

J. E. Parker

# Chemistry: Quantum Mechanics and Spectroscopy I

J.E. Parker

# **Chemistry: Quantum Mechanics and Spectroscopy**

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Chemistry: Quantum Mechanics and Spectroscopy

1<sup>st</sup> edition

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# Acknowledgements

I was pleased to respond to requests to write a textbook that introduces quantum mechanics and the physical-chemistry aspects of spectroscopy. I developed and presented lectures and tutorials on quantum mechanics and spectroscopy to our first and second year Chemistry students over many years at the Chemistry Department, Heriot-Watt University, Edinburgh, Scotland. These lectures and tutorials have formed the basis for this textbook. I would like to thank the staff of Heriot-Watt University Chemistry Department for their help and thank the students who gave me valuable feedback on these lectures and tutorials. I hope this textbook will help future students with their Chemistry, Physics, Chemical Engineering, Biology or Biochemistry degrees and then in their later careers. Most of all I would like to thank my wife Jennifer for her encouragement and help over many years.

I shall be delighted to hear from readers who have comments and suggestions to make, please email me. So that I can respond in the most helpful manner I will need your full name, your University, the name of your degree and which level (year) of the degree you are studying. I hope you find this book helpful and I wish you good luck with your studies.

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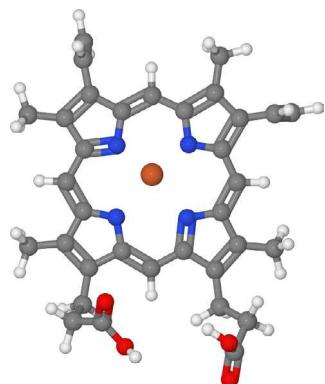
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# 1 Quantum Mechanics

Chemistry and the related subjects of physics, chemical engineering, biology and biochemistry deal with molecules, their properties, their reactions and their uses. The “molecular” world of electrons, atoms, molecules, ions, chemical bonding and chemical reaction is dominated by quantum mechanics and its consequences so that’s where we start our journey. One of our most powerful ways of exploring molecules is by using spectroscopy which is the interaction of light with molecules, so we will also need to understand some things about light. In this book I will be using the term “light” as a short-hand term to mean not just visible light but the whole spectral range of electromagnetic radiation at our disposal.

We will be using maths and drawing graphs as we explore quantum mechanics and spectroscopy and I recommend the *free* PDF books which cover the maths required in a first year chemistry, a related science or engineering degree. The three books are *Introductory*, *Intermediate* and *Advanced Maths for Chemists* (Parker 2013b), (Parker 2012) and (Parker 2013a), respectively. There are links on my website to download these books from the publisher <http://johnericparker.wordpress.com/> also you will want to look at other chemistry books for more details and I have listed some recommendations in the References. This textbook is accompanied by a companion book (Parker 2015) *Chemistry: Quantum Mechanics and Spectroscopy, Tutorial Questions and Solutions*, which should be used together with the current book, chapter by chapter.

When anyone first meets quantum mechanics they find it strange and against their everyday experience. This is because we live in a macroscopic, classical mechanics world because humans have a mass of around 60–90 kg and heights of about 1.3–2.0 m and other objects such as your car is perhaps 2–4 m long and has a mass of between 800 to 1800 kg. As we will see, quantum effects are so small as to be unmeasurable, even in principle, for macroscopic objects such as you, me and other everyday objects. Newton Laws of motion (classical mechanics) is an extremely accurate approximation to quantum mechanics for macroscopic objects.



**Figure 1.1:** haem B, O red, N blue, Fe brown, C grey, H light grey.

Molecules, however, have small masses and dimensions ranging from the hydrogen atom at  $1.674 \times 10^{-27}$  kg and a diameter of about  $1.6 \times 10^{-10}$  m; to large molecules, e.g. haem B (or heme B) at  $1.0237 \times 10^{-24}$  kg and a diameter of about  $16 \times 10^{-10}$  m. The non-SI unit angstrom (symbol Å where  $1 \text{ \AA} = 1 \times 10^{-10}$  m) is commonly used as it is of the order of the lengths of chemical bonds and atomic radii. Quantum mechanics dominates the properties of the microscopic matter such as electrons, atoms and molecules and also the interaction of matter with light and so it is of major importance for chemistry, molecular biology, and much of chemical engineering and physics.

## 1.1 The Failures of Classical Mechanics

Around 1880 it was believed: (1) that classical mechanics explained how the universe behaved; (2) that energy behaved rather like a fluid; (3) that atoms and molecules were hard-sphere objects and (4) that light was a continuous wave. Together these ideas of classical mechanics could explain all of physics, chemistry and biology.

Between about 1880 and about 1900 several experimental results showed that this complacent view was untrue and the quantum mechanics revolution was founded from 1900–1927 and is still developing. Atom, molecules and quantum mechanics then moved into centre stage with major changes in chemistry, physics and then new subjects of molecular biology and genetics. These early failures of classical mechanics and their quantum mechanics solutions are briefly covered now. Although much of what follows may appear to be “physics” to you, it is *not*, it is at the foundations of chemistry and biology! It is central to chemistry and our understanding of electrons, atoms, molecules and bonding; so “hang-on in there” and things will become clear.

### 1.1.1 Blackbody Radiation and the Quantization of Energy

When a solid material is heated it emits light, e.g. red-hot iron in a blacksmiths, the Sun and the stars. A perfect emitter and a perfect absorber of radiation would not reflect any light at all and is called a blackbody because at room temperature it looks black because most of the radiation emitted from it is in the infrared (IR). Such a perfect body does not exist but a very good approximation is a thermostatically heated hollow insulating vessel inside which the radiation is continually emitted and absorbed but with a pin-hole in it to allow some light to escape so that we can measure its spectrum.

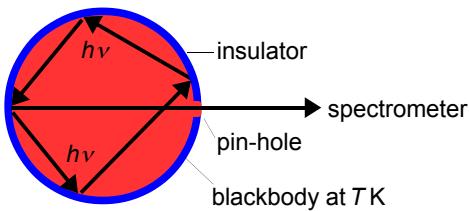


Figure 1.2: cross-section through a blackbody apparatus.

The blackbody spectrum depends only on the temperature and not on the material of the solid. The spectrum could not be explained at all by the classical view that the light could emit and absorb continuously at all frequencies  $\nu$  (Greek italic “nu” don’t confuse it with the Roman italic “vee”). The frequency  $\nu$  and the wavelength  $\lambda$  (Greek italic “lambda”) are related to the speed of light  $c = 2.9979 \times 10^8 \text{ m s}^{-1}$  through the wave nature of light (see section 1.2).

$$c = \nu \lambda \quad \text{the wave nature of light}$$

Classically it was thought that the atoms making up the solid of the blackbody have a continuous distribution of frequencies of vibration about their mean positions in the solid, which would give a radiant energy density  $\rho$  (Greek italic “rho”) of

$$\rho = \frac{8\pi k_B T}{\lambda^4}$$

where  $\rho$  is the energy at a frequency  $\nu$  per unit volume of the blackbody per unit frequency range and  $k_B$  is Boltzmann’s constant  $k_B = 1.3806 \times 10^{-23} \text{ J K}^{-1}$ . Unfortunately this equation *completely disagrees* with the experimental result which showed a maximum in the radiant energy density at a certain wavelength and this maximum wavelength varied with the temperature. Max Planck in 1900 realized that the solution to this failure was that the atoms making up the solid could only vibrate around their equilibrium positions with *certain* frequencies and not a continuum of possible frequencies. That is the atoms have *quantized* vibration energies which can only acquire an integer number ( $n$ ) of the discrete unit of energy ( $h\nu$ ).

