delta J = \pm 1$ . So, if we assume the transition is an absorption from a state with quantum number  $J$  to a state with quantum number  $J + 1$ , a photon of light that will be absorbed by our molecule must have an energy of:

$$E_{\text{photon}} = E_{J+1} - E_J$$

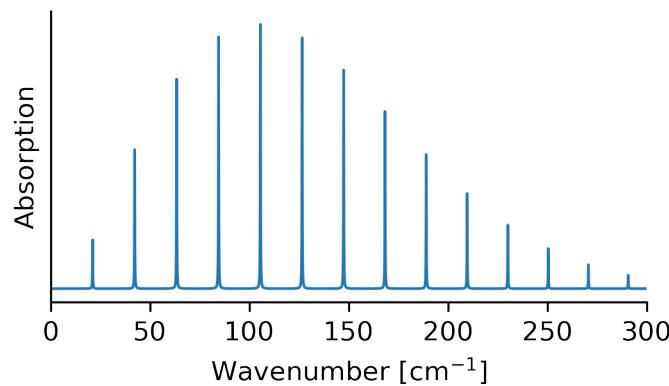
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<sup>3</sup>Rotation is all about angular momentum - and in many ways the rotation of a molecule is analogous to the rotation of an electron around an atom, which is what we learnt about last year in atomic spectroscopy.

We can then use Equation 3.1 and find:

$$\begin{aligned} E_{\text{photon}} &= B(J+1)(J+2) - BJ(J+1) \\ &= B[(J+1)(J+2) - J(J+1)] \\ &= B(J^2 + 3J + 2 - J^2 - J) \\ &= B(2J+2) \\ &= 2B(J+1) \end{aligned}$$

So, given our expression for energy levels and the selection rules, we would expect that any photon with an energy of  $2B(J+1)$  will be absorbed by our molecule and make it start rotating.  $J$  takes integer values: 0, 1, 2.... Thus, in our spectrum, we would expect to see a *series of lines that correspond to the different possible values of  $J$* , right? Let's look at the real, measured, rotational spectrum for HCl (Figure 3.4) and see if experiment matches our theory.



**Figure 3.4:** A rotational spectrum of HCl. Note the discrete set of lines corresponding to different values of  $J$ , as we predicted.

Breathtaking stuff. I wish it was my first time again.

We can go a little further and think about where these lines must be. We've predicted that the lines will have energies of  $2B(J+1)$ , where  $J = 0, 1, 2, \dots$ . Thus, the lines should be at  $2B, 4B, 6B, \dots$ . Clearly, if we can measure where the lines are, we can calculate the rotational constant – which depends on molecular properties such as bond length, which we would then be able to calculate! This process is really fundamental to this course (and we will see many examples), but it is worth noting the steps involved:

1. Take an expression for the quantised energy levels (which will be given to you in this course).
2. Consider any selection rules (also given to you) and work out an expression for the positions of the lines in the spectrum.
3. Using given spectra data, calculate molecular properties from the spectrum.

The process is the same for many kinds of spectroscopy, and we will see a lot of examples. It is important that you understand this process, and realise that it doesn't matter whether we are looking at rotational, vibrational, electronic, or whatever energy levels – its always the same idea!

### 3.2.3 Closing Remarks

Hopefully Figure 3.4 makes sense given our previous discussion, in that we see a series of lines that correspond to the different photons that can be absorbed by our molecule. But there is also lot of stuff that raises new questions, like why all the lines are different heights – we'll answer some of these questions in due course.

I appreciate this has been a whistlestop lecture with a lot of new content, so let's just summarise before we consolidate it with problems in the next session and then carry on.

- Light shining on molecules makes them move.
- We can understand this with both a wave picture (qualitative) and a photon picture (quantitative).
- The motion of molecules is quantised, and each molecule possesses a set of quantised energy levels that correspond to each type of motion. The energy of these levels depends on properties of the molecules.
- Transitions between these levels (governed by selection rules) give rise to spectra, that we can then use to work back and find out molecular properties.

Now it's time for **Problem Sheet 1**.

#### Take Home Messages

- All motion (rotation, vibration, electronic) is quantised at the atomic level.
- We can understand the interaction of light and matter quantum mechanically, by thinking about transitions between different energy levels that correspond to different kinds of motion.
- The transitions that are allowed to happen between states are governed by selection rules.

### Problem Sheet 1

1. i A laser produces light with a wavelength of 800 nm. What is the photon energy (in eV) and the frequency of this light?  
 ii An infrared source in a spectrometer produces light at  $3000\text{ cm}^{-1}$ . What is the photon energy (in J) and wavelength of this light?  
 iii What is the wavelength of a photon with an energy of 4.2 eV?  
 iv What is the energy (in  $\text{kJ mol}^{-1}$ ) of a photon of light with a wavelength of 266 nm?
2. Which of the following molecules would rotate if placed in an oscillating electric field? Explain your answers with sketches. Which of the molecules would produce a pure rotational spectrum?
 

i HF              ii CH<sub>4</sub>              iii H<sub>2</sub>O              iv CO<sub>2</sub>              v OCS
3. Light with a wavelength of 355 nm is absorbed by a molecule. The ground state of the molecule has an energy of 0.2 eV. What is the energy of the excited state populated by this absorption?
4. A sample of 1000 molecules is examined and it is found that 900 are in their electronic ground state (singly degenerate), and 100 are in the first electronic excited state (triply degenerate). The excitation was performed by a light source emitting at a wavelength of 190 nm.  
 What is the temperature of this sample of molecules?
5. This is an extended problem designed to introduce you to how we can calculate simple molecular properties from spectroscopy, we will encounter similar examples throughout this course.

The energy levels of a rotating rigid molecule are given by:

$$E = BJ(J + 1)$$

Where  $B$  is the *rotational constant* and is given by:

$$B = \frac{\hbar}{8\pi^2 c I} \quad \text{in units of cm}^{-1}$$

Where  $I$  is the **moment of inertia** of the molecule, and  $c$  is the speed of light in a vacuum. For a diatomic molecule consisting of atoms with mass  $m_1$  and  $m_2$  separated by a bond length  $r$ , the moment of inertia is given by:

$$I = \mu r^2 \quad \text{where } \mu = \frac{m_1 m_2}{m_1 + m_2}$$

The quantity  $\mu$  is known as the *reduced mass* of the system.

- i Show that the units of  $B$  are  $\text{cm}^{-1}$  if we write  $c$  as  $2.997 \times 10^{10} \text{ cm s}^{-1}$ . By using the relationship  $E = hc\nu$ , or otherwise, show that  $B$  in units of **Joules** is given by:

$$B = \frac{\hbar^2}{8\pi^2 I} = \frac{\hbar^2}{2I} \quad \text{where } \hbar = \frac{\hbar}{2\pi}$$

- ii The specific selection rule for an allowed rotational *absorption* is that  $\Delta J = +1$ . Show that the energy of the photon  $E_p$  that can cause an absorption from a state  $J$  to state  $J + 1$  is given by:

$$E_p = 2B(J + 1)$$

Is the  $J$  in this expression the quantum number of the lower state, or the upper state?

- iii The diatomic molecule nitric oxide (NO) undergoes a transition from the  $J = 0$  state to the  $J = 1$  state when irradiated with a photon of light of energy  $3.343\,90\,\text{cm}^{-1}$ . Show that the rotational constant of NO can be written as :

$$B = 1.671\,95\,\text{cm}^{-1} = 3.323\,02 \times 10^{-23}\,\text{J}$$

- iv Show that the moment of inertia of NO is  $1.674\,76 \times 10^{-46}\,\text{kgm}^2$ .
- v Given that the mass of a nitrogen atom is  $14\,\text{u}$  and the mass of an oxygen atom is  $16\,\text{u}$ , where  $1\,\text{u} = 1.6606 \times 10^{-27}\,\text{kg}$ , calculate the bond length of NO in both metres and Ångstrom.

## Lecture 4

# Interpreting Spectra

### Lecture Aims

- To understand how to read a spectrum.
- To understand how peak position, peak width, and peak area can provide chemical information.
- To calculate molecular properties from simple spectra.

Last time, we spoke about how light and matter interact, and about how all molecular motion is quantised. We ended up showing that if we take an expression for quantised rotational energy levels, that we can predict that we'd see a series of lines in a rotational spectrum.

In the problem sheet just done, we worked through an extended problem and could calculate the bond length of a diatomic molecule from information obtained from its rotational spectrum. Today we will think more about what we can learn from spectra, and consolidate what we did in this problem set.

### 4.1 Reading Spectra

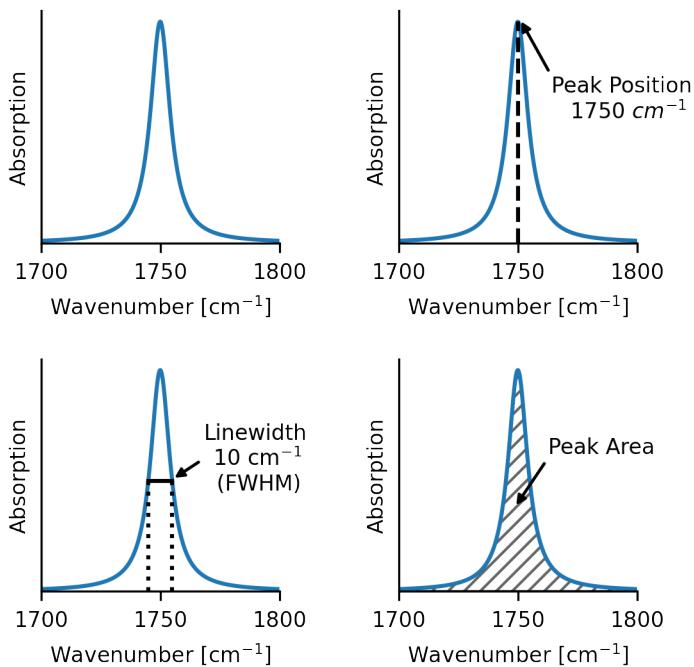
Recall CH1200, where we said some very general things about reading spectra:

- Energy (or something easily convertible to energy, like wavelength, frequency, wavenumber, or chemical shift) is on the x-axis.
- Some measure of how much light is emitted or absorbed (absorbance, emittance, transmittance, intensity) is on the y-axis.

We also know that our spectra will generally consist of a series of different peaks. There are three things that characterise each peak in a spectrum that allow us to figure out chemical information from the spectrum:

- The **position** of the peak along the energy axis.
- The **width** of the peak.
- The **area** underneath the peak.

Let us speak generally, and use a simple spectrum containing a single peak to illustrate how these things work.



**Figure 4.1:** A single spectral peak, with key features highlighted.

#### 4.1.1 Peak Position

The single **most** important thing to look at when reading a spectrum is the position of the peaks along the energy axis. We already know that the power of spectroscopy comes from being able to determine gaps between quantum mechanical energy levels in a molecule, which can then be linked to a wealth of information about the structure of said molecule. We also know that the positions of peaks in a spectrum is directly proportional to these energy gaps. Knowing the positions of the peaks, means we know the energy gaps, which allows us to get structural information:

$$\text{Peak Position} \rightarrow \text{Gaps between Energy Levels} \rightarrow \text{Structural Information}$$

The position of the peak is defined intuitively, as shown in Figure 4.1 (upper right panel).

Sometimes in spectroscopy we will measure peak positions, and then work back to find out molecular structure (as in problem 5 for the problem sheet). This approach is most common for simple molecular systems. Other times (particularly for complex molecules, or large systems like proteins), we might start by calculating which peaks we expect to see for a variety of different molecular structures, and then comparing these different calculated spectra to a 'real' experimental spectrum to decide which one matches best, and thus which structure is present. We'll see examples of this soon.

### 4.1.2 Peak Width

The **width** of a peak in a spectrum can be defined in a couple of different ways, but a common way is to define it as the **Full Width at Half Maximum (FWHM)**<sup>1</sup> of the peak. This means that we look at how wide the peak is at half of the maximum height – illustrated in Figure 4.1 (lower left panel). However, taking a step back, it's probably not clear *why* the peak has a width and isn't just a single straight line. After all, the energy gap between the different states has a well-defined energy, and the peak having width implies that photons of a range of energies can be absorbed by the molecules, not just that which exactly matches the the energy gap. So what's going on?

The answer is that all spectral lines will actually have some finite width, and this can be caused by many factors. We will group these into two groups:

- **Intrinsic** factors that relate to the molecule and system being studied.
- **Extrinsic** factors that relate to the way the spectroscopic measurement is being done.

#### Intrinsic Factors - Lifetime Broadening

The most fundamental reason that spectral lines are broadened and are not just single sharp straight lines is a phenomenon called **lifetime broadening**. When a molecule jumps up to an excited state, it will not stay excited forever. The excited state has a **lifetime**, because at some point it will randomly undergo spontaneous emission and relax back to the ground state<sup>2</sup>. This relaxation process is random in nature – when we define a lifetime it is an *average* lifetime of a large sample of molecules. These finite lifetimes result in the lines in our spectra being broadened away from infinitely sharp 'lines' and towards wider 'peaks'. The fundamental reason behind this is due to the mathematics of Fourier transforms<sup>3</sup>, but a hand-wavy intuitive explanation is as follows.

Imagine that it takes some time to accurately measure the energy of a state. If you can measure for a long time, then you are going to be very sure of the energy of the state you are measuring. Thus:

- If the state is **long-lived**, then you have a lot of time to measure it and can be very sure of the energy – thus the peak in your spectrum has a **narrow linewidth**.
- If the state is **short-lived**, then you don't have long to measure it and the state has decayed before you are very sure of the energy – the peak in your spectrum has to have a **broad linewidth** to reflect this uncertainty.

This **lifetime broadening** is what makes the spectral line look like it does, a shape which is known as a **Lorentzian** profile. Relating the measured linewidth  $\Gamma$  to a lifetime  $\tau$  can be done very approximately with:

$$\Gamma \approx \frac{1}{\tau}$$

Just remember that this means that in the absence of any other broadening mechanism:

---

<sup>1</sup>Another common measure is the **Half Width at Half Maximum (HWHM)** – this is just half of the FWHM.

<sup>2</sup>In some spectroscopies, like NMR, the spontaneous emission rate is almost negligible and this leads to cool quantum mechanical effects, which is part of why NMR is so useful.

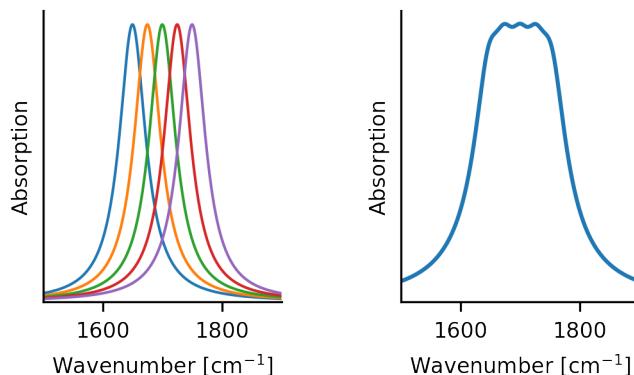
<sup>3</sup>Time and frequency (energy) are a *Fourier transform pair*, and this means that a signal that is narrow in frequency space (narrow linewidth) is broad in temporal space (long lifetime), and vice versa. See <https://www.youtube.com/watch?v=spUNpyF58BY> for a nice introduction.

- A broad line means that the excited state is short lived.
- A narrow line means that the excited state is long lived.

Lifetime broadening is always there, but often it is small compared to other sources of broadening. However, it can be influenced by the thing surrounding the molecule you are interested in - like a solvent. A solvent present in a system can collide with the excited molecules and de-excite them more quickly than they would if they were just left to their own devices. This means the lifetimes are shortened and so the linewidths increase – this is called **collisional broadening**, or sometimes **pressure broadening**<sup>4</sup>. A consequence of this is that the width of peaks in a spectrum can give you information about solvation environments – and is one reason why a lot of solution phase spectra look like big messy blobs rather than nice sharp lines.

### Intrinsic Factors - Overlapping Peaks

In modern spectroscopy we are often looking at relatively huge systems, like proteins, or other big molecules. These molecules will contain a very large number of different functional groups that can absorb or emit light – a protein might contain 40 or 50 different amide groups which all will absorb light in similar, but slightly different, regions of the infrared EM spectrum. Each of these functional groups will have its own natural linewidth, but they'll often be so closely spaced together that when you measure the spectrum they coalesce into one enormous ‘blob’ type peak.



**Figure 4.2:** Multiple closely spaced peaks (left) can overlap to produce one big combined ‘blob’ peak (right). This is common in many kinds of spectroscopy – the hint of some wiggly line on top of the combined peak is not noise, but is a teaser of some beautiful quantum mechanics you might learn about later in life.

In biological spectroscopy peak broadening due to overlapping smaller peaks, and due to collisional broadening smearing out any fine structure, is often quite significant. We'll see some examples of this later, but a key point here is that we will only really see beautiful spectra with series of sharp lines if we are working in the gas phase!

### Extrinsic Factors - Instrumental Broadening

Other sources of line broadening relate to how spectroscopic measurements are conducted. These can mostly be encapsulated under the term **instrumental broadening**. To see how this works, consider a typical experiment which relies on the following steps:

---

<sup>4</sup>As in the gas phase this process depends a lot on pressure.



**Figure 4.3:** Low resolution: a homemade UV-Vis spectrometer made of Lego and a webcam. You'll make one of these this year in the teaching labs. The resolution is probably about 5 nm at best (which is still not that much worse than a standard commercial instrument).



**Figure 4.4:** High resolution: the operating principle of the ESPRESSO instrument in the European Southern Observatory. This spectrometer looks at light from space to identify distant planets based on their spectral signatures. The resolution is about 0.002 nm – over 1000 times better!

1. Shine some light on a molecule from a light source.
2. The molecule interacts with the light in some way.
3. Detect the light that is absorbed/emitted/modified by the molecule.

Each of these steps can result in peaks being broadened, and step 2 is where all of the intrinsic broadening comes in. However, steps 1 and 3 are often those that induce most broadening and limit the spectral resolution of our spectroscopy experiments.

This happens because any spectroscopic instrument has a defined *spectral resolution*, which is defined as the smallest energy difference between two lines in a spectrum that can be distinguished. For example, a UV-Vis spectrometer might have a spectral resolution of 1 nm, which means that two lines with peaks that are less than 1 nm apart will not be distinguishable. In terms of wavelength, we give spectral resolution the symbol  $\Delta\lambda$ , with similar symbols ( $\Delta\nu$ ,  $\Delta\bar{\nu}$ ,  $\Delta E$ ) depending on the energy units used.

Overall, broadening of peaks is generally an annoyance, and we would rather have infinitely sharp peaks! However, it's a reality, and in some cases can even provide us useful information about solvation environments and other things. It's important to understand the resolution of your spectroscopic measurements, as this puts a hard limit on what you can resolve, and has a significant impact on the error in any spectroscopic experiment.

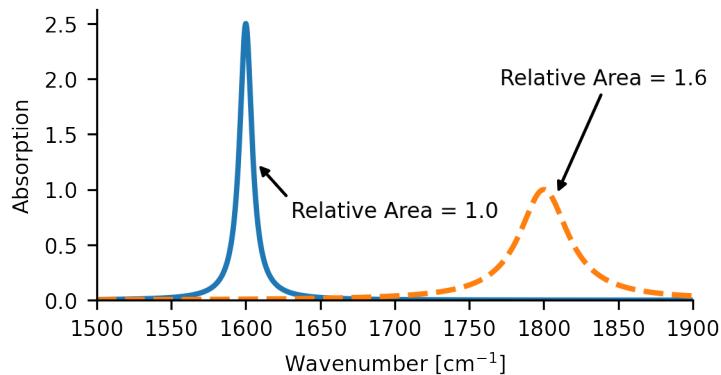
### 4.1.3 Peak Area

The area under a peak gives you an indication of how 'strong' that peak is in the spectrum, which directly relates to:

- The population of the lower state in the transition – i.e. how many molecules are in this state.
- How strongly that transition interacts with the light – i.e. how many photons are absorbed/emitted/affected by it.

