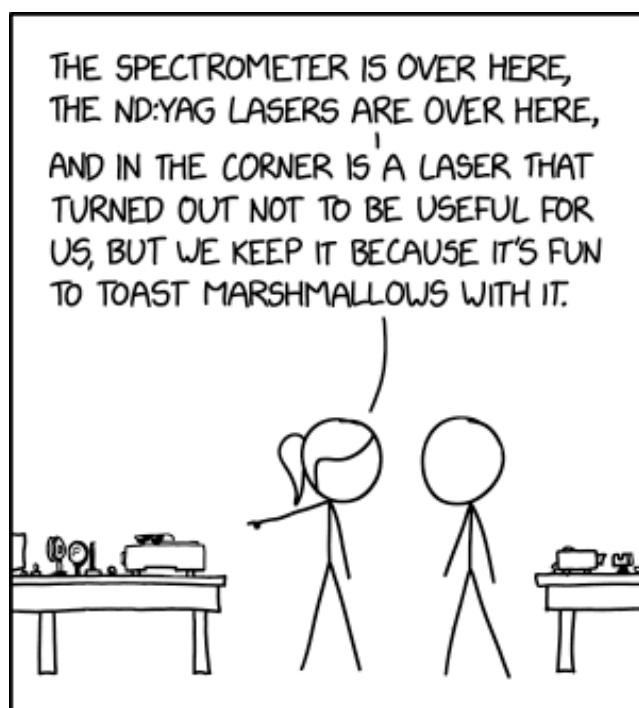


CH2200 Spectroscopy Theory and Practice

Part A

James Pickering



EVERY LAB IN EVERY FIELD HAS
SOME PIECE OF EQUIPMENT LIKE THIS.

Cartoon credit: <https://xkcd.com/2514/>

Overview

This module is called '*Spectroscopy Theory and Practice*' and is delivered by James Pickering and Alex Pulis. It is worth 30 credits, and 60% of the module is assessed by an exam, and the other 40% is assessed via coursework (two tutorials and an MCQ). This module is **heavily oriented towards problem solving**. This course has traditionally been one that students find challenging. It is therefore important that you engage with it, and in particular the problems – **the only way to learn this stuff is to wrestle with the problems!**

James' part will consist of 17 sessions. This will roughly be 11 lectures and 6 problem classes (some of which will be in a lecture style). A synopsis for James' part of the module is below.

A detailed breakdown of the sessions and assessments will be on Blackboard, as timings will differ for the UK (UoL) and Chinese (DLI) instances of the module.

Assessment

- 60% assessed via written exam. 50:50 split between James' and Alex's material on the exam. Three questions, answer all questions.
- 40% assessed via coursework:
 - 24% Multiple choice test – a mixture of James' and Alex's material. CHECK
 - 16% Two tutorials (8% each). One on James' and one on Alex's material.

Philosophy

This course will run in a more problem-focussed way than other courses you've had to date. By this, I mean that:

- Your answers to the problem sheets are **the most important resource**.
- These lecture notes are **not** the only source of examinable material.
- You will learn concepts via the problem sheets that are not explained in these notes.

Thus, **you need to engage with the problems**. You will not be able to simply read these notes and then pass the exam. There will be concepts that could arise in the exam that we will learn about through the problem sheets. To stress the point: **these notes alone do not define the examinable content**.

For my part of the course, the emphasis is not really on memorisation of material. It is more important that you can apply knowledge to unfamiliar situations, and think creatively to solve problems. In the exam, I will give you most equations you need, but will expect you to be able

to manipulate them, solve problems, and interpret the results. The equations I will expect you to know from memory are listed at the end of this booklet.

By the end of the course, you should have both this booklet, and a large set of answers to the problems which will form the basis of your revision material. There is an appendix with a few advanced topics in it at the end **that is there for interest only** - won't be on the exam.

Synopsis – James' Part

My part of this module focusses on the physical processes that underpin spectroscopy. Fundamentally it is mostly about *why spectra look they way they do*, not about *how to interpret a specific spectrum and learn some chemistry*. After this part you should be developing a broad, intuitive understanding of what spectroscopy is and why it's useful. The second part of the module will go into the specifics about how you use this stuff in real chemistry.

1. **Lecture 1:** Why Spectroscopy? Recap from level 1: photons, waves, and energy.
2. **Lecture 2:** Light and Matter I. Light interacting with molecules: wave picture.
3. **Lecture 3:** Light and Matter II. Light interacting with molecules: photon picture.
4. **Problems 1:** Converting units on the EM spectrum. Calculating transition energies.
5. **Lecture 4:** Interpreting Spectra. Peak position, lifetime, and area. Rotations.
6. **Lecture 5:** Vibrations. Vibrational spectroscopy. Rovibrational excitation.
7. **Problems 2:** Calculating molecular properties from spectral data.
8. **Extended Problems 1:** Calculating molecular properties. Complex systems.
9. **Lecture 6:** Bigger Molecules. Symmetry Elements. Point groups. Character Tables.
10. **Lecture 7:** Symmetry and Spectroscopy. Applications of group theory in spectroscopy.
11. **Problems 3:** Group theory and symmetry.
12. **Extended Problems 2:** Group theory and symmetry, complex examples.
13. **Lecture 8:** Raman Spectroscopy. Raman effect, IR vs Raman activity.
14. **Lecture 9:** Electronic Spectroscopy. Electronic excitation, UV-Vis and X-rays.
15. **Lecture 10:** Magnetic Resonance I. Molecules in magnetic fields. Chemical shift.
16. **Lecture 11:** Magnetic Resonance II. Spin-spin coupling.
17. **Problems 4:** Bringing it all together. Solving spectroscopic problems.

Recommended Reading + Resources

Textbooks

- **Physical Chemistry**, P Atkins. *Chapters 13, 14, 15 in my edition (8). Also has useful background on quantum mechanics and atomic spectroscopy which we don't cover explicitly in this course.*
- **Modern Spectroscopy**, J M Hollas. *Despite the title, a little dated now but the fundamentals haven't changed.*
- **Fundamentals of Molecular Spectroscopy**, Banwell and McCash. *Similar to above, with a nice focus on practical spectroscopy.*
- **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 and work through it for symmetry.*
- The Oxford Primers on **Molecular Spectroscopy** and **Atomic Spectroscopy**.

Other Resources

- **A link the group theory tables you'll have in the exam.** https://www3.uji.es/~planelle/APUNTS/TGS/taules_TG_oxford.pdf.
- **QED - The Strange Theory of Light and Matter**, R P Feynman. *A nice introduction to thinking about light-matter interaction at a deep fundamental level.*

Websites

- <https://symmetry.constructor.university/>. *Group theory tables, lots of example molecules, and calculators for reduction formulae. I use it a lot.*
- **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). My one is here: <https://jamesdpickering.com/pages/calculators.html>.

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.

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

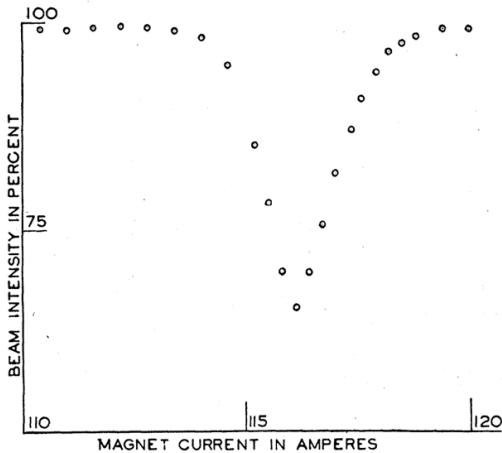


Figure 1.1: The first NMR spectrum, measured by Isidor Rabi in 1938. Humble beginnings!

rotational spectroscopy), or visible/ultraviolet light (in electronic spectroscopy), among others. The EM spectrum that we will become intimately familiar with is shown in Figure 1.2.

Region:	Radio	Microwave	Infrared (IR)	Visible	Ultraviolet (UV)	X-Ray	Gamma Ray
Wavelength:	>1 m	1mm - 1m	750nm - 1mm	400 - 750nm	10nm - 400nm	10pm - 10nm	<10pm
Frequency:	<300 MHz	0.3 - 300 GHz	0.3 - 400 THz	400 - 750 THz	0.75 - 30 PHz	30 PHz - 30 EHz	>30 EHz
Energy:	<1 μ eV	1 μ eV - 1 meV	1 meV - 1.7 eV	1.7eV - 3 eV	3 eV - 100eV	100eV - 100 keV	>100 keV
Wavenumber: (cm ⁻¹)	<0.01	0.01 - 10	10 - 13333	13333 - 25000	25000 - 10 ⁶	10 ⁶ - 10 ⁹	>10 ⁹
Timescale:	>3 ns	3ps - 3ns	2.5fs - 3ps	1.3 - 2.5fs	0.03 - 1.3fs	0.03fs - 0.03 as	<0.03as
Spectroscopy:	Magnetic (NMR, ESR)	Rotational	Vibrational	Electronic (valence)	Electronic (valence + core)	Electronic (core)	Mossbauer
Common Use:	BBC Radio 4	Ready Meals	Radiators	Your Eyes	Tanning Salons	Broken Bones	Death Star
Think:	Low Energy Low Frequency Small Wavenumber Long Wavelength Slow Oscillation	→					High Energy High Frequency Large Wavenumber Short Wavelength Fast Oscillation

Figure 1.2: The EM spectrum. Our best friend.

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 different kinds of matter**, and a lot of the fundamentals 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.

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 spectroscopy: 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 is often directly linked to a huge range of 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), and we care about measuring molecular properties because we are chemists and are interested in molecules – which is why spectroscopy is so useful to us.

Recall a few key things that arise from this model:

Key Fundamentals

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.

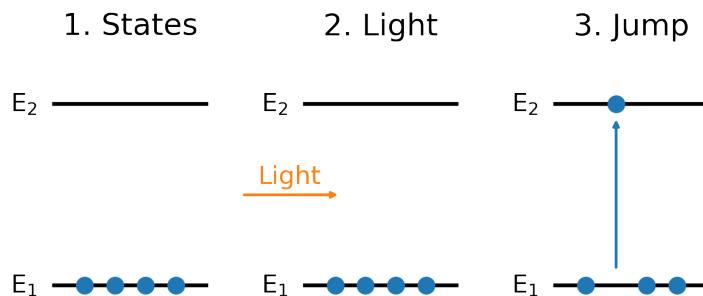


Figure 1.3: Simple model of spectroscopy. A photon of light causes a molecule to jump from one quantum state to another.

1.2.1 Energy Units

Point (1) above written mathematically says:

$$E_{\text{photon}} = E_2 - E_1$$

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

¹In many ways wavelength is a silly unit to use, and I think it should be considered harmful, but people still use it so you need to know about it.

Note the standard notation, which I'll try and stick to, however these are rules of thumb². 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 in the same units, 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, c , which has a value of $2.997 \times 10^8 \text{ m s}^{-1}$ (units of **metres per second**).
- The electronvolt is defined as $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$ (i.e there are $1.602 \times 10^{-19} \text{ Joules per electronvolt}$).

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 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!

This process of looking at units will help you work out how to do energy conversions, without having to learn tedious formulae³. 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:

²Rotational spectroscopists use both Hertz and wavenumbers, depending on their mood, and electronic spectroscopists tend to use nanometers or electronvolts depending on if they're working nearer to biology or nearer to physics.

³The units help you see where the formulae come from, much more valuable knowledge to have.

- $1 \text{ eV} = 8065.54 \text{ cm}^{-1}$
- $1 \text{ cm}^{-1} = 1 \times 10^7 \text{ nm}$
- $1 \text{ THz} = 33.36 \text{ cm}^{-1}$

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

You should get 4.66 eV, 239 GHz, and 8359 cm^{-1} .

1.2.2 Energy Gaps - Lines and Levels

We will come back to this again and again, but point (2) from our list in the *Key Fundamentals* box earlier is critical. In spectroscopy, we are always measuring the **difference in energy** between two energy states. 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 course⁴, 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 energy⁵. We normally represent states pictorially by drawing horizontal lines on paper, and jumping between these states is what we do in spectroscopy (Figure 1.3).

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.

⁴In 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.

⁵Formally, 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?

You should find that it is 4.81 eV.

1.2.3 Populations

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 T using the **Boltzmann Distribution**, as we've seen last year.

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

Where n_i is the number of molecules with energy E_i .

Boltzmann Distribution

A given molecule can exist in two states.

1. A sample of the molecules is held at 200 K. If the energy gap between the states is 300 cm^{-1} , what is the population ratio?
2. If the measured population ratio is 0.98, what is the temperature of the sample of molecules?

You should find that the ratio in Q1 is 0.12, and the temperature in Q2 is about 21 400 K. **Check your units** if you didn't get these, the factor in the exponent in the Boltzmann needs to be dimensionless.

1.2.4 Absorption and Emission

Recall than when light hits matter, there are 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 interesting⁶).

⁶For example, either the first couple of chapters of Hollas, or https://en.wikipedia.org/wiki/Einstein_coefficients is a good place to look.

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 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 jumping and 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 a little bit 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 anything at a molecular level. Neither picture is entirely 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 thinking 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

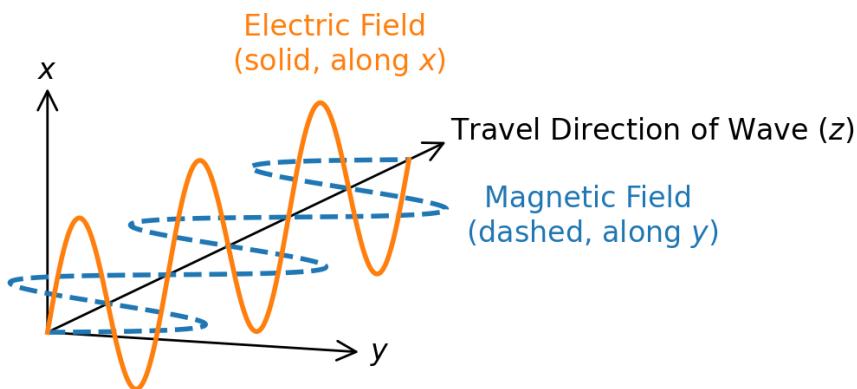


Figure 2.1: Electromagnetic radiation consists of an electric field (orange, solid line) and a magnetic field (blue, dashed line) that propagate together. In this drawing, the light wave is travelling along the z direction, with the electric field polarised along x , and the magnetic field polarised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

field oscillating along x and the magnetic field oscillating along y – the electric and magnetic fields are always perpendicular to each other¹

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 spectroscopies*, like NMR, 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 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, and Figure 1.2 showed how these quantities vary across the EM spectrum. Remembering how to convert between these is vital, and we saw how to do it last time.

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!

The wave 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.

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. We saw this in the 'states-light-jump' model last time (Figure 1.3), which I call the **jumping molecule** model. We can calculate the photon energy from the wave properties just discussed using the Planck constant, as we saw in the last lecture. To get a feel for how 'big' a photon is in terms of energy, let's think about the sun :

¹The direction of the wave oscillations can have important consequences in some kinds of spectroscopy, and is called the 'polarisation state' of the wave. We won't worry about it too much in this course, though.

Photons

The solar flux that hits the surface of the Earth on a sunny day is about 1.36 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?

You should find the answer is about 5×10^{21} . Lots of photons!

While thinking about the sun and other light sources, another question might occur to us:

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

We don't get sunburn from a radiator (or if we are wearing suncream), or feel warm if we stand in front of an LED light (and suncream doesn't stop us feeling hot while we stand in the sun), 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 frequencies 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. We saw the **jumping molecule** model (which uses the photon picture) just now. The model that uses the wave picture, I call the **jiggling molecule** model.

Remember that fundamentally spectroscopy is about light interacting with matter, and making the matter (a molecule) to do something. Different kinds of spectroscopy involve the matter doing different things:

- **Rotational** spectroscopy: light makes molecules **rotate**.
- **Vibrational** spectroscopy: light makes molecules **vibrate**.
- **Electronic** spectroscopy: light makes **electrons** in molecules (or atoms) jiggle 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.

2.2.1 Electric Fields

We said a useful picture of light is as an oscillating electric field. To understand what an oscillating electric field actually is, imagine it as a wave where the peaks and troughs are positively

charged – as shown in Figure 2.2. What would happen if you put a charged particle (say, an electron), in this field?

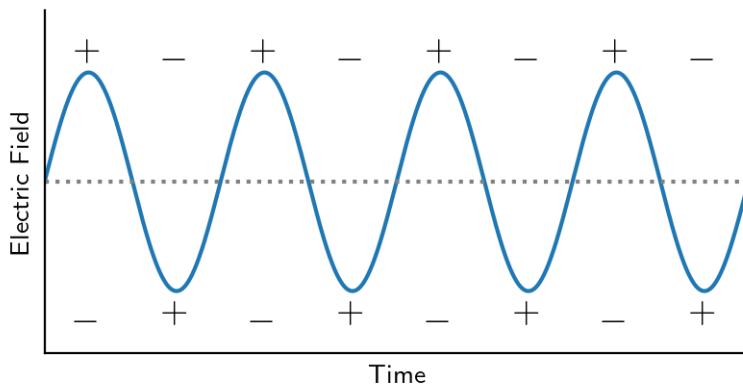


Figure 2.2: The electric field of light can be thought of as a wave where the peaks/troughs are positively charged, and change direction over the course of a cycle. A free electron in this field would oscillate (following the blue curve).

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 down². 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 Jiggle Electrons

Ok, so that's a free electron, but free electrons are boring, and most of the electrons we care about in chemistry are tied up in molecules. So what happens if we do this to molecule, which contains electrons that are already tightly held by attraction to positive nuclei? To see this, let's consider a simple molecule, which is a homonuclear diatomic (something like O₂), so has a symmetrical distribution of electrons around it (shown in grey on Figure 2.3).

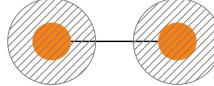


Figure 2.3: Our example molecule. Nuclei are orange, and the electrons are the grey shading.

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.

So, in the presence of a light wave, the electrons in the molecule have started jiggling around and moving. 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. As this motion happens,

²Researchers 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>.

