Chemical Spectroscopy

John Murrell

History
Our current view of the nature of light started with the pioneering work of Newton, who in the seventeenth century showed that white light was a mixture of the rainbow colours, and these could be separated by, and combined back to white light, by a prism. Other landmarks in the field were experiments by Young to show the wave nature of light by diffraction and interference patterns. The work of Faraday, Maxwell, and others showed that visible light was part of an electromagnetic spectrum of radiation with a continuum of frequencies (or wavelengths). Later, Einstein argued that Planck’s interpretation of black-body radiation through the quantization of energy could only be accepted if light was also quantized; its basic component, the photon, was not divisible. This recovered aspects of the earlier corpuscular theory of light favored by Newton.

Einstein also made important contributions to our understanding of the absorption and emission of light by matter, and this led to the development of lasers. Lasers have allowed us to probe the time domain of spectroscopy as well as the frequency domain.

Much of our current detailed knowledge about the microscopic nature of matter (e.g. very precise knowledge about molecular shapes) is derived from the interaction of light and matter. Spectroscopy was a key technique by which theories of the chemical bond were developed, and in recent years has taken forward our understanding of the mechanism of chemical reactions.

Wave form
Faraday’s (and others) experiments in the 19th century showed that light had associated electrical and magnetic fields, and it is these fields that interact with the charged particles (the electrons and protons) of atoms and molecules, and lead to absorption, emission, or scattering of light. In the wave picture of light these fields oscillate in space and time as traveling transverse harmonic waves. For a snapshot in time the electric field, E, oscillates in a direction perpendicular to the direction of travel (x) like

\[ E(x) = E_0 \sin \frac{2\pi(x+x_0)}{\lambda} \]

(1)

where \( E_0 \) is the maximum amplitude and \( x_0 \) is an arbitrary origin (called the phase). If we go from x to \( x+\lambda \), the wave repeats itself; \( \lambda \) is the wavelength. Monochromatic
light is light with a single wavelength. The magnetic component of the light has a similar mathematical form to (1).

Light travels forward at a velocity that in a vacuum is independent of the wavelength. This velocity, \( c = 2.998 \times 10^8 \text{m/s} \), is a fundamental constant of nature. For the development of Einstein’s theory of relativity it was important that not only had light a finite velocity, but that this was independent of the velocity of the source.

If the wave represented by (1) travels forward with a velocity \( c \), then after a time \( \tau = \frac{\lambda}{c} \) the pattern will repeat itself, or, if we fix our attention at a particular value of \( x \), the electric field will go up and down like a sine wave with frequency \( \nu = \frac{1}{\tau} \) (units Hertz (Hz) = \( \text{s}^{-1} \)). Thus frequency and wavelength are related by \( c = \nu \lambda \). Another commonly used measure in spectroscopy is the wavenumber \( \tilde{\nu} = \frac{1}{\lambda} \).

If the electric field oscillates in one plane the light is called plane polarized; in this case the magnetic field is also represented by a harmonic wave which oscillates in a plane perpendicular to the plane of E. Ordinary light is not plane polarized as it has electric fields oscillating in all planes perpendicular to the direction of travel, but plane - polarized light can be produced by passing ordinary light through certain crystals or other optical devices.

### The Electromagnetic Spectrum

The whole electromagnetic spectrum used by chemists spans a wavelength range of \( 10^2 \) to \( 10^{-10} \text{m} \), and it is therefore not surprising to find many different units in common use. The most common are: angstrom (Å)=\( 10^{-10} \text{m} \), nanometre (nm)= \( 10^{-9} \text{m} \), micron (µ or µm) = \( 10^{-6} \text{m} \). There is a similar choice of frequency units: terahertz (THz)=\( 10^{12} \text{Hz} \), gigahertz (GHz) = \( 10^9 \text{Hz} \), megahertz (MHz)= \( 10^6 \text{Hz} \), kilohertz (kHz) = \( 10^3 \text{Hz} \). The most common unit for wavenumber is \( \text{cm}^{-1} \).

Visible light has a small wavelength range (red = 700nm to violet = 400nm). The usable electromagnetic spectrum for chemical purposes is normally divided into sections by multiplying factors (for frequency) roughly \( 10^2 \) wide. Starting from the low-frequency end these are as follows: radio (the nuclear magnetic resonance (nmr) region); microwave (electron spin resonance (esr), and rotational spectroscopy); infra-red ((ir), vibrational spectroscopy); visible and ultra-violet ((uv), electronic spectroscopy); and X-ray (inner-shell electron spectroscopy). The reason for this division is that different devices are used for producing and detecting radiation in each region; think of detecting radio waves and visible light, for example. The important point for chemistry is that each region gives different types of information relevant to molecular structure.

### Photon Energy

Einstein’s first important contribution to spectroscopy was the photoelectron effect. By analyzing the numbers and energies of electrons emitted from a metal surface by light he showed that light consists of photons whose energy is proportional to their
frequency according to the equation $E = h\nu$, where $h$ is Planck’s constant. Photoelectron spectroscopy was revived in the 1960s and made accessible to chemists; it confirmed important aspects of the molecular orbital theory of chemical bonding.

A molecule absorbing a photon of frequency $\nu$ will increase its energy by $h\nu$; likewise it will lose this energy if a photon is emitted. If we take a typical photon of visible light, $\lambda = 500\text{nm}$ or $\nu = 6\times10^{14}\text{Hz}$, then the photon energy is $4\times10^{-19}\text{J}$ (2.5eV), or for a mole of photons (multiply by Avogadro’s number), 240kJmole$^{-1}$. This is about half the dissociation energy of a strong chemical bond. Only weak chemical bonds can be broken by visible light unless more than one photon is absorbed at the same time (a less probable event, but one that occurs with strong laser sources). The energies of radio wave photons are smaller by a factor of $10^6$ than visible light photons, and short X-ray photons have energies greater by $10^3$. Photon absorption can give energies to a molecule that are either negligible or enormous in comparison with the energy of a chemical bond.