So we can get information about how many of our molecules are in a given quantum state by looking at the area under peaks in our spectra. Note that peak *area* is a much better indicator

of this than the peak *height*, because a peak could be very high and very narrow, and actually be less intense than a shorter, much broader peak<sup>5</sup>. Ultimately a peak tells you how many photons produce a certain spectral line, and you need to add up all the photons that do this at every relevant energy to get this information – information that the area under the peak directly gives you. This is why NMR spectra always give you the **integration** of peaks rather than the height.

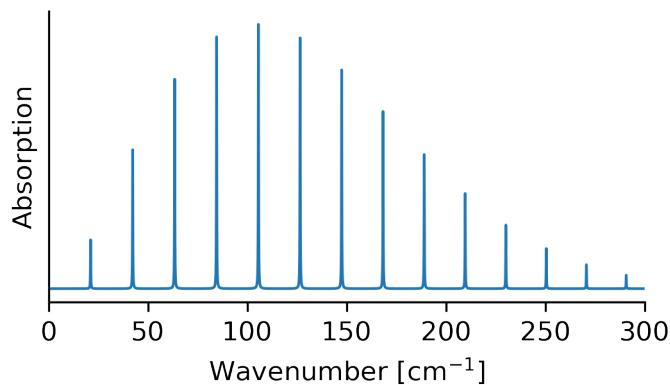


**Figure 4.5:** Two peaks of different heights – the leftmost peak (solid line) has a height of 2.5, but an area of 1.0. The rightmost peak (dashed line) has a height of 1.0, but an area of 1.6, so it is a more intense transition than the leftmost peak. Peak area is generally a better measure than peak height!

In the example above, this could tell us that we have 1.6 times more of the functional group that vibrates at  $1800\text{ cm}^{-1}$  than the one that vibrates at  $1600\text{ cm}^{-1}$ . We will see some examples of how peak area is useful to determine things like temperature and orbital occupancy later on.

## 4.2 Putting it into Practice

Lets now use what we've discussed today to look again at our rotational spectrum of HCl and try and learn some chemical information from it.



**Figure 4.6:** A rotational spectrum of HCl.

Last time, we worked out a formula for the position of each spectral line, remembering that we are always looking at the transition between two states:

$$\bar{\nu} = 2B(J + 1)$$

---

<sup>5</sup>In some cases thinking about peak height is justified, because all the peaks have the same linewidth. It is also often very difficult to accurately measure the peak area in some kinds of spectroscopy due to small signals and large amounts of noise in the measurements – often people use peak height here as they have no other choice.

Transition	Energy	Wavenumber for HCl (cm <sup>-1</sup> )
$J = 0 \rightarrow 1$	2B	21.18
$J = 1 \rightarrow 2$	4B	42.34
$J = 2 \rightarrow 3$	6B	63.48
$J = 3 \rightarrow 4$	8B	84.59

**Table 4.1:** Data obtained from the HCl spectrum in Figure 4.6

Recall that  $J = 0, 1, 2, \dots$  and that our specific selection rule was that  $\Delta J = \pm 1$ . Considering this and the equation above, we would expect to see lines at  $2B$ ,  $4B$ ,  $6B$ ,  $8B$ , etc. Thus, our lowest energy spectral line will have energy  $2B$ , and the gap between any two adjacent lines is also  $2B$ . This is tabulated in Table 4.1, along with the measured wavenumber of each line (read from the spectrum). So this explains why we see a consistent spacing of lines. Neat! Try to annotate the spectrum with the transitions that give rise to each peak.

From any of these peak positions, we can then easily work out the rotational constant for HCl, which is:

$$B = \frac{21.18}{2} = 10.59 \text{ cm}^{-1}$$

Following the same procedure as in problem 5 from problem sheet 1, we can use this rotational constant to work out the moment of inertia of HCl, and you'd find it is  $2.644 \times 10^{-47} \text{ kg m}^2$ . If we then assume that our HCl consists of a normal mixture of H<sup>35</sup>Cl and H<sup>37</sup>Cl, then we can take the mass of a chlorine atom to be 35.45 u, and thus calculate the bond length.

### Bond Length of HCl

The moment of inertia of HCl is  $2.644 \times 10^{-47} \text{ kg m}^2$ , as calculated from the measured rotational constant. If we take the mass of a chlorine atom to be 35.45 u, what is the bond length of HCl?

What would the bond length of DCI be? Would you expect the rotational spectrum of DCI to look different to HCl?

Figuring out diatomic bond lengths is cool, but it's not everything we can learn. Looking at our spectrum, it's clear that each peak has the same linewidth, so we can't really learn a lot from the linewidth (other than that our instrument has a good resolution!). However, look at the peaks - they are all different heights, and so will all have different areas. We know from earlier that the size of the peaks (area) is proportional to the population of the lower state in the corresponding transition. So, if we can identify the largest peak, that tells us the state with maximum population. The populations of the different states depends on the *temperature* of the sample of molecules (think back to the Boltzmann distribution), so we should be able to use the sizes of the peaks to work out the temperature of the molecules we are measuring the spectrum of.

It turns out (see problem sheet 2), that if we can identify the rotational state with the largest population (call it  $J_{\max}$ ) from our spectrum, we can link this directly to the temperature of the sample of molecules as follows:

$$T = \frac{2hcB}{k_B} \left( J_{\max} + \frac{1}{2} \right)^2$$

Looking at our spectrum, and counting the peaks (knowing that the first peak comes from the  $J = 0$  level, second from  $J = 1$  and so on), we see that the largest peak corresponds to the

$J = 4 \rightarrow 5$  transition (all the peaks have the same linewidth, so it's OK to look at peak height here). Thus,  $J_{\max} = 4$ , and with the formula above we can figure out that the temperature of sample of molecules is roughly 617 K<sup>6</sup>.

So, I hope you can see that you can actually learn some useful things from spectra. There are even more things we can learn, and we'll see some examples as we go along. Next time we will step away from pure rotational spectroscopy and see some more examples.

#### Take Home Messages

- Peak position, width, and area are the important things to consider when analysing spectra.
- Peak position is often the most useful, as peak position is exquisitely sensitive to molecular and system properties.
- Peak width and area are more subtle, but can also provide useful information around lifetimes and the environment of the system under investigation.

<sup>6</sup>Very roughly, because in reality we are entering a whole calculus nightmare. To derive the expression above we are treating a quantised thing as a continuous variable (illegal), and also have assumed spontaneous emission is negligible in terms of its effect on population (illegal-ish). In reality the temperature of the molecules giving that spectrum is 600 K (I know, because I simulated it), but being out by 17 K isn't too bad. Spectroscopy is complicated once you start thinking about things properly, and is part of the reason 99% of users treat it in a 'this blob means O-H, this blob means N-H, look mum, I'm a spectroscopist!' way.

## Lecture 5

# Vibrations

### Lecture Aims

- To start to understand simple vibrational spectra.
- To calculate molecular properties from simple vibrational spectra.
- To start to think about combined spectroscopies, like **rovibrational** spectroscopy.

Last time we talked about reading spectra and showed how we can calculate simple things like bond lengths from a rotational spectra. The fundamental idea, to recap, is that the positions of the peaks in the rotational spectrum depend strongly on the moment of inertia of the molecule, which depends on both the mass of the molecule and any bond lengths within it. To labour the point:

Spectra are very sensitive to physical molecular properties - if we can measure the spectrum, we can usually work out these properties.

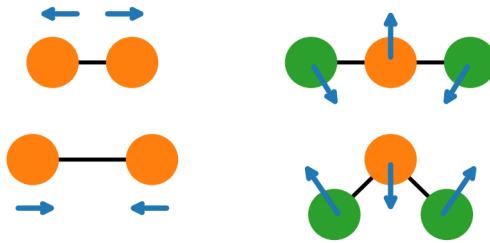
Rotational spectroscopy is a nice kind of spectroscopy to learn about initially as it's quite intuitive (you can imagine that a heavier molecule will rotate more slowly than a lighter one), and the equations are relatively simple<sup>1</sup>. However, it gets a little more complex when molecules get bigger, and actually these days is not a very common technique – I'd be surprised if many of you ever used rotational spectroscopy in your later careers, unless you go into astrochemistry. So, now we will look at a much more commonly used spectroscopy, which is **vibrational spectroscopy** – or as you probably know it, **infrared spectroscopy**.

### 5.1 Vibrational Spectroscopy

A good way to think about vibration of molecules is to imagine the atoms as balls that are connected by springs, which are the bonds. The atoms can then move relative to each other, and these motions are called **vibrations**. Vibrations can be **stretches** (one bond stretching and compressing), or **bends** (a bond angle opening and closing), or other kinds of motion – but the important thing is vibrations are nuclei moving relative to each other. Two common kinds of vibration are shown in Figure 5.1.

Molecular vibration is quantised in the same way that molecular rotation is, so molecular vibrations have well-defined energies, and happen at well-defined frequencies. However, when we

<sup>1</sup>At least, as we used them.



**Figure 5.1:** Left: a stretching vibrational mode. Right: a bending vibrational mode.

think about rotation, a molecule can actually only rotate in three ways – around each of the coordinate axes. In contrast, molecules can vibrate in many different ways, and we can work out how many ways they can vibrate by thinking about **degrees of freedom**.

### 5.1.1 Degrees of Freedom

A good way to think about a *degree of freedom* is that it is a single contribution to the energy of a molecule. The total energy of the molecule can then be broken down into contributions from all the different degrees of freedom. The energy of a molecule is inextricably linked to its motion, and so we can say that a molecule consisting of  $N$  atoms has  $3N$  *degrees of freedom*<sup>2</sup>, because each atom can move in three dimensions, and so the total number of possible ways in which the molecule can move is just three times the number of atoms. In terms of energy, this means there are  $3N$  ‘places’ that we can put energy in the molecule – you should have met this concept last year in CH1203.

Of those  $3N$  degrees of freedom, there are:

- 3 that relate to **translation** of the whole molecule (moving it around in space).
- 2 (if the molecule is linear) or 3 (if it is non-linear) that relate to the **rotation** of the whole molecule.
- The remainder relate to **vibration** of the molecule – motion of the atoms relative to each other.

We can then easily work out how many relate to vibration, given that we have  $3N$  in total and  $2 + 3 = 5$  relating to translation and rotation for a linear molecule, or  $3 + 3 = 6$  relating to translation and rotation for a nonlinear molecule. Thus, the total number of vibrational degrees of freedom in a molecule is:

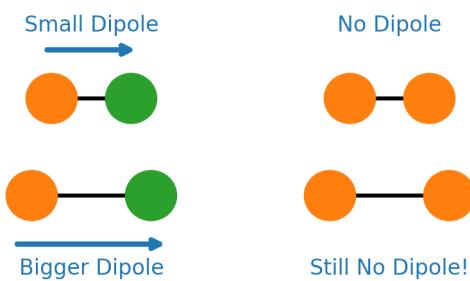
$$3N - 5 \text{ (if the molecule is linear), or } 3N - 6 \text{ (if it is non linear)}$$

The number of vibrational degrees of freedom tells us how many different ways there are that the molecule can vibrate. Let’s keep using a simple diatomic molecule like HCl as first example. How many vibrational degrees of freedom are there?

You should find there is one, because  $3N - 5 = 6 - 5 = 1$ . This means that there is only one possible vibration in HCl, so only one way in which the nuclei can move relative to each other.

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<sup>2</sup>Not counting electronic degrees of freedom, just ones that relate to the motion of the nuclei – which is fine for what we need to do here.



**Figure 5.2:** Left: a stretching vibrational mode in a polar diatomic like HCl. The dipole moment clearly changes on vibration. Right: a stretching vibrational mode in a non-polar diatomic like N<sub>2</sub>. There is no dipole moment change on vibration.

This type of vibration is called a **stretch** and is illustrated in the left hand pane of Figure 5.1, because we are stretching and compressing the bond between the two nuclei.

We call each vibrational degree of freedom a **vibrational mode**, and you'll hear people talk about the *number of vibrational modes*, or the *number of IR active modes* – they're just referring to how many possible vibrations there are in a given molecule.

#### Degrees of Freedom

How many vibrational modes are there in:

1. Water (H<sub>2</sub>O)
2. Acetone (C<sub>3</sub>H<sub>6</sub>O)
3. Neon (Ne)
4. Hemoglobin, the protein which carries oxygen in blood, which contains 4679 atoms.

#### 5.1.2 Vibrational Excitation

A simple type of vibrational mode is the one we have just seen, a **stretching mode**. There are other kinds too, like **bending modes** and **twisting modes**, but we don't need to get hung up on this, and we'll see some examples later. Continuing with our HCl molecule, we know we have one vibrational mode which is a stretch. Our aim in spectroscopy is to shine light on the molecule and make it vibrate, so is it possible for us to excite this vibration by shining light on the molecule? To work this out, we need to know what the **selection rules** are.

The gross selection rule for vibrational spectroscopy is that:

*The dipole moment of the molecule must change during the vibration.*

To understand this, let's think back to our wave picture of light causing vibration we saw in Figure 2.6. For the electric field of the light to make the molecule vibrate, the polarity of the molecule has to change a bit so that positive parts are pulled towards negative parts of the field and vice versa. It's most easy to explain this by looking at two examples – one where the dipole moment does change, and another where it doesn't.

So, to see a pure vibrational spectrum<sup>3</sup>, the dipole moment of the molecule has to change during the vibration. That's our gross selection rule, and we also have a specific selection rule which tells us exactly how the quantum state of the molecule changes during the vibration.

To understand the specific selection rule, we first have to think about the vibrational quantum states we can have, and their energies. We will treat our vibrating bond as a **harmonic oscillator**, which means that as you stretch or compress the bond (by a distance  $x$ ), the force with which the bond 'resists' that stretching or compression ( $F$ ) is given by:

$$F = -kx$$

Where  $k$  is the **force constant** of the bond. The equation above is known as Hooke's Law and you might have seen it if you did A level physics. This is a reasonable model provided that we don't stretch or compress our bond too much (as nothing in this model accounts for the possibility that the bond might break). The harmonic oscillator model is reasonable for a lot of systems, especially at low vibrational excitation. We can turn this force into a potential energy  $V$  using some elementary calculus (an exercise for you):

$$V = \frac{1}{2}kx^2$$

Which tells us that as we stretch or compress our bond (increasing or decreasing  $x$ ), the energy of our system rises quadratically with the extension. Note that  $x = r - r_e$ , where  $r_e$  is the equilibrium position of the bond (the equilibrium bond length). The quantity  $x$  therefore tells you how far from equilibrium the bond is stretched or compressed.

So, if we treat our vibrating diatomic molecule as a harmonic oscillator and do a lot of maths to solve the Schrödinger equation<sup>4</sup>, then we find we can write our vibrational energy levels  $E_v$  (in Joules) as:

$$E_v = h\nu \left( v + \frac{1}{2} \right) \quad (5.1)$$

Here  $h$  has its usual meaning,  $\nu$  is the **fundamental vibrational frequency**, and  $v$  is the **vibrational quantum number**, which takes values of  $0, 1, 2 \dots$  in integer steps and again is an index that tells us how vibrationally excited our molecule is. The value of  $\nu$  depends on physical properties of the bond that is vibrating:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

Where  $k$  is the **force constant** we met earlier and relates to the stiffness of the bond. An intuitive way to think about it is that high values of  $k$  mean that the bond is difficult to stretch or compress, and vice versa. We've already met  $\mu$  and this is the **reduced mass** of the vibrating system. Can you rationalise the form of the equation for  $\nu$  by thinking about what you would expect to happen in the case of  $k$  and  $\mu$  being low or high? Would a stiff spring vibrate with a high or low frequency?

The quantity  $\nu$  is the **classical vibrational frequency** of the bond, and tells us the 'natural' frequency that the bond will vibrate with – in Hertz (when expressed using the equation above). However, normally in vibrational spectroscopy we express things in units of wavenumbers, so it's important that we can interconvert these units comfortably.

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<sup>3</sup>As with rotation, there are ways to excite vibration that don't involve absorbing IR photons, such as in *vibrational Raman spectroscopy*.

<sup>4</sup>See Atkins MQM, or Chem Libretexts has a good entry under 'Harmonic Oscillator'.

### Vibrational Energy Units

Show that the expression for  $E_v$  given in units of wavenumbers ( $\text{cm}^{-1}$ ) is:

$$\bar{\nu} = \frac{\nu}{100c} \left( v + \frac{1}{2} \right)$$

Wavenumbers are a more common unit to use in vibrational spectroscopy. In fact, it's common to introduce a new quantity  $\omega = \nu/100c$ , so we can write the energy in wavenumbers as:

$$\bar{\nu} = \omega \left( v + \frac{1}{2} \right)$$

The quantity  $\omega$  introduced above is useful for us, as this tell us what the **fundamental wavenumber** of the vibration is (in the same way that  $\nu$  told us the fundamental frequency). The fundamental wavenumber is like the 'natural' energy the vibration has. We're now in a position to think about what these energy levels look like.

### Vibrational Energy Levels

Sketch the first 6 vibrational energy levels for a harmonic oscillator, and think about the following questions:

- What is the gap between any two adjacent vibrational energy levels?
- What is the lowest vibrational energy level a molecule can have? Can it have no vibrational energy?
- What is the maximum vibrational energy level a molecule can have? Is this physically reasonable?

How good do you think the harmonic oscillator model is, as a way to model chemical bonds?

Circling back to our main aim here, which is to think about vibrational spectra, we need to know the specific selection rule. Doing the quantum mechanics and thinking about the transition dipole moment<sup>5</sup> results in the specific selection rule being that:

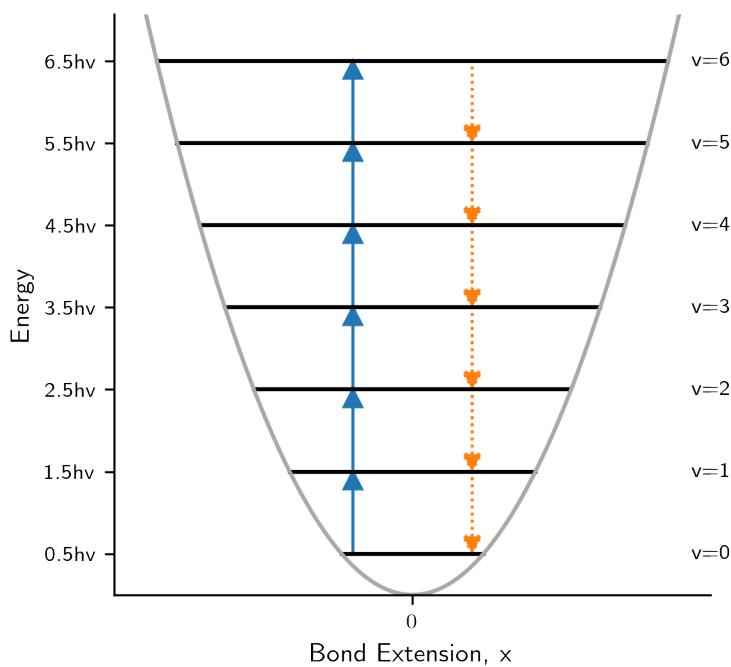
$$\Delta v = \pm 1$$

Where  $\Delta v = +1$  corresponds to absorption of an IR photon (so the molecule becomes excited and gains energy), and  $\Delta v = -1$  corresponds to emission of an IR photon (so the molecule loses energy and spits out a photon). If we consider IR absorption, then the energy gap between two levels is given by:

$$\begin{aligned} E_{v+1} - E_v &= h\nu \left( v + \frac{3}{2} \right) - h\nu \left( v + \frac{1}{2} \right) \\ &= h\nu \left( \frac{3}{2} - \frac{1}{2} \right) \\ &= h\nu \end{aligned}$$

This is interesting, because it tells us that the energy gap between vibrational states with quantum numbers  $v$  and  $v + 1$  is actually *independent of  $v$* . It doesn't matter whether we excite from

<sup>5</sup>See chapter 6 in Hollas' *Modern Spectroscopy*, or chapter 10 in edition 5 of Atkins' *Molecular Quantum Mechanics* for details.



**Figure 5.3:** Energy levels of a harmonic oscillator, with allowed transitions annotated (absorption solid blue, emission dashed orange). The harmonic potential is the grey curve.