$$E = n h\nu \quad n = 0, 1, 2, 3, \dots \quad \text{Planck's blackbody quantum equation}$$

Where  $n$  is a quantum number and can only have the integer values shown, Planck’s constant  $h = 6.6261 \times 10^{-34} \text{ J s}$  and the ellipsis ... means “and so on”. The atoms can only vibrate with an energy of  $0h\nu$ ,  $1h\nu$ ,  $2h\nu$ ,  $3h\nu$  and so on. The quantum mechanics equation for the radiant energy density  $\rho$  is shown below.

$$\rho = \frac{8\pi hc}{\lambda^5} \left( \frac{1}{\exp\left(\frac{hc}{\lambda k_B T}\right) - 1} \right)$$

Planck fitted his blackbody equation to the experimental spectra to find an experimental value for  $h$  Planck's constant. The quantum mechanical blackbody equation was a *perfect* fit at *all* temperatures for *all* wavelengths for *all* solids, this was a major triumph for quantum mechanics. Fig. 1.3 shows the blackbody spectrum for a temperature of 5000 K.

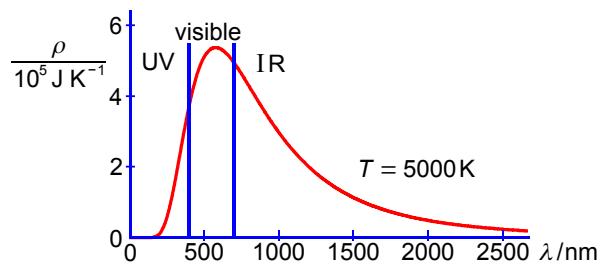


Figure 1.3: plot of radiant energy density against wavelength for a blackbody at  $T = 5000 \text{ K}$ .

### 1.1.2 The Photoelectric Effect and the Quantization of Light

Planck (1900) had introduced the idea of quantization of energy, the next step was the realization by Einstein in 1905 that *light* could be quantized as well to explain a problem that had existed for several years.

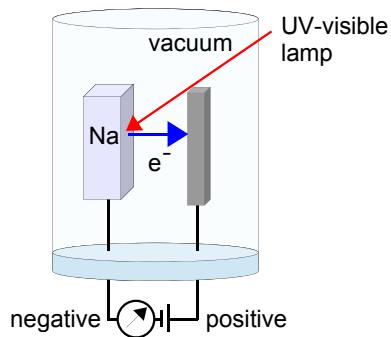


Figure 1.4: schematic of photoelectric apparatus.

The photoelectric effect uses monochromatic light of a chosen frequency  $\nu$  to hit a metal target inside a vacuum chamber and the ejected electrons have their kinetic energies measured by a grid electrode to which a negative voltage was applied to stop the electrons and so measure their kinetic energy  $E_{\text{KE}}$ . Fig. 1.4 shows the schematic apparatus but for clarity without showing the stopping electrode. Fig. 1.5 is a schematic of experimental results for sodium which shows that a *threshold frequency*  $\Phi$  (Greek italic capital “phi”) of light is required to emit any electrons at all and that the photoelectrons’ kinetic energy increases linearly with light frequency above this threshold frequency. Different metals give graphs with lines parallel to one another with identical gradients but different threshold frequencies. Increasing the light intensity did *not* alter the results in Fig. 1.5 at all. Sodium has a threshold frequency of  $\Phi = 5.56 \times 10^{14} \text{ s}^{-1}$  at a wavelength of 539 nm in the green visible region.

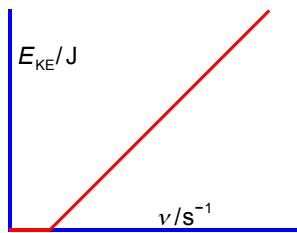


Figure 1.5: schematic plot of the photoelectron KE versus light frequency.

However, varying the intensity of the light does alter the *number* of electrons (the electric current  $I$ ) ejected from the metal target, Fig. 1.6. Again for a given metal there is a threshold frequency below which no current is obtained. Above the threshold the number of electrons (current) plateaus off and is constant.

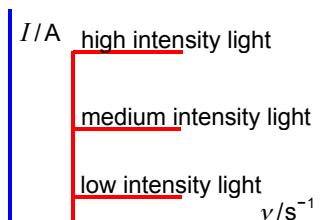


Figure 1.6: schematic of the photoelectron intensity (current) versus light frequency.

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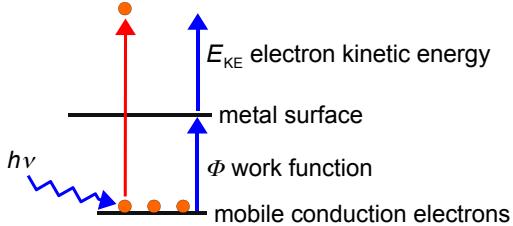
The photoelectric experimental results summarized in Figs. 1.5 and 1.6 could not be explained at all by the wave theory of light. Einstein could explain these experimental results if the light was quantized as a particle called a photon with an energy  $E$ .

$$E = h\nu \quad \text{energy of a photon}$$

This equation shows both particle and wave properties,  $E$  is the energy of the particle, the photon, but  $\nu$  is the frequency of the wave.

Metals are conductors because the valence electrons of the metal atoms are shared between all the atoms, *i.e.* they behave like a “mobile electron gas” which are attracted to the lattice of metal cations. There is a minimum energy of the photon for a given metal for it to eject an electron from the solid, this minimum energy is the *work function* of the metal  $\Phi$  which is the solid state equivalent of the ionization energy of a gas phase atom. The photon is annihilated when it is absorbed and its energy  $h\nu$  is used to overcome the work function of the metal and eject the electron from the solid with the photon’s excess energy appearing as the kinetic energy  $E_{\text{KE}}$  of the ejected electron. If we increase the number of photons of the same frequency, the light intensity, then we increase the number of electrons ejected from the metal target.

$$h\nu = \Phi + E_{\text{KE}} \quad h\nu = \Phi + \frac{1}{2}mv^2$$



**Figure 1.7:** energy balance of the photoelectric effect.

So we have a duality of light properties, with the continuous wave theory relevant for interference, refraction and diffraction but the particle photon theory is needed for the photoelectric effect and as we shall see shortly for the heat capacity of solids and for the absorption and emission of light by atoms and molecules.

*Self Test Question and Solution* on the photoelectric effect (Parker 2013b, p. 74).

### 1.1.3 Heat Capacities of Solids and the Quantization of Atom Vibrations in a Solid

The heat capacity of a solid at constant volume  $C_v$  was believed to be given by the equipartition principle and to be constant and independent of temperature (Dulong and Petit’s law 1819) which for a metallic crystalline solid is  $C_v = 3R \approx 25 \text{ J K}^{-1} \text{ mol}^{-1}$ .