**Absorption and Emission Probabilities**

The probability of a photon being absorbed on impact with a molecule varies widely. The underlying principle we deal with later, but we note here that radio waves have a very small probability of absorption (we can listen to our radio indoors), whereas uv light is strongly absorbed by most molecules. Absorption by atmospheric molecules is very important in shielding us from sun’s uv radiation. Molecules like H$_2$O, and CO$_2$ absorb more strongly in the infra red than in the visible region, and contribute to the so-called greenhouse effect by absorbing ir radiation reflected from the earth’s surface.

There is also a wide range of probabilities that a molecule in a high energy (excited) state will emit a photon and move to a lower energy state; a high probability will give a short lifetime for an excited state, a low probability will give long lifetime. If molecules are raised to an excited state by absorption of light, then a steady state can be reached in which there is a balance between absorption and emission. If, when the light source is switched off, the emission cuts off almost instantaneously, the emitted light is called fluorescence (a typical lifetime for the excited state is $10^{-9}$s). If the emission lasts for more than a few seconds it is called phosphorescence.

The probabilities of transitions between different energy states in absorption, emission, or scattering are governed by rules, which are called selection rules. Some of these are very general, and some are specific to the type of spectroscopy or to the type of atom or molecule. These will be touched on when we discuss particular cases.

Einstein’s second contribution to spectroscopy was to show the relationship between the probabilities of absorption and emission, and to show that there were two processes for emission called spontaneous, and stimulated. Stimulated emission requires the presence of an external radiation field of the same frequency as the
emitted light, spontaneous emission does not; stimulated emission is the basis of laser action.

Einstein showed that the ratio of the probabilities of spontaneous to stimulated emission had a frequency dependence proportional to $\nu^3$, so that spontaneous emission is usually dominant at high frequencies (e.g., in the UV) and stimulated is dominant at very low frequencies (e.g., in the radio region).

We can create a time variation in a light source, either by a simple method such as chopping the beam with a rotating disc, or by using a spark source. We can also use laser technology to produce light pulses of very short and precise duration, say down to a few femto seconds ($10^{-15}$ s). The development of intense spark sources in the 1950s, called flash photolysis, enabled the spectroscopic study of molecules that had a very short existence (they were unstable species like free radicals). The later use of lasers showed how energy could be transformed from one form to another, or could be transferred within a molecule from one bond to another.

The interaction of light and matter is predominantly through the electric vector of the light. The exceptions to this are for magnetic resonance spectroscopy (nmr, esr) where it is due to the interaction of the magnetic field of the light with the magnetic moments of electrons or nuclei. Also, the phenomenon of optical rotation, which is the rotation of the plane of polarized light by chiral molecules or crystals, needs both electrical and magnetic interactions; non-chiral systems have either a zero electric or magnetic interaction for all spectroscopic transitions.

**Absorption Spectroscopy**

The traditional way of studying absorption spectroscopy is to vary the frequency or wavelength of an incident beam by rotating a prism or grating, and recording the frequencies that are absorbed. Light passing through a sample is absorbed by an amount depending on the path length of the sample ($l$), and the concentration of the absorber ($c$), according to the formula

$$I = I_0 \exp(-\alpha l c)$$

(2)

where $I_0$ is the incident intensity and $I$ the emerging intensity. Instruments are usually designed so that the incident beam is split into two so that one beam can be a reference, and both $I$ and $I_0$ are measured together. Expression 2 is called the Beer-Lambert law, and $\alpha$ is the absorption coefficient. A commonly used unit, which is proportional to $\alpha$, is the extinction coefficient, $\varepsilon$. This is based on formula (2), but with the base 10 instead of the base e; it has units $\varepsilon/cm^\text{-1}mole^\text{-1}dm^\text{3}$. A plot of $\varepsilon$ or $\alpha$ against $\nu$ or $\lambda$ is called an absorption spectrum.
A more modern technique is called Fourier Transform (FT) spectroscopy. For this the sample is illuminated by light covering the whole frequency range of the source, which is pulsed (for nmr) or modulated by an interferometer (for ir). This light is absorbed in certain frequency regions, as in the conventional method, and one then looks at either the time dependence of the total absorption signal, or the decay pattern of the emitted radiation, and picks out the harmonic (sine-wave) components of this according to a mathematical procedure known as Fourier analysis. These Fourier components are the frequencies at which the light is absorbed. This type of spectroscopy is much more sensitive than the conventional swept frequency spectroscopy and is widely used for both nmr and ir spectroscopy; for ir it is particularly good for detecting low frequency bands.

**Light Scattering**

As well as absorption or emission, light can just be scattered by molecules; the same number of photons are in the incident and scattered beams. Scattering without a change of frequency is called Rayleigh scattering, and this is the basis of useful techniques to study the size of small particles such as polymers. The scattered light can also change its frequency and this is called Raman scattering. If the frequency is lowered, from $\nu$ to $\nu'$, then the molecules will take up an energy equal to $h(\nu - \nu')$. If the absorbing material contains molecules in excited states then $\nu$ can be greater than $\nu'$ and the excited molecules will lose energy.

Raman spectroscopy is important in chemistry because the probabilities of a Raman transition are different from those of absorption and emission. For example, a diatomic molecule like N$_2$ cannot absorb ir radiation but it can exhibit Raman scattering, and from this the frequency of vibration of the N - N bond can be determined. A comparison of the ir and Raman spectrum of a molecule gives valuable information about its symmetry.