$v = 0$  or  $v = 1$ , or from  $v = 9$  to  $v = 10$ , we will measure the same transition energy<sup>6</sup>. So we expect that in a vibrational spectrum, we will just see one line for every different possible vibrational mode, rather than a series of lines as we saw for rotation.

#### Vibrational Frequencies

The vibrational spectrum of HCl shows one line centred at  $2991\text{ cm}^{-1}$ . What is the force constant of the bond in HCl?

We'll see more examples of this in the problem sheet.

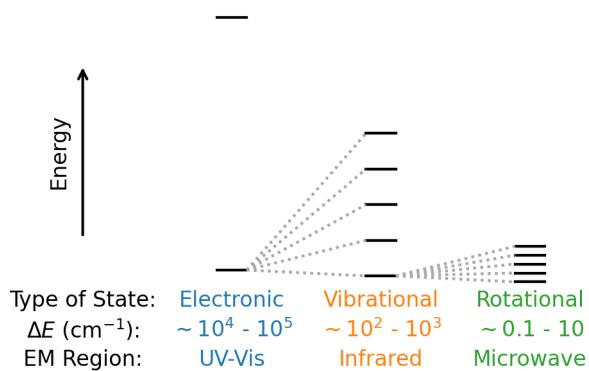
#### 5.1.3 Aside: Exam Questions

To motivate you to actually do the problems later, I want to reinforce that the calculations we have just done are ultimately going to form a lot of the bulk of the exam questions for this part of the module. If you can:

- Derive an expression for transition energies from an expression for energy levels and a selection rule.
- Use this expression to predict where lines will appear in a spectrum.
- Use this expression in conjunction with spectral data to work out molecular properties.

Then you should feel confident. We will see more examples of this, and examples with more complex equations. I will **not** be expecting you to remember all these equations, but I will expect

<sup>6</sup>Under our simple approximation where the bond is a harmonic oscillator - more on this later.



**Figure 5.4:** Energy scales of different kinds of molecular motion. Each electronic state supports a number of vibrational states, and each vibrational state supports a number of rotational states.

you to be able to convert units and use equations and data that are given to you. The focus is on solving problems, not remembering a load of crap you can just look up on Wikipedia.

## 5.2 Combined Excitation

Up until now, we have talked about rotation and vibration in isolation. This is because rotational energies are a lot lower than vibrational energies, which are a lot lower than electronic energies. When we think about a molecule, it will have quantised energy states that correspond to rotation, vibration, and electronic motion – and all of these states exist with very different energies, as illustrated in Figure 5.4.

So when exciting a rotation, we won't be giving the molecule enough energy to also excite a vibration, for example. However, if we excite a vibration, we are giving the molecule quite a lot of energy, and it is often enough to excite rotations *alongside* the excited vibration. We call this **rovibrational** excitation<sup>7</sup> because we are exciting a rotation at the same time as the vibration. This sounds a little complicated but we will introduce the idea now and then spend a lecture doing an extended problem discussing this idea in depth.

A hand-wavy explanation of this idea is that it takes a lot of energy to make a molecule vibrate, and comparatively little to start it rotating, so when you excite the vibration you're dumping a lot of energy into the molecule, and it's quite likely to start rotating too. We see this in the spectra as we will see **rotational fine structure** along with our vibrational excitation. I'll outline how this works now, and then we will see it in action in a couple of lectures time.

To start, remember our expressions for rotational energy levels ( $E_R$ ) and vibrational energy levels ( $E_v$ ):

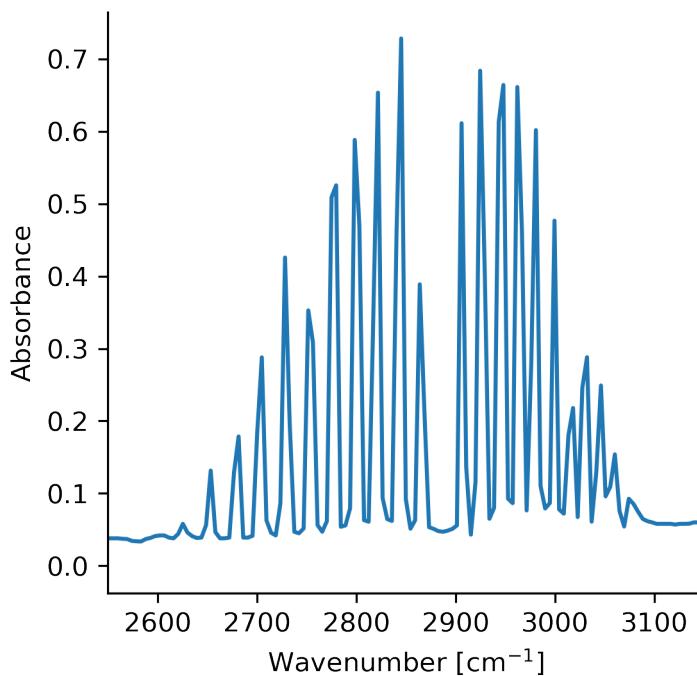
$$E_R = BJ(J + 1)$$

$$E_v = \left(v + \frac{1}{2}\right) h\nu$$

In rovibrational excitation, we are really exciting a *combined* level with vibrational quantum number  $v$  and rotational quantum number  $J$ . This combined level  $E_c$  is simply given by:

$$E_c = E_v + E_R = \left(v + \frac{1}{2}\right) h\nu + BJ(J + 1)$$

<sup>7</sup>Other options are available too, like **vibronic excitation** (vibration and electronic), and even **rovibronic** (rotation and vibration *and* electronic). All fun.



**Figure 5.5:** A high-resolution gas-phase IR spectrum of HCl, showing clear R and P branches, and no Q-branch. Data from NIST.

If we imagine having a transition from  $v \rightarrow v + 1$  and  $J \rightarrow J + 1$ , then our transition energy ( $\Delta E$ ) is given by:

$$\Delta E = h\nu + 2B(J + 1)$$

You'll prove this yourself later. What this tells us is that when we excite vibrations from  $v \rightarrow v + 1$ , we can also excite rotations and in our spectrum we would expect to see a line at  $h\nu$  (the fundamental), and then a series of lines at higher energies:  $h\nu + 2B, h\nu + 4B, h\nu + 6B$  and so on. Physically this means we are absorbing photons of higher energies than just the vibrational fundamental ( $h\nu$ ) because it takes energy to excite the rotations in addition to the vibration.

Before we look at the actual spectrum, we need to consider another option too. When we excite this vibration, we could also have the rotational selection rule be  $\Delta J = -1$ , which corresponds to rotational *emission* alongside the vibrational absorption. Doing the same calculation above for this case, we'd find that:

$$\Delta E = h\nu - 2BJ$$

So we would also see a series of lines at  $h\nu - 2B, h\nu - 4B, h\nu - 6B$  and so on. Physically this corresponds to the vibration being excited, but then you getting some energy *back* from the process due to the molecule losing energy by going to a lower rotational state. The consequence of this is that less energy is needed to excite the molecule in the first place, so you see a series of lines at lower energies than the fundamental.

In any real high-resolution gas-phase IR spectrum such as in the one for HCl in Figure 5.5, we will see both of these sets of lines around the fundamental, and they are called the **R-branch** (when  $\Delta J = +1$ ) and the **P-branch** (when  $\Delta J = -1$ ). This is easy to remember, because the *R* stands for 'Rich', and refers to the lines that are higher (richer) in energy than the fundamental. Conversely, the *P* stands for 'Poor' and refers to the lines that are lower (poorer) in energy than the fundamental.

Beautiful stuff. Note that we don't see a line actually *at the fundamental frequency* – this line would be called a **Q-branch** if it was present (as Q is between P and R in the alphabet), but the Q-branch is absent for diatomic molecules<sup>8</sup>. The absence of a Q-branch means that around the fundamental there should be a gap of width  $4B$ , which is what we see in the spectrum in Figure 5.5.

Now it's time for **Problem Sheet 2**, and after that we will spend a lecture working through the problems in **Extended Problems 1** to introduce some other concepts.

After that, though, it's time to think about bigger molecules. So far we've only really talked about diatomic molecules, which are interesting, but the majority of molecules are not diatomic...

#### Take Home Messages

- Vibrations are quantised in the same way rotations are, and the number of vibrational modes in a molecule can be worked out by considering degrees of freedom.
- By modelling the vibrations as a simple harmonic oscillator (ball and spring model), we can predict the appearance of vibrational spectra.
- Vibrations and rotations can be excited simultaneously, which leads to combination bands in the spectrum.

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<sup>8</sup>Except for some weird cases like NO where angular momentum can be put into an electronic state.

## Problem Sheet 2

1. Isotopically pure carbon monoxide ( $^{12}\text{C}^{18}\text{O}$ ) has a rotational constant  $B = 1.9316 \text{ cm}^{-1}$ .
- Calculate the bond length of carbon monoxide.
  - What are the energies of the first five lines that would be seen in the rotational spectrum of carbon monoxide?
  - How would your answer to part (ii) differ if a spectrum of  $^{12}\text{C}^{17}\text{O}$  was measured? Justify your answer with a calculation, but you do not need to re-calculate the energies of all the lines.
  - The rotational spectrum of carbon monoxide is used in astrochemistry to determine the temperature of molecular gas clouds in deep space. Outline how this might be achieved.

**Note:** You may assume that carbon monoxide behaves as an ideal rigid rotor. The rigid rotor approximation states that:

$$E = BJ(J+1) \text{ where } B = \frac{\hbar^2}{8\pi^2 I}$$

2. Hydrogen fluoride (HF) has a fundamental vibrational wavenumber ( $\omega$ ) of  $4138 \text{ cm}^{-1}$ .
- Calculate the force constant ( $k$ ) of HF.
  - The force constant of HF is experimentally observed to be same as DF (deuterium fluoride). Explain this observation.
  - Calculate the fundamental vibrational frequency of DF and comment on how the result differs to that of HF.
  - Sketch the infrared spectrum of a 2:1 mixture of HF and DF, identifying any features of note.

**Note:** You may assume that HF and DF behave as an ideal harmonic oscillators, such that:

$$E = \left(v + \frac{1}{2}\right) h\nu \text{ where } \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

3. The number of molecules  $n_J$  in rotational state  $J$  at a given temperature  $T$  is given by:

$$n_J = n_0(2J+1) \exp\left(-\frac{BJ(J+1)}{k_B T}\right)$$

Where  $n_0$  is the number of molecules in the ground state.

- Fully explain the form the above equation, specifically identifying the meaning of the  $(2J+1)$  and the exponential term.
- Show that the  $J$  level with maximum population at a temperature  $T$  will occur when:

$$\frac{dn_J}{dJ} = n_0 \left(2 - \frac{B}{k_B T}(2J+1)^2\right) \exp\left(-\frac{BJ(J+1)}{k_B T}\right) = 0$$

- Hence show that the  $J$  level with maximum population at a temperature  $T$  is given by:

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

- What is the most populated  $J$  level in a sample of molecules with  $B = 12.5 \text{ cm}^{-1}$  at 120 K?

# Extended Problems 1

1. The rigid rotor model is a simple model for rotating molecules which assumes that the bond lengths of the molecule are fixed and do not change during rotation. However, at high rotational excitation, this model breaks down because the bond lengths of the molecule start to change due to a phenomenon called **centrifugal distortion**.

- i Imagine a diatomic molecule like CO, if you spin this molecule faster and faster, would you expect the bond length to increase or decrease? Why? (Hint: think about which direction the hammer flies when an athlete does the hammer throw).
- ii The energy levels of a diatomic molecule, including the effect of centrifugal distortion, are given by:

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

Where  $D$  is the *centrifugal distortion constant*, which is a positive number.

For a molecule with  $B = 1 \text{ cm}^{-1}$ , calculate the energies of the first 6 rotational energy levels ( $J = 0 \rightarrow 5$ ) both with  $D = 0.01 \text{ cm}^{-1}$  and with  $D = 0 \text{ cm}^{-1}$  (no centrifugal distortion). Comment on the result.

- iii Derive an expression for the energy of a transition from state  $J$  to  $J+1$ , including the effect of centrifugal distortion.
- iv Sketch a typical rotational spectrum of both a diatomic rigid rotor and a diatomic non-rigid rotor, highlighting any significant differences.
- v The centrifugal distortion constant can be expressed in terms of other parameters as:

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

By considering the value of  $D$  as  $\omega$  and  $B$  are varied, justify the form of this equation (detailed calculations are not required).

2. Sketch a high resolution infrared spectrum of a typical polar diatomic molecule, showing the first four lines in both the R and P branch. Annotate on your sketch:

- The spacing between each pair of lines in units of  $B$ .
- The position of the fundamental vibrational frequency  $\omega_0$ .
- The transition that gives rise to each individual line.

3. A high resolution *infrared* spectrum of HBr shows the lines at the following energies:

2598.216, 2615.144, 2632.072, 2665.928, 2682.856, 2699.784

Determine the bond length, force constant, and centrifugal distortion constant of HBr.

How would you expect the centrifugal distortion constant of HI be different to HBr?

4. The harmonic oscillator model is a simple model for a vibrating bond, but has some key shortcomings. More sophisticated models are known as **anharmonic** models, which account for the bond not being entirely harmonic. One key anharmonic model is called the **Morse Oscillator** model.
- What are the shortcomings of the harmonic oscillator model? Under what conditions is it reasonable to assume a bond is behaving as a harmonic oscillator?
  - The energy levels of an anharmonic Morse oscillator (in wavenumbers) are given by:

$$E = \omega \left( v + \frac{1}{2} \right) - \left( v + \frac{1}{2} \right)^2 \omega x_e$$

Where  $x_e$  is the *anharmonicity constant*, which is a dimensionless positive number.

Outline how the presence of anharmonicity affects the vibrational level structure.

- Derive an expression for the energy of a transition from state  $v$  to  $v + 1$ , including the effect of anharmonicity.
- Sketch a harmonic potential and a Morse potential, and draw in the vibrational states. Highlight any features of note and differences between the two systems. (N.B. You will need to look up what a Morse potential looks like!).

## Lecture 6

# Bigger Molecules: Symmetry

### Lecture Aims

- To understand how symmetry helps us think about spectra of larger molecules.
- To be able to assign molecules to point groups.
- To be able to form basic representations.

Small diatomic molecules are ideal model systems when we are learning about spectroscopy, because we can predict spectra using relatively simple equations, and showcase a lot of key concepts very simply. However, most molecules are *not* small diatomic molecules, so for spectroscopy to be useful it needs to be applicable to big molecules too.

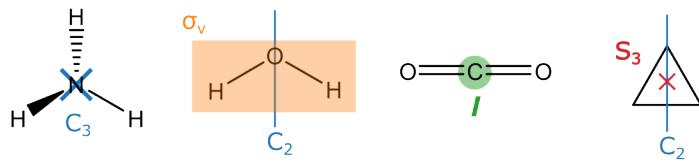
Unfortunately, the process we have looked at so far of taking expressions for energy levels, applying selection rules, and working out where lines will appear doesn't work as well for big molecules – the energy level expressions are horrendously complex (if they can be written down at all), and often selection rules end up being relaxed. For example, the heme molecule we looked at last time is of great biological importance, and spectroscopy of heme-containing systems what a lot of people in the chemistry department are studying (including me). We figured out that there would be several thousand possible vibrational modes in heme – so how do we even start to think about that?

Yet, this complexity doesn't mean that spectroscopy is hopeless. We can still learn a lot, but we have to be smarter about how we do things. Using **symmetry** to reduce the complexity of big molecules helps us a lot, and is what we're going to think about in the next couple of lectures.

### 6.1 Point Groups and Character Tables

Symmetry pops up all over chemistry, and the fundamental idea is that by classifying molecules into **groups** based on their symmetry, we can use all the mathematical machinery of **group theory** to help us think about their structure and spectra. Some treatments of group theory are very mathematical, but we don't need to do that here – we can learn a lot with some relatively simple pictures. For more, I would refer you to Vincent's book on group theory (introductory), and Atkins MQM for more mathematics.

You started learning about symmetry last year with Mark Lowe in CH1202, and we'll recap a few basics to start with. You might find a molecular modelling kit useful when thinking about symmetry!



**Figure 6.1:** Some examples of different symmetry elements. Crosses denote an axis going into/out of the plane of the page.

### 6.1.1 Symmetry Operations and Elements

In molecular symmetry, a *symmetry operation* is a transformation of a molecule that leaves it looking the same after it has been carried out. There are five different kinds of symmetry operation we can do to a molecule:

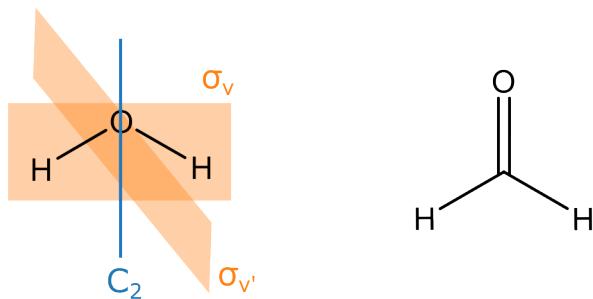
- **The identity operation,  $E$**  – the operation of ‘doing nothing’, which every molecule possesses.
- **Proper  $n$ -fold rotation,  $C_n$**  – the operation of rotating a molecule around an axis. The rotation is through  $360^\circ/n$ . The highest order rotation axis is known as the **principle axis**.
- **Reflection,  $\sigma$**  – the operation of reflection through a mirror plane somewhere in the molecule. The mirror plane is denoted as either  $\sigma_h$  (if it is perpendicular to the principle rotation axis),  $\sigma_v$  (if it is parallel to the principle axis), or  $\sigma_d$  (like  $\sigma_v$  but bisecting two other  $C_2$  axes – really just a special case of  $\sigma_v$ ).
- **Inversion,  $i$**  – the operation of taking each point in a molecule and inverting it through a *centre of inversion* to the other side.
- **Improper  $n$ -fold rotation,  $S_n$**  – the operation of doing a proper  $n$ -fold rotation, and then reflecting the molecule in a mirror plane perpendicular to the rotation axis.

Some examples of each of these are given in Figure 6.1.

These symmetry operations all happen around a given **symmetry element**. For example, if reflection through a horizontal mirror plane ( $\sigma_h$ ) leaves the molecule unchanged, then we say that the molecule possess that mirror plane as a symmetry element. Not every molecule will possess every symmetry element, so we can use the collection of symmetry elements a molecule does possess to classify it into a group. This group is called a **point group**, because all of the operations in a given group will leave at least one point in the molecule unchanged<sup>1</sup>. The benefit of doing this is that we can leverage all the power of the mathematical machinery behind group theory to help us understand and predict molecular symmetry, structure, and spectra. First though, we need to learn how to assign point groups.

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<sup>1</sup>Other kinds of symmetry groups are called **space groups**, which are used in crystallography where repeating unit cells add extra kinds of symmetry to the system.



**Figure 6.2:** Water and formaldehyde – both in the same point group. Can you see why?

### Assigning Symmetry Elements

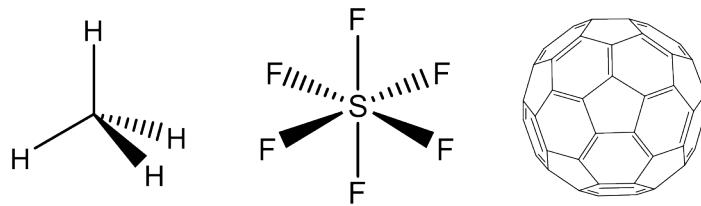
Identify the symmetry elements of the following molecules:

1. Water
2. Formaldehyde
3. 1,2-Dichloroethene (trans isomer)
4. Ethene
5. Methane
6. N<sub>2</sub>
7. Bromochlorofluoromethane

### 6.1.2 Point Groups

In the above exercise, you'll have found that both water and formaldehyde have the same set of symmetry elements:  $E, C_2, \sigma_v, \sigma'_v$  (there are two vertical mirror planes). This means that water and formaldehyde are in the same **point group**, and the point group they are in is the  $C_{2v}$  point group (Figure 6.2).

There are technically an infinite number of point groups. The naming of them is systematic, and the  $C_{2v}$  name means that in the group, the highest rotation axis is a  $C_2$  axis, and that there are only vertical mirror planes. Assigning molecules to point groups is a systematic process, and you're given a flow chart with the group theory tables you get in exams to help you do it. Let's assign the molecules from our earlier example into their point groups using this flow chart and then talk about them.