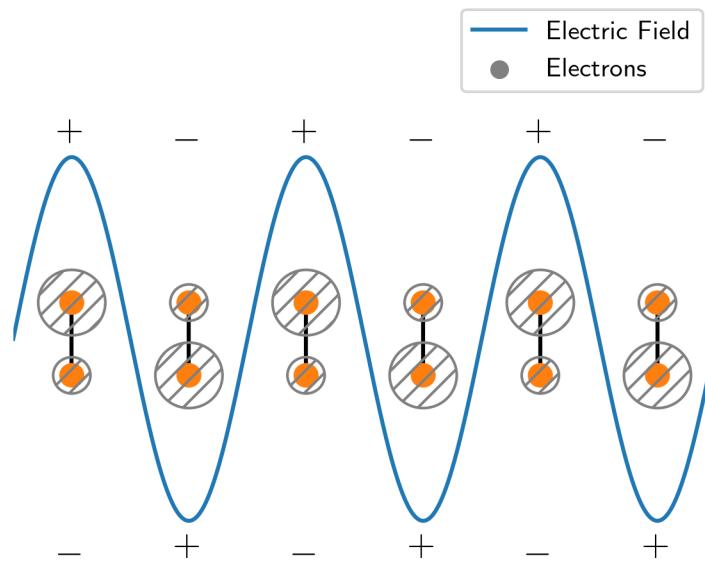


Figure 2.4: Putting the molecule in an oscillating electric field makes the electrons jiggle up and down. The molecule is polarised now due to the unequal charge distribution, and this oscillation of the molecule's polarity is called an oscillating polarisation.

the molecule becomes become **polarised**³ by the field, 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.

The polarity of the molecule changes as the field changes, and so it's an **oscillating polarisation** in the same way that our light was an **oscillating electric field**. Oscillating polarisations are essentially moving charges, and physics tells us that moving charges emit light – we can use this later to understand how things like absorption and diffraction work in this dynamic picture.

Photons and Waves → Jumping and Jiggling

The **photon** and **wave** pictures of light lead to the **jumping** and **jiggling** pictures of light-matter interaction:

- **Jumping Picture:** A photon of light is absorbed by a molecule, and the energy of the photon transferred to the molecule, causing it to become excited.
- **Jiggling Picture:** The electric field of the light pushes around electrons on the molecule, causing it to move (oscillating polarisation), gain energy, and become excited.

³You 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. Something like iodine, big and floppy, is polarisable. Something like hydrogen, small and hard, is not.

2.2.3 Resonance

In our simple picture above, electrons jiggle up and down at the same frequency as the driving light wave, but in fact, 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 ‘keep up’ and follow it (so no interaction happens). Conversely, it could be so slow that the electrons don’t move much 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 bullet train travelling at 300 km h^{-1} , then no matter how fast you tried to run, you couldn’t keep up with it
- 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.

This idea of a molecule being able to ‘follow’ the oscillating light field is an important one. The electrons in the molecule have intrinsic, natural, frequencies at which they want to jiggle around which are related to the energy of a transition between different states of the molecule. When the frequency of the oscillating field of the light matches one of these natural frequencies, we say that the light is **resonant** with the transition in the molecule. At resonance, energy transfer from the field to the electrons is most efficient, and the jiggling of the electrons is as strong as it can be, and the absorption of the light by the molecule is very strong.

Mathematically, the resonance condition is basically that:

$$\nu_{\text{light}} = \nu_{\text{molecule}}$$

Where ν_{molecule} is a natural frequency of the molecule. We can relate a natural frequency of the molecule to the energy of a specific transition, ΔE :

$$\nu_{\text{molecule}} = \frac{\Delta E}{h}$$

We can combine the two above expressions to arrive back at the familiar $E_{\text{photon}} = \Delta E$ expression from Lecture 1. Really, the resonance condition is just the dynamic, jiggling-picture version of that $E_{\text{photon}} = E_2 - E_1$ condition from the jumping molecule picture that we explained with energy conservation. So overall we have two complementary ways to think about spectroscopy:

- The energy of the photon has to match the energy between two states of the molecule (jumping picture)
- The frequency of the light field has to match the natural frequency of the molecule (jiggling picture)

These two pictures are describing the same thing in different ways. The photon (jumping) and wave (jiggling) picture of light lead to these complementary pictures of light matter interaction.

Resonance and Energy Gaps

Show that a combination of the resonance condition:

$$\nu_{\text{light}} = \nu_{\text{molecule}}$$

and the definition of the natural frequency of a given transition:

$$\nu_{\text{molecule}} = \frac{\Delta E}{h}$$

lead to the familiar expression:

$$E_{\text{photon}} = E_2 - E_1$$

Next time we will build on this picture and see how we can understand **rotational** spectroscopy through it, leading to us being able to predict the appearance of our first spectrum. Exciting times.

Take Home Messages

- We need two pictures (photon and wave) to describe how light behaves, and so there are two corresponding pictures of spectroscopy (jumping and jiggling).
- Light consists of oscillating electric and magnetic fields, and we mostly care about the electric one (unless doing NMR).
- When the photon energy matches the energy gap between two states, or when the frequency of a light field matches the natural frequency associated with a transition, we have resonance and our light-matter interaction is strong.

Lecture 3

Light and Matter II

Lecture Aims

- To understand how the ideas of jiggling electrons and resonance can make molecules move.
- To understand that all motion at the molecular scale is quantised.
- To understand how these two things result in the appearance of spectra.

Last time we ended by looking at the wave picture of light and discussed the idea of **resonance** where the molecule was oscillating at the same frequency as the light field. Specifically, we looked at electrons moving (which results in electronic spectroscopy). Today, we are going to see how this light can make molecules **rotate**.

3.1 Rotating Molecules

Imagine we now have a polar diatomic molecule, so it has an asymmetric electron distribution (i.e. a dipole moment). If we put this molecule in our oscillating field (Figure 2.2), what would 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 3.1. 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.

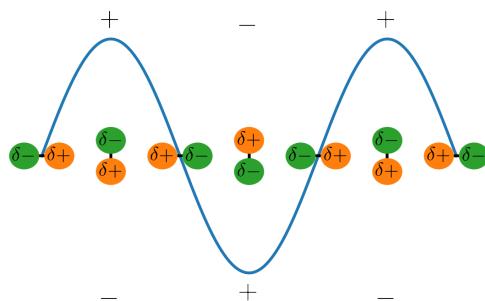


Figure 3.1: A polar molecule in an electric field resonant with the rotational level spacing will start to rotate.

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 *ridiculous* that exposing a molecule to light could make it start to rotate, right? Later on we will look at how to understand other kinds of molecular motion in this context too, like vibration (Figure 5.1).

Rotation

1. 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)?
2. Would a non-polar molecule rotate when exposed to EM radiation?

You should find that the rotational period is 10 ps, and that a non-polar molecule would **not** rotate.

3.2 Quantised Molecular Motion

3.2.1 Particle in a Box

At the atomic scale, we already know that things behave differently to how they behave at the macroscopic scale. We saw last year how the motion of an electron becomes quantised if you trap it in a box, and the same thing happens if you trap it in a molecule (i.e. hold it in an orbital).

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 became **quantised** as a result of needing to fit the wavefunction of the particle into the box. The idea is that the **matter wave** that describes the particle (the wavefunction) was confined between two boundaries so only certain waves were allowed, and so the energy is quantised. 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*, and so on. There are three important things to understand from this picture:

- The energies of the particle **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.
- **The quantisation arises from the confinement of matter waves by boundaries.** Matter waves are the waves that describe particles and their motion.

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**, as they can all be described as different kinds of waves that get confined by boundaries. 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.

A Disclaimer

What I am saying here might sound weird, that a rotating molecule can only rotate with specific, well defined energies. This is quite weird, but it's the reality. A rotating molecule can only rotate at certain speeds that are defined by the physical properties of the molecule (e.g. mass, bond lengths, etc.) 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 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 (and are described by quantum numbers n , l , m_l , and m_s). We know all of this is real by looking at spectra, and over the next few lectures you will see these spectra and see for yourself. Later in this course, and in CH2203 and CH3203, you'll cover more of the maths and physics that underpins this. For now, I hope now that you can just trust me as we go forward.

3.2.2 An Example: Quantised Rotation

To give you a concrete example of what I mean, let's think about rotating molecules. It turns out¹ 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 integer value from zero to infinity.

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 – it's a **spectroscopic constant**:

$$\text{Energy} = \text{Spectroscopic Constant} \times \text{Quantum Numbers}$$

We'll see lots of equations that have this general form.

Anyway, we can calculate the first few energies using Equation 3.1 and see that we have a lot of different levels in Figure 3.2. 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.

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 is:

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

¹See Chapter 1 of Hollas' *Modern Spectroscopy*, or look up 'Diatom Rigid Rotor Model' online for a derivation.

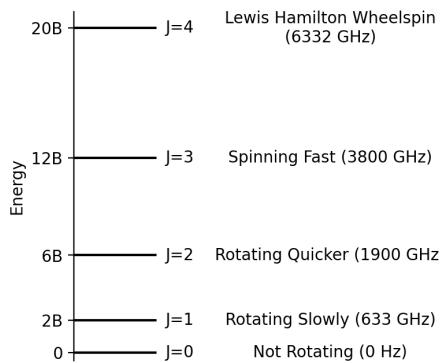


Figure 3.2: Rotational energy levels, with the rotational speeds of HCl annotated for info (1 GHz is 1 billion rotations per second – molecules spin fast!).

The answer here is simple, and maybe you can already see it. **The energies of light that are resonant with the transitions** are the ones that make the motion happen. As we've seen, the energy of the photon that causes the jump has to exactly match the energy gap between the lower and the upper state (the resonance condition):

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

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. **Experimental spectroscopy is fundamentally about measuring energies of light and working out molecular properties from them.**

Rotational Excitation

A photon of light causes a molecule of HCl undergo a transition from a rotational state with energy 0.635 THz to an excited state with energy 1.905 THz. What is the frequency of the photon?

You should find it is 1.27 THz.

3.3 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 1.27 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 1.27 THz, we are in resonance and 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 3.3, which is a part of the **rotational spectrum** of HCl.

Later we will see how we can use this energy 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).

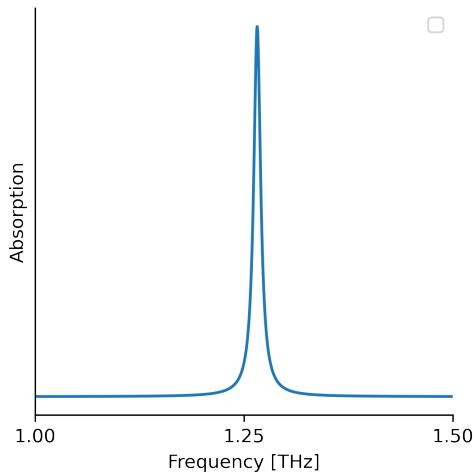


Figure 3.3: The spectrum we would obtain if we shone light with frequencies from 1 to 1.5 THz at our HCl molecule and measured how much was absorbed. HCl absorbs light at 1.27 THz, leading to a peak in the absorption spectrum.

- 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 a photon is absorbed (resonance condition). We almost always measure the amount of absorbed light rather than the molecular motion directly.

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 tried to use a totally different energy of light to excite the molecule?

3.3.1 Selection Rules

Looking at our diagram for the possible rotational energy levels (Figure 3.2), 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 if we used different energies of light. Are all of these transitions possible?

We have already seen the resonance condition, that the photon energy of the light exactly matches the energy gap between the two states:

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

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**:

Selection Rules

- **Gross selection rules** determine which broad classes of molecules can produce a certain kind of spectrum.
- **Specific selection rules** determine which specific transitions between states are allowed.

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*² rotational spectrum of a molecule, the molecule needs to be polar. **This is the gross selection rule for pure rotational spectroscopy.**

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 momentum³, 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 is the **specific selection rule for pure rotational spectroscopy**. The allowed transitions are shown in Figure 3.4.

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

3.3.2 Real Rotational Spectra

To take stock, we know what the rotational energy levels are (from Equation 3.1 and Figure 3.2), 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:

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

²'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 solely on absorption, such as rotational Raman scattering, that can rotationally excite non-polar molecules.

³Rotation 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.

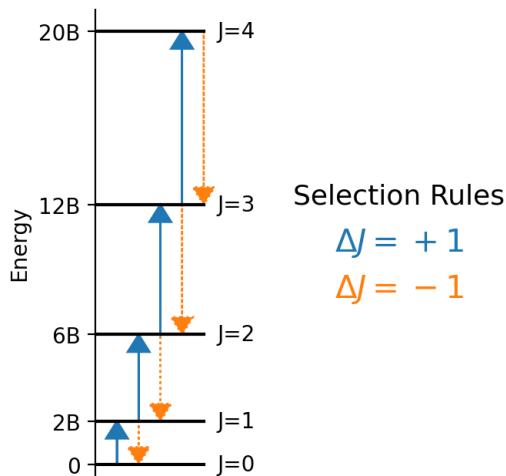


Figure 3.4: Allowed transitions in rotational spectroscopy. Absorptions ($\Delta J = +1$) are shown in blue solid, and emissions ($\Delta J = -1$) are shown in orange dashed.

We 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 3.5) and see if experiment matches our theory.

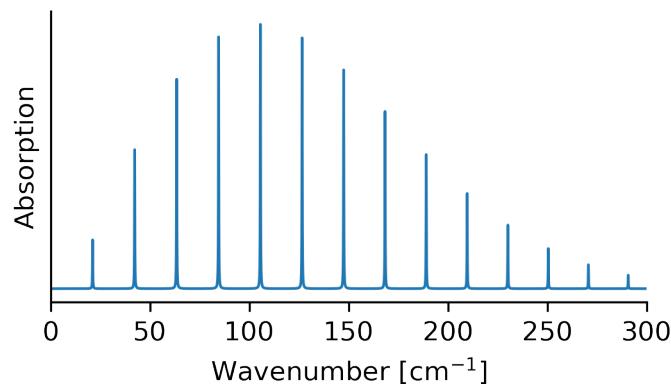


Figure 3.5: A rotational spectrum of HCl. Note the discrete set of lines corresponding to different values of J , as we predicted. I've plotted it against wavenumber not frequency now, just to emphasise that people use different units and it can be annoying.

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 and 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, especially when small molecules are being investigated. Even when we have big molecules and can't find good expressions for the energy levels directly, the spectral lines still relate to molecular properties – which is why spectroscopy is so useful. 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 – it's always the same idea: **two states that the molecule jumps between after being hit by some light**.

3.3.3 Closing Remarks

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 and a photon picture.
- 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 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 kJ mol^{-1}) of a photon of light with a wavelength of 266 nm? How does this energy compare to a typical chemical bond strength?
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 CH₄ iii H₂O iv CO₂ 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, and 100 are in the first electronic excited state. 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. The available **thermal energy**, ϵ , at a temperature T is given by:

$$\epsilon = k_B T$$

Where k_B is the Boltzmann constant. Calculate

- a) The available thermal energy at a temperature of 1000 K.
- b) The temperature that would correspond to the energy of a 190 nm photon of UV light

Comment on the result.

6. 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:

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

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 μ is known as the *reduced mass* of the system.

- i Show that the units of B are 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:

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

- 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 $1.674\,76 \times 10^{-46} \text{ kg m}^2$.

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

Problem Sheet 1 - Numerical Solutions and Hints

1. i $E = 1.55 \text{ eV}$, $\nu = 374.7 \text{ THz}$.
ii $E = 5.952 \times 10^{-20} \text{ J}$, $\lambda = 3333 \text{ nm}$.
iii $\lambda = 295 \text{ nm}$.
iv $E = 449.096 \text{ kJ mol}^{-1}$
2. All except methane and carbon dioxide would rotate and thus produce a pure rotational spectrum. Sketches should indicate dipoles and how the molecule rotates in an oscillating field.
3. $E = 3.693 \text{ eV}$
4. $T = 34\,500 \text{ K}$ (roughly).
5. The available thermal energy at 1000 K is about 8 kJ mol^{-1} or 0.08 eV . The temperature that corresponds to the energy of a 190 nm photon is about 75 000 K. This is the temperature you would have to be at to achieve the same excitation that absorption of the UV photon gives you – hot!
6. i Combine equation for B and $E = hc\nu$, rearrange to answer.
ii Consider $\Delta E = E(J+1) - E(J)$ if the selection rule is $\Delta J = +1$ for absorption. The J in the expression is the quantum number of the lower state.
iii Use expression from (ii) to find rotational constant. Rearrange to give it in both wavenumbers and Joules.
iv Trivial :)
v Take care with units, and find that the bond length is $1.163 \times 10^{-10} \text{ m}$ or 1.163 \AA .

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 5 on problem sheet 1, you 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-axis¹.

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 in energy space.
- The **area** underneath the peak.

¹Sometimes, a measure of how the molecule itself responds is on the y-axis – this is called *action spectroscopy*.

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

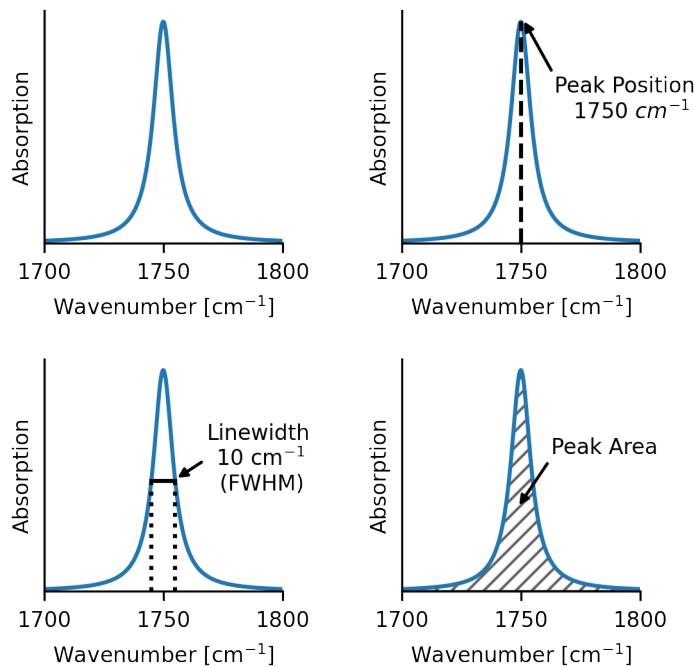


Figure 4.1: A single spectral peak, with key features highlighted.

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 states 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 molecular (often structural) information:

Peak Position → Gaps between Energy States → Molecular 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)**² 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 state³. 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 transforms⁴, but a *non-rigorous, hand-wavy* way to remember how it works could be 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.

I emphasise that **this isn't really the reason** – it's not like measuring a spectrum for a longer time will give you narrower lines. But it's a useful way to remember which way around it goes.

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 Γ (in Hz) to a lifetime τ (in seconds) can be done approximately with:

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

²Another common measure is the **Half Width at Half Maximum (HWHM)** – this is just half of the FWHM.

³In 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.

⁴Time 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, or look in the appendix to these notes.

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

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

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**⁵. 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, materials, or other big molecules. These systems 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 EM spectrum. Each of these functional groups will have its own natural linewidth, but because they are so closely spaced they can coalesce together to look like one large broad peak (Figure 4.2, top panels).