**Molecular Energies**

Quantum theory shows that molecules exist in discrete energy states, and it is this that leads to discrete bands in an absorption spectrum, discrete frequencies of emission, or discrete frequency changes in Raman spectroscopy. The word discrete needs some qualification; bands are not totally sharp (have zero width) for many reasons, both instrumental (the resolution of the spectrometer), and from the motion of the molecules. The important point is that an absorption or emission spectrum has peaks and troughs. Take the visible spectrum, for example, the phenomenon of colour arises because some frequencies are absorbed or reflected more strongly than others (eg, absorbing blue light from white light makes the transmitted light red).
The essential point about absorption and emission of light is that energy must be conserved. Thus if a molecule is in a state of energy $E_1$, it can only absorb a photon of frequency $\nu$ if there is a higher energy state available of energy $E_2$ such that

$$h\nu = E_2 - E_1$$  \hspace{1cm} (3)

Conversely, in emission, if a molecule has energy $E_2$ it can emit a photon of frequency $\nu$ only if there is an energy state $E_1$ available, satisfying the same equation. This equation is called the Planck - Einstein equation, and is the basis for the quantum mechanical interpretation of spectroscopy. Quantum theory leads to discrete energy states; the gaps between these states can be linked to the frequencies of spectroscopy by equation (3).

**The Energy Ladders**

From quantum theory we can deduce that the total energy of a molecule can be subdivided into a number of distinct parts; this division is approximate but good enough to interpret spectroscopic phenomena for most molecules. It is important to realize that there is a hierarchy for these energy components. We can think of energy ladders (the rungs indicating the discrete energies) and different components of the energy have ladders with different patterns of rungs. The hierarchy is such that we start with the ladder whose rungs are most widely separated and move to ladders with smaller gaps. A small-gap ladder rests on one of the rungs of the next higher gap ladder (big fleas have little fleas on their backs to bite ‘em, little fleas have lesser fleas, and so on ad infinitum).

**Electronic Energies**

The top of the energy hierarchy is the electronic energy ladder. Electronic energies are generally more widely spaced than the energies associated with the dynamics of the nuclei because electrons are much lighter than nuclei (the ratio of the proton to the electron mass is 1836). This separation of electron and nuclear energies is known as the Born - Oppenheimer approximation.

The patterns of rungs on the electronic ladder are often quite simple for atoms, as will be seen later, but they are not generally simple for molecules. However, one common feature is that they always close up towards a limit, which is the ionization potential. This is the minimum energy required to eject an electron; beyond this the energies are continuous ie, there are no energy gaps.

Stable molecules, typically those that we can keep in bottles, have a large energy gap between the lowest energy electronic state (the ground state) and the next highest state on the electronic ladder. If this gap is less than about 1eV the molecule is likely
to be chemically unstable; if it is less than $3\text{eV}$ the molecules will be coloured (absorb in the visible region of the spectrum); if it is greater than $6\text{eV}$ the molecule is likely to be very unreactive (eg hexane). Transitions from the ground state to excited states generally give absorption bands in the visible or uv regions of the spectrum. Conversely, the reverse process gives emission bands in these regions. However, transitions involving inner-shell electrons involve much greater energies and give absorption or emission bands in the X-Ray region.

**Vibrational and Rotational Energies**

The energy levels of a molecule which arise from the dynamics of its nuclei can usually be separated into two ladders, vibrations (the larger spacing) and rotations (the smaller spacing). The exception is for a few floppy molecules for which no such separation is possible. To picture the vibrations and rotations of molecules we can think of a set of masses (the nuclei) joined by springs (the bonds).

Rotational energies depend on the equilibrium geometry of the molecule and the atomic masses, the connection between energies and frequencies being made through quantities called the moments of inertia of the rotating body. If an atomic mass $m_i$ is at distance $r_i$ from an axis, this contributes $m_i r_i^2$ to the moment of inertia about that axis, the total moment being obtained by summing all such terms. A molecule generally has three moments of inertia (with respect to a set of perpendicular axes going through the centre of mass), and these can be deduced from the rotational spectrum, although the analysis is simple only for linear molecules. Pure rotational spectroscopy (that is when there is no accompanying change in electronic or vibrational energy) gives frequency changes in the microwave region.

Vibrational energy levels depend on the geometry of the molecule, the atomic masses, and the force constants for bond stretching and angle bending. The force constant of a spring is the force required to extend the spring by a small amount, divided by the extension. If we use the notation of calculus and concentrate attention on the potential energy of the system, then the force constant is $\frac{d^2V}{ds^2}$, where $V$ is the potential energy of the spring and $s$ is the extension. For molecules we have force constants for changes in bond lengths and changes in bond angles.

Molecules having many atoms and bonds have many vibrational energy ladders, the precise number and patterns we will see later. Changes in vibrational energies without changing an electronic energy give rise to spectra in the IR region.

When we excite a molecule to a higher electronic state (by visible or UV radiation), we may simultaneously change the vibrational and rotational states, and these changes will give fine structure to the electronic band although this is not necessarily resolved. There can likewise be vibrational and rotational structure on an
electronic emission band. Similarly, if we excite vibrations by ir radiation we may change the rotational level and see rotational fine structure (only usually resolved for small molecules in the gas phase). An important point to make is that the geometry of the molecule and the strength of its bonds depends on what electronic state it is in, so that different electron states have different vibrational and rotational ladders (different in both the patterns and separations of the rungs). Thus molecular spectroscopy (electronic, vibrational, and rotational), contains a vast amount of information which reveals the details of how electrons and nuclei interact in the molecule.

**Magnetic Resonance**

Electrons, and many nuclei possess magnetic moments and these can interact with an external magnetic field giving quantized energy levels whose separation is proportional to the strength of the magnetic field. For both the electron and the proton only two energy states are possible which we interpret qualitatively as the magnetic moments lining up parallel or anti-parallel (opposed to) the field. We attribute the magnetic moments to the spin of the electron or proton, and assign quantum numbers with the two spin states of 1/2 and -1/2. Magnetic resonance spectroscopy is due to a transition between these two states stimulated by the magnetic component of the radiation. The spectrum is usually obtained by having a fixed frequency and varying the magnetic field until a resonance condition is obtained (the energy gap is equal to $h\nu$).