Although approximately true for many solids at or above room temperature, the heat capacity of all solids decreases with decreasing temperature and approaches zero at zero kelvin. This decrease with temperature could not be explained classically. Einstein (1906) with improvements by Peter Debye (1912) realized that the solid is made of molecules which are vibrating in three dimensions around their average positions. The molecules do not have a continuous range of vibration frequencies but have *quantized* vibration energies ( $n\hbar\nu$ ) of  $n$  quanta of energy  $\hbar\nu$  with quantized frequencies  $\nu$  ranging from zero up to a maximum frequency  $\nu_M$ . The molecular rotations and translations are quenched by collisions with the neighbouring molecules in the crystal lattice for nearly all solids. This quantized vibration mechanism, using Planck's vibration energy quantization of blackbody radiation, explained *quantitatively* the  $T$  variation in  $C_V$  for all solids.

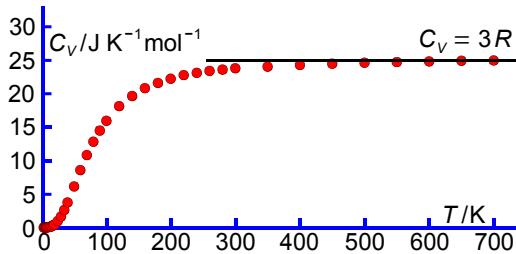


Figure 1.8:  $C_V$  versus  $T$  for copper.

The gas constant  $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$  appears in many situations in science that don't involve gases! Its name is purely historical and the reason for its appearance is that the gas constant is a disguise for the much more fundamental Boltzmann's constant  $R = N_A k_B$  ( $N_A$  is Avogadro's constant  $6.0221 \times 10^{23} \text{ mol}^{-1}$ ). Boltzmann's constant  $k_B$  applies to *individual* atoms or molecules whether they be gas, liquid or solid and the gas constant is "Boltzmann's constant for a mole" of atoms or molecules whether they be gas, liquid or solid.

*Self Test Question and Solution* on heat capacity (Parker 2012, p. 76).

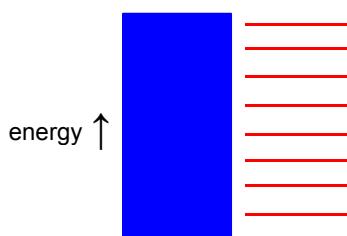
### 1.1.4 Atomic and Molecular Spectra and their Quantization of Electronic Levels

Classical mechanics says that when we excite an object it should emit or absorb light in a continuous series of wavelengths. However, we know that fireworks emit light from *isolated* atoms or ions and are of various different colours depending upon the metal salt used to make them. The Sun's spectrum has a blackbody distribution of light of an object at 5778 K, but superimposed upon this the Sun has about 1000 absorption lines from the *isolated* atoms in the Sun's atmosphere. These lines' wavelengths were accurately measured by Fraunhofer and Ångstrom. Spectra in the lab from *isolated* atoms and molecules can be measured using electric discharges or flames and they showed the presence of lines, *e.g.* a sodium salt held in a Bunsen burner flame is yellow and consists of two closely spaced lines at 588.9950 nm and 589.5924 nm, these yellow lines are also the light from a Na street lamp. Note the typical *precision* of spectroscopic measurements typically to seven significant figures.



**Figure 1.9:** Na atom emission spectrum, gap between the Na lines is exaggerated.

The unit for the wavelength of visible and UV light is the nanometre (symbol nm) with  $1 \text{ nm} = 10^{-9} \text{ m}$ . These line emissions and absorptions mean that isolated atoms and molecules have quantized absorption and emission, but *why*? The simplest explanation is that atoms and molecules can only absorb energy into quantized energy levels rather than continuously and so can only emit the energy as discrete quanta of light.



**Figure 1.10:** continuous (left) and quantized (right) energy levels.

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## 1.2 Wave-Particle Duality of Light

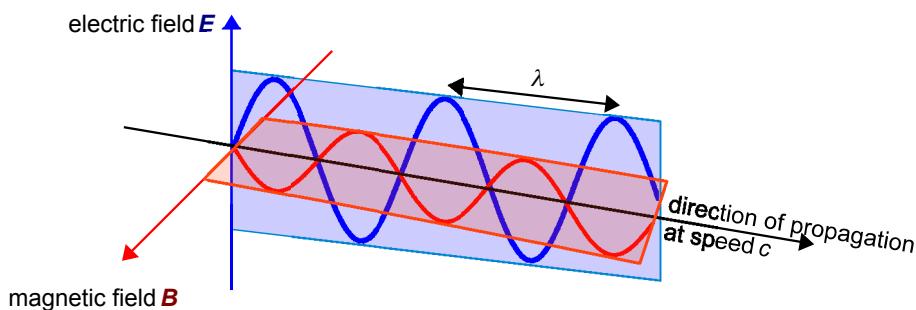
### 1.2.1 The Wave Nature of Light

Light acts as a wave in: refraction (e.g. the apparent bending of a stick at an air-water interface); interference (e.g. the colours of a thin film of oil on water); and diffraction (e.g. X-ray diffraction).

*Self Test Question and Solution on X-ray diffraction (Parker 2013a, p. 70).*

The light wave has a wavelength  $\lambda$  (the distance between two equivalent points on the wave) and a frequency  $v$  (the number of waves per second). A light wave consists of an electric field ( $E$ ) and a magnetic field ( $B$ ) whose intensities vary like sine waves but at right angles to one another. These electric and magnetic fields are moving in-phase at the speed of light  $c = 2.9979 \times 10^8 \text{ m s}^{-1}$  in a vacuum. In other media such as air or water the electromagnetic wave moves at a lower velocity, the wavelength  $\lambda$  decreases but the frequency  $v$  remains constant. When we say the speed of light we mean in a vacuum unless specified otherwise.

$$c = v \lambda \quad \text{the wave nature of light}$$



**Figure 1.11:** electromagnetic radiation (light).

To characterize the light we can use either the frequency or wavelength, it is also useful to quote the number of complete waves (peak plus trough) per centimetre which is called the wavenumber  $\bar{v}$  ("nu bar"). The wavenumber unit is  $\text{cm}^{-1}$  pronounced as "centimetres to the minus one" (or "reciprocal centimetres") and wavenumber is the commonly used practical unit, even though it is a non-SI unit.

$$\bar{v} \text{ cm}^{-1} = \frac{1}{\lambda \text{ cm}} \quad \text{the wavenumber of light}$$

The regions of the electromagnetic spectrum vary only in their wavelengths, frequencies or wavenumbers. In Fig. 1.12 frequency increases to the right and wavelength increases to the left.

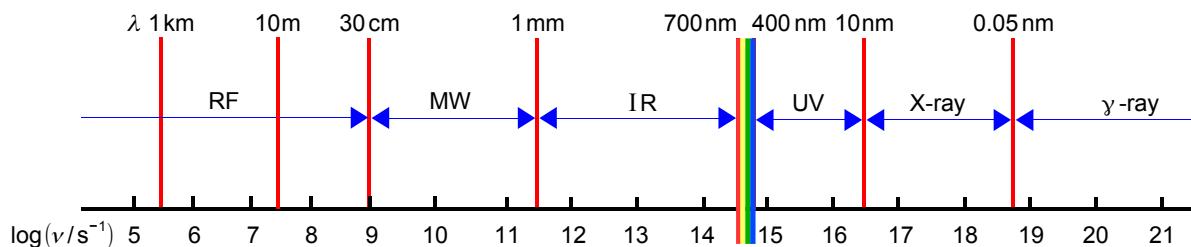


Figure 1.12: the electromagnetic spectrum.