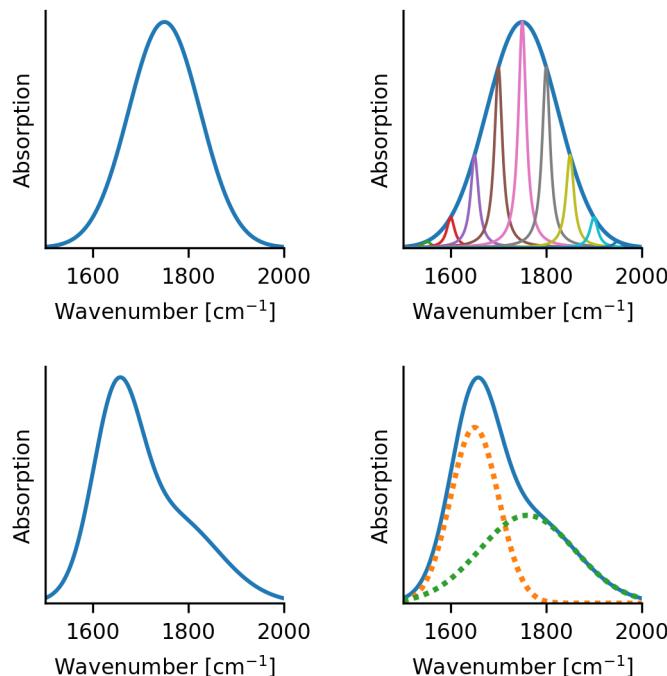


Figure 4.2: One broad peak (top left), might actually be a collection of lots of closely-spaced peaks (top right - only some of the closely-spaced peaks shown for clarity). The presence of a 'shoulder' on a peak (bottom left) is evidence of another peak nearby that you aren't resolving (bottom right).

In a lot of real spectroscopy peak broadening due to overlapping smaller peaks, and due to collisional broadening smearing out any fine structure, is often quite significant. A very common

⁵As 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 isn't that bad, given that the spectrometer is held together with blu-tack).

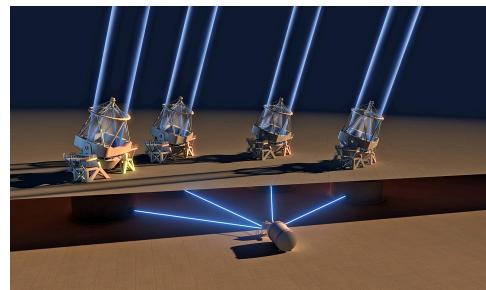


Figure 4.4: High resolution: the operating principle of the ESPRESSO instrument in the European Southern Observatory. This spectrometer looks at light from space to identify distant planets based on their spectral signatures. The resolution is about 0.002 nm – over 1000 times better than the Lego one.

thing to see, especially in electronic spectroscopy, is a *shoulder* on a peak (Figure 4.2, lower panels) – this is evidence of two closely spaced peaks that aren't individually resolvable. 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, or doing (idealistic) calculations!

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:

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 ($\Delta\nu$, $\Delta\bar{\nu}$, ΔE) 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. the number of molecules in this state.
- How strongly that transition is driven by 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 peak⁶. 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.

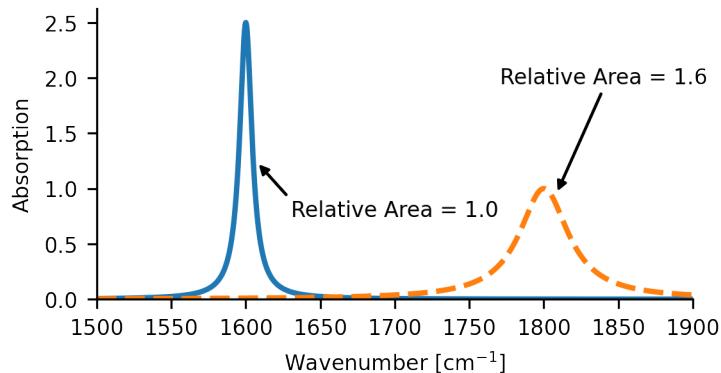


Figure 4.5: Two peaks of different heights - the leftmost peak (solid line) has a height of 2.5, but an area of 1.0. The rightmost peak (dashed line) has a height of 1.0, but an area of 1.6, so it is a more intense transition than the leftmost peak. Peak area is generally a better measure than peak height!

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

Interpreting Spectra

There are three key things to be aware of when interpreting peaks in spectra:

- The **position** of the peaks in the spectra along the energy axis.
- The **linewidth** of the peaks.
- The **area** underneath the peaks.

⁶In 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^{-1})
$J = 0 \rightarrow 1$	$2B$	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

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.

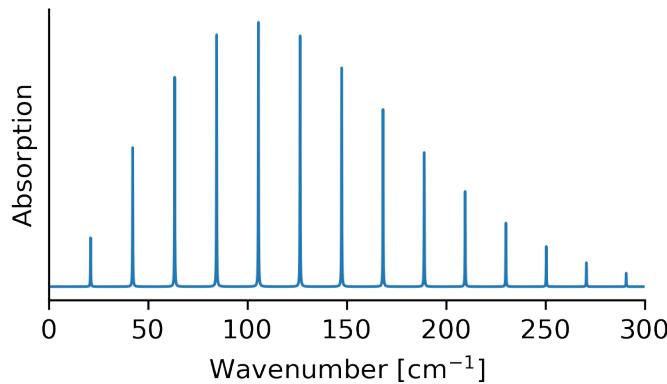


Figure 4.6: A rotational spectrum of HCl.

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:

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

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^{35}Cl and H^{37}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 2.644×10^{-47} kg m², 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?

You should find that the bond length is about 1.3 Å. The bond length of DCI will be the same, but the rotational spectrum will look different (you can explain why).

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 under them) is proportional to the population of the lower state in the corresponding transition. The populations of the different states depends on the *temperature* of the sample of molecules (Boltzmann distribution), so we can use the sizes of the peaks to work out the temperature of the molecules we are studying. This is how we know things like the temperature of stars and gas clouds in outer space.

It turns out that for a diatomic rigid rotor, 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 (leaving the derivation as a challenge for you):

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

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 expression above we can figure out that the temperature of sample of molecules is roughly 617 K⁷. **Note that the expression above only applies for the specific case of a diatomic rigid rotor.** In general when you see the word 'temperature' in this course, think: **Boltzmann Law**.

So, I hope you can see that 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.

⁷ 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 95% of people treat it in a 'this blob means O-H, this blob means N-H, woo spectroscopy go brrr' way.

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.

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 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 simple¹. However, it gets a little more complex when molecules get bigger, and actually these days is not a very common technique in chemistry outside of some specialist areas like astrochemistry and fundamental chemical physics. 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

To start with, let's think back to our wave picture of light, and how it would interact with a molecule like CO₂. This molecule is non-polar, so it won't rotate in the oscillating field. Looking at the polarity, can you imagine what will happen?

As the field oscillates (Figure 5.1), the negative parts of the dipoles are pushed and pulled up and down. The bond angle opens and closes, and the molecule is **vibrating**. As before, the frequency of the light affects the frequency of the vibration, because the molecule 'follows' the field of the light. It's the same idea as in the rotational case – the oscillating electric field drags charges in the molecule around and makes the molecule move.

¹At least, as we used them.

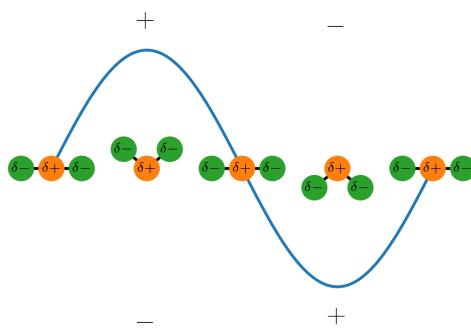


Figure 5.1: CO_2 in an electric field, it starts to bend and vibrate.

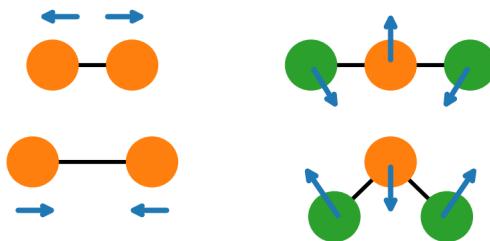


Figure 5.2: Left: a stretching vibrational mode. Right: a bending vibrational mode.

Vibration

A ketone absorbs light with a wavenumber of 1715 cm^{-1} and starts to vibrate. How many times does the ketone vibrate per second?

The frequency is about 51 THz , so 51×10^{12} times per second. Quick!

Vibrating Molecules

To think more deeply about vibration of molecules is to imagine the atoms as masses 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 (like **torsion**) – but the important thing is vibrations are *nuclei moving relative to each other, without the overall molecule moving through space*. Two common kinds of vibration, a *stretch* and a *bend*, are shown in Figure 5.2.

Molecular vibration is quantised in the same way that molecular rotation is, so molecular vibrations have well-defined energies, and produce peaks in spectra with well-defined frequencies. However, in the case of 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. If we only think about energy from the motion of the nuclei (not electronic energy), we can say that a molecule consisting of N atoms has $3N$ degrees of freedom², 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.

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 nonlinear) 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:

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

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. This type of vibration is called a **stretch** and is illustrated in the left hand pane of Figure 5.2, 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* – 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_2O)
2. Acetone ($\text{C}_3\text{H}_6\text{O}$)
3. Neon (Ne)
4. Haemoglobin, the protein that makes blood red (4769 atoms).

You should find there are 3, 24, 0, and 14301. Proteins are massive.

5.1.2 Vibrational Excitation

Our aim in vibrational spectroscopy is to shine light on the molecule and make it vibrate, so having established that there are one or more vibrational modes in our molecule, we now have

²Again, 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.

to ask: is it possible for us to excite this vibrational mode by shining light on the molecule? To work this out, we need to know what the **selection rules** are.

The gross selection rule for pure vibrational (infrared) 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 5.1. 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 - shown in Figure 5.3.

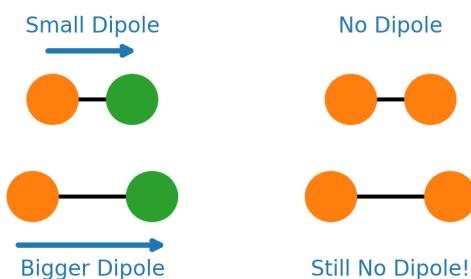


Figure 5.3: Left: a stretching vibrational mode in a polar diatomic like HCl. The dipole moment clearly changes on vibration. Right: a stretching vibrational mode in a non-polar diatomic like N₂. There is no dipole moment change on vibration.

So, to see a pure vibrational (infrared) spectrum³, 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.

The Harmonic Oscillator

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 $x = r - r_e$, where r is the stretched or compressed bond length and r_e is the equilibrium bond length), 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 it's 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) – it works well 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.

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

So, if we treat our vibrating diatomic molecule as a harmonic oscillator and do a lot of maths to solve the Schrödinger equation⁴, then we find we can write our vibrational energy levels E_v (in Joules) as:

$$E_v = h\nu \left(v + \frac{1}{2} \right) \text{ where } v = 0, 1, 2 \dots \quad (5.1)$$

Here h has its usual meaning, ν is the **fundamental vibrational frequency**, and v is the **vibrational quantum number**, which is basically an index that tells us how vibrationally excited our molecule is. Note that this equation has the same format of:

$$\text{Energy} = \text{Spectroscopic Constant} \times \text{Quantum Numbers}$$

that we saw earlier for rotation. The specific value of ν depends on physical properties of the bond that is vibrating, for a harmonic oscillator:

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

Where k is the **force constant** we met earlier and relates to the stiffness of the bond⁵. We've already met μ in problem sheet 1 and this is the **reduced mass** of the vibrating system. The quantity ν is the **classical vibrational frequency** of the bond, and tells us the natural frequency that the bond will vibrate at (the one we need our light to be resonant with).

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. Can you rationalise the form of the equation for ν by thinking about what you would expect to happen in the case of k and μ being low or high? Would a stiff spring vibrate with a high or low frequency?

We expressed the frequency ν above in Hertz, however, normally in vibrational spectroscopy we express things in units of wavenumbers, so it's important that we can interconvert these units comfortably.

Vibrational Energy Units

Show that the expression for E_v given in units of wavenumbers (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 ω introduced above is useful for us, as this tell us what the **fundamental wavenumber** of the vibration is (in the same way that ν told us the fundamental frequency). The fundamental wavenumber is the natural energy the vibration has.

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

⁵You solved the classical equation of motion for this system $\mu \frac{d^2x}{dt^2} = -kx$ last year in maths, and probably arrived at this frequency if you got it right.

Vibrational Energy Levels

Look at the energy levels of the harmonic oscillator in Figure 5.4 and think about the following:

- 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 moment⁶ results in the specific selection rule being that:

$$\Delta v = \pm 1$$

Where $\Delta v = +1$ corresponds to absorption of a photon (so the molecule becomes excited and gains energy), and $\Delta v = -1$ corresponds to emission of a photon (so the molecule loses energy and spits out a photon). If we consider 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* within the harmonic oscillator approximation. It doesn't matter whether we excite from $v = 0$ or $v = 1$, or from $v = 9$ to $v = 10$, we will measure the same transition energy. 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 cm^{-1} . What is the force constant of the bond in HCl?

You should find the force constant is about 494 N m^{-1} . Force constants for bonds are normally around this range (hundreds of N m^{-1}).

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

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

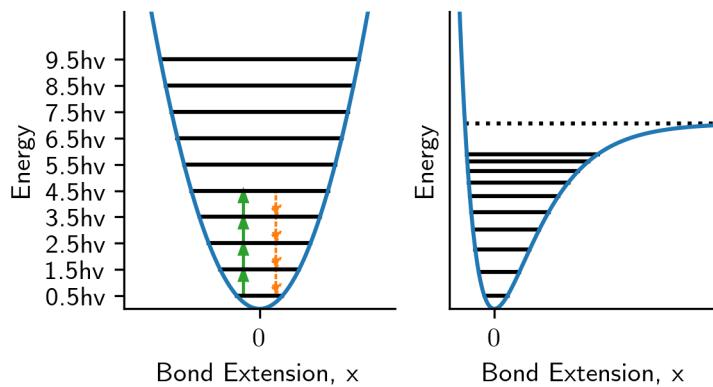


Figure 5.4: Potential and first ten energy levels for a harmonic oscillator (left), and an anharmonic oscillator (right). The first few allowed transitions are annotated on the harmonic oscillator diagram (absorption solid green, emission dashed orange). The dashed line on the anharmonic diagram (right) is the energy at which the bond is broken.

Vibrational Spectroscopy

- Vibrational spectroscopy measures the energies with which atoms in molecules move relative to each other: stretching, bending, twisting...
- The harmonic oscillator model describes these energies in terms of the mass of the atoms moving and the force constant (stiffness) of the bonds connecting them.
- Because atoms have different masses, and bonds have different stiffnesses depending on the surrounding molecule, vibrational spectroscopy is sensitive to different kinds of functional groups.

5.2 Beyond the Harmonic Oscillator

You've probably realised by now that the harmonic oscillator model isn't great when we have highly excited molecules or when we are close to bond breaking – nothing in the model can account for that. If you are measuring highly accurate vibrational spectra and want to match your spectra to calculation, it also isn't a great model and your calculations won't match the real data. **Really, the harmonic model is just the simplest model that helps give us intuition** – it's not 'wrong', and the conclusions we drew about masses and force constants and bond stiffness are all basically correct, but it doesn't capture the whole picture.

5.2.1 Anharmonicity

To improve on it we have to find more sophisticated models for the potential energy of a vibrating molecule using **anharmonic** models. These models essentially add correction terms to the harmonic energies from Equation 5.1 to better account for the real behaviour of the molecules. The energy with the first correction term added would be:

$$E_v = E_{\text{harmonic}} + E_{\text{correction}} = \omega \left(v + \frac{1}{2} \right) - \omega x_e \left(v + \frac{1}{2} \right)^2 \quad (5.2)$$

where x_e is the **anharmonicity constant** and accounts for the deviation from harmonic behaviour. We'll look into this in more depth in the lecture, and sketch some potentials and see the impact it has on spectra – but an anharmonic potential is shown on the RHS of Figure 5.4 for

now. In extended problem sheet 1, we will also look at the rotational analogue of anharmonicity: **centrifugal distortion**.

Anharmonicity

Starting from Equation 5.2, derive the energy for a line in a spectrum of an *anharmonic* oscillator, i.e:

$$\Delta E = E_{v+1} - E_v$$

How does the result differ from the harmonic result derived earlier?

You should find that now the energy of the line *depends on v*.

Anharmonicity also relaxes our original selection rules and enables us to see transitions with $\Delta v = \pm 2, \pm 3$ (these are called *overtones*), and allows excitation to more than one vibrational state simultaneously (which are called *combination bands*). The degree of anharmonicity can also tell us interesting things about the system, and is particularly relevant in a modern kind of spectroscopy called 2D-IR spectroscopy. Here you measure a two-dimensional IR spectrum and can learn about the couplings of different vibrational motions – a story for another time.

5.3 Combined Excitation

To end, let's briefly discuss an assumption we've made without realising it. Up until now, we have talked about rotation and vibration in isolation. This is because rotational energies are a lot lower than vibrational energies, so if we excite a rotation we won't normally have enough energy to also excite a vibration. 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 5.5. Under something called the *Born-Oppenheimer Approximation*⁷, these energies are independent and contribute individually to the overall energy of the molecule:

$$E_{\text{total}} = E_{\text{rotation}} + E_{\text{vibration}} + E_{\text{electronic}}$$

As a rule of thumb, the energy gaps between these states differ by a factor of 1000 or so:

$$\Delta E_{\text{electronic}} \approx 10^3 \Delta E_{\text{vibrational}} \approx 10^3 \Delta E_{\text{rotational}}$$

Looking at Figure 5.5 and the relationships above, it's clear that 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 roughly 1000 times more energy than is needed to excite a rotation, and so we can excite rotations *alongside* the excited vibration. We call this **rovibrational** excitation⁸ because we are exciting a rotation at the same time as the vibration.

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 structure** along with our vibrational excitation, or we might see **vibrational structure** in an electronic spectrum. We'll meet this again in more detail later on, and in the problems.

⁷A pedant would say that this isn't really Born-Oppenheimer separation, but whatever. See CH2203 lectures next semester for more...

⁸Other options are available too, like **vibronic excitation** (vibration and electronic), and even **rovibronic** (rotation, vibration, and electronic). All fun.