The electrons in an atom or molecule couple together to give a total electron magnetic moment. For most stable molecules the electrons are spin-paired (for every +1/2 electron there is a −1/2 electron) and this gives a total magnetic moment of zero. Free radicals have an odd number of electrons so there is always one unpaired electron spin and a net magnetic moment. Typical magnetic fields used to study free radicals are about 1T (Tesla = 10000 Gauss). The magnetic moment of the electron is 9.27x10^{-24} JT^{-1}, and this gives an energy gap that is spanned by a photon of frequency 14GHz, which is in the microwave region. The spectroscopy is called electron spin resonance (esr), or electron paramagnetic resonance (epr). A molecule with more than one unpaired electron has a spin quantum number $S$ that is an integer or a half integer, and such a spin state has $2S+1$ components that will separate in a magnetic field and can also give an esr spectrum.

The hydrogen atom has a single proton in its nucleus but other atoms have several protons and neutrons (these also have a spin) and, as for electrons, their spins couple together to give a net spin for the nucleus. This is described by a quantum number $I$ which has $2I+1$ components; $I$ can have the same values as $S$ for the electron spin. The nuclear spin quantum numbers for some of the nuclei (including important isotopes) of the first row atoms are as follows:
The proton magnetic moment is smaller than that of the electron moment by a factor of 700, so that with the same strength of magnetic field the transitions occur in the radio region. There are advantages in using as large a magnetic field as possible and 25T is common. The spectroscopy is called nuclear magnetic resonance (nmr).

Nuclear spin transitions can appear as fine structure in an esr spectrum, and in a molecule with several different magnetic nuclei there are several nmr energy ladders; in both forms of spectroscopy the frequency pattern can be quite complicated, but it contains a wealth of information.

**Atomic spectroscopy**

Atomic spectroscopy was first seriously studied in the latter part of the 19th century, and was the main plank in the foundations of quantum theory. The key step in spectral analysis was the realization that the frequencies of absorbed or emitted light could be expressed as the difference of two quantities. In 1885 Balmer made the inspired observation that the frequencies of lines in the emission spectrum of the hydrogen atom could be fitted to the formula

$$\nu = R c \left( \left( \frac{1}{n_1} \right)^2 - \left( \frac{1}{n_2} \right)^2 \right)$$

where $n_1$ and $n_2$ are integers. The frequencies of the four lines known at that time were obtained by taking $n_1=2$ and $n_2=3,4,5,6$. The value of $R$, which is called the Rydberg constant, is $109678 \text{cm}^{-1}$.

The first successful explanation of expression (4) was by Bohr in 1913. He solved the equations of classical mechanics for an electron orbiting a proton but imposed a constraint that only orbits for which the angular momentum was quantized to be integer multiples of $\hbar/2\pi$, were allowed. He found that the energies of these orbits, relative to the ionization limit as zero, were given by the formula

$$E_n = - \frac{R \hbar c}{n^2}$$

From Bohr’s theory $R$ was given by an expression involving the mass and charge of the electron, and its value agreed exactly with the spectroscopic value for the Rydberg constant.
Bohr theory worked perfectly for the energy levels of the hydrogen atom (also other one-electron systems like He\('\)), but it was, at best, only qualitatively successful for atoms having more than one electron. The full explanation of atomic spectroscopy only came after the development of modern quantum theory by Schrödinger and others in the 1920s.

Schrödinger derived an equation for the wave nature of the electron (which had been postulated in 1924 by de Broglie). It is a differential equation whose solution gives the quantized energy levels of the system and the wave functions associated with those levels.

The solutions of the Schrödinger equation for the electron in the hydrogen atom are called atomic orbitals, and these are identified by labels that are called quantum numbers, (n,l,m). The first of these describes the wave features of the orbital with respect to its distance from the nucleus (the number of wave oscillations increases as n increases). The energy of the orbital also depends on n; the same expression (5) is obtained from Bohr and Schrödinger theory. The value of n can be any positive integer, n=1 being the lowest energy orbital of the atom.

The quantum numbers l and m are connected with the wave nature of the orbital in respect of its angular variation around the nucleus. They are also connected with the angular momentum of the electron in the orbital. The number l can take the value 0, 1, 2, ..., up to n-1. Thus if n=1 the only value allowed is l=0; if n=2, then there are two values l=0, and l=1; if n=3, then l=0, 1, and 2. For historical reasons, which originated in the nature of atomic spectral lines, symbols are used to distinguish orbitals on the basis of their l values, as follows:

\[
\begin{align*}
l &= 0, 1, 2, 3, \ldots \\
\text{spectroscopic label} &= s, p, d, f, \ldots
\end{align*}
\]

Combining the information we have about the n and l quantum numbers, we can identify the orbitals of the hydrogen atom in an obvious way as follows: 1s, 2s, 2p, 3s, 3p, 3d, ... etc.

For an atom with more than one electron there is no exact analytic solution of the Schrödinger equation, although very accurate numerical solutions can be obtained. However, it is still useful to define atomic orbitals for many-electron atoms as the wave functions of an electron moving under the influence of the attractive nuclear potential and the average repulsive potential of all the other electrons, and these orbitals are given the same spectroscopic labels as those of the hydrogen atom. The main difference between one-electron atoms and many-electron atoms is that the energy of an orbital depends only on n for the former, but on both n and l for the latter; for a given value of n, energy increases as l increases.
Lastly, the m quantum number can have $2l+1$ values, in the series

$$m = l, l-1, l-2, \ldots, -l$$

Thus s orbitals come in sets of 1 (only $m = 0$), p orbitals come in sets of 3 ($m = 1, 0, -1$), d orbitals come in sets of 5, etc. Colloquially we can say that the m quantum number identifies the direction of an orbital in space, so that if there are no external applied fields (e.g. electric or magnetic), then all orbitals in the set of a given $n$ and $l$ have the same energy; the orbitals are said to be degenerate.