The various regions are “separated” only because they use different instrumental techniques and also they affect atoms and molecules in different ways. These effects are: radiofrequency (RF) the magnetism of atomic nuclei; microwave (MW) the rotations of molecules around their centre of mass; infrared (IR) the vibrations of bond lengths and angles; visible and ultraviolet (UV) the excitation and ionization of outer shell electrons; X-rays the excitation and ionization of inner shell electrons; and gamma rays ( $\gamma$ -rays) the excitation of atomic nuclei energy levels.

*Self Test Question and Solution* on light waves (Parker 2013b, p. 14).

### 1.2.2 The Particle Nature of Light

Blackbody radiation, the heat capacity of solids, the photoelectric effect and the line spectra in the absorption and emission of light by atoms and molecules can *only* be explained by light being made of irreducible packets of electromagnetic energy (a particle of light), the photon. The photon travels at the speed of light  $c$ , it has a rest mass of zero but has measurable linear momentum  $p = h\nu/c$ , it exhibits deflection by a gravitational field, and it can exert a force. It has no electric charge, has an indefinitely long lifetime, and has a spin ( $s = 1$ ) of one unit of  $h/2\pi$ . The component of the spin vector  $m_s = \pm 1$ . These correspond to right-handed or left-handed circularly polarized light depending upon whether the spin direction is the same as the direction of motion  $c$  (Fig. 1.13, left) or against the speed of light vector  $c$  (see the right-hand rule, section 1.7.6). The photon spin angular momentum quantum number of unity and its components  $m_s = \pm 1$  are important when we consider spectroscopy. For help with vectors see Parker (Parker 2013a, p. 127).

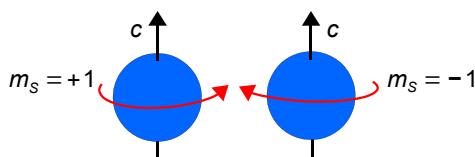


Figure 1.13: right-handed and left-handed circularly polarized photons.

*Self Test Question and Solution* on the particle and wave properties of light see Parker (Parker 2013b, p. 29).

### 1.3 The Bohr Model for the Hydrogen Atom

The explanation of the line spectra of atoms and molecules has its origins from Balmer, Lyman, Paschen and Brackett measuring the wavelengths of the visible, UV and IR emission lines of excited hydrogen atoms formed in electric discharges through H<sub>2</sub>.



Figure 1.14: Balmer visible emission spectrum of the hydrogen atom.

Wavelength is not proportional to the energy of the light, we could use frequency which is proportional to energy, but  $400 \text{ nm} = 7.495 \times 10^{14} \text{ s}^{-1}$  to  $700 \text{ nm} = 4.283 \times 10^{14} \text{ s}^{-1}$  which is not user friendly. Wavenumber  $\bar{v}$  is proportional to the energy of light and  $400 \text{ nm} = 25,000 \text{ cm}^{-1}$  to  $700 \text{ nm} = 14,285 \text{ cm}^{-1}$  is more convenient, hence the use of this practical but non-SI unit. Rydberg brought the experimental work together by finding that the wavenumber  $\bar{v}$  of the spectral lines of the H-atom in the UV, visible and IR could *all* be fitted *perfectly* to an equation involving only two integer terms,  $n_1$  and  $n_2$ .

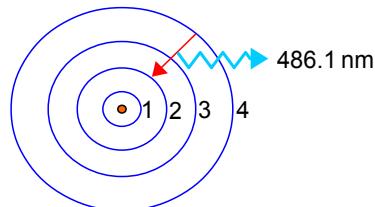
$$\bar{v} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \text{where } n = 1, 2, 3, \dots \quad \text{the Rydberg equation}$$

"I studied English for 16 years but...  
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Jane, Chinese architect

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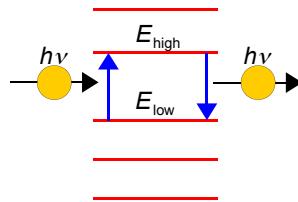
where Rydberg's constant is  $R_H = 109,737 \text{ cm}^{-1}$ . Niels Bohr in 1913 noted that the Rydberg equation could be modelled if the H-atom had a quantized electron energy and the electron could *only* occupy one of several stable circular orbits which are characterized by the principal quantum number  $n = 1, 2, 3, \dots$  (but not  $n = 0$ ).



**Figure 1.15:** the Bohr model of the H-atom.

Fig. 1.15 shows the second Balmer line  $n = 4$  to  $n = 2$  (cyan) at 486.1 nm. The UV Lyman lines are transitions to  $n = 1$ ; the visible Balmer to  $n = 2$ ; the IR Paschen and Brackett are to  $n = 3$  and 4, respectively. Absorption arises when the H-atom converts the energy of the absorbed photon into electronic excitation energy and the electron makes a quantum jump *up* to a higher energy level with a higher quantum number  $n$ .

Emission arises when an excited H-atom, *e.g.* from an electric discharge, converts its electronic excitation energy into light by the electron making a quantum jump *down* to a lower energy level with a lower quantum number  $n$ . The difference in electronic energy is converted to a photon of light given by Planck's equation.



**Figure 1.16:** quantized light absorption (left) and emission (right).

The Bohr model explained the line spectra of the H-atom and introduced the idea of atoms and molecules having quantized electronic energy levels and that emission and absorption involved jumps between these quantum states. But it is only a first approximation as the Rydberg equation *only* worked for the H-atom and other one-electron atoms such as  $\text{He}^+$  or  $\text{Li}^{2+}$  and the Bohr theory was superseded in 1924 as quantum mechanics developed.

*Self Test Question and Solution* on the Rydberg equation (Parker 2013b, p. 32).

## 1.4 The Wave-Particle Duality of Matter, the de Broglie Equation

Louis de Broglie (1924 in his PhD thesis, awarded the Nobel prize in 1929!) had an inspirational insight when he realized that if light has both wave and particle properties then perhaps particles of *matter* such as electrons, atoms and molecules should also have wave properties. Up to then matter had always been thought of as particles which behaved like hard-spheres. A particle of mass  $m$  moving with a velocity  $v$  in a straight line acts like a “matter wave” with a wavelength  $\lambda$  given by the de Broglie equation.

$$\lambda = \frac{h}{m v} = \frac{h}{p} \quad \text{the de Broglie equation}$$

where  $h$  is Planck's constant,  $p$  is the momentum  $p = mv$  with  $m$  the mass and  $v$  the velocity. Let's calculate some de Broglie wavelengths,  $h$  is in J s,  $m$  in kg and  $v$  in m s<sup>-1</sup> giving  $\lambda$  in metres. I will also quote the wavelengths in ångstroms where 1 Å = 1×10<sup>-10</sup> m to give us a feel for the size of the de Broglie wavelength in terms of the size of atoms and molecules.