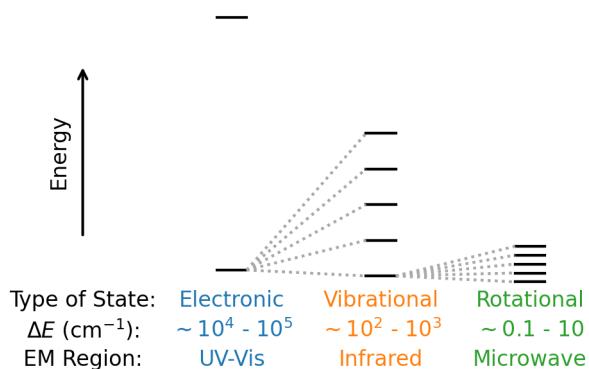


Figure 5.5: Energy scales of different kinds of molecular motion. Each electronic state supports a number of vibrational states, and each vibrational state supports a number of rotational states.

In the next lecture, we are going to talk about symmetry. **I am going to assume that you know about symmetry elements and point groups from CH1202 last year – have a look back at that material before this lecture if it is unfamiliar.**

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.
- Corrections to the harmonic model to better describe vibrations of real molecules are called anharmonic corrections.

Problem Sheet 2

1. Isotopically pure carbon monoxide ($^{12}\text{C}^{18}\text{O}$) has a rotational constant $B = 1.9316 \text{ cm}^{-1}$.
 - i Calculate the bond length of carbon monoxide.
 - ii What are the energies of the first five lines that would be seen in the rotational spectrum of carbon monoxide?
 - iii 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.
 - iv 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: The selection rule for pure rotational spectroscopy is $\Delta J = \pm 1$. You may assume that carbon monoxide behaves as an ideal rigid rotor. The rigid rotor approximation states that:

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

2. Hydrogen fluoride (HF) has a fundamental vibrational wavenumber (ω) of 4138 cm^{-1} (*Hint:* take care with units throughout this question).
 - i Calculate the force constant (k) of HF.
 - ii The force constant of HF is experimentally observed to be same as DF (deuterium fluoride). Explain this observation.
 - iii Calculate the fundamental vibrational frequency of DF and comment on how the result differs to that of HF.
 - iv 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. Under the harmonic oscillator and rigid rotor approximations, the energy of a combined **rovibrational** level is given by:

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

- i Explain what is meant by the terms *rovibrational level*, *harmonic oscillator approximation* and *rigid rotor approximation*.
- ii Show that for a transition where $\Delta v = +1$ and $\Delta J = +1$, the transition energy is:

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

- iii Show that the spacing between two adjacent lines where $\Delta J = +1$ (the spacing between a $J \rightarrow J+1$ line and $J+1 \rightarrow J+2$ line) is equal to $2B$.
- iv The spacing between two such lines in HI is $12.852\,74 \text{ cm}^{-1}$. Calculate the bond length of HI. (*Hint:* the mass of iodine is 127 amu).

Problem Sheet 2 - Numerical Solutions and Hints

1. i 1.1011×10^{-10} m.
 ii 3.8632 cm^{-1} , 7.7264 cm^{-1} , 11.5896 cm^{-1} , 15.4528 cm^{-1} , 19.316 cm^{-1} ,
 iii The bond length would be the same (why?), but rotational constant would be higher ($1.977\ 08 \text{ cm}^{-1}$) due to decreased reduced mass. Energies of all lines would be higher.
 iv Think about how intensities of lines can lead to information about populations (Boltzmann?).
2. i Take care with units, using the formula given requires ω to be given in Hertz, not wavenumbers. Will find that $k = 959.16 \text{ N m}^{-1}$.
 ii Are isotopes chemically different? Why or why not?
 iii 89.92 THz or 2999 cm^{-1} . Much lower - what would you expect?
 iv Key features
 - Two lines, DF at lower energy.
 - Area under HF line is double that of DF.
3. i
 - A rovibrational level is a combined rotational and vibrational energy levels, denoted by two quantum numbers v and J .
 - The harmonic oscillator approximation is a simple model used to explain vibrations of molecules. It is a simple model because it does not account for the possibility of a bond being stretched/bent so far that it breaks. It is valid as long as molecule is not too vibrationally excited.
 - The rigid rotor approximation is a simple model used to explain rotations of molecules. It is a simple model because it assumes that the bond length of a molecule remains fixed as it rotates. It is valid as long as molecule is not too rotationally excited.
 ii Set up problem:

$$\Delta E = E(v+1, J+1) - E(v, J) = (v + \frac{3}{2})h\nu + B(J+2)(J+1) - (v + \frac{1}{2})h\nu + BJ(J+1)$$

Rearrange to final answer.

- iii Set up problem (call the line spacing ΔL , or whatever):

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

Rearrange to final answer.

- iv Find that $I = 4.357 \times 10^{-47} \text{ kg m}^2$, and then that the bond length is 1.65 \AA .

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 ω and B are varied, justify the form of this equation (detailed calculations are not required).

2. 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.

- a) 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?
- b) 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.

- c) Derive an expression for the energy of a transition from state v to $v + 1$, including the effect of anharmonicity.
 - d) 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.
 - e) Outline how you would expect a vibrational spectrum of a pure harmonic oscillator to differ to that of an anharmonic Morse oscillator (no numerical calculations needed).
3. Hooke's Law states that the restoring force of a spring behaving as a harmonic oscillator F_{Hooke} is given by:

$$F_{\text{Hooke}} = -kx$$

Where k is the force constant of the spring, and x is the extension of the spring.

- a) Using the relationship:

$$U = \int -F dx$$

Derive an expression for the energy of a harmonic oscillator as a function of x , and sketch it for a range of values of k .

- b) Newton's second law states that the force acting on an object F_{Newton} is given by:

$$F_{\text{Newton}} = \mu \frac{d^2x}{dt^2}$$

Where μ is the mass of the object. **Harmonic motion** occurs when:

$$F_{\text{Newton}} = F_{\text{Hooke}}$$

Use the above and the expressions for F_{Newton} and F_{Hooke} to write down a second-order differential equation for $x(t)$.

- c) Using a trial solution of the form:

$$x = A \cos(\omega t)$$

or otherwise, solve the differential equation above and show that the frequency of the harmonic motion ω is given by:

$$\omega = \sqrt{\frac{k}{\mu}}$$

Extended Problems 1 - Numerical Solutions and Hints

1. i Thought experiment :)
- ii Without distortion, in wavenumbers: 0, 2, 6, 12, 20, 30. With distortion: 0, 1.96, 5.64, 10.56, 16, 21.
Clearly distortion lowers rotational energy, but has a higher impact at higher values of J - does this make sense?
- iii $\Delta E = 2B(J+1) - 4D(J+1)^3$
- iv Use answers from ii and iii to sketch.
- v A nice question to think about :) Is a bond with a low vibrational frequency 'floppy' or 'stiff'?
2. i Harmonic oscillator assumes bond will never break. Harmonic oscillator model is reasonable at low levels of vibrational excitation.
- ii Anharmonicity affects the level structure in an analogous way to the centrifugal distortion constant (can you see how?). Positive values of x_e reduce the energy of each vibrational state, and change the gaps between levels.
- iii $\Delta E = \omega - (v + 2)\omega x_e$
- iv See lecture for annotated sketch.
- v Key points are that energies shift to lower energies, and we might start seeing progressions of lines as transitions are no longer independent of the quantum number v .
3. A test of how much maths you remember...
 - a) Remember that F is a function of x .
 - b) When you see the words 'write down' in a question, no thinking is required.
 - c) Back your mathematical ability!

Lecture 6

Bigger Molecules: Symmetry

Lecture Aims

- To understand what is meant by **symmetry representation**.
- To be able to form basic representations.
- To understand how symmetry helps us think about spectra of larger molecules.

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 haemoglobin we looked at in an example last time is in a class of proteins of great biological importance, and spectroscopy of haem-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 haem – how do we even start to think about interpreting a spectrum of that?

However, 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 Alan Vincent's book 'Molecular Symmetry and Group Theory' – **everyone should work through this book**.

You started learning about symmetry last year in inorganic chemistry (CH1202), and we'll recap a few basics to start with. You might find a molecular modelling kit useful when thinking about symmetry, if you're like me and find these things hard to visualise in your head. **You are going**

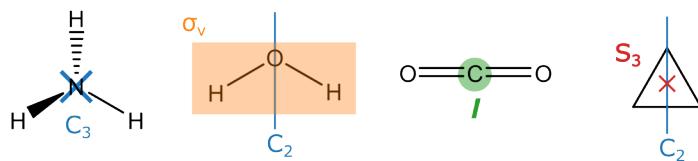


Figure 6.1: Some examples of different symmetry elements. Crosses denote an axis going into/out of the plane of the page.

to need to know this stuff, both in this course, and in CH2202, CH2203, CH3202, CH3203, and all of the Y4 courses¹.

6.1.1 Recap: 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. To recap, there are five different symmetry operations we can do to a molecule:

- **The identity operation, E** – the operation of ‘doing nothing’.
- **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 **principal axis**.
- **Reflection, σ** – the operation of reflection through a mirror plane somewhere in the molecule. The mirror plane is denoted as either σ_h (if it is perpendicular to the principal rotation axis), σ_v (if it is parallel to the principal axis), or σ_d (like σ_v but bisecting two other C_2 axes – really just a special case of σ_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 (σ_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 unchanged². 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. However, we need to be able to assign point groups, but we hopefully can already do this after last year (look back at CH1202 if unfamiliar).

¹Don't do what one of my third year students did last year and panic right before the final exams because you 'didn't think it was worth learning as it wouldn't come up again'...

²Other 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.

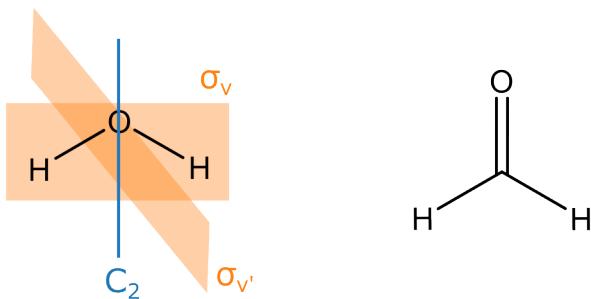


Figure 6.2: Water and formaldehyde – both in the same point group.

Assigning Symmetry Elements

Identify the symmetry elements of the following molecules:

1. Water
2. Formaldehyde

6.1.2 Recap: 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 , σ_v , σ'_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 (σ_v) 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 some molecules to their point groups using this flow chart and then talk about them.

Assigning Point Groups

Identify the point group of each of the following molecules:

1. 1,2-dichloroethene (trans isomer)
2. Ethene
3. Methane
4. N_2

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 nC_2 rotation

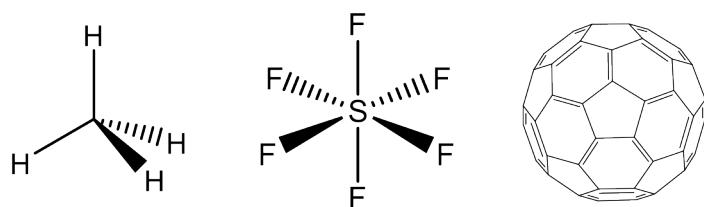


Figure 6.3: High symmetry point groups. From left to right: methane (tetrahedral point group: T_d), SF_6 (octahedral point group, O_h), buckminsterfullerene (icosahedral point group, I_h).

axes *perpendicular* to the principal axis. The *h* refers to the horizontal mirror plane.

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 ∞ 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?

To understand why grouping molecules into point groups is useful, we need to understand 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 σ and π 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 here³. 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 and work out the **character** of the axis under that operation:

³It ultimately doesn't matter for the calculations we are going to do – the important thing is that you are consistent once you have picked a set of coordinates.

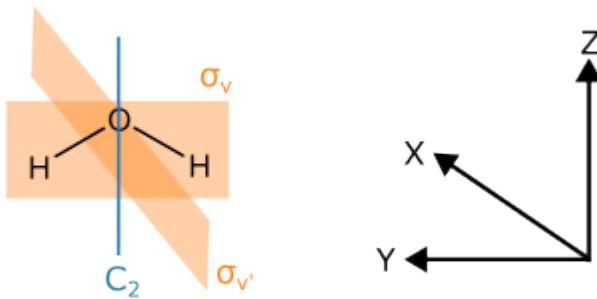


Figure 6.4: Water with co-ordinate axes. The axes can be figured out by noting that the principal axis aligns with z , and using the right-hand rule. The positions of the x and y axes are less critical, here x is perpendicular to the plane of the molecule.

- If the axis is unchanged (mapped onto itself), then the character of that transformation is +1.
- If the axis is mapped onto a reversed (180° rotation) version of itself, then the character is -1.
- If the axis is moved to a new location, so doesn't map onto a rotated version of itself, then the character is 0.
- If the axis is rotated by an angle θ but *not* moved to a new location, then the character is $\cos(\theta)$.
 - The first two rules come from this: $\cos(0) = +1$, and $\cos(180) = -1$.

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	σ_v	σ'_v
$\Gamma(z)$	+1	+1	+1	+1

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

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 by a systematic calculation using a **reduction formula** 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 (can you see why?).

Symmetry Representations

A **symmetry representation** is a way to represent the symmetry of an object by how it transforms under all the symmetry operations of its point group. The **character** under each operation denotes how the object transforms:

- +1 if the object is unchanged by the operation.
- -1 if the object is inverted by the operation.
- 0 if the object is moved by the operation.
- $\cos(\theta)$ if the object is rotated by an angle θ but is not moved to a new location.

Representations can be expressed as a sum of **irreducible representations** (irreps), which are found in the *character tables* in your group theory booklet.

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 σ orbital in H_2 ($D_{\infty h}$ point group).
3. An anti-bonding σ orbital in H_2 ($D_{\infty h}$ point group).

You should find that the three coordinate axes have A_u (z) and B_u (x,y) symmetry in C_{2h} . The molecular orbitals in H_2 have Σ_g^+ (bonding) and Σ_u^+ (anti-bonding) symmetry – which is why they are called σ bonds.

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.

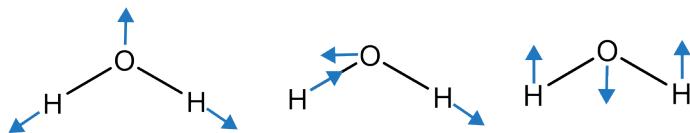


Figure 6.5: Normal modes of water. From left to right: symmetric stretch (3585 cm^{-1}), asymmetric stretch (3506 cm^{-1}), and bend (1885 cm^{-1}).

6.2.1 Normal Modes

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).
- **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.

You should find that the symmetric stretch and the bend have A_1 symmetry, and the asymmetric stretch has B_2 symmetry.

6.2.2 Predicting Spectroscopic Activity

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 absorption of a photon of 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?

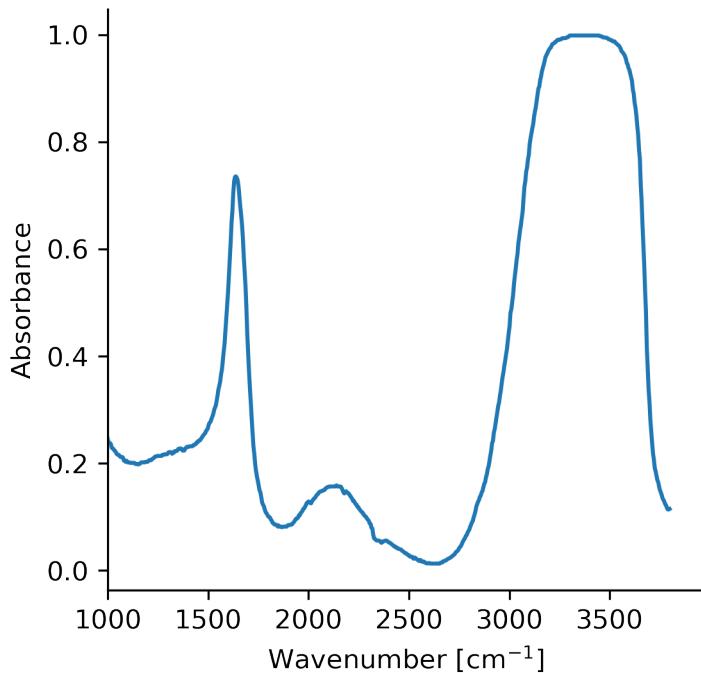


Figure 6.6: IR spectrum of liquid water. It looks like three bands, but in reality the two stretching modes overlap in the big peak at around 3500 cm^{-1} . The small band at 2100 cm^{-1} is actually a *combination band*.

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 modes only applies in the case that we are exciting the *fundamental* of each normal mode (i.e. the $\nu = 0 \rightarrow \nu = 1$ 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 can 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 moves to a new location, 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:

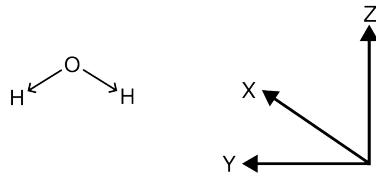


Figure 7.1: Water with arrows drawn in place of the bonds. This picture will help us predict the stretching vibrations of water.

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

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.

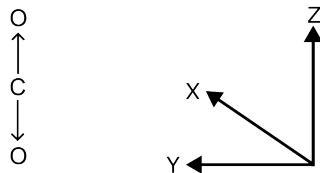


Figure 7.2: Carbon dioxide with arrows drawn in place of the bonds. This picture will help us predict the stretching vibrations of carbon dioxide. Note that it doesn't matter if the bonds are single or double – they are all just 'bonds' as far as we care.

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_∞	σ_v	i	S_∞	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 case¹.

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, or at least a hint). 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_2 , 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 energies² 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 Ψ 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 can 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), that 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

¹You can do a similar process to this for finding out symmetry of non-stretching modes, you'll do this next year.

²Most of the time...

something called the **transition dipole moment (TDM)**:

$$\text{TDM} = \int \psi_f \hat{\mu} \psi_i d\tau \quad (7.1)$$

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.

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 (an even function), 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 etc.

7.2.2 TDM: What You Need to Know

If you skipped the above, 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 via the **Raman effect**, 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 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 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?

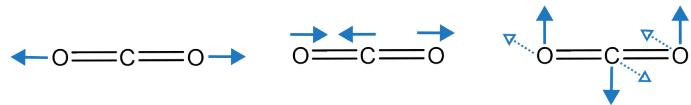


Figure 7.3: Normal modes of carbon dioxide. From left to right: symmetric stretch (1480 cm^{-1}), asymmetric stretch (2565 cm^{-1}), and bend (526 cm^{-1}). Note that the symmetry of the molecule means that there are two *degenerate* bending modes.