Atomic spectroscopy is governed by a number of selection rules, some that are rigorous and some that are approximate. An important rule is that for allowed transitions between orbitals, in either absorption or emission, the $l$ quantum number must change by +1 or -1. Thus an electron in an s orbital can only jump to a p orbital; an electron in a p orbital can jump to an s or a d orbital etc.

Atoms with more than one electron can have several states for a given orbital occupation, these states differing in the way that the electron spins and orbital angular momenta couple together. These couplings give rise to various types of splittings in the atomic spectral lines. Thus an electron transition from a p orbital to a d orbital (say) gives several spectral lines, some well separated from one another and some very close. There are important selection rules describing the angular momenta changes that can occur in many-electron spectroscopy.

**Molecular Electronic Spectroscopy**

From molecular electronic spectroscopy we obtain information about the nature of the chemical bond and, in particular, whether electrons are tightly bound in the molecule or weakly bound. Generally speaking if a molecule absorbs in the visible or near uv it has some weakly bound electrons, and these are often associated with interesting aspects of chemical reactivity. For example, the first absorption band of benzene is at 260nm, and that of cyclohexane is at 170nm; undoubtedly benzene has more interesting chemistry than cyclohexane.

One cannot discuss molecular electronic spectroscopy in isolation from the theory of the chemical bond, so there are only a few generalisations to be made here. There are broadly two classes of molecule that show low energy electronic transitions, and these are transition metal ions and their complexes, and unsaturated organic molecules. The reasons are quite different in the two cases.

Transition metals are elements in the periodic table that have incomplete d shells. If we take Mn$^{2+}$, for example, then this ion has four outer electrons that can be arranged in the five 3d orbitals with different spins in 210 ways. Many of these arrangements
have the same energy, but it can be shown that there are 16 different energy states for
the ion in the gas phase, and even more if the ion is surrounded by solvent molecules
or attached ligands. As many of these states have very similar energies, it is not
surprising that there are several that can give absorption bands in the visible region
of the spectrum.

The most important use of electronic spectra in organic chemistry is to identify
molecules with conjugated unsaturated bonds. In a planar molecule like benzene, the
most weakly bound electrons are those associated with the $\pi$ orbitals; these are
orbitals which change sign on reflection in the molecular plane. They are weakly
bound because the overlap of $2p\pi$ atomic orbitals on adjacent carbon atoms is
relatively small.

Ethene, the simplest molecule of this kind, has its first absorption band with a
maximum at 175nm, just outside the accessible range of most standard
spectrometers, and in molecules with more than one C - C double bond which are
separated (not on adjacent atoms) the first absorption band is in the same region.
However, if the double bonds are on neighbouring atoms (we say they are
conjugated), as in benzene or butadiene, then the first absorption band comes down
into the accessible region. For example, if one looks at the wavelengths of the linear
all trans polyenes, we see that the longer the conjugated chain the longer the
wavelength of the first band

\[
\text{Number of conjugated bonds} = \begin{array}{cccccc}
2 & 3 & 4 & 5 & 6 \\
\lambda /\text{nm} = & 217 & 268 & 304 & 334 & 364 \\
\end{array}
\]

$\beta$-carotene, the yellow colour in carrots, has eleven conjugated double bonds and $\lambda =
452\text{nm}$. The theory of $\pi$ electron molecules is well developed and in its simplest form
is associated with the so-called Huckel model. From such spectra one can deduce a
great deal of useful structural information, such as whether conjugated bonds possess
cis or trans arrangements, and on the nature and positions of any substituent groups.

**Rotational spectra**

Rotational spectroscopy is not a widely used analytical tool because it is largely
confined to molecules in the gas phase, and generally small molecules at that; in
solution molecules do not rotate freely; bump around would be a better description.
In solids they do not rotate at all except for a few special cases. Rotational
spectroscopy is largely the interest of specialist spectroscopists but it is important in
giving very accurate data about molecular bond angles and bond lengths.
The rotational energies of molecules depend on their moments of inertia. If we measure distances from the centre of mass, then the moment of inertia about an axis through the center of mass is given by

$$\sum m_i r_i^2$$  \hspace{1cm} (6)

the summation being over all atoms of mass $m_i$ where $r_i$ is the perpendicular distance of the atom from the axis. With this definition the moment of inertia depends on the choice of axis. Three so-called principal moments of inertia can be found for three perpendicular axes, and for molecules with high symmetry the principal axes of inertia coincide with the symmetry axes of the molecule (there are recipes to find the principal moments for low symmetry molecules).

Molecules having tetrahedral or octahedral symmetry have three equal moments of inertia and are called spherical tops. If two moments of inertia are equal and one different, then the molecule is a symmetric top (ammonia is an example of this). For a linear molecule (the most important being diatomic molecules) the moment of inertia about the molecular axis is zero (all $r_i$ about this axis are zero) and the other two are equal.

For a diatomic molecule the moment of inertia is equal to

$$I = \mu r^2$$  \hspace{1cm} (7)

where $r$ is the bond length and $\mu$, the reduced mass, is given by

$$\mu = m_A m_B / (m_A + m_B)$$  \hspace{1cm} (8)

For spherical and symmetric tops, and linear molecules the rotational energy ladders are relatively simple. In other cases, when all three moments of inertia have different values, the rotational energy pattern can be very complicated.