**Figure 6.3:** High symmetry point groups. From left to right: methane (tetrahedral point group:  $T_d$ ),  $SF_6$  (octahedral point group,  $O_h$ ), buckminsterfullerene (icosahedral point group,  $I_h$ ).

### Assigning Point Groups

Identify the point group of each of the following molecules:

1. Water
2. Formaldehyde
3. 1,2-Dichloroethene (trans isomer)
4. Ethene
5. Methane
6. N<sub>2</sub>
7. Bromochlorofluoromethane

We've already discussed water and formaldehyde, which are in the  $C_{2v}$  point group. Looking at 1,2-Dichloroethene, we should find from the flowchart that this is in the  $C_{2h}$  point group – the highest order rotation axis is still  $C_2$ , but now we have no vertical mirror planes and have a horizontal mirror plane instead. Hence, this molecule is in the  $C_{2h}$  point group. What point group is the cis isomer of 1,2-Dichloroethene in?

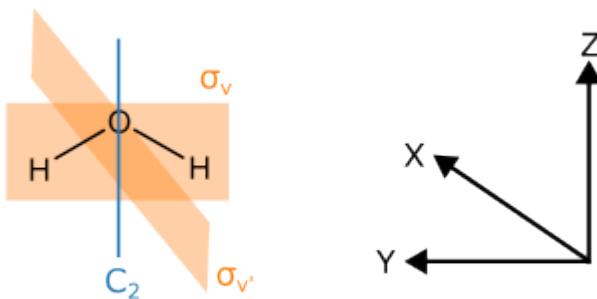
Ethene, in contrast, is in a different point group to dichloroethene. Ethene belongs to the  $D_{2h}$  point group. The point groups that begin with  $D$  all have the feature that there are  $n C_2$  rotation axes *perpendicular* to the principle axis. The  $h$  refers to the horizontal mirror plane. What point group is cyclopropane in?

Methane is an interesting molecule, we should all know that methane is tetrahedral, and actually it is very symmetrical. It has a lot of different symmetry elements (24), and belongs to the  $T_d$  point group. There are special point groups for molecules with high symmetry:  $T_d$  for tetrahedral,  $O_h$  for octahedral (common in inorganic chemistry), and  $I_h$  for icosahedral molecules.

Diatomic nitrogen is a linear molecule, and there are two special point groups for linear molecules:  $C_{\infty v}$  and  $D_{\infty h}$ . A linear molecule has an infinite-fold rotation axis that runs along the internuclear axis, hence the  $\infty$  in the point group name. Then, there is either a horizontal mirror plane perpendicular to this axis (so that the molecule is  $D_{\infty h}$ ), or there isn't, in which case it is  $C_{\infty v}$ . What point group is HCl in?

Finally, bromochlorofluoromethane has no symmetry elements except the identity, and so is in the  $C_1$  point group.

To understand why grouping molecules into point groups is useful, we need to understand



**Figure 6.4:** Water with co-ordinate axes. The axes can be figured out by noting that the principle axis aligns with  $z$ , and using the right-hand rule. The positions of the  $x$  and  $y$  axes are less critical, here  $x$  is perpendicular to the plane of the molecule.

something called the **character table** associated with each point group. These are the tables you get in your group theory booklets, and are the things that help us most in using symmetry to predict molecular structure and spectra.

### 6.1.3 Symmetry Representations and Character Tables

We've classified molecules into point groups on the basis of their symmetry elements, but we can go further than this and classify other properties of molecules (such as their molecular orbitals, or vibrational modes) based on how they transform under the symmetry elements of the point group. You already do this without knowing it when you talk about s, p, and d orbitals, or  $\sigma$  and  $\pi$  bonds – these are just symmetry labels that tell you how the orbitals transform under the symmetry elements of the point groups of atoms or molecules. Symmetry is all around you!

Identifying how a given molecular property transforms under the symmetry elements of a point group is called making a **representation** of the property in the given point group. We'll see how this works in a moment, but to do this we need to be careful about how we define coordinate axes ( $x, y, z$ ) around our molecule. Conventionally, we define the principal rotation axis as the  $z$  axis, but the other two axes are less easy to standardise. Usually, the  $x$  axis is perpendicular to the plane of the molecule, and we will use that convention here. Let's consider a simple case of working out how an arrow in line with the each of the coordinate axes transforms under the  $C_{2v}$  point group.

Starting with the  $z$  axis, to find out how it transforms under the symmetry operations of the point group, we simply apply each operation to it. If the axis is unchanged (mapped onto itself), then we say that the **character** of that transformation is +1, and if it is mapped onto a reversed version of itself, then we say the character is -1, and if it is moved so it doesn't map onto itself or a reversed version of itself, the character is 0<sup>2</sup>. Doing this for every symmetry operation forms our **representation** of the  $z$  axis ( $\Gamma(z)$ ) in the  $C_{2v}$  point group, which we can write down in a table

Representation	$E$	$C_2$	$\sigma_v$	$\sigma'_v$
$\Gamma(z)$	+1	+1	+1	+1

Doing the same thing for the  $x$  and  $y$  axes will lead to:

<sup>2</sup>This is a bit of an oversimplification, but will be fine for our purposes.

Representation	$E$	$C_2(z)$	$\sigma_v(xz)$	$\sigma'_v(yz)$
$\Gamma(z)$	+1	+1	+1	+1
$\Gamma(x)$	+1	-1	+1	-1
$\Gamma(y)$	+1	-1	-1	+1

Now we have a *representation* of all three coordinate axes in our point group. It's called a representation because it is a way of *representing* the coordinate axes in terms of how they transform under the symmetry operations of the point group. You're actually already familiar with this idea too, whenever you write the coordinates of a point as  $(x, y)$ , you are writing a representation of that point in terms of the unit vectors  $x$  and  $y$ .

However, it's really cumbersome to write these representations out with all the numbers every time, and actually any representation we make is formed from a certain number of **irreducible representations** (or *irreps*) of the group. These irreducible representations have shorter names and are what you find in the **character tables** in your group theory booklets. Any representation can be reduced into a sum of different irreducible representations, but we aren't going to go into how to do that here (a topic for next year). However, our representations of the coordinate axes don't actually *need* reducing, because they are irreducible representations already!

Looking at your group theory tables for the  $C_{2v}$  point group, can you see that our representation for the  $z$  axis  $\Gamma(z)$  is the same as the  $A_1$  irreducible representation? And that the  $x$  and  $y$  axes have  $B_1$  and  $B_2$  symmetry? In fact, we can find this information without forming the representation because the character table helpfully provides it to us – can you see where?

That process of considering how an object or property transforms under a point group is a useful one, both for spectroscopy and molecular orbital theory later on, so we will do some practice before we continue.

### Forming Representations

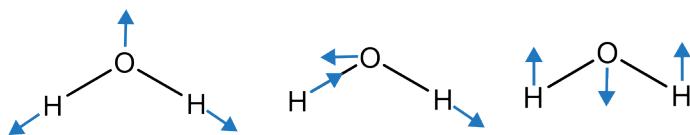
Form representations of the following, stating the corresponding irreducible representations:

1. The three coordinate axes in the  $C_{2h}$  point group.
2. A bonding  $\sigma$  orbital in  $H_2$  ( $D_{\infty h}$  point group).
3. An anti-bonding  $\sigma$  orbital in  $HCl$  ( $C_{\infty v}$  point group).

## 6.2 Symmetry and Spectroscopy

'Ok' I can hear you sigh, '*this is all fascinating but what on earth does any of it have to do with spectroscopy?*'. To answer this question, we're going to think about vibrations of molecules. Let's consider water as an example case again. Water has 3 atoms, and is nonlinear, so has  $9 - 6 = 3$  vibrational modes, or **normal modes**. A normal mode is defined as a mode of vibration that satisfies three criteria:

- They leave the center of mass of the molecule unchanged (so the molecule does not start translating through space as a result of the vibration).
- They involve all atoms moving coherently (i.e. the motion of each atom is linked in a fixed way to the others).



**Figure 6.5:** Normal modes of water. From left to right: symmetric stretch ( $3585\text{ cm}^{-1}$ ), asymmetric stretch ( $3506\text{ cm}^{-1}$ ), and bend ( $1885\text{ cm}^{-1}$ ).

- They transform as an irreducible representation of the molecule's point group.

You can think of a normal mode as just another term for vibrational mode, really. A good way to think about it is that any vibrational motion of the molecule can be decomposed into a sum of motions of each individual normal mode, they're the kind of 'basis' from which all other vibrations are built up. Water has three normal modes, a symmetric stretch, an asymmetric stretch, and a bending mode.

So, we want to figure out which irreducible representations correspond to these modes, and we do it in the way we did for the simpler case of coordinate axes. We consider how each normal mode is transformed by the symmetry operations of the group. We'll work through this in the lecture but we'd find out that the symmetric stretch and the bend both have  $A_1$  symmetry, and that the asymmetric stretch has  $B_2$  symmetry. So far, so good. But why is this useful?

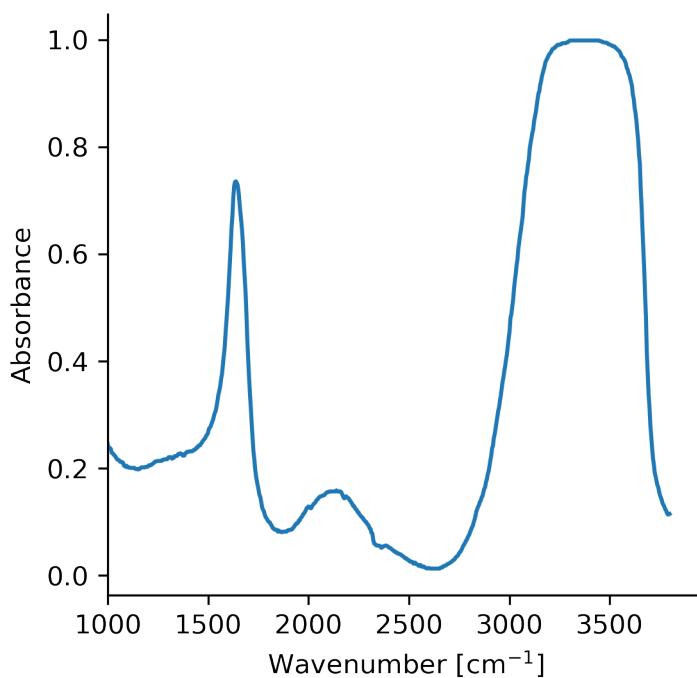
#### Normal Mode Symmetries

Identify the symmetry of the three normal modes of water (Figure 6.5) in the  $C_{2v}$  point group.

This way of classifying vibrations by symmetry actually helps us predict the appearance of spectra, because even though we know there are three possible vibrations, not every vibration will necessarily show up in an IR spectrum. We need to be able to drive the vibration with infrared light if we want to see it in our IR spectrum – we talked about this in the context of selection rules a couple of lectures ago. Group theory and the character tables give us a way to quickly and conveniently determine if that is possible. It turns out that **any normal mode that transforms as the same symmetry as either  $x$ ,  $y$ , or  $z$  is infrared active**. 'Infrared active' means that it can be excited by irradiation with infrared light. For water, you can see from the character table that all three normal modes are infrared active, so in an IR spectrum of water we would expect to see three bands, so do we?

From Figure 6.6, we see three bands, but actually one of them is fooling us (spectroscopy is always annoying like this). The very small band between the two big bands is a **combination band**, where multiple normal modes are excited simultaneously, and the two normal stretching modes overlap in the large broad band on the right. Combination bands are forbidden under harmonic oscillator selection rules, but we'll see later how these rules can end up being relaxed.

We'll continue looking at this next time, but there are a couple of important technical points to mention here. Firstly, the symmetry and group theory **don't tell you anything about how intense a band in a spectrum is, or where the band lies**. All it can tell you is if there is a band or not, rather than anything more detailed – but this is often very useful information to have. Secondly, the rule we have just learned for predicting the presence of IR active normal



**Figure 6.6:** IR spectrum of liquid water. It looks like three bands, but in reality the two stretching modes overlap in the big peak at around  $3500\text{ cm}^{-1}$ . The small band at  $2100\text{ cm}^{-1}$  is actually a *combination band*.

modes only applies in the case that we are exciting the *fundamental* of each normal mode (i.e. the  $v = 0 \rightarrow v = 1$  transition). However, most of the time this is reasonable, and we'll see some cases where this isn't the case next time.

#### Take Home Messages

- Classifying molecules into point groups based on their symmetry helps us understand molecular structure and spectroscopy.
- Forming representations of things in point groups helps us understand their properties.
- We can predict the presence or absence of bands in vibrational spectra by looking at symmetries of normal modes.

## Lecture 7

# Symmetry and Spectroscopy

### Lecture Aims

- To understand how symmetry is applied in vibrational spectroscopy.
- To be able to predict IR and Raman active vibrational modes using group theory.
- To start to use group theory to solve chemical problems.

Last time we introduced some basic group theory and talked about forming representations, and showed that we can form representations of normal modes of water. However, in doing this we assumed we already knew what the normal modes looked like – it's more useful to be able to *predict* the symmetry of normal modes without already knowing what they look like!

Today we are going to do just that, continue forming representations and see how we can predict the appearance of vibrational spectra. We will restrict ourselves to thinking about stretching vibrations in this course, as that keeps the mathematics more simple, but the same principles apply to other vibrations too.

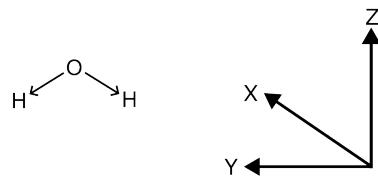
### 7.1 Stretching Modes

A stretching vibration is one where chemical bonds only lengthen and shorten (as opposed to *bending* modes which involve changes in bond angle). We can use group theory to predict the number of stretching modes in a molecule, and we do this by considering how the bonds in the molecule transform under the symmetry operations of the molecule's point group. The best way to understand this is to just do some examples and see how it works, so let's do that.

#### 7.1.1 Water

For our first example, let's consider water again. There are two O-H bonds in water, and to start predicting the number of stretching vibrations, we consider how these bonds transform. Let's draw the water molecule with two arrows in place of the O-H bonds, as shown in Figure 7.1. Now let's think about the representation of these bonds in the  $C_{2v}$  point group, remembering that a bond contributes +1 to the character under each symmetry element if it is unchanged, 0 if it transforms into something else, and -1 if it is transformed onto a reversed version of itself. We should find that the representation of the two O-H bonds is given by:

Representation	$E$	$C_2$	$\sigma_v$	$\sigma'_v$
$\Gamma(O - H)$	+2	0	0	+2



**Figure 7.1:** Water with arrows drawn in place of the bonds. This picture will help us predict the stretching vibrations of water.

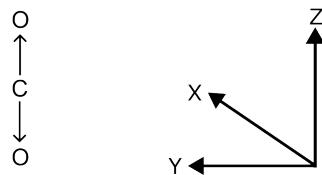
Now, this representation isn't one of the irreps of the point group, but we know that every representation can be written as a combination of different irreps. Inspection of the character table for  $C_{2v}$  shows that we can write this representation as:

$$\Gamma(O - H) = A_1 + B_2$$

So, we have one stretching vibration with  $A_1$  symmetry, and another with  $B_2$  symmetry, which is what we found before – these are the symmetric and asymmetric stretch respectively.

### 7.1.2 Carbon Dioxide

Carbon dioxide is a linear molecule, in the  $D_{\infty h}$  point group. As before, we consider the two C-O bonds and look at how they transform under each symmetry element in the point group.



**Figure 7.2:** Carbon dioxide with arrows drawn in place of the bonds. This picture will help us predict the stretching vibrations of carbon dioxide. Note that it doesn't matter if the bonds are single or double – they are all just 'bonds' as far as we care.

Drawing the diagram in Figure 7.2, and thinking about it in terms of the character table, you should find that the representation of the two C-O bonds is as below:

Representation	$E$	$C_\infty$	$\sigma_v$	$i$	$S_\infty$	$C_2$
$\Gamma(C - O)$	+2	+2	+2	0	0	0

Now, we can again look at the character table for  $D_{\infty h}$  to find out how to write this representation as a sum of irreps:

$$\Gamma(C - O) = A_{1g} + A_{1u}$$

So we expect to vibrational modes, one of  $A_{1g}$  symmetry and another of  $A_{1u}$  symmetry. In total, though, we'd expect there to be three vibrational modes (why?), so we must have another non-stretching mode – which is a bending mode, in this case<sup>1</sup>.

<sup>1</sup>You can do a similar process to this for finding out symmetry of non-stretching modes, but its more complicated and beyond the scope of what we want to do here – have a look at Hollas (chapter 4) for an introduction to it.

Now, there are a few things to think about here. Firstly, we have always done the reduction of a representation into its constituent irreps by inspection, but this isn't always easy to do. In harder cases, there is a **reduction formula** that can be used to allow you to work out how to break down a given representation into constituent irreps. In this course, we won't see any examples where you need to use the formula (and if there is anything more complex, I'll give you the constituent irreps). Next year, you'll learn how to use this in more detail in CH3203.

Secondly, we've found the symmetry of the vibrational stretching modes of CO<sub>2</sub>, but we haven't done anything useful with this information. Let's do something more useful with it now.

## 7.2 IR and Raman Activity

Last time we ended on saying something a bit vague about how a vibrational mode with the same symmetry as one of the coordinate axes ( $x, y, z$ ) would be **infrared active**. We're going to put this on a more formal footing now, and I'm going to show you the maths (because its fun) but please don't stress about it – 90% of people doing this only need to understand the final result, so feel free to just skip down to the '*What You Need To Know*' section below and have a rest while I get into the quantum mechanics.

### 7.2.1 Transition Dipole Moments: Some Detail

At a quantum mechanical level, spectroscopy is all about transitions happening between different quantum states. These quantum states have well-defined energies<sup>2</sup> and this is why we often talk about transitions between energy levels as a shorthand. However, really it is the quantum mechanical states that we are looking at transitions between, and any quantum mechanical state is described using a wavefunction. We can imagine then, that what we are doing is looking at a transition between two wavefunctions:

$$\Psi_{\text{initial}} \rightarrow \Psi_{\text{final}}$$

Where  $\Psi$  is the wavefunction of the initial or final state (as the subscripts describe). For example, these could be  $v = 0$  and  $v = 1$  state of a particular vibrational mode, or the  $J = 1$  and  $J = 2$  state of a rotation.

For a transition to happen, these states need to be *coupled* in some way, so that population can move between them. One way we can accomplish this is by photon absorption, and what the photon is doing in this case is coupling the two states together, and creating something that is known as a **coherence** between the two states. This coherence can ultimately result in population being transferred from the initial to the final state. Think of the photon as creating a connection between the two states, tying them together so that population can move from one state to another. Mathematically we represent this connection using something called an **operator**.

In the case that we are absorbing one photon (which is mostly what we are doing, Raman spectroscopy is a bit different), the operator is called the **dipole moment operator**, and has the symbol  $\hat{\mu}$ . The initial and final states are coupled together in the following way to form something called the **transition dipole moment (TDM)**:

$$\text{TDM} = \int \Psi_f \hat{\mu} \Psi_i d\tau \tag{7.1}$$

Don't worry too much about the exact mathematical form of this for now, the important thing to understand is what this represents, and what it means for us.

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<sup>2</sup>Most of the time...

You can think of the TDM as a quantity that tells you how big the change in dipole moment is when there is a transition between the two states. Most importantly though, **the intensity of a spectroscopic transition is given by the square of the transition dipole moment**. If the TDM is zero, then no transition can happen. The TDM is ultimately the origin of all the spectroscopic selection rules, but the details of all this are beyond the scope of his course.

One of the beautiful things about symmetry and group theory is that it's applicable in so many places, and we can use it to help us simplify integrals – we did this without realising it last year when we talked about even and odd functions. Without getting too deeply into the maths, we can define the symmetry of the final state, initial state, and dipole moment operator (i.e. each term in Equation 7.1), and then determine the overall symmetry of the integral using direct products. If the overall symmetry is odd, the integral is zero and no transition can happen. The upshot of this is that we can determine which vibrational transitions are allowed based on the symmetries of the normal mode and dipole moment operator.