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 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 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} symmetry³, 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 CO_2 , and one in a Raman spectrum. Spectra are shown in Figure 7.4.

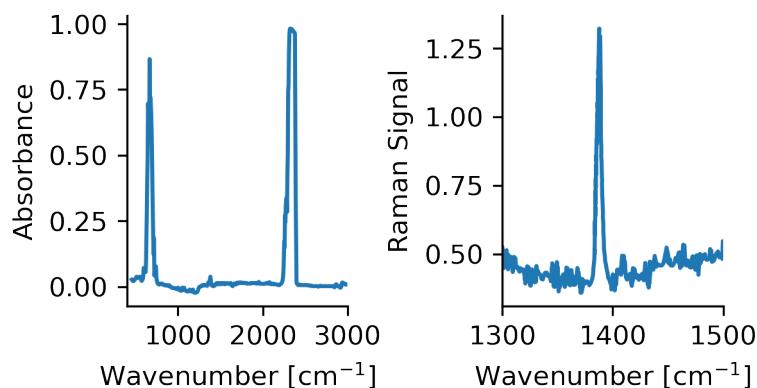


Figure 7.4: Vibrational spectra of CO_2 in the gas-phase. Left: IR spectrum. Right: Raman spectrum. Data from NIST.

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.

³You can work this out in an analogous way, by working out the symmetry representation of the motion of every atom in 3D (next year).

Transition Dipole Moments

- Any vibrational mode that transforms with the same symmetry as a **linear Cartesian component** (x, y, z) is **IR active**.
- Any vibrational mode that transforms with the same symmetry as a **quadratic Cartesian component** (x^2, xy, xz etc...) is **Raman active**.

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.

7.3.1 Distinguishing Isomers of CH_2^+

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. CH_2^+ could have either a linear or a bent structure (Figure 7.5). The IR spectrum of 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 CH_2^+ ion?

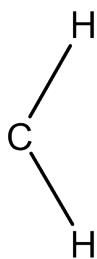
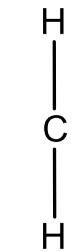


Figure 7.5: Different possible isomers of CH_2^+ .

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.

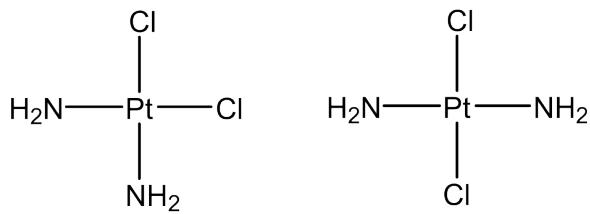


Figure 7.6: Left: cisplatin. Right: transplatin.

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 CH_2^+ would have stretching vibrations with A_{1g} and A_{1u} symmetry ($D_{\infty h}$ point group), and that bent CH_2^+ would have stretching vibrations with A_1 and B_2 symmetry (C_{2v} point group). Looking at the character table, if 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 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 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 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:

HCN, CS₂, CF₄, C₂H₂, C₂H₂F₂ (both isomers), PF₅ (both isomers), C₆₀, W(CO)₆

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 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:

CH₄, benzene, CDH₃, fluorobenzene, 1,4-dichlorobenzene, 1,3-diiodobenzene

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

Problem Sheet 3 - Numerical Solutions and Hints

1. i HCN: $C_{\infty v}$
 ii CS₂: $D_{\infty h}$
 iii CF₄: T_d
 iv C₂H₂: $D_{\infty h}$
 v C₂H₂F₂: C_{2h} (trans), C_{2v} (cis)
 vi PF₅: D_{3h} (trigonal bipyramidal), C_{4v} (square pyramid)
 vii C₆₀: I_h
 viii W(CO)₆: O_h

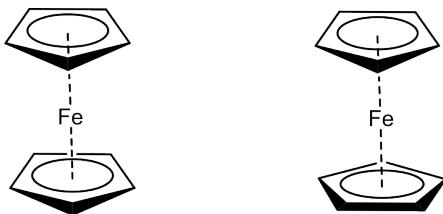
2. i C_{3v}
 ii Find representation as:

C_{3v}	E	$2C_3$	$3\sigma_v$
$\Gamma(N-H)$	3	0	1

- iii Easy :)
- iv Check which irreps transform as linear or quadratic Cartesian components.
- v Three - use $3N - 6$ rule.
3. Do similar calculation to above for both geometries of ammonia. Excited state has D_{3h} symmetry. Find that there is one more IR active mode for the ground state than excited state, so can be distinguished.
4. Perform similar analysis as above for C-H stretches in methane. Find that the C-H stretch representation is $A_1 + T_2$. Hence expect one band in the IR spectrum, two bands in the Raman spectrum. The T_2 band appears in both spectra.
5. i CH₄: all equivalent
 ii CDH₃: all equivalent
 iii Fluorobenzene: three sets of equivalent hydrogens
 iv 1,4-dichlorobenzene: all equivalent
 v 1,3-diiodobenzene: three sets of equivalent hydrogens

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 $\text{Ni}(\text{CN})_4^{2-}$ in the C-N stretching region shows two bands, neither of which are present in the IR spectrum.
Using a group theoretical analysis, determine the 3D structure of $\text{Ni}(\text{CN})_4^{2-}$.
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 Spectroscopy

Lecture Aims

- To understand the principles of Raman spectroscopy.
- To understand the difference between infrared and Raman excitation of vibrations.
- To understand the technical differences between infrared and Raman spectroscopy experiments.

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 relevant in research today.

However, the majority of people using spectroscopy today are looking at bigger systems, or more complex systems – proteins, or materials, or solutions containing many different molecules. So, the final few lectures are going to focus on different kinds of spectroscopy – Raman techniques, electronic spectroscopy, 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, looking at something called the **Raman effect**.

8.1 Spectroscopy Apparatus

Before we dive into the discussion in the next few lectures, it'll be useful to remind ourselves how a typical spectroscopic measurement is actually done. All spectroscopy apparatus has a couple of key common features:

1. **A source of the EM radiation (light) that is being used.** This could be as simple as an LED or a lamp, or as complex as a laser or large synchrotron source.
2. **A way to detect the radiation after interaction with a sample.** Either by measuring the change in an amount of light after absorption by a sample, or by measuring emission of new light from the sample.

A very simplistic, cartoon-style figure of how this works is shown in Figure 8.1. Obviously, this

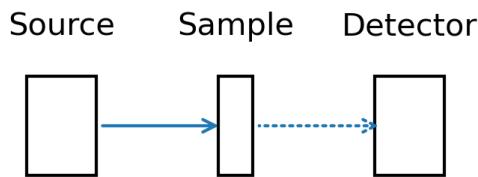


Figure 8.1: (very) Generic spectroscopy apparatus. A light source produces light which interacts with a sample, the change to the light is detected by the detector.

is a simplistic picture and things like an actual NMR or IR spectrometer are more complex than just two boxes and a sample, but the general principle is true. We need a **light source** capable of generating light of the right energy, and a way to detect that light after it's interacted with a sample. It's useful to have some idea of what kinds of sources and detectors are used, especially before we start discussing Raman spectroscopy.

8.1.1 Light Sources

The light source is the most fundamental bit of apparatus you use in spectroscopy. The light source needs to be able to generate light of the right energy to excite the transition you want. For example, if you want to do infrared absorption spectroscopy, you need an infrared light source. If you want to do X-ray spectroscopy, you need an x-ray light source. For NMR spectroscopy, you actually need a source of radio waves (more on this later).

Some examples of typical light sources are shown in Figure 8.2. These vary from the cheap and easy (LEDs), to the less cheap and easy (lasers), to sources so expensive that *you* have to bring your experiment to the source (the synchrotron and free-electron laser complex – basically a particle accelerator that produces high intensity X-ray radiation).

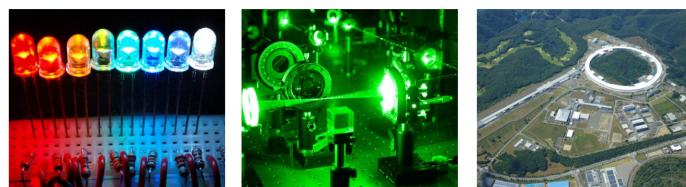


Figure 8.2: Light sources in spectroscopy. From left to right: some visible LEDs, a visible laser, and the Spring8 synchrotron and SACLAA free-electron laser in Japan (for reference, the circle is a synchrotron (1.5km circumference) and the long straight building a free-electron laser (700m long). Some of these sources are more expensive and difficult to get hold of than others!

The key considerations when picking a light source are that it produces light of the energy you need, and that it produces *enough* of the light (high enough intensity). Then factors like cost and ease of use come into play.

8.1.2 Detectors

Once you have made your light, you need to detect it using a **detector**. Light detectors are also specific to certain ranges of the EM spectrum. These detectors always will measure light by converting the incident light signal into an electrical signal. In the visible region, you can use a detector that's fundamentally the same as the camera on your smart phone. In the infrared region, you can use similar kinds of infrared cameras (but these are much more expensive¹), and more exotic and expensive solutions are generally needed in other ranges of the EM spectrum. Some examples are shown in Figure 8.3.



Figure 8.3: Detectors used in spectroscopy. From left to right: a CCD camera (similar to the one on your phone), an infrared photodiode array (the large red cylinder is to hold liquid nitrogen, as these need to be cold to function effectively), and a drawing of the probe from an NMR spectrometer - which houses both the source of the radio waves and the radio detector needed (see later in the course).

The key considerations when picking a detector are that it's sensitive to the kind of light you want to measure, and also *how* sensitive it is. Some kinds of spectroscopy rely on measuring very small amounts of light. Humans are very good at making visible region detectors (think about all the cameras in the world) - so if you can use these to do your experiment it helps. Which brings us onto the main topic for today: **Raman spectroscopy**.

8.2 Raman vs Infrared Excitation

8.2.1 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. IR absorption is quite a good way to excite vibrations, because:

- Many molecules have big absorption cross sections in the IR region, so you don't need much sample in order to absorb a lot of light and produce a big signal in your spectrum.
- For the same reason, you can use an infrared lamp (which is basically a glorified blowtorch) as a light source, which is cheap and relatively easy.

However, the downsides are that:

- Not all vibrations are infrared active.

¹Also, the same technology is used to make the guidance systems on ballistic missiles. Thus, there was a global shortage of these detectors when the war in Ukraine broke out - which was bad news for everyone trying to build infrared spectrometers.

- 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 much harder to get hold of than really powerful visible light sources.
- IR light detectors are also quite crappy, and expensive, when compared to visible light detectors.

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

8.2.2 Raman Excitation

The Raman effect is different a way to excite molecules using EM radiation. Instead of looking at 'pure' absorption of a single photon, we end up needing two photons, one that's absorbed and another that's emitted. In the photon picture, it looks a bit like that shown in Figure 8.4.

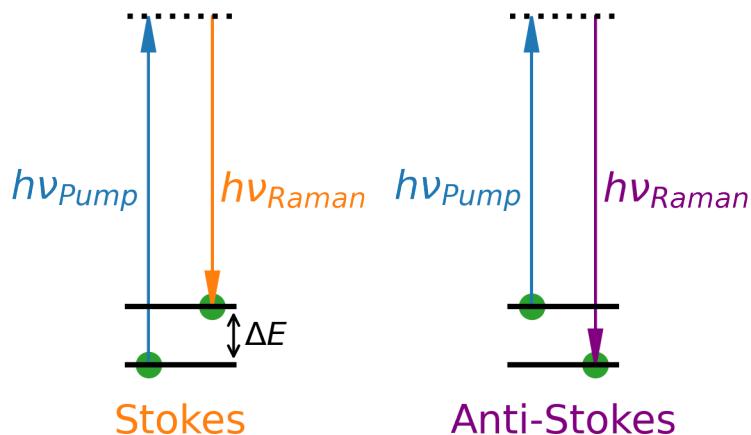


Figure 8.4: The Raman effect. Pump light excites the molecule, and then light is emitted at either longer wavelengths (Stokes, left panel), or shorter wavelengths (Anti-Stokes, right panel). Stokes transitions result in population (green circle) transfer to higher energy states, and vice versa for anti-Stokes transitions.

So, we send in a photon of one energy, and rather than being absorbed, it ends up losing/gaining a small amount of energy to/from 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 energy to the incident light – this process is called the **Raman effect**, after its discoverer, the Indian physicist Chandrasekhara Raman².

Crucially, in the Raman effect, 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*)

²Who won the Nobel Prize for this discovery in 1930. He famously said he wore a turban to prevent his ego from swelling up from all the excess praise he received.

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 ΔE 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 by ΔE), this is called **Stokes transition**. Conversely, if the scattered photon loses energy (and thus de-excites the molecule by ΔE), 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). Performing spectroscopy by measuring the emitted Stokes or Anti-Stokes photon is called **Raman spectroscopy**.

It's important to understand that the Raman effect can excite **any** kind of transition. You can have rotational, vibrational, and electronic Raman spectroscopy – however vibrational Raman is probably the most common, and so when a lot of people say 'Raman spectroscopy' they mean vibrational Raman spectroscopy, which is what we are talking about today.

The Raman Effect

The **Raman effect** is a way to excite molecules via a two-photon process (absorption then emission). It is most commonly used as a way to excite vibrations that are not IR active.

8.2.3 Raman Selection Rules

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 active³. 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 vibration is IR active (panel A of Figure 8.5). In the case of an IR inactive vibration (panel B of Figure 8.5), the vibration cannot be driven by IR light alone because the dipole moment of the molecule won't change on vibration. In this case, sometimes the vibration can be driven by the Raman effect. To understand this, remember that in the Raman case we have two electric fields now (the incident light and the emitted light). So think about it as follows:

1. The incident, first, 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 second electric field (that ends up being emitted) 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

³And the quantity we care about is called the **transition polarisability moment**, not the TDM.

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. This idea is illustrated in panels (C) and (D) of Figure 8.5.

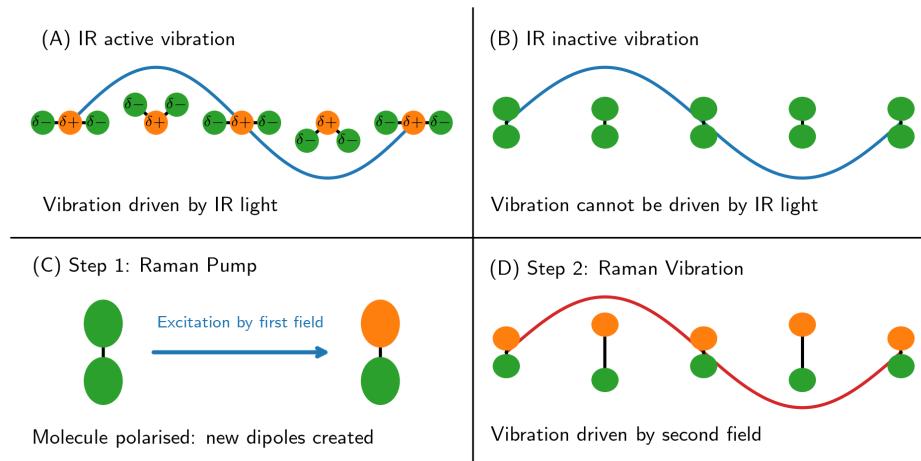


Figure 8.5: The Raman effect. Pump light excites the molecule, and then light is emitted at either longer wavelengths (Stokes, left panel), or shorter wavelengths (Anti-Stokes, right panel). Stokes transitions result in population (green circle) transfer to higher energy states, and vice versa for anti-Stokes transitions.

8.2.4 Raman Scattering?

There's a lot to talk about here and we can't go fully into all the physics, but note where I am talking about the interaction with a second, emitted, field, I don't mean that we are necessarily physically shooting two different kinds of light at the molecule. The emitted field can arise spontaneously, via spontaneous emission, and is emitted in all directions around the molecule - so it appears that the light is scattered by the molecule. This is the most common way that Raman spectroscopy is done, and is why you'll often hear it referred to as **Raman scattering**. In fact, it is so common that you'll often hear Raman referred to as a 'scattering technique' – it isn't necessarily, but is most often used like this.

A major downside of traditional spontaneous Raman scattering 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 light⁴. A typical spontaneous Raman scattering signal would be about 4 or 5 orders of magnitude smaller than the corresponding pure IR signal, due to this reliance on spontaneous emission. A way around this is to send in multiple beams of light to your sample, which requires the use of multiple overlapped laser beams. This is called **stimulated Raman spectroscopy**, and is an increasingly common technique as it produces bigger signals, and also signals that are more directional (not scattered everywhere), so are easier to detect.

A typical Raman scattering spectroscopy setup is shown in Figure 8.6 – the weak Raman signals are detected at right angles to the intense pump light, to avoid saturating the detector with the intense pump. This isn't necessary if you're doing a stimulated Raman experiment.

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

⁴What really happens here is that a *vacuum fluctuation* stimulates the emission. Vacuum fluctuations happen randomly so the emission looks spontaneous. You can think of a vacuum fluctuation as the universe suddenly sneezing and making excited molecules de-excite themselves.

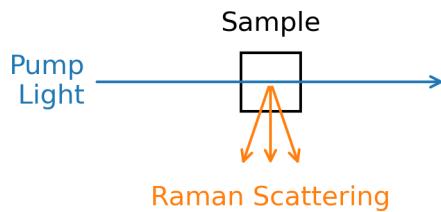


Figure 8.6: A typical Raman spectroscopy setup. The intense pump light is fired at the sample, and the weak scattered Raman signal is detected at right angles to it.

- Raman spectroscopy works via two-photon process (absorption then emission) rather than the single-photon absorption only process.
- 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 using the Raman effect than can be excited using IR absorption.

For example, you can excite the N-N vibration in N_2 using Raman excitation, which is impossible using pure IR.

8.2.5 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** – as we saw earlier, we are good at making these.
- Due to this, we can use a visible region detector to detect the light, and we are good at making cheap and effective visible light detectors. This avoids the need for expensive and noisy infrared detectors.
- 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.

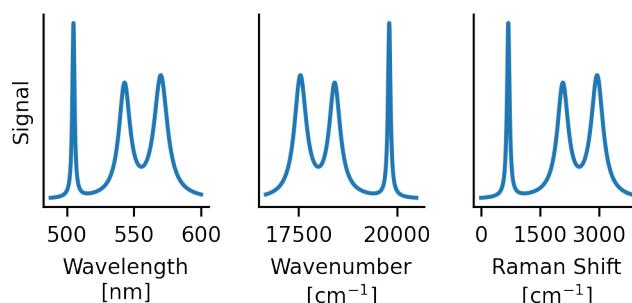


Figure 8.7: Converting raw Raman spectra to something more useful. Left: raw spectrum in wavelength units. Middle: converted to wavenumber units (so subtraction is simple). Right: with excitation wavenumber subtracted off, to give the Raman shift.