For a linear molecule the rotational energy levels follow the recipe

$$E_J = B J (J + 1)$$  \hspace{1cm} (9)

where $B$ (called the B-value) is proportional to the reciprocal of the moment of inertia, and the quantum number $J$ is zero or an integer. For a diatomic molecule the B-value determines the bond length. Note that the rungs on the rotational energy ladder get wider apart as $J$ increases.

Transitions between the rotational levels of a diatomic molecule can give absorption or emission of radiation in the microwave region but only if the molecule has a
dipole moment (homonuclear diatomics give no bands). In addition there is a selection rule that allowed bands require $\Delta J = +1$ or $-1$. Thus we can go from $J=0$ to $J=1$ (energy $2B$), or $J=1$ to $J=2$ (energy $4B$) and so on, giving a series of bands separated by $2B$.

**Vibrational energies**

If there are $N$ atoms in a molecule then there are $3N-6$ vibrational energy ladders. The reason for this is that the position of each atom is specified by 3 coordinates (so $3N$ in total), but in describing the vibrations we can forget about the position of the whole structure in space (3 coordinates for the centre of mass) and the overall orientation (3 rotational coordinates). Linear molecules are a special case as their orientation needs only 2 coordinates, so they have $3N-5$ vibrational ladders.

We associate these ladders with $3N-6(5)$ normal modes of vibration. A normal mode is a vibration of the whole structure in which all atoms vibrate with the same frequency, which is the frequency of the mode. If we apply light of frequency $\nu$ it can be absorbed by a vibrational mode of that frequency.

A diatomic molecule ($N=2$) has only one mode of vibration, which is associated with the stretching and contraction of the bond. For small movements of the nuclei (low vibrational energies) the increase in potential energy on changing the bond length from its equilibrium position is proportional to the square of the change. The potential energy curve is a parabola with its minimum at the equilibrium distance; this is called the harmonic approximation. The curvature of the parabola is called the force constant $(d^2V/dr^2) = k$. The vibrational energies depend on $k$, and the atomic masses, and a quantum number $n$ which can be $0,1,2,3,…$ etc. The rungs on the vibrational energy ladder are equally spaced according to the formula

$$E_n = (n + \frac{1}{2})\hbar \nu_0 \quad (10)$$

where

$$\nu_0 = (1/2\pi)(k/\mu)^{1/2} \quad (11)$$

and $\mu$ is the reduced mass, defined by expression (8)

Expression (11) for $\nu_0$ is the same as the classical vibration frequency of a spring of force constant $k$ with an attached mass $\mu$. Notice that the lowest energy state, $n=0$, has an energy $(1/2)\hbar \nu_0$, which is called the zero point energy.

Every vibrational mode of a molecule has an energy ladder with rungs defined by (10) and (11), but with different values for $k$ and $\mu$, and hence $\nu_0$; these quantities are determined by the atomic masses and equilibrium geometry of the molecule. The
procedure for finding normal mode frequencies is straightforward, but not appropriate for a description here.

The overall vibrational state of a molecule is specified by a set of 3N-6(5) quantum numbers, \( n_1, n_2, n_3, \) etc, one for each mode, and the total vibrational energy is the sum of the mode energies. Thus the ground state can be designated \((0,0,0,\ldots)\), each mode being in its lowest energy state, and this has a total energy which is the sum of the zero point energies for each mode. If one mode is excited this gives a state classified by a symbol such as \((0,1,0,\ldots)\), and transitions from the ground state to this are stimulated by ir radiation with the appropriate frequency \( \nu_0 \). This gives rise to what is called a fundamental absorption band in the spectrum. These are the most important vibrational bands because they appear with greatest intensity. Exciting a mode by two or more quanta (eg to give a state like \((0,2,0,\ldots)\)) gives rise to overtone bands, and exciting more than one mode (eg to a state like \((1,1,0,\ldots)\)) gives combination bands. Both of these are generally much weaker (and forbidden in the harmonic approximation).

Although normal modes can, in principle, involve all the atoms in a molecule, in practice they are often localized in bonds or over a few atoms so that we can assign many bands in a spectrum to the stretching of individual bonds. For example, stretching C-H bonds gives bands in the region of 3000 cm\(^{-1}\), and stretching C = O bonds gives bands around 1700 cm\(^{-1}\); in both cases the spread of frequencies depends on the other atoms in the molecule. At lower frequencies other bands can be assigned to angle bending. However, in a molecule like benzene, the C-C stretches are indeed spread over all carbon atoms and span in this case the wavenumber range 1000-1600 cm\(^{-1}\).

Vibrational transitions are subject to a number of very specific selection rules for the absorption or emission of light, and these depend on the symmetry of the molecule. It follows that one can deduce certain aspects of molecular symmetry from the appearance of an ir spectrum.

The underlying principle behind ir selection rules is that the vibrational mode must change the dipole moment of the molecule. Take the simplest case of a homonuclear diatomic molecule like N\(_2\); because the two atoms are equivalent they cannot have any net charge and the molecule has no dipole moment. As this is true for all distances between the nuclei, there can be no dipole moment change for the N-N stretching vibration; homonuclear diatomic molecules have no ir spectra.

If a polyatomic molecule has no dipole moment at its equilibrium configuration then some of its modes of vibration will maintain this zero dipole and these will not give ir bands; others will lower the symmetry and produce a dipole and these will give ir bands. Take CO\(_2\), for example. This is a linear molecule with two equal C-O bonds,
and hence in its equilibrium position it has no dipole moment (the two oxygen atoms must have the same net charge, and their contributions to the total dipole cancel). If the two bonds stretch and contract in phase, (we call this the symmetric stretch), the symmetry is maintained and at no time in the vibration is a dipole moment produced. The symmetric stretch vibration does not therefore give a band in the ir spectrum. We say the symmetric stretch mode is ir inactive. However, if one bond stretches as the other is compressed (ie the two bonds are stretching and compressing out of phase) then the two bonds have different dipoles and will not cancel; there will be a net dipole moment for the molecule along the direction of the O-C-O axis except at the equilibrium configuration. This so-called antisymmetric stretch is ir active and gives a band in the spectrum at 2349cm\(^{-1}\).