*Worked Example:* what is the de Broglie wavelength of a 70 eV electron which is a typical electron energy used in a mass spectrometer? We must calculate its kinetic energy, then its velocity, then its de Broglie wavelength.

$$\begin{aligned} E_{\text{KE}} &= (1.602 \times 10^{-19} \text{ C})(70 \text{ V}) = 1.121 \times 10^{-17} \text{ J} \\ E_{\text{KE}} = \frac{1}{2} m v^2 &\quad v = \sqrt{\frac{2 E_{\text{KE}}}{m}} = \sqrt{\frac{2 \times 1.121 \times 10^{-17} \text{ J}}{9.109 \times 10^{-31} \text{ kg}}} = 4.961 \times 10^6 \text{ m s}^{-1} \\ \lambda = \frac{h}{m v} &= \frac{6.626 \times 10^{-34} \text{ J s}}{(9.109 \times 10^{-31} \text{ kg})(4.961 \times 10^6 \text{ m s}^{-1})} = 1.466 \times 10^{-10} \text{ m} \end{aligned}$$

The de Broglie wavelength of the 70 eV electron is 1.5 Å and is of atomic dimensions. See for yourself if you can calculate the de Broglie wavelengths for the objects shown below?

particle	$m/\text{kg}$	$v/\text{m s}^{-1}$	$\lambda/\text{m}$	$\lambda/\text{\AA}$
1 V electron	$9.1 \times 10^{-31}$	$5.9 \times 10^5$	$1.2 \times 10^{-9}$	12
100 V electron	$9.1 \times 10^{-31}$	$5.9 \times 10^6$	$1.2 \times 10^{-10}$	1.2
10 kV electron	$9.1 \times 10^{-31}$	$5.9 \times 10^7$	$1.2 \times 10^{-11}$	0.12
100 V proton	$1.67 \times 10^{-27}$	$1.38 \times 10^5$	$2.9 \times 10^{-12}$	0.029
H <sub>2</sub> at 200 °C	$3.3 \times 10^{-27}$	$2.4 \times 10^3$	$8.4 \times 10^{-11}$	0.84
22 rifle bullet	$2 \times 10^{-3}$	320	$1.0 \times 10^{-33}$	$1.0 \times 10^{-23}$
golf ball	$45 \times 10^{-3}$	30	$4.9 \times 10^{-34}$	$4.9 \times 10^{-24}$
human	~70	1.34	$7.1 \times 10^{-36}$	$7.1 \times 10^{-26}$

As one increases the velocity but keeps the mass constant, e.g. the electrons, the wavelength decreases but is still of atomic dimensions. Increasing the mass, e.g. from the electron to the proton and the hydrogen molecule, the wavelengths decrease but they are still of an atomic and molecular size. However, for *macroscopic* objects, e.g. the bullet, golf ball and humans, the wavelength is  $10^{-23}$  to  $10^{-26}$  m. These wavelengths are so small as to be meaningless in the sense that they cannot be measured, compare them to the radius of an electron at about  $10^{-15}$  m and an atomic nucleus about  $10^{-14}$  to  $10^{-15}$  m. So macroscopic matter may be safely treated with the classical mechanics of Newton but we *must* use quantum mechanics for *microscopic* matter.

What experimental evidence is there that matter does have wave properties? In 1927 Davisson and Germer, Fig.1.17 left, observed in the US a diffraction pattern when an electron beam was “reflected” from the front surface of a metal consisting of large nickel crystals. Independently, whilst in Aberdeen GP Thomson, Fig. 1.17 right, found a diffraction pattern when an electron beam was passed *through* a thin polycrystalline film of gold or aluminium, the end-on view of the pattern is shown on the extreme right.

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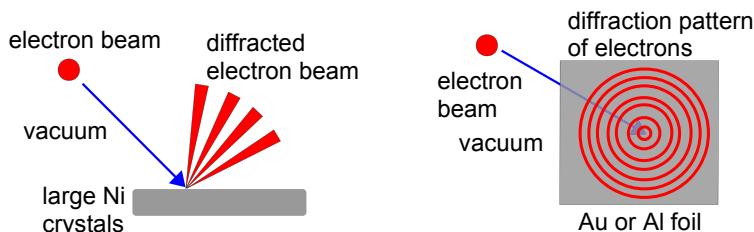




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**Figure 1.17:** electron diffraction patterns: Davisson and Germer (left) and GP Thomson (right).

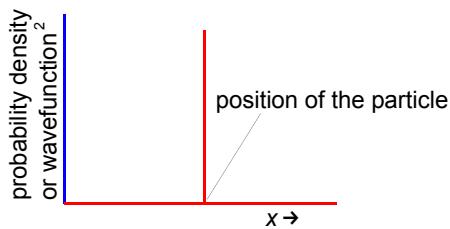
These experiments agreed with previous X-ray diffraction measurements of the samples (X-rays are light acting as waves in diffraction experiments). Interestingly, JJ Thomson received one of the first Nobel Prizes in 1906 for proving the existence of the electron and showing it was a *particle* and his son GP Thomson received a Nobel Prize in 1937 (sharing it with Davisson) for showing that the electron could also have *wave* properties!

## 1.5 Heisenberg's Uncertainty Principles

The physical meaning of these particle-waves was supplied by Max Born whose explanation is based on the work of Louis de Broglie, Arthur Compton and Werner Heisenberg. Arthur Compton (1923) had showed that photons, which have zero mass, nevertheless have momentum  $p$  from scattering experiments of a beam of X-ray photons by a beam of electrons where the X-rays lost energy and had a longer wavelength than the initial X-rays.

$$p = \frac{h\nu}{c} = \frac{h}{\lambda} \quad \text{photon momentum}$$

Werner Heisenberg (1927) realized that there was a fundamental limit to the information you could obtain about particle-waves. Imagine a particle, e.g. an electron, moving freely through space with a constant wavelength  $\lambda$  and its wavefunction (section 1.6) is a sine wave  $\sin(2\pi/\lambda)$  and the wavefunction of the electron is spread through space and it has no definite position. From de Broglie's equation ( $\lambda = h/mv$ ) the particle has a definite momentum  $p = h/\lambda$ . So if we know the momentum exactly we have no idea of its position. Conversely, we may know the position of a particle exactly as in Fig. 1.18.

**Figure 1.18:** Heisenberg's uncertainty principle.

The wavefunction for Fig. 1.18 is zero everywhere except at the particle's position. In order to get this result we need to add an infinite number of wavefunctions each of  $\sin(2\pi/\lambda)$  with wavelengths ranging from  $\lambda = 0$  to  $\lambda = \infty$ . So we know nothing about the momentum of the particle  $p = h/\lambda$  as  $\lambda$  is unknown but we know the particle position exactly. Heisenberg summarized the situation.

It is impossible to specify with *arbitrary* precision both the momentum and position of a particle simultaneously (at the same time).

If  $\Delta x$  is the uncertainty in position on the  $x$ -axis and  $\Delta p$  the uncertainty in momentum also along the  $x$ -axis then the following inequality holds.

$$\Delta x \Delta p \geq \frac{h}{4\pi} \quad \text{Heisenberg's uncertainty principle}$$

The above equation in terms of the  $x$ -axis does not tell us anything about the positions and momenta of the orthogonal  $y$ -axis and  $z$ -axis which must each be treated separately by the uncertainty principle. Position and momentum are complementary quantities, as are time and energy and the uncertainty principle may be written in an alternative form.

$$\Delta t \Delta E \geq \frac{h}{4\pi} \quad \text{Heisenberg's uncertainty principle}$$

There is a huge amount of experimental evidence confirming the validity of Heisenberg's uncertainty principle. The uncertainty principle has *nothing* to do with experimental precision or accuracy, it is a fundamental intrinsic property of nature. Sometimes you may see the symbol  $\hbar$  ( $h$  bar) used where  $\hbar = h/2\pi$  (called the reduced Planck's constant).