For a vibrational mode to be IR active, it has to transform as the same symmetry as one of the Cartesian coordinates  $x$ ,  $y$ , or  $z$ , because if this happens then the overall integral shown in Equation 7.1 will be totally symmetric, and so will be non-zero. Similarly, for a vibrational mode to be Raman active, it has to transform as the same symmetry as one of the quadratic Cartesian components,  $xy$ ,  $yz$ ,  $xz$ ,  $x^2$ . More mathematical detail on this will be provided in an Appendix but please don't feel you have to know all of this maths – the end result is the most important thing for us as spectroscopy.

### 7.2.2 TDM: What You Need to Know

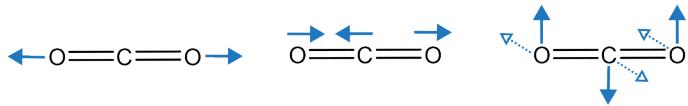
The bottom line is that we can use symmetry to determine if certain vibrational modes are IR or Raman active. 'IR active' means that the vibrational mode can be excited by absorbing one IR photon, and 'Raman active' means that it can be excited through Raman scattering, which is a process we'll discuss more in a couple of sessions time. What this means for us is that:

- Any vibrational mode that transforms with the same symmetry as a linear cartesian component ( $x$ ,  $y$ , or  $z$ ) will be **IR active**.
- Any vibrational mode that transforms with the same symmetry as a quadratic cartesian component (i.e.  $xy$ ,  $y^2$  or similar) will be **Raman active**.

We can get this information from the character table, so let's see an example of how it works. Again we'll start with water, which we know has two stretching vibrations with  $A_1$  and  $B_2$  symmetry. From the character table for  $C_{2v}$  we can see that  $A_1$  is the symmetry of  $z$  and three quadratic terms, so the  $A_1$  vibration is **both IR and Raman allowed**. The  $B_2$  vibration is also both IR and Raman allowed. The exact Cartesian coordinates also tell you about the direction the transition dipole moment moves in, which has some important consequences in more advanced kinds of spectroscopy, but for now this is fine.

A more interesting example is  $\text{CO}_2$ , which we found has stretching vibrational modes with  $A_{1g}$  and  $A_{1u}$  symmetry. From the character table, we can see that the  $A_{1g}$  mode does not share symmetry with any linear Cartesian component, so it is **not** IR active. However, it does share symmetry with some quadratic components, so it is Raman active. The opposite is true for the  $A_{1u}$  mode, which is IR active but not Raman active. We can use this information to identify these two stretching modes - one must be the symmetric stretch and the other the asymmetric stretch. Can this information tell us which is which?

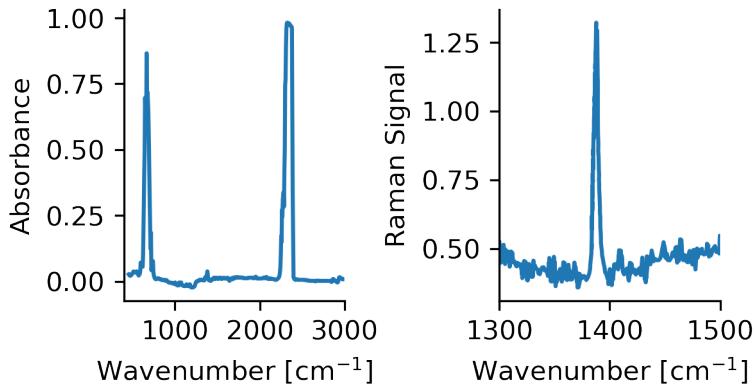
It can, because we know that if a vibrational mode is IR active, the dipole moment of the molecule must change during the vibration (gross selection rule). If we think about it, it will



**Figure 7.3:** Normal modes of carbon dioxide. From left to right: symmetric stretch ( $1480\text{ cm}^{-1}$ ), asymmetric stretch ( $2565\text{ cm}^{-1}$ ), and bend ( $526\text{ cm}^{-1}$ ). Note that the symmetry of the molecule means that there are two *degenerate* bending modes.

change for the asymmetric stretch, so this mode must be the IR active mode, which is the one with  $A_{1u}$  symmetry. Thus, we can make the mode assignments shown in Figure 7.3, based on our group theoretical analysis.

Finally, we can predict the appearance of an IR or Raman spectrum of  $\text{CO}_2$  using this information – if we focussed solely on the stretching vibrations, we would expect to see one peak in each spectrum. However, there is a third vibrational mode which corresponds to the bending of the molecule (opening and closing the O-C-O bond angle). This mode has  $E_{1u}$  symmetry<sup>3</sup>, looking at the group theory table, we can see that this mode will be IR active and **not** Raman active – which should also make sense if we think about the dipole moments moving. Thus, we expect to see two bands in an IR spectrum of  $\text{CO}_2$ , and one in a Raman spectrum. Spectra are shown in Figure 7.4.



**Figure 7.4:** Vibrational spectra of  $\text{CO}_2$  in the gas-phase. Left: IR spectrum. Right: Raman spectrum. Data from NIST.

Neat. Right, to help this sink in, we are going to work through some problems for the remainder of this lecture and the next, showcasing some interesting concepts along the way.

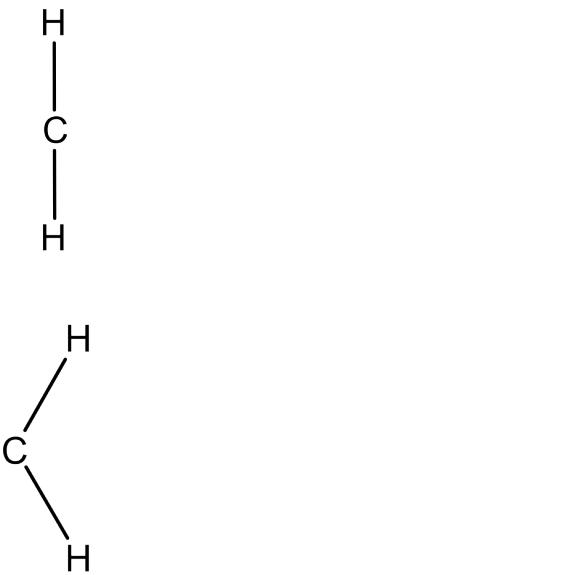
### 7.3 Applied Symmetry in Spectroscopy

The examples below showcase a couple of interesting cases which show how symmetry is actually useful to spectroscopists, and is not just an interesting curiosity that nobody really cares about. Each is presented like a question, and these are the kinds of things I might ask you in an exam.

<sup>3</sup>You can work this out in the usual way, but it's a bit trickier due to some angle dependence - take my word for it for now.

### 7.3.1 Distinguishing Isomers of $\text{CH}_2^+$

$\text{CH}_2^+$  is a molecule that is very abundant in deep space, and is a molecule that astrochemists can use to detect the presence of certain kinds of planets and interstellar gas clouds.  $\text{CH}_2^+$  could have either a linear or a bent structure (Figure 7.5). The IR spectrum of  $\text{CH}_2^+$  in space shows two bands, which are both also present in the Raman spectrum. Both spectra were measured in the C-H stretching region. What is the structure of the  $\text{CH}_2^+$  ion?



**Figure 7.5:** Different possible isomers of  $\text{CH}_2^+$ .

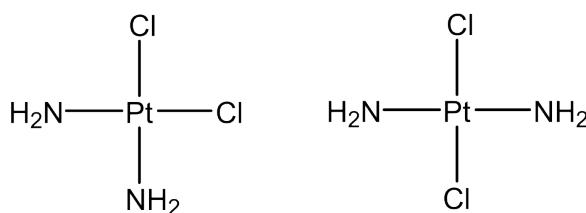
To answer this question, we follow a logical sequence of steps:

1. Draw both isomers and determine their point groups.
2. Work out a representation of the C-H stretches in both point groups.
3. Look at which bands are IR and Raman active and see if we can determine the structure.

We'll go through this in detail in the lecture, but we'd find that linear  $\text{CH}_2^+$  would have stretching vibrations with  $A_{1g}$  and  $A_{1u}$  symmetry ( $D_{\infty h}$  point group), and that bent  $\text{CH}_2^+$  would have stretching vibrations with  $A_1$  and  $B_2$  symmetry ( $C_{2v}$  point group). Looking at the character table, if  $\text{CH}_2^+$  was linear, we would see one band in Raman spectrum, and a different band in the IR spectrum – neither band would be present in both. Conversely, if  $\text{CH}_2^+$  was bent, we would see two bands in the IR spectrum, which are both also present in the Raman spectrum. Given our experimental data from the question, we can conclude that  $\text{CH}_2^+$  is **bent**.

### 7.3.2 IR Spectra of Square Planar Complexes

Cisplatin (Figure 7.6, left) is a powerful anti-cancer drug that is being synthesised by a pharmaceutical chemist. The chemist needs to find a way to determine whether or not they have



**Figure 7.6:** Left: cisplatin. Right: transplatin.

successfully made cisplatin, or the other isomer, transplatin (Figure 7.6, right), which is not medically useful. Could they tell these isomers apart using an IR spectrum taken in the Pt-Cl stretching region?

Again, we're going to follow a similar set of steps:

1. Draw both isomers and determine their point groups.
2. Work out a representation of the Pt-Cl stretches in both point groups.
3. Look at which bands are IR active and see if this could distinguish the isomers.

We'll go through in detail in the lecture, but we'd find the following:

- Cisplatin is in the  $C_{2v}$  point group, and transplatin is in the  $D_{2h}$  point group.
- The Pt-Cl vibrations have the following symmetries:
  - In cisplatin:  $A_1$  and  $B_2$ .
  - In transplatin:  $A_g$  and  $B_{2u}$ .

Thus, looking at the character tables, in cisplatin we'd expect to see two bands in the IR spectrum, as both stretches are IR active. Conversely, in transplatin only the  $B_{2u}$  stretch is IR active, so we would only see one band in the IR spectrum. So yes, the pharmaceutical chemist could tell which isomer they had made based on the IR spectrum in the Pt-Cl stretch region!

That's it for today, and now its time for **Problem Sheet 3**, followed by **Extended Problem Sheet 2**, where we will do some more group theory and see some more interesting things. After that, our final few lectures will focus on some different kinds of spectroscopy.

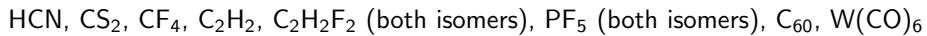
#### Take Home Messages

- We can work out predicted stretching vibrations of molecules by drawing them and thinking about how the bonds transform under the operations of the point group.
- We can determine whether or not vibrational modes are IR or Raman active from the character table.
- The origin of selection rules in IR spectroscopy is the **transition dipole moment**.

### Problem Sheet 3

You will find a molecular modelling kit very helpful for some of these problems.

1. Identify the point groups of the following molecules, sketching the symmetry elements where possible:



2. This question is about the stretching vibrations of ammonia.

- i Draw the structure of ammonia and identify its point group.
- ii By drawing arrows on each of the N-H bonds, or otherwise, construct the representation of the N-H stretches of ammonia in its point group.
- iii Show that this representation reduces to the combination of irreps  $A_1 + E$ .
- iv Are these modes IR active, Raman active, both, or neither? Why?
- v The  $E$  irrep is a **degenerate irrep**. What does this mean for the vibrational mode it corresponds to?
- vi How many non-stretching vibrational modes would you expect ammonia to have?

3. Upon electronic excitation, ammonia changes from having a trigonal pyramidal geometry to a trigonal planar geometry. Can IR spectroscopy of the N-H stretching region be used to distinguish between ground-state and excited-state ammonia? Justify your answer.

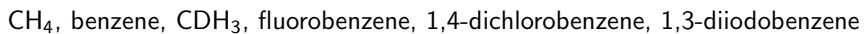
4. How many bands would you expect to see in the following spectra:

- i An IR spectrum of the C-H stretching region of methane.
- ii A Raman spectrum of the C-H stretching region of methane.

Are there any bands that would appear in both spectra?

5. Symmetry has an important application in NMR spectroscopy where any nuclei that can be interconverted through a symmetry operation of the molecule's point group are termed. **chemically equivalent**. Chemically equivalent nuclei will exhibit peaks at the same position in an NMR spectrum.

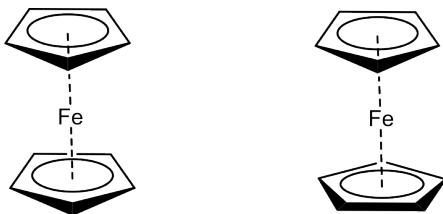
Identify the chemically equivalent hydrogen atoms in the following molecules, showing your reasoning:



You'll learn more about this with Alex later on.

## Extended Problems 2

1. This question is based on the stretching vibrations of benzene.
  - a) Draw the structure of benzene and identify its point group.
  - b) Form a representation of the C-H stretches in benzene. Show that this representation reduces to:
$$A_{1g} + E_{2g} + B_{1u} + E_{1u}$$
Assign the IR/Raman activity of these modes, and hence predict the appearance of an IR and Raman spectrum of benzene.
  - c) A synthetic chemist is attempting to fluorinate benzene. Could they use vibrational spectroscopy (IR or Raman) to distinguish benzene from fluorobenzene, based on the C-H stretching vibrations? Justify your answer with a group theoretical calculation.
2. The Raman spectrum of  $\text{Ni}(\text{CO})_4$  in the C-O stretching region shows two bands, neither of which are present in the IR spectrum.  
Using a group theoretical analysis, determine the 3D structure of  $\text{Ni}(\text{CO})_4$ .
3. Ferrocene (below) can exist as either a staggered (right -  $D_{5d}$ ) or eclipsed (left -  $D_{5h}$ ) conformation.



Can IR spectroscopy of the C-H stretching region of ferrocene distinguish these isomers?  
Justify your answer.

4. (*Hard! Not directly examinable, but here for the spectroscopy heroes among you*) This question will introduce you to using **direct products** to find out more detailed information about the symmetry of IR allowed molecular vibrations.

The idea is that the **transition dipole moment** must be **non-zero** if a transition is IR allowed. As the TDM is simply an integral, we can utilise symmetry properties of integrals to determine whether or not a transition is allowed. To do this, we consider the symmetry representation of each part of the integrand:

$$TDM = \int_{\infty} \Psi_f \hat{\mu} \Psi_i d\tau \rightarrow \Gamma(\Psi_f) \otimes \Gamma(\hat{\mu}) \otimes \Gamma(\Psi_i)$$

Where  $\otimes$  represents a **direct product**. Direct product tables are found at the back of your group theory booklet. Thus, we need to determine the representations of our final and initial wavefunctions, and the dipole moment operator. If the direct product of these representations contains the totally symmetric irreducible representation (TSIR), then the integral will be non-zero and the vibration is IR active. Some key pieces of information:

- The symmetry of the  $v = 0$  vibrational state is always the TSIR.
- The symmetry of the  $v = 1$  vibrational state is the same as the symmetry of the normal mode.
- The dipole moment operator has three components, and the symmetry of each component is given by the symmetry of the corresponding Cartesian coordinate axis.

We will illustrate this process using symmetric stretching vibration of water.

- a) What is the point group of water? What is the TSIR in this point group?
- b) Write down the symmetry of the symmetric stretching normal of water (lecture 6).
- c) What is the symmetry representation of this stretching mode in both the  $v = 0$  and  $v = 1$  state?
- d) Explain why the dipole moment operator has the following symmetries in water's point group:

$$\Gamma(\hat{\mu}_x) = B_1 \quad \Gamma(\hat{\mu}_y) = B_2 \quad \Gamma(\hat{\mu}_z) = A_1$$

- e) By using direct product tables, show that for the symmetric stretch of water:

$$\begin{aligned} \Gamma(v = 1) \otimes \Gamma(\hat{\mu}_x) \otimes \Gamma(v = 0) &= B_1 \\ \Gamma(v = 1) \otimes \Gamma(\hat{\mu}_y) \otimes \Gamma(v = 0) &= B_2 \\ \Gamma(v = 1) \otimes \Gamma(\hat{\mu}_z) \otimes \Gamma(v = 0) &= A_1 \end{aligned}$$

- f) Hence, explain why the symmetric stretch of water is IR allowed, with transition dipole moment along  $z$ . Can you reconcile this picture with a sketch of the normal mode?
- g) (Bonus) Explain why the asymmetric stretch is IR allowed, but with transition dipole moment along  $y$ .

## Lecture 8

# Raman and Electronic Spectroscopy

### Lecture Aims

- To understand the difference between infrared and Raman excitation.
- To understand the principles of Raman spectroscopy.
- To start to understand electronic spectroscopy, and how it differs from vibrational and rotational spectroscopy..

So far in this course we've spoken quite generally about spectroscopy, and have focussed on looking at rotational and vibrational spectroscopy, in what is quite a traditional way to learn spectroscopy. Rotations and vibrations lend themselves well to learning the basics, as the spectra of simple molecules are very predictable and they create a nice set of examples to illustrate key concepts. Furthermore, a lot of what we've already learned about rotational and vibrational spectroscopy is still applicable, especially in astrochemistry and in studying fundamental chemical physics.

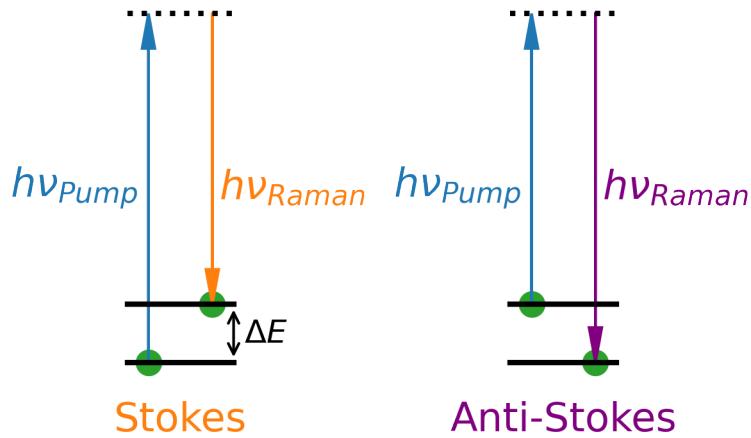
However, the majority of people using spectroscopy today are looking at bigger systems, or more complex systems – proteins, or materials, or solutions containing many molecules. So, the final few lectures are going to focus on different kinds of spectroscopy – vibrational, electronic, and NMR – and we'll introduce some new concepts and showcase how these are used *today*. By the end, you'll hopefully understand things like why NMR is king for organic structure determination, but vibrational spectroscopy still wins if you need to look at reactions that happen very quickly. Today, let's take a deeper dive into vibrational spectroscopy.

## 8.1 Raman vs Infrared Excitation

### 8.1.1 Pure Infrared Excitation

We've talked about vibrational spectroscopy already, and we mentioned selection rules for *pure infrared transitions*, which means that a vibration is excited by absorbing an IR photon (in the photon picture). In the wave picture, the electric field of the IR light interacts with the molecule, and can drive a vibration if the dipole moment of the molecule changes on vibration. This is how *IR spectroscopy* works, and is what you do in the teaching labs when you measure an IR spectrum. It's a good way to excite vibrations, because:

- Lots of common molecules have big absorption cross sections in the IR region so you don't need a large amount of sample to produce a big signal in your spectrum.



**Figure 8.1:** The Raman effect. Pump light excites the molecule, and then light is emitted at either longer wavelengths (Stokes, left panel), or shorter wavelengths (Anti-Stokes, right panel). Stokes transitions result in population (green circle) transfer to higher energy states, and vice versa for anti-Stokes transitions.

- For the same reason, you can use an infrared lamp (which is basically a glorified blowtorch) as a light source, and don't *need* a laser or something similar.

However, downsides are that:

- Not all vibrations are infrared active.
- Sometimes the molecule you care about (e.g. a protein) might absorb in the same region as the solvent it is in (e.g. water). So you can't distinguish the spectrum of the molecule from the spectrum of the solvent.
- If you need a lot of light for some reason, really powerful IR sources are harder to get hold of than really powerful visible sources.
- IR light detectors are also quite crap (and expensive) compared to visible light detectors.

A way to circumvent these problems is to excite vibrations using something called the **Raman effect**.