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 to have to use multiple kinds of spectroscopy to answer your chemical questions.

8.2.6 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 scattering 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 8.7.

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.

Next time, we are going to stick with the visible region of the EM spectrum and talk about **electronic spectroscopy**.

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.
- Different vibrations can be excited via the Raman effect than can be excited through pure IR absorption.

Lecture 9

Electronic Spectroscopy

Lecture Aims

- To understand the principles of electronic spectroscopy.
- To understand how solvent effects can impact spectra.
- To have a first look at X-ray techniques.

So far we've looked at rotational and vibrational spectroscopy, mostly of small molecules. Today we are going to go up a few orders of magnitude in energy and think about **electronic spectroscopy**.

9.1 Basic 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 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?

9.1.1 It's Complicated

The problem is that electronic spectroscopy is *complicated*¹. In vibrational and rotational spectroscopy, we can make some reasonable assumptions and predict the appearance of spectra fairly accurately – even with 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 from the first few lectures.

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.

¹I realise I keep saying stuff is complicated, but in this case it really is.

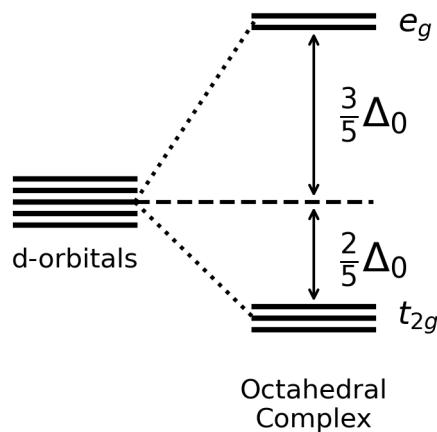


Figure 9.1: Splitting of d-orbitals (left) in an octahedral ligand field (right).

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 normally² can't extract the same detail about molecular structure from the spectra that we can from other forms of spectroscopy like NMR.

Firstly, we're going to talk a bit about some d-block spectroscopy to illustrate a couple of useful concepts, and then briefly have a first look at X-ray techniques.

9.1.2 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 should also already know that when you put these atoms into a crystal field or ligand field (i.e. by 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 9.1. 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’ – shown in Figure 9.2 for a range of complexes containing Vanadium in different oxidation states. With your new spectroscopy expertise, you should now also be able to explain why the wavelength of these transitions (and hence the colour of the complex) depends on the magnitude of the *ligand field splitting parameter*, Δ_o . The magnitude of the splitting is determined by both the oxidation state of the metal, and by the ligands, 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:

²However 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.



Figure 9.2: Vanadium complexes are colourful due to these d-d transitions – the colour depends on the oxidation state.

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

So, what are the selection rules?

9.1.3 Electronic Selection Rules

You're familiar with the selection rules for atomic spectroscopy from last year³, but what you find is that as the molecules get bigger, everything becomes more annoying and less pretty: 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:

- $\Delta S = 0$ - 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, adn 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. The parity is denoted by the *g* or *u*, and you can think of it as telling you about the inversion symmetry of the wavefunction⁴ 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?

³ $\Delta n = \text{anything}$, $\Delta l = \pm 1$ and all that jazz.

⁴This notation comes from the German for 'even' (gerade) and 'odd' (ungerade). Photons have odd parity, so if you absorb a photon the parity has to change. Think of even parity as like the number +1 and odd as -1, the overall product of parities of the final and initial orbital and photon needs to be totally symmetric (+1 - think back to the TDM). So if the photon parity is -1, the only way our overall product can end up with a parity of +1 if is the product of the initial and final parities is -1, so they must be different.

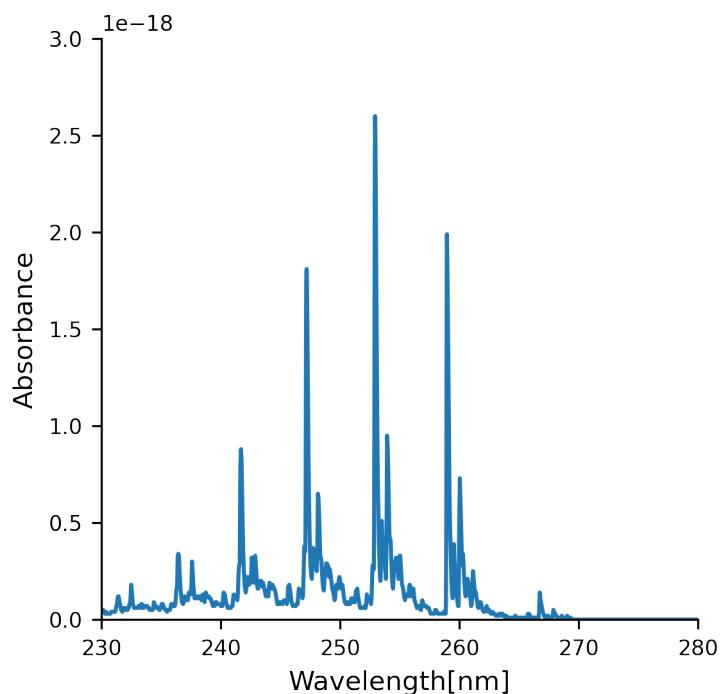


Figure 9.3: Electronic spectrum of gas-phase benzene. Beautiful sharp lines corresponding to different vibrations and rotations that accompany the electronic transition.

9.1.4 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**⁵. 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 – which is why the complexes look coloured.

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 (atomic number bigger than about 30), then a phenomenon called **spin-orbit coupling** becomes 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 about the details 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 9.3.

The spectrum shown in Figure 9.3 is in the gas-phase, though. Gas-phase means that the

⁵ROtational, VIBrational, and electRONIC.

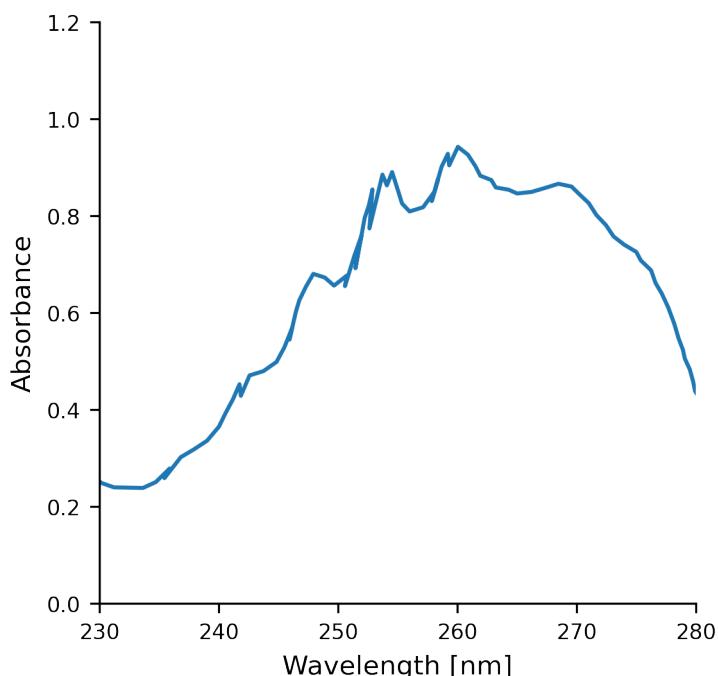


Figure 9.4: Electronic spectrum of solution phase benzene. A big blobby mess of crap due to collisional broadening. A higher resolution spectrometer wouldn't help you here!

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 9.4.

9.1.5 Solvation Effects

So where we once had a beautiful series of sharp lines (Figure 9.3), we now have a big ugly blob (Figure 9.4). 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. However, there are cases where electronic spectroscopy can be a lot more diagnostic - especially when you start exciting core electrons using X-rays.



Figure 9.5: The UK synchrotron, and main high-intensity X-ray source: The Diamond Light Source in Oxfordshire. Many of your lecturers regularly go there to do measurements. I hold the world record for the fastest bicycle time-trial around the perimeter.

Relaxing Selection Rules

Most spectroscopic selection rules are derived using approximations in quantum mechanics that assume molecules behave ideally, or ignore complications like spin-orbit coupling.

Deviations from these ideal conditions result in **relaxation** of the selection rules, and formally forbidden transitions can be visible in spectra. Relaxation of selection rules becomes more common as molecules get bigger.

9.2 X-Ray Techniques

9.2.1 X-Ray Spectroscopy

In UV-Vis spectroscopy, we are exciting electrons in the **valence orbitals** of a molecule – i.e. the outer electrons. The binding energies of these valence electrons correspond to ultraviolet and visible wavelengths (1-10 eV). However, we can also excite **core electrons** in our molecule if we use much higher energy photons (100-10 000 eV). These high energy photons are in the **X-Ray** region of the EM spectrum⁶. So absorption of an X-ray photon will excite an electron from a core level, or from the **inner shell**.

This kind of spectroscopy is a lot more diagnostic than UV-Vis, in general, because the core energy levels of atoms of different elements are very different, and depend a lot on the oxidation state of the atom. As such, X-ray absorption and emission spectroscopies can be very sensitive to specific atoms in a larger molecule, and so they are some of the most widely used diagnostic techniques. This is especially in materials science and biological chemistry, where you might want to look at a material doped with a small amount of a particular atom, or a particular metal inside a large protein. The main downside of X-ray techniques is that it's *really hard* to make X-rays with high intensities in a normal university lab, so to do most X-ray spectroscopy requires that you travel to a large facility like a synchrotron (Figure 9.5) or X-ray Free-Electron Laser (XFEL).

⁶This region gets split into 'deep UV' at the low energy end, to 'vacuum UV' (VUV), then 'extreme UV' (XUV), then 'soft X-ray', and then 'hard X-ray'. After that you're in gamma ray territory.

9.2.2 X-Ray Crystallography

Before we end this brief discussion - it's worth mentioning **X-ray crystallography**, because that's probably the place where you've heard about X-rays in chemistry before (and is a commonly used technique in synthesis). Crystallography is a technique where you determine the 3D structure of a crystal by looking at how X-rays diffract from it. Measuring the diffraction pattern and doing some maths can then reveal the atomic structure. Crystallographic techniques are very powerful and widely used across science - but strictly, it isn't spectroscopy (even though it is a light-matter interaction), so we won't talk about it more here.

Anyway, next time we're going to see a different kind of spectroscopy that produces very sharp, beautiful, and informative spectra. We're going to look at the **magnetic resonance** spectroscopies, like NMR.

Take Home Messages

- Electronic spectroscopy is spectroscopy where atoms and molecules are excited to different electronic states.
- UV-Vis spectroscopy is electronic spectroscopy where valence electrons are excited using UV and visible light.
- X-ray spectroscopy is electronic spectroscopy but where core electrons are excited using X-rays.

Lecture 10

Magnetic Resonance I

Lecture Aims

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

In our last two lectures we are going to 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 the most widely used kind of spectroscopy in 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 **dipoles** on molecules. Magnetic Resonance (MR) spectroscopies are a bit different – they are **magnetic dipole** spectroscopies, where the **magnetic field** of the light interacts with the molecule.

Our plan for these two lectures is:

- Today: understand the basic principles of MR spectroscopy, and understand **shielding** and **chemical shift**.
- Next time: understand **coupling** and why we get **multiplets** in our spectra.

For these two lectures we aren't really bothered about *what* the NMR spectrum means (Alex will do that much better than I could), but we are going to understand *why* it looks like it does, so you can appreciate the underlying principles. We are going to focus on **nuclear magnetic resonance (NMR)**, but the principles apply to other MR spectroscopy too.

10.1 Spin

Like in all spectroscopy, in NMR spectroscopy we need two quantum states that transitions can 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**, and the **nuclear spin quantum number** normally has the symbol I – it's

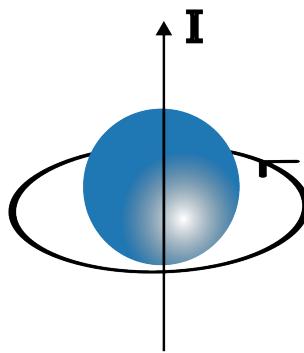


Figure 10.1: The angular momentum I of a nucleus spinning on its axis is a technically incorrect, but often quite useful, way to think about nuclear spin.

a quantum number just like n , v , J , and so on from before. Different nuclei have different spin quantum numbers, and we're going to talk mostly 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 10.1 is why it's called *spin*, in any case.

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

10.1.1 Quantised Spin States

Given a nucleus with a nuclear spin I , quantum mechanics tells us¹ that there are $2I+1$ different **orientations** that spin can take². Each of these orientations has a value m_I associated with it:

$$m_I = -I, -I+1, \dots, I \text{ in integer steps}$$

If $I = 1/2$, then $2I+1 = 2$ and we have two spin orientations (spin states):

- $m_I = \frac{1}{2}$ (spin up)
- $m_I = -\frac{1}{2}$ (spin down)

A good way to picture these spin states is as like little bar magnets³ that are oriented in different directions depending on the value of m_I . This is why we draw spins as arrows in MO diagrams, at least.

¹See any textbook on atomic structure under ‘space quantisation’ and quantised angular momentum for an explanation.

²It is exactly analogous to how an electron with orbital angular momentum ℓ has $2\ell+1$ orientations, which is why in an atom there are 3 p-orbitals, and 5 d-orbitals, etc...

³Later on in NMR you'll be thinking about the **magnetic moment** of a sample, and how you can manipulate it by firing pulses of radio-frequency light at it. The magnetic moment of a nucleus μ is given by $\mu = \gamma I$.

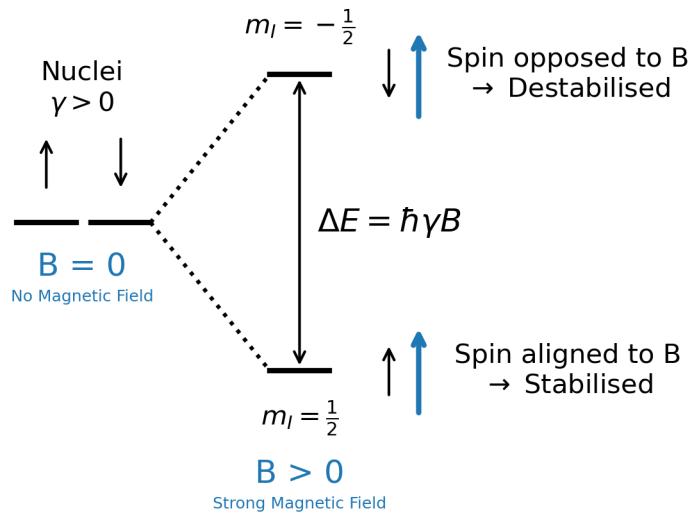


Figure 10.2: In a magnetic field, the degeneracy of nuclear spin states is lifted. For a nucleus like a proton with $I = 1/2$ and $\gamma > 0$ (shown here), this results in two states with a gap between them that depends on the strength of the B field.

The energy of these spin states is given by Equation 10.1:

$$E = -m_I \hbar \gamma B \quad (10.1)$$

Where m_I is the spin orientation⁴ (either $\pm 1/2$ for the cases we'll see in this course, a unitless number), \hbar is the *reduced Planck constant*, which is $\frac{h}{2\pi}$, γ is a constant called the **gyromagnetic ratio** (in units of radians per second per Tesla), and B is the magnetic field strength (in Tesla). Equation 10.1 implies that the energy of both spin states is the same (zero) if $B = 0$. So what would happen if we put a collection of these nuclei into a magnetic field?

Equation 10.1 shows these two states will end up with different energies: one is stabilised by the field and another is destabilised (shown Figure 10.2), which should be intuitive if we think of it as one bar magnet being aligned to the field direction and another being opposed to it. Figure 10.2 shows the case for a nucleus where $\gamma > 0$, which is the case for the ${}^1\text{H}$ nucleus (protons) we mostly care about⁵.

NMR Units

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

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

⁴Technical term: the projection of the spin angular momentum I onto the spin quantisation axis, which is the axis defined by the strong magnetic field in this case.

⁵Other nuclei may have $\gamma < 0$ and so the spin alignments that correspond to the stabilised and destabilised states are reversed – this is also the case for the spin of an electron. So for an electron, the spin being aligned to the B -field is actually *destabilising*, and vice versa.

10.1.2 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:

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

In Hertz (more common in NMR).

NMR Lines

The gyromagnetic ratio of a proton is $267.5 \times 10^6 \text{ rad s}^{-1} \text{ T}^{-1}$. What is the energy gap (in Joules), and the corresponding resonance frequency (in Hertz) between the two nuclear spin states of a proton, in a magnetic field of strength 7.0460 T?

You should find it is $1.98 \times 10^{-25} \text{ J}$ or 300 MHz.

This is the energy where we'll see a line in our NMR spectrum, or in the dynamic picture, is the resonance frequency at which those nuclear spins are jiggling around.

Resonance Frequency

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

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

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

Anyway, you'll have noticed that the energy gap between the spin states we calculated ($1.98 \times 10^{-25} \text{ J}$) was bloody tiny. So now let's think about the **populations** of those two spin states.

NMR Populations

Calculate the Boltzmann populations of the two states mentioned above at 298 K. Comment on the result.

You should find that the population ratio is about 0.99995.

From the above example, we note two things:



Figure 10.3: Low resolution: a benchtop NMR spectrometer with a proton resonant frequency of 80 MHz. These are relatively recent invention and are surprisingly expensive.



Figure 10.4: Higher resolution: the NMR spectrometer you use in the teaching labs, with a proton resonant 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.

1. Gaps between nuclear spin states are *tiny* compared to other kinds of spectroscopy.
2. Both states have essentially equal population (the difference is on the order of 1 part in 100000).

These two points have some important consequences. Firstly, the tiny energy gap means that spontaneous emission from an excited nuclear spin 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 states⁶. It also means that it's impossible to make an NMR measurement quickly⁷ – more on this in the Appendix for interest.

Secondly, both states having similar populations means that we need a large amount of nuclei to observe a change in the population. To understand this, imagine having two shelves, each covered with an almost-equal large number of grains of rice (say, 10000 grains on each shelf). 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 (Figure 10.5, left panel).

In contrast, in electronic or vibrational spectroscopy, the energy gap is several orders of magnitude larger and 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 (Figure 10.5, right panel). So we don't need to excite as many molecule in electronic or vibrational spectroscopy to observe a change. 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 slow measurements and need for large amounts of sample are obviously not catastrophic issues because NMR is used by everyone all the time in chemistry. So why is it so useful?

10.2 Why is NMR everywhere?

The fundamental reason is that NMR is **exquisitely** sensitive to molecular structure, more than any other spectroscopic technique, and we're about to see why.