*Worked example:* if the lifetime of a molecule in an excited electronic state is  $1\times 10^{-8}$  s what is the uncertainty in the energy of this state?

$$\begin{aligned} \Delta t \Delta E &\geq \frac{h}{4\pi} & \Delta E &\geq \frac{6.626 \times 10^{-34} \text{ J s}}{4\pi \times 1 \times 10^{-8} \text{ s}} \geq 5.273 \times 10^{-27} \text{ J} \\ \Delta E &\geq (5.273 \times 10^{-27} \text{ J})(6.022 \times 10^{23} \text{ mol}^{-1}) \geq 3.175 \times 10^{-3} \text{ J mol}^{-1} \end{aligned}$$

Typical energies of electronic states are 100s of  $\text{kJ mol}^{-1}$ , so we know the energies of these states accurately.

## 1.6 Physical Meaning of the Wavefunction of a Particle

Think of the waves in water, by their very nature they have an amplitude (height) which goes up and down and they have positive and negative parts measured from a zero level at their average height. For the particle-waves of de Broglie this amplitude is called the *wavefunction* of the particle with the symbol  $\psi$  (Greek italic “psi”). From Heisenberg’s uncertainty principle we know that we can only talk about probabilities for a particle’s position or momentum which led Max Born (1926) to realize the wavefunction is a *probability amplitude*. The *probability density*  $P(x)$  of finding the particle at a given position  $x$  is equal to the *square* of the magnitude (or modulus) of  $\psi(x)$ . If the wavefunctions are written as complex numbers (Parker 2013a, p. 52) the star indicates that the complex conjugate must be used. Fig. 1.19 is an example of  $\psi(x)$  and  $|\psi(x)|^2$  of a one-dimensional standing wave of length  $x = l$ . The wavefunction  $\psi$  in Fig. 1.19 is like the first overtone standing wave of a guitar string, it oscillates between the two extremes shown. The wavefunction  $\psi$  has one node in the middle, a node is where the wavefunction passes *through* zero, not where it is zero. So at  $x = 0$  and  $x = l$  they are not nodes as  $\psi$  does not pass through these points. The probability density  $|\psi(x)|^2$  is always positive as you cannot have a negative probability!

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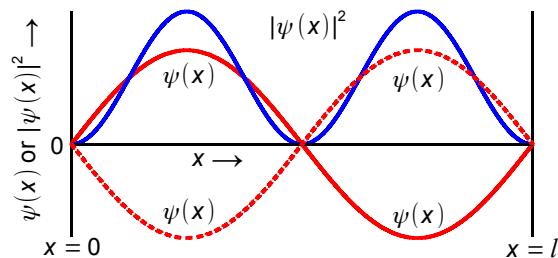
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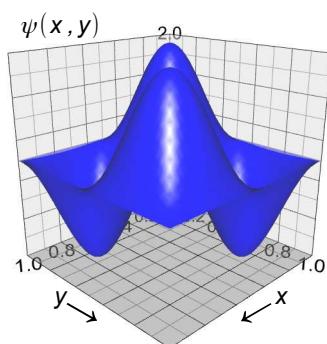
$$P(x) = |\psi(x)|^2 \quad \text{or} \quad P(x) = \psi^*(x) \psi(x) \quad \text{Born's interpretation of a wavefunction}$$



**Figure 1.19:** wavefunction  $\psi(x)$  in red and probability density  $|\psi(x)|^2$  in blue.

*Self Test Question and Solution* for a one-dimensional wavefunction (Parker 2012, p. 48).

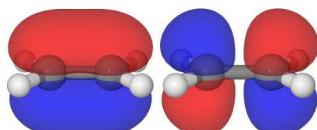
Fig. 1.20 shows a two-dimensional example of a wavefunction with one complete wavelength fitting into both the  $x$  and  $y$  unit distances and it is like one of the standing waves from striking a square metal plate with a hammer. Only the wavefunction is shown, the probability density  $|\psi|^2$  would have four maxima.



**Figure 1.20:** two-dimensional wavefunction  $\psi(x,y)$  with one complete wave in both  $x$  and  $y$ .

*Self Test Question and Solution* for a two-dimensional wavefunction (Parker 2012, p. 15).

You have probably (pun intended) been using three-dimensional probability diagrams in school when we talk about an atomic orbital (AO) or a molecular orbital (MO), e.g. Fig. 1.21 shows the *highest occupied molecular orbital* (HOMO) and the *lowest unoccupied molecular orbital* (LUMO) of ethene, more about MOs later on. The MO calculations in this book are carried out with MOPAC2012 (Stewart, JJP 2013). The MOs are displayed with Jmol (Jmol, 2014). Both software packages are free to academic students and staff.



**Figure 1.21:** ethene wavefunctions of the HOMO, left and LUMO, right.

## 1.7 Schrödinger's Wave Equation

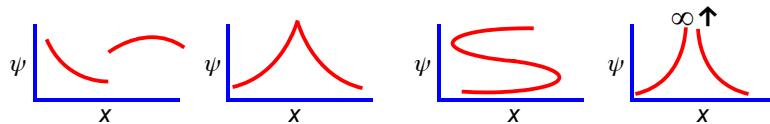
From Max Born we have the physical reality that the probability density  $|\psi|^2$  of a particle is the only thing we can experimentally measure about its position. The particle has a total energy  $E$  and a potential energy  $V$  what about its kinetic energy? Erwin Schrödinger (1926) showed that for one-dimensional, time-independent motion, *i.e.* a standing wave, that the wavefunction  $\psi$ , the total energy  $E$  and the potential energy  $V$  are related to the kinetic energy (the first term on the left side of the equation below).

$$-\frac{\hbar^2}{8\pi^2 m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad \text{the Schrödinger equation}$$

Although this equation may look frightening we shall see from some examples that it is quite simple! In one-dimension the wavefunction  $\psi$  and the potential energy  $V$  are functions of the distance  $x$ , however for clarity this is often not shown explicitly.

$$-\frac{\hbar^2}{8\pi^2 m} \frac{d^2\psi}{dx^2} + V\psi = E\psi \quad \text{the Schrödinger equation}$$

The *time-independent* Schrödinger equation, (where the amplitude does not vary with time) applies to standing wave situations. In order for  $|\psi|^2$  to correspond to the probability density of a particle then  $\psi$  must be “well-behaved”, *i.e.* fulfil certain common sense conditions called *boundary conditions*.



**Figure 1.22:** unacceptable conditions for an allowed wavefunction.

Fig. 1.22 from the left; the wavefunction must be continuous without any breaks in it; the slope must be continuous and smooth without any “kinks” in it; it must have a single value at all points in space; and it must be finite at all points. Acceptable wavefunctions  $\psi$  which meet these boundary conditions are called *allowed* solutions (eigenfunctions) and the energies  $E$  of these allowed solutions are the *allowed* energy levels (eigenvalue) with eigen being German for characteristic or allowed in English. It is in the process of the wavefunction  $\psi$  meeting its particular boundary conditions that quantum numbers appear for the allowed solutions.