### 8.1.2 Raman Excitation

The Raman effect is a way to excite molecules via the scattering of EM radiation. Instead of looking at 'pure' absorption, we end up looking at light that is scattered by the molecule. In the photon picture, it looks a bit like that shown in Figure 8.1.

So, we send in a photon of one wavelength, and rather than being absorbed, it ends up losing/gaining a small amount of energy by inelastic scattering off the molecule. The photon then flies out with slightly more or slightly less energy than it came in with, and so we detect light

of a different wavelength to the incident light – this process is the Raman effect. Crucially, the amount of energy the photon gains or loses is exactly the amount of energy the molecule loses or gains. Thus, if we send in a photon (known as the *pump*) with energy  $h\nu_{\text{pump}}$ , and detect a Raman scattered photon at a lower energy  $h\nu_{\text{Raman}}$ , we know that the energy  $\Delta E$  the molecule has gained is:

$$\Delta E = h\nu_{\text{pump}} - h\nu_{\text{Raman}} \quad (8.1)$$

If the incident photon loses energy (and thus excites the molecule), this is called **Stokes transition**. Conversely, if the scattered photon loses energy (and thus de-excites the molecule), it's called an **Anti-Stokes transition**. Almost all of the time you'll see more Stokes transitions than Anti-Stokes (as Anti-Stokes means that the molecule has to already be excited before the measurement starts). It's important to understand that this method of exciting a molecule can excite **any** kind of transition. You can have rotational, vibrational, and electronic Raman spectroscopy – however vibrational Raman is probably most common, and so when a lot of people say 'Raman' they mean vibrational Raman, which is what we are talking about here.

The selection rules for vibrational Raman spectroscopy are different than for pure IR, due to the different nature of the excitation. For pure IR, we had the idea that a dipole moment has to change on vibration for it to be IR active. For vibrational Raman, the rule is that the **polarisability** of the molecule has to change on the vibration for it to be Raman active<sup>1</sup>. We mentioned polarisability at the start of the course – think of it as a measure of how 'easy' it is to push the electrons around a molecule.

To understand this, it's most intuitive to think in the wave picture. With pure IR, the picture was that the electric field of the light drags the dipoles in the molecule around, which can make the molecule vibrate if the symmetry and geometry of the molecule is correct (if the vibration is IR active). With Raman spectroscopy, we have two electric fields now (the incident light and the scattered light). So think about it as follows:

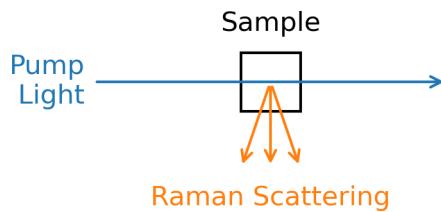
1. The incident electric field interacts with the electrons on the molecule and polarises them, creating instantaneous dipoles which are different to the dipoles in the ground state of the molecule (which are what the field interacts with in pure IR).
2. The scattered electric field interacts with these instantaneous dipoles and can make the molecule vibrate, if the geometry and symmetry are correct.

Essentially, it's the same process as pure IR but with an extra initial step where the dipoles in the molecule are shifted around by the first incident field. Then, if a vibration changes these new dipoles, it can be excited by interaction with the second field. A good way to think about it is that you use the first electric field to create some new dipoles, that give you access to different vibrations than you'd get if you just interacted with the ground state dipoles.

There's a lot in this and we can't go fully into all the physics, but note where I am talking about the interaction with a second, scattered, field, I don't mean that we are necessarily physically shooting two different kinds of light at the molecule. The scattered field can arise spontaneously, via spontaneous emission. In fact, a major downside of traditional spontaneous Raman spectroscopy is that the signals are **very very weak**, because you rely on spontaneous emission to spontaneously create the second field after you shoot in the incident light. A typical spontaneous Raman signal would be about 4 or 5 orders of magnitude smaller than the corresponding pure IR signal, due to this reliance on spontaneous emission. Ways around this are to send in multiple beams of light to your sample, in what is called **stimulated Raman spectroscopy**, but that's beyond the scope of what we want to chat about today. A typical

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<sup>1</sup>And the quantity we care about is called the **transition polarisability moment**, not the TDM.



**Figure 8.2:** A typical Raman spectroscopy setup. The intense pump light is fired at the sample, and the weak scattered Raman signal is detected at right angles to it.

Raman spectroscopy setup is shown in Figure 8.2 – the weak Raman signals are detected at right angles to the intense pump light, to avoid saturating the detector with the intense pump!

Anyway, that's a lot of new information. The key things you need to understand are that:

- Traditional Raman spectroscopy works via *scattering* of photons rather than absorption.
- A vibration does not need to cause a change in dipole moment to be Raman active, but does need to cause a change in the *polarisability* of the molecule.
- The above results in different selection rules, so different vibrations can be excited.

For example, you can excite the N-N vibration in  $\text{N}_2$  using Raman excitation, which is impossible using pure IR.

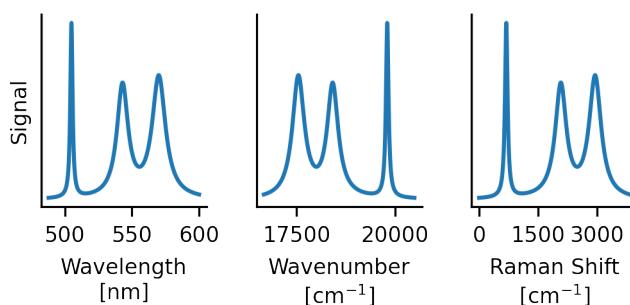
### 8.1.3 Why Raman?

Why is any of this extra complexity useful? Well, aside from being able to excite a different set of vibrations:

- You can excite vibrations using a **visible region light source** – we are good at making these, and are good at making light detectors that work in the visible region.
- You can often avoid problems like absorption of light by the solvent that plague pure IR spectroscopy.
- You can selectively excite vibrations on specific components of a multi-component system by choosing the right incident light source.

Alright, that sounds cool. It does however, come at a cost:

- You need more powerful light sources (i.e. lasers). These are more expensive than IR lamps.
- You can still end up with low signals, depending on the system being studied.
- Raman signals often end up on top of signals from other, competing, processes, like fluorescence. This can complicate interpreting the spectra.



**Figure 8.3:** Converting raw Raman spectra to something more useful. Left: raw spectrum in wavelength units. Middle: converted to wavenumber units (so subtraction is simple). Right: with excitation wavenumber subtracted off, to give the Raman shift.

There are always benefits and drawbacks – each spectroscopy is like a tool in a toolbox. The more tools you have, the more problems you can solve. It's very common nowadays to have to use multiple kinds of spectroscopy to answer your chemical questions.

#### 8.1.4 Raman in Practice

To finish up our brief encounter with Raman, let's look at some examples of how we use it, including some typical calculations.

The way spontaneous Raman experiments are conducted is that a laser with a fixed wavelength is fired at a sample, and the scattered light (usually at longer wavelengths, Stokes transitions) is detected using a spectrometer and sensitive camera. The spectrum you obtain then has an energy axis that is relative to the wavelength of the incident light, and you need to convert the units to figure out the true energy of the vibrations. The thing you care about is the energy of the scattered light *relative to the incident light*, which is called the **Raman shift** of the light. The basic idea is shown in Figure 8.3.

##### Raman Units

A sample of cyclohexane was irradiated with a laser operating at 488 nm, and a strong peak in the spectrum of the scattered light occurred at 566.90 nm.

What is the energy of the transition that gave rise to this peak, in wavenumbers?

We'll go through in detail in the lecture, but it is really as easy as converting everything to wavenumbers and adding/subtracting as necessary.

## 8.2 Electronic Spectroscopy

You met some forms of electronic spectroscopy last year – we talked about atomic spectroscopy and the Rydberg equation in CH1200, and you talked about coordination chemistry and d-block complexes being colourful with Mark and Greg in CH1202. As a form of spectroscopy, it's seemingly an easy one to understand – literally just electrons jumping between states – so why have we not mentioned it until now?

### 8.2.1 Difficulty

The problem is that electronic spectroscopy is *complicated*<sup>2</sup>. In vibrational and rotational spectroscopy, we can make some reasonable assumptions and predict the appearance of spectra fairly accurately – even with very rudimentary models that it's not hard for us to write down on paper. This is because when you quantise the motion of nuclei (which is what vibrational and rotational states are), you tend to end up with a fairly structured set of energy levels that follow nice patterns – remember our rotational spectra and R and P branches.

However, in anything more complicated than an atom, when we quantise the motion of the electrons to find the **electronic states**, we don't get a nice structured set of states, with an equation that describes them we can easily write down. Therefore, interpreting electronic spectra in anything more than a rudimentary way is very difficult without computational chemistry to guide us (and even then, it's hard). On top of this, we can excite vibrations and rotations *alongside* our electronic states, which adds to the complexity.

Despite this, all is not lost. We can still learn things from electronic spectra – and actually it is very widely used. It's just that we normally<sup>3</sup> can't extract the same detail about molecular structure from the spectra that we can from other forms of spectroscopy like NMR.

Today we're just going to talk a bit about some d-block spectroscopy to illustrate a couple of useful concepts.

### 8.2.2 d-Block Spectroscopy

You already know that in the d-block, you have metal atoms that have five degenerate d-orbitals in their valence shell. You also should already know that when you put these atoms into a crystal field or ligand field (i.e. bonding stuff to them), then these degenerate d-orbitals split to form other sets of orbitals. If the metal atom is in an octahedral complex, then the d orbitals split into two sets of orbitals that have symmetry labels  $e_g$  and  $t_{2g}$ , as shown in Figure 8.4.

There are other options too, in different shaped complexes. It all just comes from symmetry that you'll learn about later on.

You also know that d-block complexes are often colourful because there are transitions between these orbitals, the so-called 'd-d transitions'. With your new spectroscopy expertise, you should now also be able to explain why the wavelength of these transitions depends on the magnitude of the splitting parameter,  $\Delta_0$ . The magnitude of the splitting is determined by the ligands<sup>4</sup>, and we can rank the ligands by how much they split the orbitals in something called the *spectrochemical series*. We'll see this in one of the problems.

Anyway, we are now at point 2 of our usual strategy of:

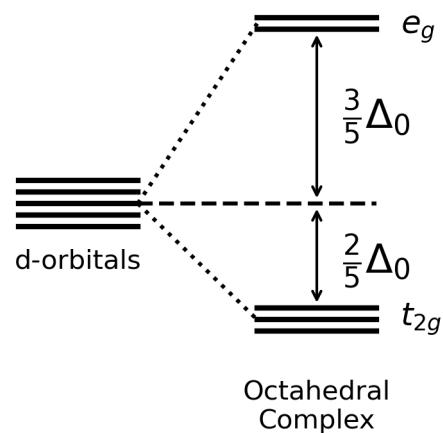
1. Find two levels.
2. Find selection rules.
3. Figure out where the peaks in the spectrum are.

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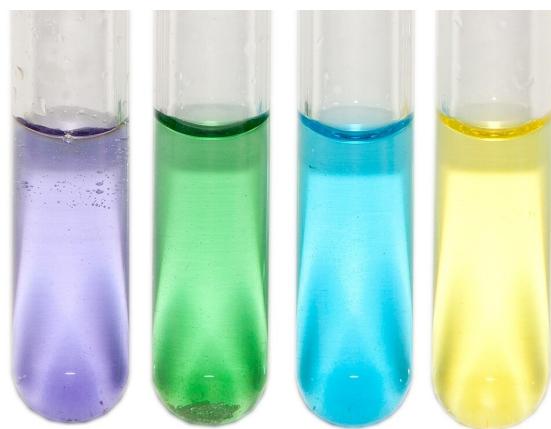
<sup>2</sup>I realise I keep saying stuff is complicated, but in this case it really is.

<sup>3</sup>Electronic spectroscopists may disagree, but in general I'm right. However there are people like Alkwin Slenczka who are much cleverer than me and can do beautiful work like this: <https://doi.org/10.1039/D2CP02256G>. However, it still takes quite a lot of effort, and if you were just interested in molecular structure, there are better ways to do it.

<sup>4</sup>I never really understood how a ligand on an octahedral complex is different to like, a hydrogen atom on a methane, but there we are. It's all just bonds at the end of the day, innit?



**Figure 8.4:** Splitting of d-orbitals (left) in an octahedral ligand field (right).



**Figure 8.5:** Vanadium complexes are colourful due to these d-d transitions – the colour depends on the oxidation state.

So, what are the selection rules?

### 8.2.3 Electronic Selection Rules

You're familiar with the selection rules for atomic spectroscopy, and what you find is that as the molecules get bigger, everything becomes more annoying and less pretty and we start losing symmetry and thus losing quantum numbers and thus losing selection rules. Pretty much the only selection rules left by the time we've made a d-block complex are that:

- $\Delta S = 0$  - the spin selection rule, we can't undergo a transition that changes the spin state of the molecule by absorbing a photon.
- Selection rules relating to the symmetry of the orbitals we are transitioning between.

For us, an for now, the selection rule relating to this second point that we care about is that an allowed transition **has to change the parity** of the orbital (because . The parity is denoted by the  $g$  or  $u^5$  label on the state (i.e.  $e_g$ ). So, in principle, the only allowed transitions are those where the parity changes from  $u$  to  $g$  and vice versa.

Those of you still awake will realise that this means that *in theory, a transition from an  $e_g$  orbital to a  $t_{2g}$  is forbidden!* Which it is, in theory. So why are d-block complexes still coloured?

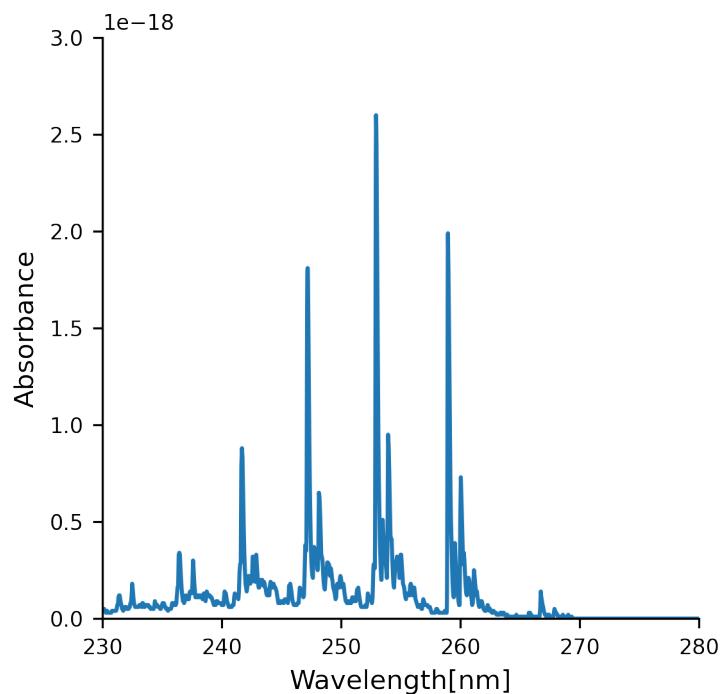
### 8.2.4 Relaxing Selection Rules

We can observe these d-d transitions because we are able to relax these selection rules. It's important to understand that these selection rules only make sense if our complex is rigid, perfectly octahedral (or whatever shape) and that when we excite the complex we only excite the electron and nothing else.

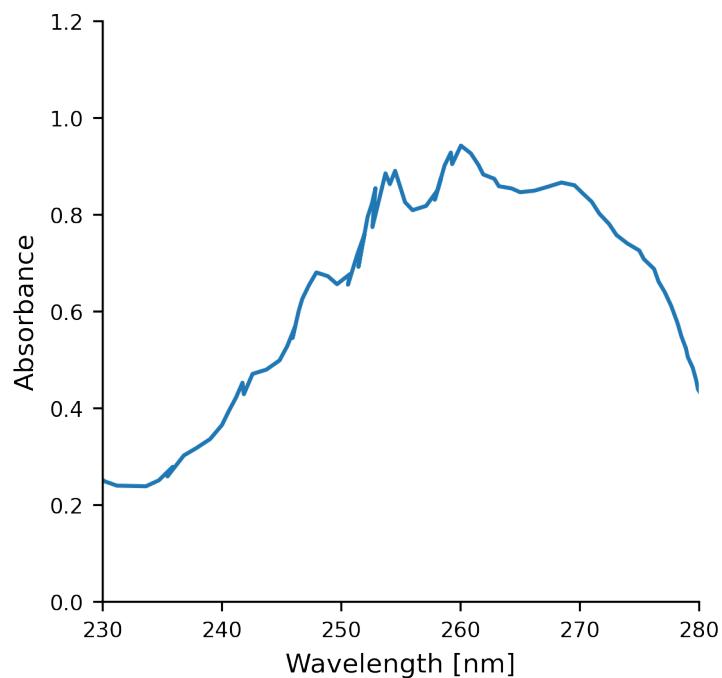
Unfortunately, in practice, this doesn't happen. Recall how we could excite rotations alongside vibration, because when we excite vibrations we generally put in a lot of energy and it's enough to co-excite some rotations. The same thing happens with electronic excitation, where we excite an electronic state and simultaneously excite some vibrations and rotations - a phenomenon called **rovibronic coupling**<sup>6</sup> These vibrations can distort the complex away from its perfect octahedral geometry and thus relax the remaining selection rules even further. Thus, we can see those d-d transitions even though they are theoretically forbidden.

Not content with just relaxing one selection rule, we can actually also relax our spin selection rule. In the case that the molecule we are exciting contains some heavy atoms (like iodine), then a phenomenon called **spin-orbit coupling** becomes very significant, and it relaxes away that spin selection rule. This happens because the spin-orbit coupling effectively provides a 'route' for the molecule to transition between spin states. It's useful to know this exists, but don't worry too much for now. The bottom line is that we can often see a lot of lines in gas-phase electronic spectra, due to the rovibronic coupling and the relaxed selection rules – as in the example of benzene in Figure 8.6.

The spectrum above is in the gas-phase, though. Gas-phase means that the molecules are isolated and don't interact with each other. Electronic spectroscopy in solutions, where there can be interactions with solvent and other molecules is a bit different, as shown in Figure 8.7.



**Figure 8.6:** Electronic spectrum of gas-phase benzene. Beautiful sharp lines corresponding to different electronic states, and their constituent vibrations and rotations.



**Figure 8.7:** Electronic spectrum of solution phase benzene. A big blobby mess of crap due to collisional broadening. A higher resolution spectrometer wouldn't help you here!

### 8.2.5 Solvation Effects

So where we once had a beautiful series of sharp lines (Figure 8.6), we now have a big ugly blob (Figure 8.7). Unfortunately, that's the reality of solution phase electronic spectra. Electronic states already have short lifetimes (so broad peaks), and collisions with solvent or other molecules in solution only serve to shorten lifetimes even further, and thus broaden peaks further. You're only really going to see pretty and sharp electronic spectra if you work in the gas phase (and even then, not always).

Electronic spectroscopy isn't useless though. Lots of molecules produce characteristic bands in spectra, even if we don't quite know *what* those bands actually correspond to. If all you need to do is monitor the progress of a reaction by seeing if a peak at 220 nm in a UV-Vis spectrum is there or not, then you don't really need to worry about exactly what that peak physically means.

Next time, we're going to see a different kind of spectroscopy that produces *much* more sharp and beautiful (and informative) spectra. We're going to look at the magnetic resonance spectroscopies, like NMR.

#### Take Home Messages

- The Raman effect allows us to excite vibrations (and other energy levels) via *scattering* of photons, rather than direct absorption.
- For a vibration to be Raman active, the polarisability of the molecule has to change during the vibration.
- Electronic spectroscopy is generally less straightforward to predict and explain than vibrational spectroscopy, but can still be very useful for some systems – such as metal complexes.

<sup>5</sup>This notation comes from the German for 'even' (gerade) and 'odd' (ungerade).

<sup>6</sup>Ro = ROTational, vib = VIBRational, onic = electrONIC.