There is a third mode of vibration of CO\(_2\), which is the bending of the molecule and as this also produces a dipole (perpendicular to the O-C-O axis) the mode is also ir active; this gives a band at 667cm\(^{-1}\). Bending modes of linear molecules occur in equivalent pairs, corresponding to bending in two perpendicular planes. Thus CO\(_2\) (N=3, 3N-5=4) has four normal modes; two stretches (one ir active and one non active), and a doubly-degenerate active bend.

The symmetric stretch of CO\(_2\) can be seen in its Raman spectrum at 1388cm\(^{-1}\). There is a very useful rule for molecules which have a centre of symmetry (molecules which have a centre such that if there is a nucleus with coordinates at (x,y,z) then there is an identical nucleus at (-x,-y,-z)); any mode which is ir active cannot be Raman active, and vice versa.

For a molecule like H\(_2\)O which has a dipole moment, all vibrational modes change that dipole and hence all modes are ir active (and also Raman active). Thus H\(_2\)O has (N=3,3N-6=3) three fundamental bands in its ir spectrum, a symmetric stretch (3652cm\(^{-1}\)), an antisymmetric streetch (3755cm\(^{-1}\)), and a bending mode (1595cm\(^{-1}\)).

**Nuclear Magnetic Resonance**

We deal only with the nmr of spin I=1/2 nuclei as these are the simplest and the most important for analytical studies. We give examples only for protons but the same principles apply to other spin 1/2 nuclei like F, and P, and also to the 1% natural abundance of \(^{13}\)C. A single spin 1/2 nucleus in a uniform magnetic field B has two energy states

\[
E_2 = \gamma \hbar B/2 \\
E_1 = -\gamma \hbar B/2
\]  

where \(\gamma\) is called the magnetogyric ratio (\(\gamma \hbar/2\) is the magnetic moment of the nucleus). Following the Planck-Einstein energy conservation rule (3), transitions
between these two states will be stimulated by light of frequency $\nu = \gamma B/2\pi$; this is called the Larmor frequency. Each isolated nucleus would absorb at a frequency characteristic of its own magnetogyric ratio. However, nuclei in molecules are not isolated as they are surrounded by electrons, which in the presence of an applied magnetic field will circulate, and these circulations give rise to their own magnetic fields. Thus the actual magnetic field experienced by a nucleus is made up of the external field $B_0$ and the net field from electron circulation. These net fields depend on the electron environment of the nucleus in the molecule; not all protons experience the same net field and therefore not all protons have the same Larmor frequency. However, chemically equivalent protons (eg the six protons in benzene) do have the same frequency.

The difference between the external magnetic field $B_0$ and the field experienced by a nucleus is represented by

$$B = B_0 (1 - \sigma)$$  \hspace{1cm} (15)

where $\sigma$ is called the chemical shift; it is a dimensionless parameter of the order of $10^{-6}$. It is standard practice to record chemical shifts in parts per million (ppm) with reference to a standard which for protons is usually the signal from TMS (Si(CH$_3$)$_4$). Thus if $\nu_{\text{ref}}$ is the TMS frequency and $\nu$ the frequency being measured,

$$\delta = 10^6 (\nu - \nu_{\text{ref}})/\nu_{\text{ref}}$$  \hspace{1cm} (16)

where $\delta$ is related to $\sigma$ by

$$\delta = 10^6 (\sigma_{\text{ref}} - \sigma)$$  \hspace{1cm} (17)

(neglect $\sigma_{\text{ref}}$ compared with 1 in the denominator).

The resonance condition for magnetic resonance can be met either by finding a frequency to match a fixed applied field, or by finding a field to match a fixed frequency. The latter is used in most instruments and so chemical shifts are usually described in terms such as ‘low-field’, meaning that one needs a low external field to obtain resonance (the protons are substantially deshielded relative to TMS), or ‘high-field’ (there is heavy shielding by the electrons); in practice this means a signal close to that of TMS as this is on the high field side. In the former class one has aromatic protons, which are heavily deshielded by the circulation of the $\pi$ electrons, and in the latter one has most alkyl group protons.

For a molecule fixed in its orientation with respect to the external magnetic field the chemical shift depends on the orientation, and if all orientations are present the nmr signal will be a broad range of frequencies; this is usually the situation for solids. However, in solution the molecules will be rotating to all orientations with respect to
the external field and the nmr signal is sharp corresponding to the rotational average of \( \sigma \) values.

Before we look at further complications, we can say that to a first approximation a proton nmr spectrum consists of one absorption band for each hydrogen atom and each of these has the same intensity (the probabilities of absorption are equal for each proton). Chemically equivalent hydrogen atoms absorb at the same frequency, so the intensity of a band is proportional to the number of hydrogen atoms of that type in the molecule. For example, in this approximation, CH\textsubscript{3}CH\textsubscript{2}OH, would have three bands with intensities in the ratios 3:2:1. However, there is an important caveat to this result; nmr is a very slow form of spectroscopy, and if protons are exchanging quickly between different chemical environments then one sees a signal with a chemical shift which is the time average of the chemical shifts of the different positions it adopts.