### 1.7.1 Translational Motion of a Particle with no Boundary Conditions

We use the term “particle” in quantum mechanics as a general name for an electron, atom, molecule or ion when we are not being specific about its nature. Translational motion is the movement of the particle through “space” so it alters at least one of its  $x$ ,  $y$  or  $z$  coordinates. Let’s firstly look at a worked example of a particle with no boundary conditions, let us solve the Schrödinger equation and find  $E$  for a free moving particle in outer space in a region of constant  $V$  well away from any other object? As  $V$  is constant let’s choose  $V = 0$ . The available space is effectively infinite compared with the size of the particle. Help with differentiation is available (Parker 2013b, pp. 85, 92). Starting from the general equation for a wavefunction (in radians) with  $A$  and  $B$  as constants we differentiate twice.

$$\begin{aligned}\psi &= A \cos \frac{2\pi x}{\lambda} + B \sin \frac{2\pi x}{\lambda} \\ \frac{d\psi}{dx} &= -\frac{2\pi}{\lambda} A \sin \frac{2\pi x}{\lambda} + \frac{2\pi}{\lambda} B \cos \frac{2\pi x}{\lambda} \\ \frac{d^2\psi}{dx^2} &= -\frac{4\pi^2}{\lambda^2} A \cos \frac{2\pi x}{\lambda} - \frac{4\pi^2}{\lambda^2} B \sin \frac{2\pi x}{\lambda}\end{aligned}$$

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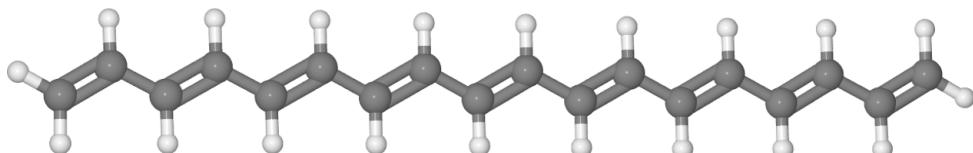
We multiply both sides by  $-h^2/(8\pi^2m)$  and take out any common factors outside the brackets.

$$\begin{aligned} -\frac{h^2}{8\pi^2 m} \frac{d^2\psi}{dx^2} &= \frac{h^2}{2m\lambda^2} \left( A \cos \frac{2\pi x}{\lambda} + B \sin \frac{2\pi x}{\lambda} \right) \\ &\text{the term in brackets is } \psi \\ -\frac{h^2}{8\pi^2 m} \frac{d^2\psi}{dx^2} &= \frac{h^2}{2m\lambda^2} \psi \\ \text{this is the } V = 0 \text{ Schrödinger equation with } E &= \frac{h^2}{2m\lambda^2} \\ -\frac{h^2}{8\pi^2 m} \frac{d^2\psi}{dx^2} &= E \psi \text{ and from de Broglie's equation } \lambda = \frac{h}{mv} \\ E &= \frac{1}{2}mv^2 \end{aligned}$$

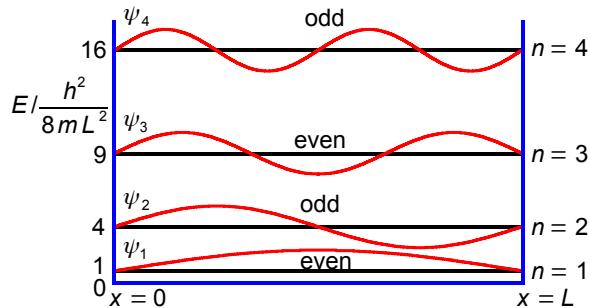
So a particle with no boundary conditions moving in “infinite” space is *not* quantized, the total energy is just the continuously variable classical kinetic energy. This is an example of the *Correspondence Principle* that as the confining box of the particle gets larger the quantum levels gets closer together until eventually it smoothly become a classical mechanics situation. So there is no sharp boundary between quantum and classical mechanics, it depends upon the size of the particle and the “box” in which it is confined, in this case the box is infinite.

### 1.7.2 Translational Motion of a Particle in a One-Dimensional Box

What do I mean by a one-dimensional box? An example would be the  $\pi$ -electrons which can move freely along the length of a conjugated polyene, Fig. 1.23. The  $\pi$ -electrons have one degree of translational motion (along the length of the polyene molecule) and are characterized by one quantum number. Another example is a molecule trapped inside a carbon nanotube the application of which is important for various Chemistry and Physics processes and devices. Help with the Maths for a particle in a box is available (Parker 2013b, pp. 48 and 113).



**Figure 1.23:** polyene molecule with mobile  $\pi$ -electrons.



**Figure 1.24:** the lower four wavefunctions for a particle in a 1-D box.

Fig. 1.24 the labels “odd” and “even” we will be using later. The box’s length is from  $x = 0$  to  $x = L$ . The potential energy inside the box is constant, let’s choose  $V = 0$  and with infinitely high potential energy walls  $V = \infty$  outside the one-dimensional box, so it is impossible for the particle to leave the box. In order for the particle to exist inside the box then the wavefunction  $\psi$  must persist through time which means that  $\psi$  must be a *standing wave* or one that has  $\psi = 0$  at both ends of the box. Otherwise, the original wave and the wave reflected from the wall will interfere with one another and cancel out. So we can apply the following boundary conditions to our general equation for wave motion. To have a standing wave there must be an *integral* number of *half-wavelengths* fitting into the box with a minimum of one half-wavelength.

$$L = n \frac{\lambda}{2} \quad n = 1, 2, 3, 4, \dots$$

Let’s label the allowed solutions as  $\psi_1, \psi_2, \dots$  corresponding to the quantum numbers  $n$ . Note the quantum numbers arise simply from applying the boundary conditions, *i.e.* from confining the particle. We start with the general wavefunction in radians.

$$\psi(x) = A \cos \frac{2\pi x}{\lambda} + B \sin \frac{2\pi x}{\lambda}$$

At the beginning of the box  $x = 0$  and  $\sin(0) = 0$  which is fine but  $\cos(0) = 1$  which does not fit the boundary conditions. So we need to remove the cosine term from the general solution by making  $A = 0$  and the wavefunction is then.

$$\psi(x) = B \sin \frac{2\pi x}{\lambda}$$

At the right hand end of the box  $x = L = n\lambda/2$  and substituting for  $x$  into the wavefunction gives us  $\psi(L)$ .

$$\psi(L) = B \sin(n\pi) \quad n = 1, 2, 3, \dots$$

The value of an allowed wavefunction at any intermediate point along the box is then found by multiplying the argument of the sine function by the dimensionless ratio of the lengths  $x/L$ .

$$\psi_n = B \sin \frac{n\pi x}{L} \quad n = 1, 2, 3, \dots$$

The other condition for a probability is that the total probability over all the particle's available space must be unity, *i.e.* the particle must be inside the one-dimensional box because the walls are infinite. The value for the constant  $B$  to get this *normalized* wavefunction is called the *normalization constant*  $N$ .

$$\int_0^L |\psi|^2 dx = 1 \quad \int_0^L N^2 \sin^2 \left( \frac{n\pi x}{L} \right) dx = 1 \quad n = 1, 2, 3, \dots$$