## Lecture 9

# Magnetic Resonance Spectroscopy

### Lecture Aims

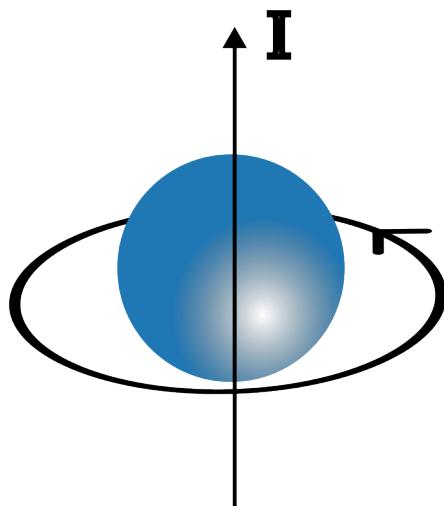
- To understand the basic principles of magnetic resonance spectroscopy.
- To understand basic concepts of shielding, deshielding, and chemical shift.
- To start to understand why NMR is so common in chemistry.

Today, in our last lecture, we are going to change direction somewhat and talk about **magnetic resonance spectroscopy**. This will underpin a lot of what you will learn with Alex in the other half of this module, about **nuclear magnetic resonance (NMR)**. NMR is probably the most widely used kind of spectroscopy in chemistry (at least, in synthetic chemistry), but there are other kinds of magnetic resonance spectroscopy too, like **electron paramagnetic resonance (EPR)** spectroscopy. So far, we've talked about **electric dipole** spectroscopies – all our IR, UV-Vis, and rotational spectroscopy are electric dipole spectroscopy, where they can be understood by the **electric** field of the light interacting with electrons or dipoles on molecules. Magnetic resonance spectroscopies are a bit different – in these spectroscopies, the **magnetic field** of the light is what interacts with the molecules.

In this lecture we are going to understand how putting molecules in a magnetic field and shooting light at them produces spectra. We're not going to learn to interpret NMR spectra or anything like that, but are instead going to be focussed on understanding *how* an NMR spectrum arises when you put a molecule in a magnetic field and fire some radio waves at it. The basic principles are the same for any kind of magnetic resonance spectroscopy, but we'll use NMR as our example all the way through as this is what you'll come across most often.

### 9.1 Spin

Like all spectroscopy, NMR is fundamentally governed by quantum mechanics, which results in two states that transitions happen between. The way these states are produced in NMR is via something called **spin**, or **spin angular momentum**. Spin is a slightly weird phenomenon in that it doesn't have a classical analogue, it's just a property of a particle like mass, or charge. In NMR we are worried about **nuclear spin**, which normally has the symbol  $I$  – which is a quantum number like  $n$ ,  $l$ ,  $J$ , and so on. Different nuclei have different spin quantum numbers, and we're going to talk about hydrogen nuclei (protons) which have a spin of  $I = 1/2$ . A good way to think about spin is as some kind of intrinsic angular momentum that a particle has – so you can imagine the particle spinning on an axis (giving rise to an angular momentum). A picture like the one shown in Figure 9.1 is why it's called *spin*, at least.



**Figure 9.1:** The angular momentum  $I$  of a nucleus spinning on its axis is a technically incorrect, but often quite useful, way to think about nuclear spin.

Like other kinds of motion at the atomic scale, spin is quantised.

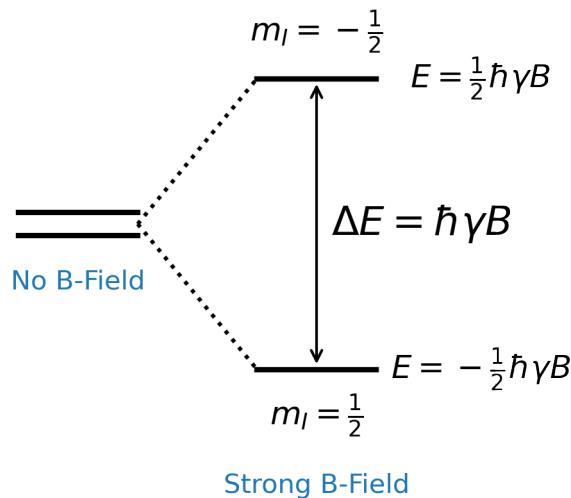
### 9.1.1 Quantised Spin States

Recall when we talked in CH1200 about orbital angular momentum of an electron  $l$ , and said that the level defined by a certain  $l$  consists of  $2l + 1$  different states ( $m_l$ ).  $m_l$  in this context is the projection of the angular momentum  $l$  onto an axis, and takes values from  $-l$  to  $+l$  in steps of  $1^1$ . An exactly analogous argument applies to spin angular momentum, and a level with spin quantum number  $I$  consists of  $2I + 1$  different spin states ( $m_I$ ). So, if we have a proton ( $I = 1/2$ ), we have two different possible spin states ( $m_I = -1/2$  or  $+1/2$ ).

A neat, if not entirely accurate, way to picture these spin states is as like little bar magnets that are oriented in different directions depending on the value of  $m_I$ . In the absence of any external magnetic field, these two states are degenerate (have the same energy). However, if we put the nucleus in a strong magnetic field, then these two states will end up with different energies: one is stabilised by the field and another is destabilised (Figure 9.2). Magnetic field strength usually has the symbol  $B$ , and magnetic fields are often referred to as *B-fields* for this reason.

From Figure 9.2, it's clear that we have our two states. Now we just need to know the energies of the states and selection rules for transitions so that we can figure out the energies of transitions, and thus the positions of lines in our NMR spectrum.

<sup>1</sup>This is called **space quantisation**, see any textbook (e.g. Atkins) on atomic structure if you're interested in learning more (you will learn a bit more in CH2203 and CH3203 next year).



**Figure 9.2:** In a magnetic field, the degeneracy of nuclear spin states is lifted. For a nucleus like a proton with  $I = 1/2$  (shown here), this results in two states with a gap between them that depends on the strength of the B field.

The energy  $E$  of a single spin state in Joules is given by:

$$E = -m_I \hbar \gamma B$$

Where  $m_I$  is the projection of the spin quantum number  $I$  (either  $\pm 1/2$  for the cases we care about, a unitless number),  $\hbar$  is the reduced Planck constant (in units of Joule seconds per radian),  $\gamma$  is a quantity called the **gyromagnetic ratio** (in units of radians per second per Tesla), and  $B$  is the strength of the magnetic field (in Tesla). Tesla is the unit of magnetic field strength.

### NMR Units

Show that the frequency of the spin state with energy  $E$  in Hertz is given by:

$$\nu = -\frac{m_I \gamma B}{2\pi}$$

The gyromagnetic ratio,  $\gamma$  is a quantity that determines how fast the nucleus 'spins' when its placed in the magnetic field - as is clear from the units (radians per second per Tesla). When a nucleus is put in a magnetic field it will spin (technical term: *precess*) at a frequency called the **Larmor frequency**. The Larmor frequency is just the product of  $\gamma$  with the magnetic field strength.



**Figure 9.3:** Low resolution: a benchtop NMR spectrometer with a proton Larmor frequency of 80 MHz. These are relatively recent inventions and are surprisingly expensive.



**Figure 9.4:** Higher resolution: the NMR spectrometer you use in the teaching labs, with a proton Larmor frequency of 500 MHz. The most powerful NMR system at the University of Leicester is an 800 MHz system in the Institute for Structural and Chemical Biology.

### Larmor Frequency

The gyromagnetic ratio of a proton is  $267.5 \times 10^6 \text{ rad s}^{-1} \text{ T}^{-1}$ . What is the Larmor frequency of this proton in:

1. A 7.0460 T magnetic field?
2. A 11.7534 T magnetic field?

How do you convert these frequencies from angular frequency (radians per second) to temporal frequency (per second)?

As an aside, the example above gives you the Larmor frequency of a proton in two different magnetic fields. In NMR spectroscopy, we are usually detecting protons, and actually we *define* the NMR spectrometer by the Larmor frequency of a proton in it. Different spectrometers have different field strengths (higher field is better, or higher resolution), but rather than talk about them in units of Tesla, we talk about them in units of the proton Larmor frequency – this makes it easier to think about differences between different spectrometers.

#### 9.1.2 NMR Transitions

So, we have the expression for our energy levels:

$$E = -m_I \hbar \gamma B$$

And I can tell you that the selection rule for an allowed transition is that:

$$\Delta m_I = \pm 1$$

So, what is the expression for the position of a line in our NMR spectrum? Hopefully by now you can figure out that it's:

$$\Delta E = \hbar \gamma B$$

In units of Joules, or:

$$\Delta E = \frac{\gamma B}{2\pi}$$

In Hertz (more common).

**NMR Lines**

What is the energy gap between the two nuclear spin states of a proton, in a magnetic field of strength 7.0460 T?

The example above shows that an isolated proton in a magnetic field will produce a peak *at the Larmor frequency* in our NMR spectrum. We'll come back to this shortly, but first, it's useful to think about these energy gaps.

**NMR Populations**

What is the energy gap between the two states in the example above in Joules?  
Calculate the Boltzmann populations of the two states at 298 K. Comment on the result.

From the above example, we learn two things:

1. Gaps between nuclear spin states are *tiny* compared to other kinds of spectroscopy.
2. Both states have essentially equal population.

These two points have some important consequences. Firstly, the tiny energy gap means that spontaneous emission from an excited NMR state is really slow, which means that states remain excited for a long time: giving us sharp lines, and the possibility to exploit interesting quantum mechanical effects due to long-lived coherences between states<sup>2</sup>. It also means that it's impossible to make an NMR measurement quickly<sup>3</sup> – more on this next time.

Secondly, both states having similar populations means that we need a large amount of nuclei to observe a change in the population – imagine having two shelves, each covered with an almost-equal number of grains of rice. Moving one grain from one shelf to the other isn't going to be noticeable, so you need to move many to observe a change – this is what we are doing in NMR. In contrast, in electronic or vibrational spectroscopy, our two shelves are not equally covered, the higher shelf would have almost no grains of rice on it – moving one grain to it *would* be noticeable. The bottom line is that this means NMR is relatively *insensitive* as a technique – we need a large amount of sample to record an NMR spectrum (compared with other kinds of spectroscopy).

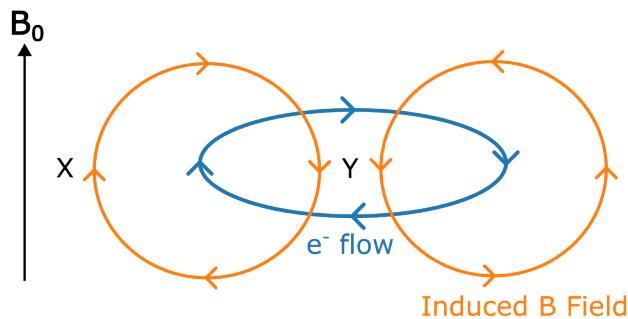
That said, the lack of time resolution and need for large amounts of sample are obviously not catastrophic because NMR is used by everyone all the time. So why is it so useful?

## 9.2 Why is NMR everywhere?

The fundamental reason is that NMR is **exquisitely** sensitive to molecular structure, and we're about to see why.

<sup>2</sup>This is beyond the scope of today, but it's the foundation of 2D-NMR and other fun things you'll learn about later.

<sup>3</sup>Depending on your definition of 'quickly'. For me, a microsecond is an essentially infinite amount of time, so NMR really doesn't cut it.



**Figure 9.5:** Example of how shielding/deshielding arises. The applied field  $B_0$  can induce an electron flow in a molecule (blue arrow). The electron flow induces a new magnetic field (orange arrows), which results in a nucleus at X being deshielded, and a nucleus at Y being shielded. The electron and magnetic field directions can be derived using the right-hand rule.

### 9.2.1 Shielding and Deshielding

Coming back to our expression for the transition between two nuclear spin states, we can see it depends on  $\gamma$  and  $B$ .

$$\Delta E = \frac{\gamma B}{2\pi}$$

$\gamma$  is the same for all nuclei of a given type, and is just an intrinsic property (it doesn't depend on the molecule the nucleus is in).  $B$  is *mostly* defined by the magnet in the spectrometer, however, it is not entirely defined by this. The environment surrounding a given nucleus influences the *local* magnetic field experienced by the nucleus quite substantially. Thus, nuclei in different *chemical environments* will experience different local magnetic fields. We can write down the relationship between the local magnetic field at a given nucleus  $B_{\text{loc}}$  and the strong field from the spectrometer  $B_0$  as:

$$B_{\text{loc}} = B_0 - \sigma B_0 = (1 - \sigma)B_0$$

Where  $\sigma$  is called the **shielding constant**.  $\sigma$  depends on the environment around the nucleus in question, and generally will have contributions from neighbouring atoms and bonds, the solvent, and perhaps contributions from the electrons around the nucleus. These contributions can either:

- Oppose the applied field  $B_0$  ( $\sigma > 0$ , so  $B_{\text{loc}} < B_0$ ), which is termed **shielding**. These contributions are known as **diamagnetic**.
- Augment the applied field  $B_0$  ( $\sigma < 0$ , so  $B_{\text{loc}} > B_0$ ), which is termed **deshielding**. These contributions are known as **paramagnetic**.

The origins of these terms should be obvious – if the environment around a nucleus protects it from feeling the full force of  $B_0$ , then it is *shielding* it from that field. An example of how these different terms might arise is shown in Figure 9.5.

To take stock, we know that:

1. The position of the line in our NMR spectrum depends on the energy gap between two nuclear spin states.
2. This energy gap depends on the magnetic field experienced by the nucleus in question.

3. The magnetic field is affected strongly by neighbouring atoms and bonds around the nucleus.
4. Thus, **the position of a line from a certain nucleus in an NMR spectrum is very sensitive to the structure of a molecule around that nucleus.**

NMR is exquisitely sensitive to small changes in molecular structure, which is why it is so useful - even if you do need lots of sample to get a measurement. Before we end, there is one last thing to cover in any introductory NMR lecture. You'll maybe know that the energy units given on NMR spectra are not Hertz, but 'ppm' – a quantity termed **chemical shift**.

### 9.2.2 Chemical Shift

To understand why this is, recall that the position of a line in an NMR spectrum will *depend on the strength of the applied magnetic field*. The consequence of this is that if we showed NMR spectra in Hertz, spectra from different spectrometers wouldn't be comparable. So instead, what we do is report the positions of peaks relative to a **reference** molecule, which is defined to have a chemical shift of zero. In proton NMR, that reference molecule is usually tetramethylsilane (TMS)<sup>4</sup>. The chemical shift,  $\delta$ , is then defined as:

$$\delta = \frac{\nu - \nu_{\text{ref}}}{\nu_{\text{ref}}} \times 10^6$$

Where  $\nu$  is the transition frequency of a nucleus,  $\nu_{\text{ref}}$  is the transition frequency of the reference molecule, and the  $10^6$  is there because chemical shifts are tiny and so reported in units of parts-per-million (ppm).

#### Chemical Shift

The frequency of the TMS reference is observed to be 500 MHz in a given NMR spectrometer.

What is the chemical shift of an NMR signal observed at 1000 Hz higher than this reference frequency?

Finally, it's useful to think about how to interpret chemical shift values.

#### Interpreting Chemical Shift

Would a very shielded nucleus have a low or a high chemical shift? Justify your answer.

We'll go through the reasoning in the lecture, but you should find that a more shielded nucleus has a lower chemical shift than a more deshielded nucleus. Thus, high values of  $\delta$  imply that a nucleus is deshielded relative to the reference compound.

With Alex you'll talk a lot more about how different functional groups and different molecules give different chemical shifts, and learn how to interpret NMR spectra to get molecular structure out. You'll also learn about **spin-spin coupling**, which is great fun.

Now, we are done with most of the course. Our final lecture will be a bit shorter, and will focus on something close to my heart: **time-resolved spectroscopy**. It's a bit more advanced, but it will give you a flavour of the kind of cutting-edge spectroscopy that is done today (by people like me).

<sup>4</sup>Different reference molecules are used in solvents where TMS isn't soluble.

**Take Home Messages**

- Putting nuclei in magnetic fields allows transitions between different spin states to be measured.
- The energy of this transition is incredibly sensitive to the structure of the molecule surrounding the nucleus, and thus the spectrum provides a large amount of structural information.
- NMR spectrometers are defined by the Larmor frequency, and NMR spectra are reported in units of chemical shift to account for differences between spectrometers.

## Lecture 10

# Time-Resolved Spectroscopy

Finally, we're going to end this course with a first look at a more modern application of spectroscopy – time-resolved spectroscopy.

By 'modern' here, I don't mean that this is a particularly recent invention, but that nowadays it is quite a common thing for people to do (where in the past it was really the preserve of specialist researchers). It's also what a few of us who do spectroscopy at Leicester (for example, me, Phil Ash, and Andrew Hudson) spend our time doing when we're not teaching you<sup>1</sup>.

### 10.1 Why Time Resolution?

The fundamental idea behind any time-resolved spectroscopy is that you are measuring the spectrum of something *as a function of time*. For example, you might mix two compounds together, and then measure the spectrum over a period of minutes as a reaction occurs. You'll see the spectrum *change over time*, which will allow you to watch the product of that reaction forming. You can then maybe learn about how fast the reaction is, and what mechanism it goes by (among other things).

It is fairly intuitive as to why this is useful, I think. Static spectroscopy is great if you have a stable molecule or you are interested in the ground state structure, but more and more often chemists are interested in what happens when molecules *do stuff*. We call this looking at the **dynamics** of a molecule rather than looking at a static spectrum. To look at dynamics, you need to make the molecule do something and then measure the spectrum over time.

#### 10.1.1 Pump-Probe Methods

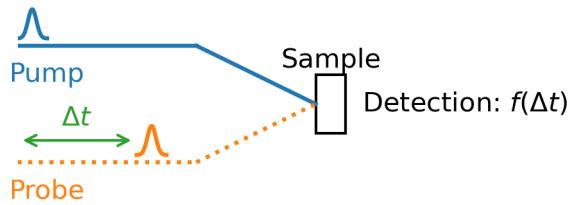
The process of initiating some change and then measuring the spectrum over time called **pump-probe** methodology. We start some sort of change using a **pump**, and then come in at a series of later times with a **probe** that measures the state of the system (Figure 10.1).

A good analogy is to think about taking photos of a sprinter. The sprinter starts running at the sound of a starting pistol (the **pump**), and then you take photos as they run (each photo is a **probe**). Afterwards, you have a series of photos of the sprinter that you can use to look at how they ran. A classic example of this is the series of photos of a galloping horse (Figure 10.2) taken by Eadward Muybridge<sup>2</sup>, used to show that when a horse gallops, it does take all four legs off the ground at some point (apparently this was a question people cared about in 1878).

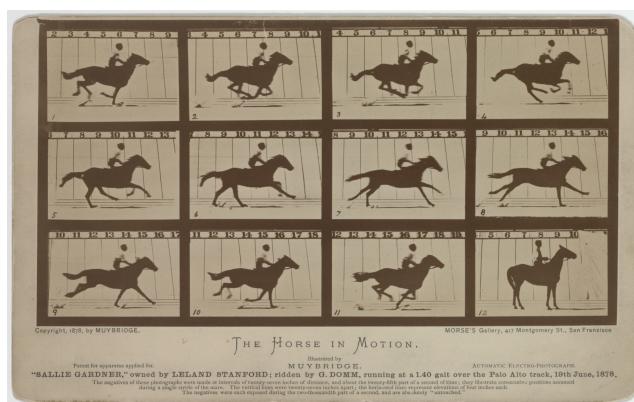
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<sup>1</sup>Or doing soul-destroyingly boring admin tasks.

<sup>2</sup>Which is used in the introductory talk of every PhD student doing ultrafast chemistry, ever.



**Figure 10.1:** Pump-probe principle. A process is started using a pump (blue), and then measured using a probe at a later time (orange). The time delay  $\Delta t$  between the pump and the probe is varied to build up a picture of the dynamics.



**Figure 10.2:** A horse in motion: the camera shutter speed needs to be fast enough that each photo is well-resolved and not blurry.

Obviously, for this to be useful, our pump needs to initiate the motion promptly (so we know when our dynamics start), and the probe needs to be fast enough that each ‘photo’ is meaningful. Imagine taking a photo of a sprinter where the camera shutter speed was too slow - it would be a blur and not anything useful. The combination of these two factors will define the **time resolution** of your measurement.