⁶This is beyond the scope of today, but it's the foundation of 2D-NMR and other fun things you'll learn about later.

⁷Depending on your definition of 'quickly'. For me, a microsecond is an essentially infinite amount of time, so NMR really doesn't cut it.

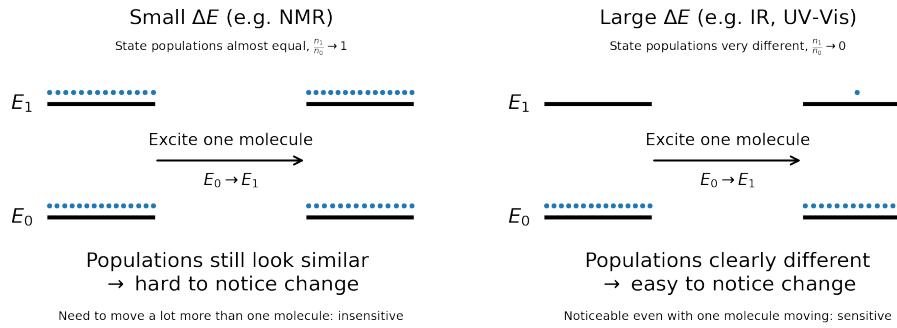


Figure 10.5: Left: exciting one molecule between two near-equally populated states is not very noticeable (e.g. in NMR). Right: exciting one molecule into an empty upper state is noticeable (e.g. in IR/UV-Vis). NMR is an insensitive technique compared to spectroscopies that probe larger energy gaps.

10.2.1 Shielding and Deshielding

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

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

γ 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 (we'll call the field applied by the magnet B_0), 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 and the strong field from the spectrometer B_0 as:

$$B = B_0 - \sigma B_0 = (1 - \sigma)B_0$$

Where σ is called the **shielding constant** and is usually very small ($\sigma \ll 1$). σ 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 $B < B_0$), which is termed **shielding**.
- Augment the applied field B_0 ($\sigma < 0$, so $B > B_0$), which is termed **deshielding**.

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 10.6. If there is no shielding at all, then $B = B_0$, and the magnetic field felt by the nucleus is entirely coming from the external magnet.

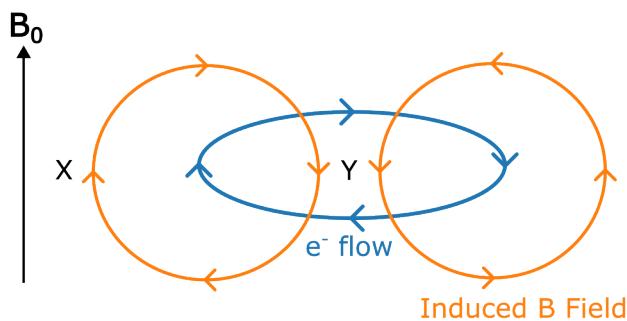


Figure 10.6: One example of how shielding/deshielding arises. The applied field B_0 can induce an electron flow in a molecule (blue arrow). The electron flow induces a new magnetic field (orange arrows), which results in a nucleus at X being deshielded (feels a stronger field than B_0), and a nucleus at Y being shielded (feels a weaker field than B_0). The electron and magnetic field directions can be derived using the right-hand rule. This effect is called a **ring current** and is common in aromatic molecules.

Shielding and Deshielding

Shielding effects change the NMR frequency of the nucleus and hence the position of its corresponding line in the NMR spectrum:

- **Shielding** is when local magnetic fields oppose the applied field B_0 .
 - $\sigma > 0, B < B_0$
- **Deshielding** is when local magnetic fields augment the applied field B_0 .
 - $\sigma < 0, B > B_0$

An NMR active nucleus can be either shielded or deshielded by neighbouring atoms, solvent effects, the wider molecular structure, and other things.

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 due to these small changes in shielding, and due to **coupling** (next time), 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 or Joules, but 'ppm' – a quantity termed **chemical shift**.

10.2.2 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 with different field strengths 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)⁸. The chemical shift, δ , is then defined as:

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

Where ν is the resonance frequency of a nucleus, ν_{ref} is the resonance 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?

You should find the answer is 2 ppm.

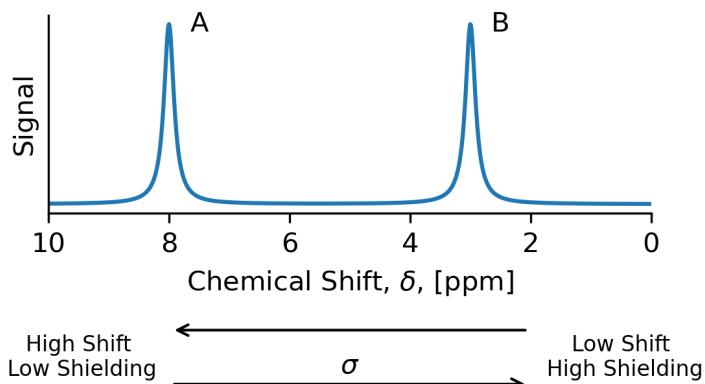


Figure 10.7: An example simple NMR spectrum, of a system containing two nuclei (A and B). Conventionally chemical shift increases from right to left, so nucleus A has a higher shift and is less shielded (more deshielded) than nucleus B.

Finally, it's useful to think about how to interpret chemical shift values and see an example NMR spectrum (Figure 10.7). NMR obviously also has some annoying conventions to deal with, like every other kind of spectroscopy, and one of these is that normally you plot spectra such that the chemical shift axis *decreases* from left to right. A high chemical shift implies that there's a high frequency transition, and so the shielding is lower, and vice versa. Remembering that **high shift → high frequency → less shielding** and vice versa is main thing⁹.

Next time, we will end by talking about **spin-spin coupling** and **multiplets**. Exciting.

⁸Different reference molecules are used in solvents where TMS isn't soluble.

⁹So the axis would be the 'normal' way around if it was plotted against the shielding parameter, to be fair.

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 spectra are reported in units of chemical shift to account for differences between spectrometers. A high chemical shift implies the nucleus is deshielded and vice versa.

Lecture 11

Magnetic Resonance II

Lecture Aims

- To understand the basic idea of **coupling** in magnetic resonance spectroscopy.
- To understand why coupling results in **multiplets** in spectra.

This last lecture is a short one where we'll talk about **coupling** in NMR spectroscopy. Last time we ended talking about **chemical shift**. We saw that the chemical shift of a nucleus in an NMR experiment was very sensitive to the structure of the molecule around that nucleus due to shielding and deshielding. These shifts are incredibly useful in helping us figure out what molecule we have, but the fun does not stop there.

11.1 Coupling

Recall that an **NMR active nucleus** is one that has nonzero nuclear spin. This nonzero nuclear spin leads to the nucleus behaving like a tiny magnet when placed in a strong magnetic field – it has a **magnetic moment**. In any molecule, there is almost always more than one NMR active nucleus. Each of these nuclei will have their own magnetic moments (they all behave like little magnets), and all these tiny magnets will interact: they *influence, and are influenced by, each other*. This phenomenon is called **coupling**.

11.1.1 A Motivating Example

Consider the simple molecule methanol, CH_3OH . Imagine we are measuring the ^1H NMR spectrum, and that the carbon atom is ^{12}C (so is NMR inactive)¹ There are two distinct environments that the protons in this molecule are in: attached to the CH_3 group, and attached to the OH group. The set of CH_3 protons are **chemically equivalent** because there is free rotation around the C-O σ bond and so these protons will all have the same chemical shift on an NMR timescale. Alex will talk a lot more about chemical equivalence (and you might have mentioned it briefly last year), but we can define it here anyway.

¹The oxygen is also NMR inactive: the only NMR active isotope of oxygen has incredibly low abundance.

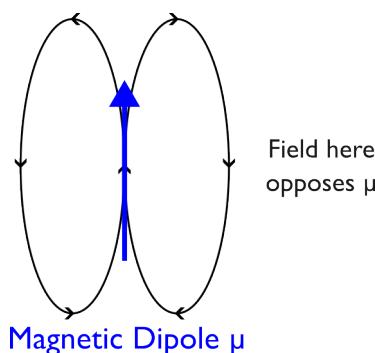


Figure 11.1: A magnetic dipole μ (blue) produces a magnetic field (black lines). At the side of this field (perpendicular to the dipole), the produced field is in the opposite direction to μ .

Chemical and Magnetic Equivalence

Two nuclei are **chemically equivalent** if either:

- There is a symmetry element present in the molecule that would interconvert them (rotations, reflections, etc.)
- There is molecular motion that would interconvert the positions of the nuclei (rotation around σ bonds, ring flipping, etc.).

Chemically equivalent nuclei will have the same chemical shift.

Nuclei are **magnetically equivalent** if they are already chemically equivalent, and have the same **coupling** to all other nuclei in the molecule. We'll discuss what **coupling** means today.

The two distinct environments should give rise to two distinct resonances in our NMR spectrum (one for the CH_3 protons and one for the OH proton). However, in reality, we see **six resonances** in our NMR spectrum! The reason is because **coupling** between the nuclei causes more resonances to appear.

11.1.2 Magnetic Moments and Fields

To understand coupling, we need to understand a little more about how nuclear spin makes nuclei behave like tiny magnets. The nuclear spin vector \mathbf{I} gives rise to a **magnetic moment**, $\boldsymbol{\mu}$:

$$\boldsymbol{\mu} = \gamma \mathbf{I}$$

The direction of $\boldsymbol{\mu}$ is the same as the direction of \mathbf{I} in the case that $\gamma > 0$ (like it is for ^1H , ^{13}C , ^{31}P , and ^{19}F), and is in the opposite direction to \mathbf{I} in the case that $\gamma < 0$ (like it is for the electron and ^{15}N). We will focus on the case where $\gamma > 0$ given we are focussing on interpreting ^1H NMR.

$\boldsymbol{\mu}$ is a magnetic dipole that you can think of like a tiny bar magnet with a north and south pole. The magnetic field produced by this dipole might be familiar from school physics and looks like Figure 11.1.

The key thing to understand for our coupling is that the magnetic moment $\boldsymbol{\mu}$ creates a magnetic field that loops around from the tip of the arrow back to the tail. You can see what magnetic fields would be experienced by objects in the vicinity of $\boldsymbol{\mu}$: something at the side of $\boldsymbol{\mu}$ would

feel a field in the opposite direction to μ , and something above or below μ would feel a field in the same direction as μ .

11.1.3 Coupling Intuition: Dipolar Coupling

To understand coupling, we first start with a simple system: AX. Two different nuclei, A and X, that are both NMR active but have different resonance frequencies, ν_{A0} and ν_{X0} . In the absence of coupling between the nuclei we'd expect to see just two lines in our spectrum, corresponding to these two resonance frequencies.

Let's focus on one of these resonances, ν_{A0} , shown on the left of Figure 11.2. This resonance originates from the transition $A \uparrow \rightarrow A \downarrow$. If we include the influence of the other nucleus, X, on this transition, then we have two options:

1. $A \uparrow X \uparrow \rightarrow A \downarrow X \uparrow$, call the transition frequency $\nu_{A,\uparrow}$.
2. $A \uparrow X \downarrow \rightarrow A \downarrow X \downarrow$, call the transition frequency $\nu_{A,\downarrow}$.

We can only flip one spin at a time due to the selection rules², so that makes life a bit easier. We just have to imagine the X spin sitting alongside the A spin as it flips, as shown above. So how does that affect the transition energies?

Let's imagine that our applied B-field (B_0) is going upwards in Figure 11.2. Think about the magnetic moment of nucleus X and the field it produces, and whether those fields oppose B_0 (shielding nucleus A) or augment B_0 (deshielding nucleus A). Remember that if a nucleus experiences a greater effective magnetic field, the splitting between the ground and excited state increases (so the ground state gets lower in energy and the excited state gets higher).

- In option 1, the field from nucleus X opposes B_0 , and so nucleus A experiences a smaller magnetic field than it would in the absence of nucleus X.
 - So we expect that the energy gap shrinks and the resonance frequency $\nu_{A,\uparrow} < \nu_{A0}$
- In option 2, the field from nucleus X augments B_0 , and so nucleus A experiences a larger magnetic field than it would in the absence of nucleus X.
 - So we expect that the energy gap rises and the resonance frequency $\nu_{A,\downarrow} > \nu_{A0}$

So overall, due to the coupling, we'd expect to see two resonances, $\nu_{A,\uparrow}$ and $\nu_{A,\downarrow}$, either side of where we'd expect to see ν_{A0} . Nucleus A does the same thing to the resonance ν_{X0} , so our overall spectrum, with the inclusion of coupling, looks like the right hand side of Figure 11.2. These resonances are called **doublets**, each original resonance is split into two (doubled).

You can see that the effect of the coupling on the spin states is that:

- States with paired spins ($A \uparrow X \downarrow$ or $A \downarrow X \uparrow$) are **stabilised**.
- States with parallel spins ($A \uparrow X \uparrow$ or $A \downarrow X \downarrow$) are **destabilised**.

We'll talk through this in some detail in the lecture, as it's easier to annotate and draw on a blackboard than describe in text.

²We can't simultaneously flip the spin of X and A during the transition.

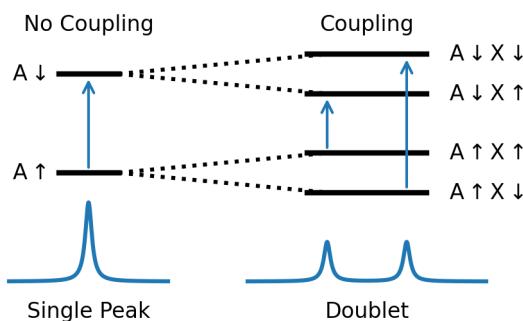


Figure 11.2: In the absence of coupling, the resonance $A \uparrow \rightarrow A \downarrow$ produces a single peak (left panel). With coupling to a neighbouring nucleus X, the single peak splits into a **doublet** (right panel), because the spin of nucleus X can either augment or oppose the original field B_0 , raising or lowering the transition energy respectively.

11.1.4 Coupling Constants

An obvious question now is *what is the splitting between each pair of lines in our doublet?*

That is defined by something called the **coupling constant**, J_{AX} , which tells you the degree of the coupling between nucleus A and nucleus X. J_{AX} has units of frequency, and a bigger value implies that there is a bigger amount of coupling between the nuclei (and hence a larger splitting of the two resonances in the spectrum). Importantly, the coupling constant between two nuclei is **independent of the strength of the applied B-field from the spectrometer** – it only depends on the degree of coupling. Coupling constants can be positive or negative, but this doesn't affect the appearance of a simple 1D NMR spectrum. A positive J_{AX} is the case we have described above: antiparallel nuclear spins are stabilised, parallel nuclear spins are destabilised.

To understand more about coupling constants, we need to understand a bit more about the precise mechanisms by which coupling happens.

11.2 Coupling Mechanisms

11.2.1 Dipolar Coupling

The mechanism of coupling alluded to above, where the magnetic field from nucleus X directly interacts with the magnetic field from nucleus A, is called **dipolar coupling**. Dipolar coupling is important in the solid state, and for understanding relaxation mechanisms in NMR (topic for next year, and the year after). However, this mechanism *cannot happen in the solution phase* because our molecules are all tumbling around very fast and their orientations relative to the applied magnetic field will average out. So there must be a different mechanism that produces the coupling effect in solution (as we still see our NMR lines split into multiplets in solution). That mechanism is called **scalar coupling**.

11.2.2 Scalar Coupling

The overall effect of scalar coupling for a nucleus with $\gamma > 0$ is analogous to what we just described for dipolar coupling:

- States with paired spins ($A \uparrow X \downarrow$ or $A \downarrow X \uparrow$) are **stabilised**.
- States with parallel spins ($A \uparrow X \uparrow$ or $A \downarrow X \downarrow$) are **destabilised**.

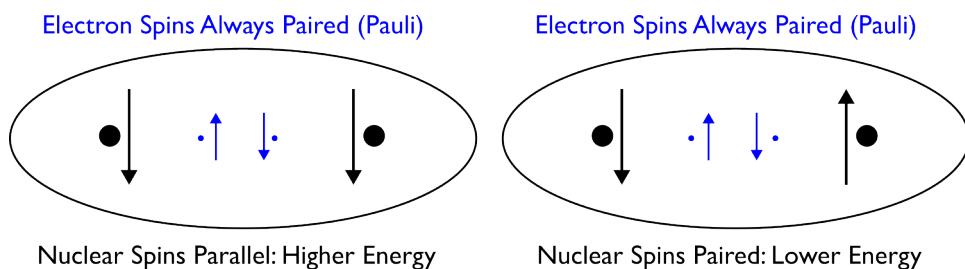


Figure 11.3: Simple cartoon of scalar coupling between two nuclei (black dots and arrows) and the electrons (blue dots and arrows) bonding them together. The electrons must always be paired to satisfy the Pauli principle, and the Fermi contact interaction causes the case where the nuclear spins are paired to be lower in energy than the case where they are parallel.

However the magnitude of the effect is much smaller and the mechanism much more subtle. The coupling between nuclei is *mediated by electrons between the nuclei*: i.e. the **coupling is transmitted through chemical bonds**. This kind of through-bond coupling is why coupling and multiplet patterns can tell us about which nuclei are bonded to which other nuclei in NMR spectroscopy.

The precise mechanism of scalar coupling requires more quantum mechanics than we have time to discuss in this lecture course³. We will simply state that the origin is in something called the **Fermi contact interaction**, the strength of which, A , is given by:

$$A \propto -\gamma_e \gamma_n \mathbf{I} \cdot \mathbf{S}$$

Where γ_e and γ_n are the gyromagnetic ratios of the electron and nucleus, and \mathbf{I} and \mathbf{S} are the nuclear and electron spin vectors. The contact interaction stabilises states where the nuclear and electron spins are paired, and because the spins of two electrons *have* to be paired to satisfy the Pauli Principle, the contact interaction leads to the most stable arrangement of *nuclear spins* being the arrangements where they are paired.

Contact Interaction

Show that for a nucleus with $\gamma_n > 0$, the contact interaction will stabilise states where the nuclear and electron spins are paired, and destabilise states where they are parallel.

Note that \mathbf{I} and \mathbf{S} are vector quantities: their sign denotes the direction they point in.

The precise way in which the contact interaction produces specific coupling constants (see below) is complex and requires rigorous calculations of ground and excited state electronic wavefunctions for the molecule: not the kind of calculation it is easy to do on paper!