The matter of time resolution in spectroscopy emerges from the Heisenberg Uncertainty Principle. The normal form of this is that the product of the accuracy \( \Delta q \) to which the position of a particle can be measured multiplied by the accuracy \( \Delta p \) to which its momentum can be measured is of the order of Planck’s constant (\( \Delta q \Delta p \approx h \)). An alternative statement is that the product of the accuracy of the energy of a quantum state and its lifetime is also of the order of \( h \), and as energy is of dimension \( h \nu \), it means that \( \Delta \nu \Delta t \approx 1 \). To collapse, or average out, signals in an nmr spectrum, which are in the frequency region of \( 10^8 \)Hz, one only needs lifetimes shorter than about \( 10^{-8} \)sec, which is quite a slow exchange in molecular terms. For example, the OH proton in ethanol exchanges rapidly with the protons of any water present and its chemical shift therefore depends on the water concentration; one only sees an OH signal characteristic of ethanol alone in very dry solvents.

The first nmr measurements on molecules were made in 1945 and chemical shift patterns were soon revealed. However, improvements in the resolution of instruments quickly showed that many bands were split due to the interactions between protons attached to neighbouring atoms. The origin of this lies in spin-spin coupling; the energy to turn over a proton spin depends on the spin states of the neighbouring protons. Spin-spin coupling is measured by a quantity \( J \) called the coupling constant, whose magnitude is independent of the strength of the magnetic field.

We take as an example the molecule CHCl\textsubscript{2}CHO. The two protons have chemical shifts separated by \( \delta = 2.8 \)ppm (in a fixed frequency of 30MHz), that attached to the carbonyl group being to low field (the electronegative oxygen withdraws electrons from the neighbouring proton so there are fewer electrons to circulate in the external field). Due to spin-spin coupling the frequency for turning over the spin of this proton is less by an amount \( J/2 \) if the alkyl proton spin is initially parallel to the
external field and greater by $J/2$ if it is initially antiparallel to the field; the difference between these two signals is therefore $J$ which has been measured to be 2.9Hz. Likewise turning over the spin of the alkyl proton depends on whether the carbonyl proton is initially parallel or antiparallel to the field, and the alkyl signal is also split into two, separated also by $J$. In summary, the spectrum consists of two doublets, all four lines being about equal in intensity.

Let us look at this pattern in terms of the spin states; we use an arrow $\uparrow$ to indicate a spin magnetic moment parallel to the field, and an arrow $\downarrow$ for one antiparallel. There are four total spin states, in order of increasing energy $\uparrow\uparrow$, $\downarrow\uparrow$, $\uparrow\downarrow$, and $\downarrow\downarrow$. The four lines mentioned above arise from the transitions first to second state and third to fourth state (turning over the first spin), and first to third and second to fourth (turning over the second spin). If the coupling constant is small compared with the chemical shift difference then the four lines have equal intensity; this is called an AX system. If the coupling constant is comparable to the chemical shift difference the two central lines have greater intensity then the outer lines; this is called an AB system. As the chemical shift difference gets smaller the intensity builds up in the central lines at the expense of the outer, and when this difference is zero (an $A_2$ system), the spectrum collapses to a single line for the two chemically equivalent protons.

Let us now turn to the splitting patterns produced by groups of equivalent protons. A $\text{CH}_2$ group for example has four spin arrangements, which in the symbolism used above can be designated as follows:

$$\uparrow\uparrow \quad \uparrow\downarrow \quad \uparrow\downarrow \quad \downarrow\downarrow$$

The frequency for turning over the spin of any other proton coupled to these will depend on the spins of the $\text{CH}_2$ group in that particular molecule at that particular time, but as the two states in the middle are energetically equivalent, these give rise to the same frequency. We therefore end up with a triplet spectrum for a proton coupled to a $\text{CH}_2$ group, three peaks with intensities in the ratios 1:2:1 each separated by the coupling constant, $J$.

Let us now turn to the splitting patterns produced by groups of equivalent protons. A $\text{CH}_3$ group for example has four spin arrangements, which in the symbolism used above can be designated as follows:

$$\uparrow\uparrow\uparrow \quad (\uparrow\uparrow\downarrow \quad \uparrow\downarrow\uparrow \quad \downarrow\uparrow\uparrow) \quad (\uparrow\downarrow\downarrow \quad \downarrow\uparrow\downarrow \quad \downarrow\downarrow\uparrow \quad \downarrow\downarrow\downarrow)$$

where we have bracketed together energetically equivalent arrangements. Any proton coupled to this group will have a four line spectrum; a quartet of lines equally spaced by $J$, with intensities in the ratio 1:3:3:1. Combining the conclusions for these two cases we can see that an ethyl group $\text{C}_2\text{H}_5$ has a spectrum, consisting of a quartet (total intensity 2) from the $\text{CH}_2$ group, and a triplet (total intensity 3), from the $\text{CH}_3$
group. If the chemical shifts of the two protons are greater than J these ‘ideal’ patterns are found (called $A_3X_2$ spectra), but if the chemical shift difference is smaller than J the intensities are not ‘ideal’ and one has an $A_3B_2$ spectrum, but one whose pattern is usually clearly attributable to an ethyl group.

The intensity patterns of a proton coupled to an $H_n$ group are given by the binomial coefficients (the coefficients in the expansion of $(a+b)^n$) and are simply derived from the Pascal triangle.

Coupling constants are very sensitive to geometry. For example, in ethene derivatives cis coupling constants are about 10Hz, and trans couplings about 14Hz. They also generally get smaller as the atoms get farther apart. For benzene protons ortho values are about 12Hz, meta about 3 Hz, and para less than 1Hz. One can generally ignore coupling between protons separated by more than two carbon atoms. In conclusion, coupling constants provide very important evidence for molecular structure.

Finally, a note on esr, the magnetic resonance of free radicals which arises from the energy levels of the electron spin in a magnetic field. The coupling between electron and nuclear spins gives rise to fine structure in the esr spectra. The theory of this is very similar to that we have just described for J coupling in nmr, with the simplification that all splitting patterns conform to the ideal binomial intensities.