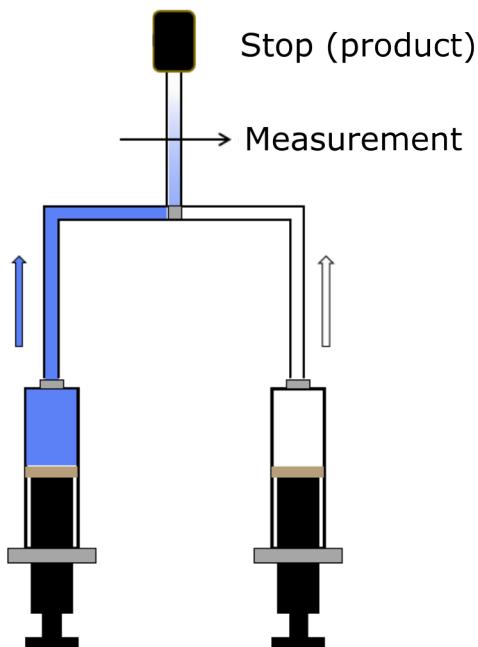
To bring this back to chemistry, we can use this approach to look at things like:

- How chemical reactions proceed over time.
- How molecules respond to external stimulus, like having a bond broken.

This is very powerful. Studying reaction kinetics and molecular dynamics like this is a very direct way to do measurements. All we need to do is:

- Have a way of initiating a reaction or changing a molecule.
- Have a way of measuring the effect that change has over time.

How we do this in practice depends on what we want to measure, and we'll look at a few examples.



**Figure 10.3:** Stopped-flow kinetics. Two reactants are rapidly mixed and then the progress of the reaction monitored as a function of time.

### Stopped-Flow Methods

An easy example to understand at first is the **stopped-flow** measurement, shown in Figure 10.3. In this measurement, two syringes containing reactant and rapidly shot into a vessel and mixed, and then the reaction is measured over time. The reaction could be measured by (non-exhaustive list):

- UV-Vis or IR spectroscopy.
- NMR spectroscopy (if the reaction is slow enough).
- Observing fluorescence or other light emitted by the sample.

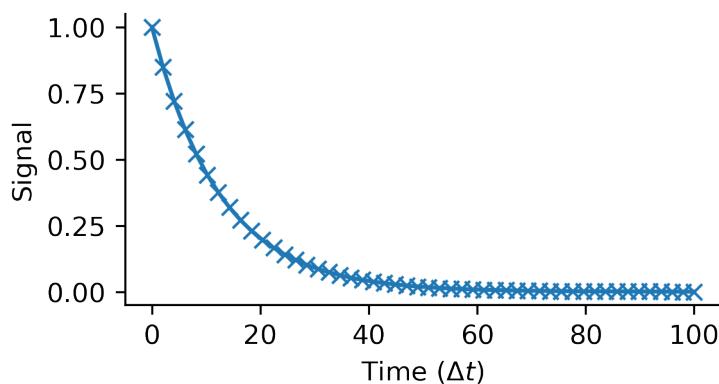
Stopped-flow methods are good if you want to study a reaction with a half-life down to around 1 ms or so (rate of around  $1000\text{ s}^{-1}$ ). Anything faster than this, and you need another method, because the time resolution is limited by how fast you can mix together the reactants from the syringes.

### Flash Photolysis Methods

For faster reactions, you need to be able to initiate the reaction more quickly than you can by simple mixing. This requires using fast electronics or optics to **flash** the reaction mixture with a pulse of light<sup>3</sup> (the pump pulse) that causes a photochemical reaction to occur. Then you measure the absorption (for example) of the reaction mixture with another flash of light

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<sup>3</sup>Usually, you could also use something like an electrical discharge I guess.



**Figure 10.4:** Typical pump-probe data: signal changes as function of the time delay  $\Delta t$ .

Methodology	Timescale (s)	Notes
Stopped-Flow	>1ms	Can be used with "slow" probes such as NMR
Flash Photolysis	>1ns	Electronic timing expands range of usable pumps
Femtochemistry	>1fs	Requires use of lasers. Can be IR or UV-Vis.

**Table 10.1:** Some different methods used in time-resolved spectroscopy.

(the probe pulse). This technique is called **flash photolysis**, and was invented shortly after the Second World War, and actually our very own **George Porter** (who the building is named after), won a Nobel Prize for the development of it in 1967.

Flash photolysis is great, and using electronics to control the timing of the pulses means that you can measure reactions that happen in as fast as a few nanoseconds (rate of around  $1 \times 10^9 \text{ s}^{-1}$ ). However, we know from earlier in this course that vibrating and rotating molecules often move even faster than this – a vibrating diatomic might undergo a vibration once every picosecond ( $1 \times 10^{-12} \text{ s}$ ). What if we want to look at motions of nuclei on their natural timescale?

### Ultrafast Methods: Femtochemistry

The advent of the **femtosecond laser** in the late 1980s/early 1990s changed the face of this field forever. These lasers use optical timing methods to produce pulses that are on the order of a femtosecond ( $1 \times 10^{-15} \text{ s}$ ) in duration. To put that in context, there are about as many femtoseconds in a second as there are seconds in the age of the universe. It's a *short* amount of time – and is why these lasers are called **ultrafast lasers**.

With this technology, you can do flash photolysis but start reactions on a much faster timescale<sup>4</sup>, using optical timing methods. The methodology is mostly just standard pump-probe (as shown in Figure 10.1), but with these lasers the pump and the probe are very very short in time, allowing very very fast changes in the reaction to be monitored. In any of these techniques, you'll measure data as a function of time (example in Figure 10.4) – just the timescales involved will be different.

Most of what I do now is ultrafast chemistry, trying to look at the dynamics of molecules on very short timescales. To summarise – we have a whole range of different kinetic methods available to us, depending on what exactly we want to achieve, which are tabulated in Table 10.1.

<sup>4</sup>It is even possible to do **attosecond** measurements with this methodology, which means  $1 \times 10^{-18} \text{ s}$ , with the right lasers. So far this is mostly used in atomic physics rather than in chemistry, though.

To end this course, we're going to talk about one kind of time-resolved measurement in a bit more depth: **transient absorption spectroscopy**. This is a really common experiment (and one you might end up doing later if you pick the right MChem supervisor...).

## 10.2 Transient Absorption Spectroscopy

Transient Absorption Spectroscopy (TAS) is a kind of pump-probe measurement where you use pulses of light (mostly from a laser nowadays) to interrogate the dynamics of some chemical system. The system could range from isolated small atoms in the gas phase, to big proteins floating around in solution. Fundamentally:

- A pump laser pulse comes in and starts some dynamics.
- A second laser pulse comes in at a series of later times and measures the dynamics by measuring the absorption spectrum of the system.

The wavelength of the laser pulses can be picked to match what you want to do. Generally speaking, the pump pulse will be some kind of UV or visible region pulse that will put the molecule in an excited state and start it doing something. The probe pulse could be (among others):

- Infrared (vibrational TAS).
- UV or Visible (electronic TAS).
- UV or Visible with a third pulse (vibrational Raman TAS).

This methodology is only possible because vibrational and electronic transitions happen very quickly. You can't do NMR transient absorption really, because it takes a long time for an NMR measurement to be made. The best timescales you can really hope to resolve with NMR are on the order of milliseconds, which is essentially an infinite amount of time if you care about molecular dynamics. **NMR is rubbish for most time-resolved measurements**, which is why we still use IR and UV-Vis, even though they are **objectively worse than NMR** at characterising molecular structure. It's all a trade-off between different things. In terms of time resolution:

- NMR is hopeless, unless your reactions happen quite slowly (longer than a second).
- IR, UV-Vis, and microwave (sort of) can all be ultrafast, with the right laser technology.

However, in terms of structural resolution, the opposite applies. NMR is **much better** than the optical spectroscopies at determining molecular structure. It's just so slow!

### 10.2.1 TAS Equipment

A typical transient absorption setup looks exactly like the one we saw in Figure 10.1, but there are a few interesting points to think about regarding the equipment used here. Firstly, the sources of light need to be appropriate, which means:

- The wavelength of the pump pulse has to be of the right energy to initiate the dynamics we want to see.



**Figure 10.5:** Typical chopping scheme: every other pump pulse is removed, so that a sequence of spectra with and without the pump is recorded. The difference between the spectra with pump on and pump off is what we measure in TAS.

- The probe pulse either needs to contain a range of wavelengths (a *broadband* pulse), or have a wavelength that can be scanned so that the spectrum can be built up.
- Both pulses need to be short enough in time to be able to resolve the dynamics we want to measure.

Note we have to think about the temporal duration of the light pulses, and also the energy (colour, wavelength, whatever) of them. So we have to think simultaneously in time and energy space – this is common, so get used to it! The timescales spanned by a TA measurement can range from milliseconds to attoseconds, and the thing that determines the time resolution in almost all cases is the temporal duration of the light pulses.

The way we detect the signal in the TAS measurement is by measuring the spectrum of the probe light pulse whilst **chopping** out every other pump pulse (Figure 10.5). In that way, we can measure the difference in absorption of the probe when the pump is present and when it isn't. This gives us a **difference spectrum** that tells us the effect that the pump has on our system.

To be quantitative, the overall signal we measure is the change in absorbance  $\Delta A$ :

$$\Delta A = A_{\text{pump}} - A_{\text{no pump}}$$

The detection can happen on a standard spectrometer, similar to the ones you have used in the teaching lab (although slightly more customised, and with less annoying proprietary software required to control them).

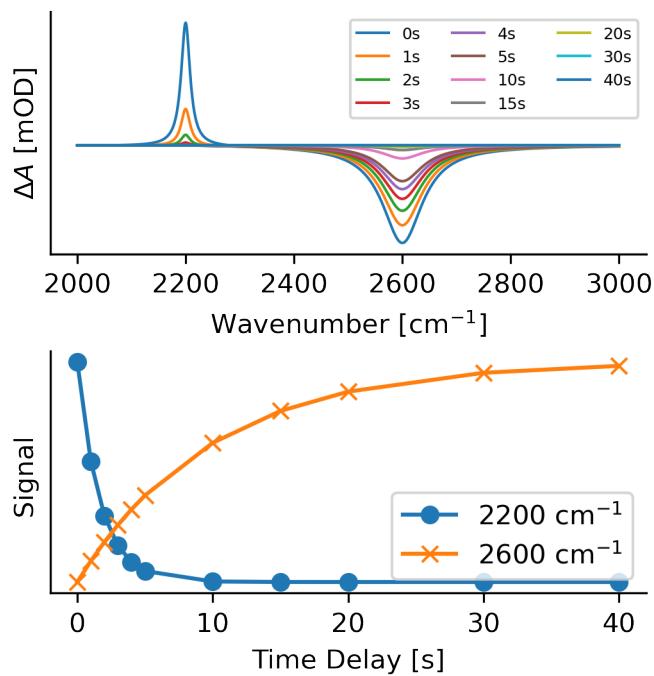
### 10.2.2 Interpreting TA Spectra

So, when we do a TA measurement, our data output is a series of spectra as a function of time. We can represent this in a few different ways. We could look at the whole spectrum at once and plot many different time steps at the same time (top panel of Figure 10.6). Alternatively, we could select bands in the spectrum we care about and look at the height/area<sup>5</sup> of those bands as a function of time (bottom panel of Figure 10.6).

Then, we can learn a few things. We can see the presence/absence of characteristic peaks as time goes on – which can tell us about the dynamics that are occurring. We can also look at an individual peak and see how the peak intensity changes with time – this can tell us about the

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<sup>5</sup>Depending on how accurate we can be.



**Figure 10.6:** Typical TAS data (simulated). Top: A series of spectra measured as a function of time. Bottom: the time-evolution of the two peaks in the spectrum.

timescale of any dynamics that are occurring. In the (fictional) case shown in Figure 10.6, we see that the lower energy peak decays fast, but that the higher energy peak rises more slowly. So there is not a 1:1 correspondence between the decay times - which tells us that it's not as simple as the lower energy peak 'turning into' the higher energy peak. We'll see another example of this in the problems.

Also, the signal in our difference spectrum can tell us some interesting things too:

- If the signal in the difference spectrum is positive, then it means that there was more absorption when the pump was present than when it wasn't. This can be due to:
  - **Product absorption**, where the product of a reaction started by the pump absorbs more light than the reactants did.
  - **Excited state absorption**, where the excited state of a molecule absorbs more light than the ground state did.
- If the signal in the difference spectrum is negative, then it means that there was less absorption when the pump was present than when it wasn't. This can be due to:
  - **Ground state bleaching**, where so many ground state molecules have been reacted/excited away ('bleached') by the pump, that there are less there to absorb light.
  - **Stimulated emission**, where the pump causes the molecule to emit light, which looks the same as 'less absorption' as far as the experiment is concerned.

Anyway, that's more than enough for now, I just wanted to give you a flavour of the kinds of spectroscopy people do in 2023. This is the last lecture, but the course is not over! We still have problems to go through, and these problems will touch on some things we haven't yet covered.

**Take Home Messages**

- Measuring spectra as a function of time allows *chemical dynamics* to be studied.
- To do this we need a pump (to initiate the dynamics) and a probe (to measure the dynamics)
- A common methodology for this is transient-absorption spectroscopy, which measures changes in an absorption spectrum over time.

# Problem Sheet 4

1. Using group theory, **or otherwise**, determine which of the following vibrations are Raman active. Justify your answers.
  - i The H–Cl stretch in HCl.
  - ii The O=O stretch in O<sub>2</sub>.
  - iii The symmetric stretch in CS<sub>2</sub>.
2. A molecule with the formula CX<sub>2</sub> is excited using a laser with a wavelength of 505.0 nm. The resulting vibrational Raman spectrum shows peaks at 521.1, 560.9, and 608.7 nm.
  - i Explain why the Raman spectrum is measured at longer wavelengths than the excitation wavelength.
  - ii Determine the vibrational wavenumber of each peak (i.e. the Raman shift relative to the excitation wavelength).
  - iii By looking up vibrational Raman wavenumbers on NIST (or similar), determine the identity of the atom X.
3. An <sup>1</sup>H NMR spectrum of an aromatic molecule was measured in an NMR spectrometer with a Larmor frequency of 500 MHz. The frequency of a proton attached directly to the aromatic ring was measured to be 500.003 50 MHz, and the frequency of a proton attached to an alkyl side chain was measured to be 500.001 25 MHz.
  - i Calculate the chemical shift of both protons.
  - ii How would the chemical shifts of these protons change if the same molecule was measured using a spectrometer operating at a Larmor frequency of 350 MHz? Justify your answer.
  - iii Which nucleus is the more shielded nucleus?
  - iv Calculate the strength of the magnet in the 500 MHz spectrometer. Why is it beneficial to use a spectrometer with as high a magnetic field as possible?  
**Note:** the gyromagnetic ratio of <sup>1</sup>H is  $267.5 \times 10^6 \text{ rad s}^{-1} \text{ T}^{-1}$ .
4. Suggest appropriate methods for studying each of the following sets of dynamic chemical phenomena, justifying your answers:
  - i The structure of an organic molecule which is isomerising over a period of days.
  - ii The catalytic activity of a peroxidase enzyme, which decolourises a solution of dye molecules at a rate of around 100 s<sup>-1</sup>.
  - iii The reaction of a metal d-block complex with formula M(CO)<sub>6</sub>. The reaction appears instantaneous when studied using stopped-flow techniques.
  - iv The photodissociation of iodobenzene following irradiation with UV light. Calculation suggests that the dissociation happens with a timescale between 1 and 10 ps.

## Extended Problems 3

1.  $\text{CuF}_6$  is a coordination compound.

a) Assuming that  $\text{CuF}_6$  is octahedral, determine:

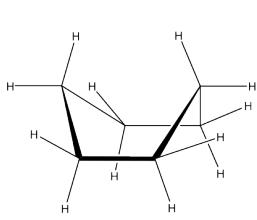
- The number of bands you would expect to see in the Cu-F stretching region of the IR spectrum of  $\text{CuF}_6$
- The number of bands corresponding to d-d transitions you would expect to see in the UV-Vis spectrum.

b) The corresponding measured spectra of  $\text{CuF}_6$  show:

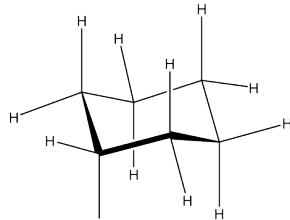
- Two bands in the Cu-F stretching region of the IR spectrum.
- Two bands in the UV-Vis spectrum that correspond to d-d transitions.

Do these observations agree with your predictions? Explain these observations **fully**.

2. Cyclohexane can exist as two conformers, known as the **chair** and **boat** forms (below)



Boat Conformation



Chair Conformation

a) The point groups of these conformers are  $D_{nd}$  and  $C_{mv}$ . Assign the point groups of the two conformers, and draw symmetry elements on the structures.

b) A representation of the C-H stretching vibrations of each conformer is given by:

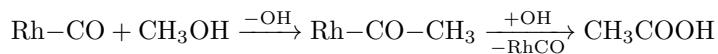
$$\Gamma(C - H)_{\text{Boat}} = 4A_1 + 2A_2 + 4B_1 + 2B_2$$

$$\Gamma(C - H)_{\text{Chair}} = 2A_{1g} + 2E_g + 2A_{2u} + 2E_u$$

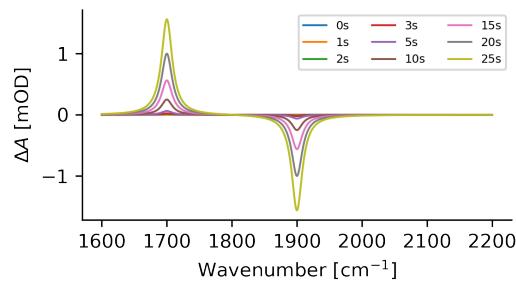
Justify these assignments. Could the two conformers be distinguished using vibrational spectroscopy? Explain your answer fully.

- c) At room temperature, the  $^1\text{H}$  NMR spectrum of cyclohexane shows only a single peak, which splits into two peaks as the temperature is lowered. Explain this observation.
- d) Is NMR or vibrational spectroscopy a more suitable technique for studying the structure of cyclohexane in solution?

3. Ethanoic acid can be produced from methanol using a Rhodium catalyst with a CO ligand. An **idealised**<sup>6</sup> reaction scheme is as follows:



This process was initiated under an atmosphere of excess CO and then an IR transient absorption spectrum of the system was measured.



Explain the form of this transient absorption spectrum given the mechanism above, paying specific attention to the following points of interest:

- The chemical origins of the two peaks.
- The reason for the sign of the two peaks as a function of time.
- The absence of any other peaks.

**Note:** you may find the following information useful:

Vibration	IR Frequency ( $\text{cm}^{-1}$ )	Notes
CO stretch	2143	In free CO.
CO stretch	1600-1800	In organic molecules.
CO stretch	1800-2100	When coordinated to a metal ion.

4. The strength of the magnetic field of the Earth in the UK is around  $47 \mu\text{T}$ .
- Calculate the Larmor frequency of a  $^1\text{H}$  nucleus in the Earth's magnetic field.
  - Hence, calculate the Boltzmann population ratio of the two spin states of  $^1\text{H}$  in the Earth's magnetic field.
  - Why is the magnetic field of the Earth generally not useful for NMR spectroscopy?
  - Define what is meant by the term **NMR active nucleus**.
  - Four commonly used NMR active nuclei are:

$$\begin{array}{ll} ^1\text{H} (\gamma = 267.5 \times 10^6 \text{ rad s}^{-1} \text{ T}^{-1}) & ^{19}\text{F} (\gamma = 251.8 \times 10^6 \text{ rad s}^{-1} \text{ T}^{-1}) \\ ^{13}\text{C} (\gamma = 67.3 \times 10^6 \text{ rad s}^{-1} \text{ T}^{-1}) & ^{31}\text{P} (\gamma = 108.3 \times 10^6 \text{ rad s}^{-1} \text{ T}^{-1}) \end{array}$$

- Calculate the Larmor frequency of these nuclei in a spectrometer with field strength of  $11.74 \text{ T}$ . Rank the nuclei in order of how sensitive they would be in an NMR measurement.
- Why is  $^1\text{H}$  the most commonly used NMR active nucleus?

<sup>6</sup>Don't show this to a real chemist please.