We'll leave NMR coupling and multiplets here for now, the main aim today was that you have some kind of feel for the mechanism by which these things occur. In the other half of the course you'll go into much more detail about how to practically use coupling in NMR to solve chemical problems. In particular, you'll learn how to predict multiplet patterns, and how to relate them to chemical structure – it is a hugely powerful tool in the toolbox of the synthetic chemist.

³See Hore's *Nuclear Magnetic Resonance*, Section 3.6, for more detail.

Coupling in Magnetic Resonance

Coupling in magnetic resonance is the phenomenon where nuclear spins 'feel' each other and so affect each other's chemical shift. Coupling leads to the splitting of resonances into **multiplets**, and the pattern in the multiplet can be very diagnostic of molecular structure.

Nuclei can couple **directly** (dipolar coupling) in the solid state, but in solution phase we have **scalar coupling**. Scalar coupling is where the **coupling is transmitted through chemical bonds**. The degree of coupling between two nuclei A and X is denoted by the **coupling constant**, J_{AX} .

Anyway, that's it for my part of the course. I hope you've enjoyed it, and **please do the problems!** They are the only way to really learn this material and are the best way to prepare for the exam. Enjoy the rest of the course with Alex where you will learn more about *what* a spectrum tells you, rather than *why* the spectrum is the way it is. I'll see you again next year for advanced physical chemistry.

Take Home Messages

- Coupling between nuclei produces multiplets in our NMR spectra and reveals a wealth of information about the connectivity between different kinds of nuclei in our molecule.
- There are through-space and through-bond mechanisms for coupling between nuclei, and the through-bond mechanisms are most important to us as chemists.
- Coupling constants tell us about the strength of the coupling, and are independent of spectrometer field strength.

Problem Sheet 4

1. Using group theory, or otherwise, determine which of the following vibrations are Raman active. Justify your answers.
 - i The two stretching vibrations in OCS.
 - ii The O=O stretch in O₂.
 - iii The four C-H stretching vibrations in ethene.
2. A molecule 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 The measured spectrum shows three sharp peaks, which sit on top of a broad background signal. Suggest a physical origin for this background.
3. UV-Vis spectra of the four Chromium complexes Cr(H₂O)₆³⁺, Cr(NH₃)₆³⁺, Cr(Cl)₆³⁻, and Cr(en)₃³⁺ have been measured, but the samples were mislabelled and mixed up.
Using your knowledge of the spectrochemical series, assign the absorbance maxima given below to each of the four complexes. State the likely colour of each complex.

Sample	λ_{max} (nm)
1	730
2	465
3	575
4	457

4. An ¹H 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 ¹H is $267.5 \times 10^6 \text{ rad s}^{-1} \text{ T}^{-1}$.

Problem Sheet 4 - Numerical Solutions and Hints

1. i Both are Raman active.
ii Yes it is Raman active.
iii Two are Raman active, two are not.
2. i Because these are Stokes lines - molecule is being excited and so scattered photon loses energy relative to the incident photon.
ii In order from question: 611, 1973, and 3373 cm^{-1}
iii Plausible suggestions include fluorescence, or external scattered light.
3. The metal centre is always the same, so think back to the spectrochemical series and which ligands are strong and weak field, and think about how this must affect the absorption in the UV-Vis (d-d transition).
4. Samples 1 → 4 in order are: Cr(Cl)_6^{3-} , $\text{Cr(NH}_3)_6^{3+}$, $\text{Cr(H}_2\text{O)}_6^{3+}$, Cr(en)_3^{3+} .
5. i Ring proton: 7 ppm. Side chain proton: 2.5 ppm.
ii Calculate and see :)
iii Shielded means feels a lower B field - how will this affect the Larmor frequency?
iv Around 11.7 T. High B field means bigger signals and better resolution.

Extended Problems 3

1. CuF₆ is a coordination compound.

a) Assuming that CuF₆ is octahedral, determine:

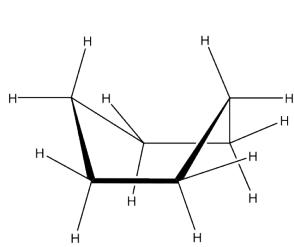
- The number of bands you would expect to see in the Cu-F stretching region of the IR spectrum of CuF₆
- The number of bands corresponding to d-d transitions you would expect to see in the UV-Vis spectrum.

b) The corresponding measured spectra of CuF₆ show:

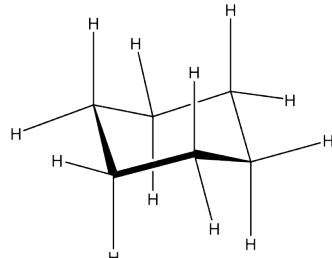
- Two bands in the Cu-F stretching region of the IR spectrum.
- Two bands in the UV-Vis spectrum that correspond to d-d transitions.

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 ¹H 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. The strength of the magnetic field of the Earth in the UK is around $47 \mu\text{T}$.
- Calculate the Larmor frequency of a ^1H nucleus in the Earth's magnetic field.
 - Hence, calculate the Boltzmann population ratio of the two spin states of ^1H 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 T. Rank the nuclei in order of how sensitive they would be in an NMR measurement.
- Why is ^1H the most commonly used NMR active nucleus?

Equations to Know

The equations and relationships listed here are assumed knowledge, and will not be given to you in an exam.

- **Energy unit conversions:** $E = h\nu$, $E = \frac{hc}{\lambda}$, $\bar{\nu} = \frac{1}{\lambda}$. Definitions of wavenumber, wavelength, frequency, etc from CH1200. In general I expect you to be comfortable converting units.

- **Boltzmann Distribution:**

$$\frac{n_i}{n_0} = \exp\left(-\frac{E_i - E_0}{k_B T}\right)$$

- **Beer-Lambert Law:**

$$A = \ln\left(\frac{I_0}{I}\right) = \epsilon c L$$

- **Energy of a Line (Bohr Condition):**

$$\Delta E = E_{\text{Upper}} - E_{\text{Lower}}$$

- **Mathematics:** I expect that you are able to perform all the basic calculus learnt in CH1204 (differentiation and integration), and are comfortable manipulating and solving algebraic equations.

Appendix A

Linewidths and Lineshapes

Linewidths

The most fundamental lineshape is that shown in Figure 4.1 – a **Lorentzian** lineshape. A Lorentzian lineshape L in frequency units is given by:

$$L(\omega) = \frac{\Gamma}{\Gamma^2 + (\omega - \omega_0)^2} \quad (\text{A.1})$$

Where Γ is the HWHM linewidth, and ω_0 is the central frequency of the line. We say this is the most fundamental lineshape as any spectral line, even in the most ideal, ultracold, high resolution conditions will fundamentally look like this if you had a spectrometer that could resolve it. To understand why and how this arises, we can do a thought experiment.

Imagine we have a collection of atoms (M) that are all happily sitting in an excited state (M^*), where the only way that they can decay is via spontaneous emission, like:



The population, n^* of excited state atoms M^* would be given by the solution to the first-order rate equation:

$$\frac{dn^*}{dt} = -kn^*$$

where k is a decay constant, here the rate constant of the spontaneous emission process. The solution to this equation is:

$$n^*(t) = n_0^* e^{-kt} \quad (\text{A.3})$$

Where n_0^* is the initial population of excited atoms, and $n^*(t)$ is the population of excited atoms at time t . Whenever an atom decays, it a photon of light with energy $h\nu$ by equation Equation A.2. The light intensity, I , is therefore directly proportional to the number of excited atoms we have:

$$n^*(t) \propto I(t)$$

And so the light intensity as a function of time is given by:

$$I(t) = I_0(t) e^{-kt} \quad (\text{A.4})$$

So if we were to measure the emission of light over time, we would see that our light intensity follows the exponential decay in Equation A.4. From Equation A.4 we can recognise that the spontaneous emission rate constant k will be inversely proportional to our state lifetime, τ :

$$k = \frac{1}{\tau}$$

Anyway, Equation A.4 shows us our measured light intensity $I(t)$ (the emission of the atoms) as a function of time. But usually in spectroscopy, we don't measure things in the **time domain** (as a function of time), we measure things in the **frequency domain** as a function of *frequency* (energy). To convert between the time and frequency domain, we do a *Fourier Transform*. The Fourier Transform of Equation A.4 is:

$$\mathcal{F}[I(t)](\omega) = \frac{k}{k^2 + (\omega - \omega_0)^2} \quad (\text{A.5})$$

at least up to a constant (factors of π make these really annoying). Equation A.5 is the expression for the Lorentzian lineshape that we saw in Equation A.1. Ultimately, that Lorentzian line you see is the frequency-domain representation of the time-domain behaviour: an exponentially decaying burst of light looks like a Lorentzian peak in frequency (energy) space, which is what you measure in your spectrum. Comparing Equation A.5 to Equation A.1, we can identify that $\Gamma = k = \frac{1}{\tau}$ - so the linewidth Γ is directly proportional to the decay rate, or inversely proportional to the lifetime τ .

Lineshapes

We saw the *Lorentzian* lineshape previously, which is the most fundamental spectroscopic lineshape. Other lineshapes are available though, and it's also common to see a *Gaussian* lineshape in cases where you have many overlapping Lorentzian lineshapes that are inhomogeneously broadened (so every individual Lorentzian has its central frequency shifted slightly differently). Essentially what happens here is you get a Gaussian distribution of Lorentzians, as was shown in Figure 4.2 (reproduced below). These two peak shapes are undoubtedly the two most common,

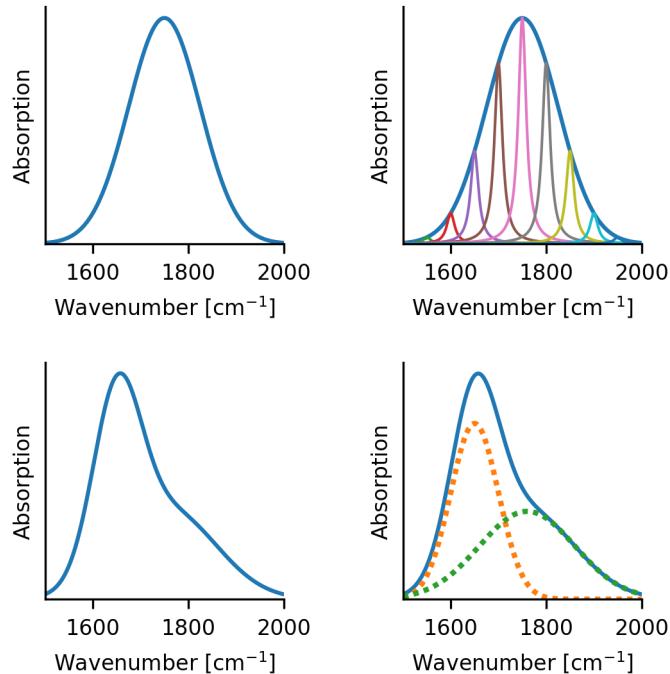


Figure A.1: A Gaussian distribution of different Lorentzians (top right), can end up just looking like a single Gaussian (top left). Two Gaussian distributions can combine together to give a peak with a shoulder (lower panels).

and the ones you'll see in 99.9% of cases.

You may think that it would be easy to work back from the broad Gaussian in the top left panel to reproduce the underlying Lorentzians. Unfortunately, it is often not that simple – in reality, the broadened Gaussian in the top left is not simply a sum of the individual Lorentzians as the figure implies. Each spectroscopic peak will interfere with every other one, so that it is not easy to deconvolute the overall Gaussian into a series of underlying Lorentzian peaks.

A good analogy is to think of it as like multiplication: if all you know is that two numbers multiply together to give you 12, you don't know whether those numbers were 1 and 12, or 3 and 4, or 6 and 2. Same idea here – it's not trivial to go from the top left panel in Figure 4.2 to the top right without having some additional information about our system, or doing some more sophisticated modelling.

Appendix B

Time-Resolved Spectroscopy

Everything following this message is not going to be examined! For interest only.

Here we are going to take a first look at a 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 you¹.

B.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.

B.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 B.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 B.2) taken by Eadward Muybridge², 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).

¹Or doing soul-destroyingly boring admin tasks.

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

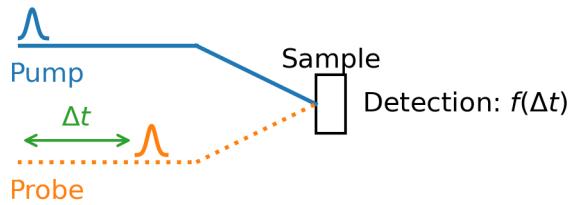


Figure B.1: Pump-probe principle. A process is started using a pump (blue), and then measured using a probe at a later time (orange). The time delay Δt between the pump and the probe is varied to build up a picture of the dynamics.

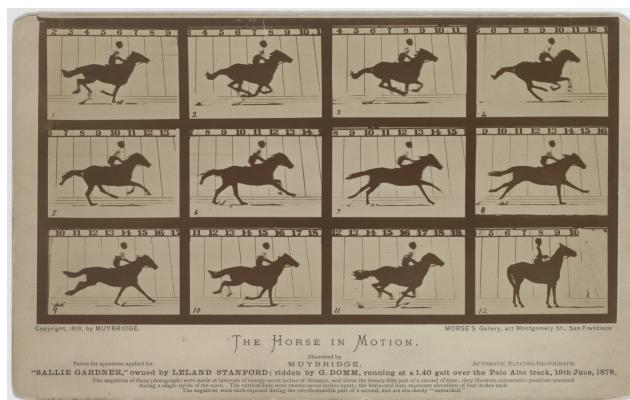


Figure B.2: A horse in motion: the camera shutter speed needs to be fast enough that each photo is well-resolved and not blurry.

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.

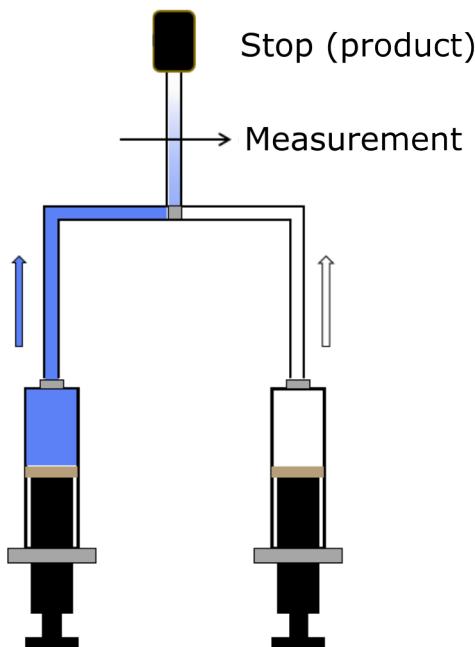


Figure B.3: Stopped-flow kinetics. Two reactants are rapidly mixed and then the progress of the reaction monitored as a function of time.

Stopped-Flow Methods

An easy example to understand at first is the **stopped-flow** measurement, shown in Figure B.3. In this measurement, two syringes containing reactant are 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 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 light³ (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

³Usually, you could also use something like an electrical discharge I guess.

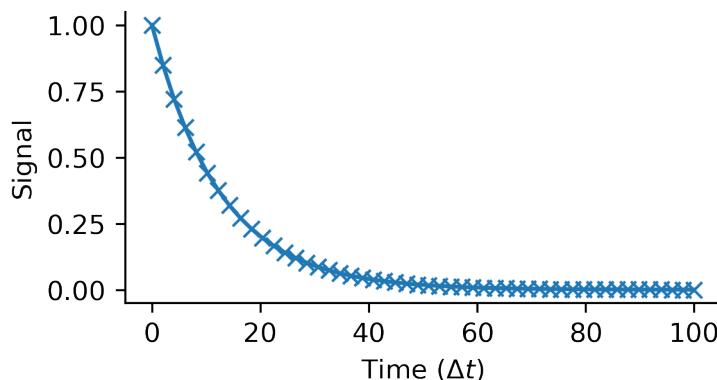


Figure B.4: Typical pump-probe data: signal changes as function of the time delay Δt .

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 B.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 timescale⁴, using optical timing methods. The methodology is mostly just standard pump-probe (as shown in Figure B.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 B.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 B.1.

To end this course, we're going to talk about one kind of time-resolved measurement in a bit

⁴It 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.

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...).

B.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!

B.2.1 TAS Equipment

A typical transient absorption setup looks exactly like the one we saw in Figure B.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.
- 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.

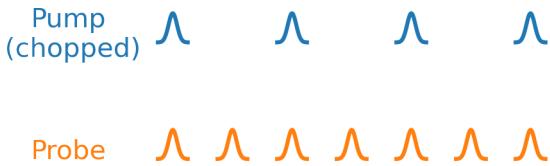


Figure B.5: Typical chopping scheme: every other pump pulse is removed, so that a sequence of spectra with and without the pump is recorded. The difference between the spectra with pump on and pump off is what we measure in TAS.

- Both pulses need to be short enough in time 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 B.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 ΔA :

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

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).

B.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 B.6). Alternatively, we could select bands in the spectrum we care about and look at the height/area⁵ of those bands as a function of time (bottom panel of Figure B.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 timescale of any dynamics that are occurring. In the (fictional) case shown in Figure B.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.

⁵Depending on how accurate we can be.

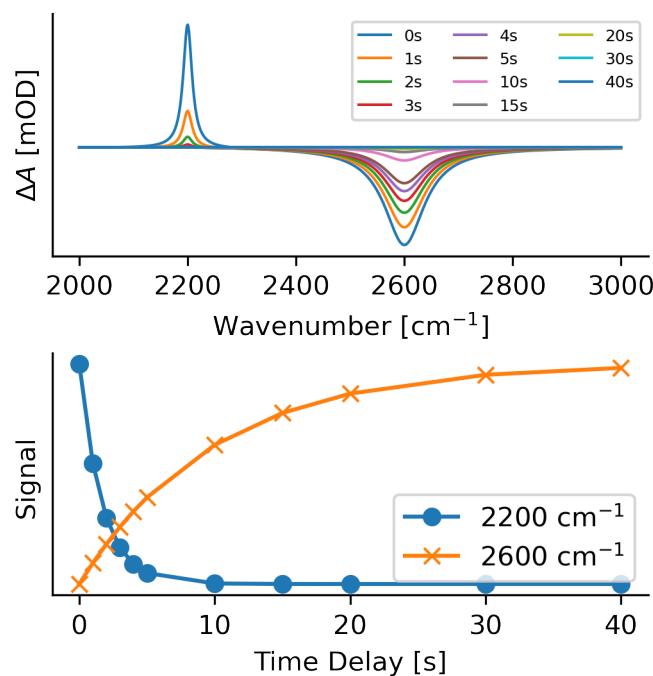


Figure B.6: Typical TAS data (simulated). Top: A series of spectra measured as a function of time. Bottom: the time-evolution of the two peaks in the spectrum.

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.