This integration is shown in detail (Parker 2013b, pp. 113, 117) where we obtain  $N = \sqrt{2/L}$  for the normalization constant which gives the normalized wavefunction,

$$\psi_n = \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi x}{L} \right) \quad n = 1, 2, 3, 4, \dots \quad \text{wavefunctions for a particle in a 1-D box}$$

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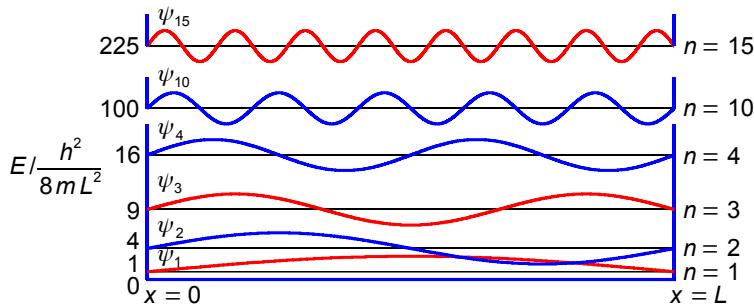
We now have the wavefunction or eigenfunction for our particle in a one-dimensional box, e.g. the  $\pi$ -electrons in a polyene molecule, but what about the allowed energies or eigenvalues? From the boundary condition and de Broglie's equation we find the momentum, the kinetic energy, and so the total energy  $E$  as we have set  $V = 0$  for the  $\pi$ -electrons.

$$n \frac{\lambda}{2} = L \quad \lambda = \frac{h}{m v} \quad m v = \frac{n h}{2 L}$$

$$E_{\text{KE}} = \frac{1}{2} m v^2 \quad E_{\text{KE}} = \frac{(m v)^2}{2 m} \quad E_{\text{KE}} = \frac{n^2 h^2}{8 m L^2}$$

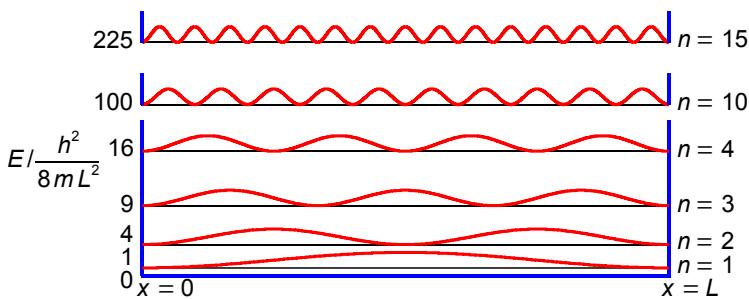
$$E_n = \frac{n^2 h^2}{8 m L^2} \quad n = 1, 2, 3, 4, \dots \quad \text{energies for a particle in a 1-D box}$$

Note that  $n = 0$  is *not* allowed for a particle in a one-dimensional box. There are two ways of looking at this, firstly, from the boundary conditions that the smallest number of half-wavelengths is one. Secondly, if the particle could have a quantum number  $n = 0$  then  $E = 0$  and  $\Delta E = 0$  and so the  $\Delta p = 0$  which from the uncertainty principle would mean  $\Delta x = \infty$  so the particle would *not* be trapped in the box. The lowest allowed energy level,  $n = 1$ , is called the *zero-point energy* it is the *ground state energy* of the particle in the box.



**Figure 1.25:** wavefunctions for a particle in a 1-D box.

Fig. 1.25, there are *nodes* where the wavefunction passes *through* zero, so  $\psi_1$  does not have any nodes as the wavefunction does not pass through zero. For clarity the “even” wavefunctions are red and the “odd” ones are blue.



**Figure 1.26:** probability density  $|\psi|^2$  for a particle in a 1-D box.

In Fig. 1.26 there are  $n$  maxima and  $(n-1)$  nodes in  $|\psi_n|^2$ . Classically the particle has an equal chance of being anywhere within the box, but for  $n = 1$  the most probable place is in the middle. When  $n$  is large such as  $n = 15$  then the probability is spread out over the whole box. When  $n$  is large and so  $E$  is large then the quantum mechanics gets closer to classical mechanics this is another example of the Correspondence Principle.

*Worked Example:* 1,3-butadiene is the smallest conjugated polyene, let's consider the  $\pi$ -electrons in a one-dimensional box this is also called the *free electron molecular orbital* (FEMO) model. 1,3-butadiene has two  $\pi$ -bonds with four  $\pi$ -electrons, from Pauli's exclusion principle, two electrons go into  $n = 1$  and two into  $n = 2$  which is the HOMO. If 1,3-butadiene absorbs a photon of the correct energy then *one* electron from  $n = 2$  the HOMO will be promoted into the empty  $n = 3$  the LUMO, both orbitals are shown in Fig. 1.27. The HOMO looks like the line formula of  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$  with the two conjugated double bonds whereas the LUMO has an isolated double bond between the two interior C-atoms. So the excited electronic state of 1,3-butadiene has one electron in  $\psi_3$  and one in  $\psi_2$  and still has two electrons in  $\psi_1$ .

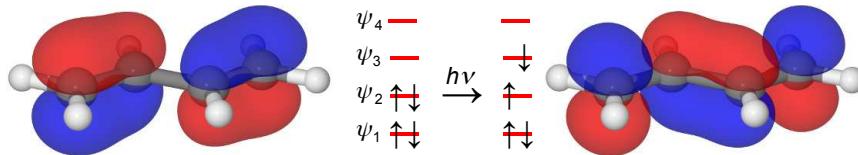


Figure 1.27: 1,3-butadiene  $\psi_2$  HOMO, left and  $\psi_3$  LUMO, right, energy not to scale.

We can calculate this photon energy within the limitations of the FEMO model if we know the length  $L$  of the 1,3-butadiene molecule. Making the rough approximation that  $L$  is equal to the sum of the average lengths of one C-C single bond and two C=C double bonds, plus the  $\pi$ -electrons don't stop dead at the carbon nuclei of the terminal atoms but go out to the "radius" of each terminal C-atom, *i.e.* they can travel beyond the nucleus of each of the terminal C-atoms by about half a C-C bond length at each end of the molecule gives us a box length of  $L = 5.78 \text{ \AA} = 5.78 \times 10^{-10} \text{ m}$ .

$$E = \frac{n^2 h^2}{8 m L^2} \quad E_{2 \text{ HOMO}} = \frac{4 h^2}{8 m L^2} \quad E_{3 \text{ LUMO}} = \frac{9 h^2}{8 m L^2}$$

$$\Delta E_{3,2} = \frac{5 h^2}{8 m L^2} = \frac{5(6.626 \times 10^{-34} \text{ J s})^2}{8(9.109 \times 10^{-31} \text{ kg})(5.78 \times 10^{-10} \text{ m})^2} = 9.02 \times 10^{-19} \text{ J}$$

$$E_{\text{photon}} = h\nu = \Delta E_{3,2} \quad \nu = \frac{9.02 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = 1.36 \times 10^{15} \text{ s}^{-1}$$

$$c = \lambda\nu \quad \lambda = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{1.36 \times 10^{15} \text{ s}^{-1}} = 2.20 \times 10^{-7} \text{ m} \quad \lambda = 220 \text{ nm}$$

This crude FEMO model gives approximate agreement with the experimental wavelength of 217 nm, but this is fortuitous as the agreement with the larger polyenes is poorer. However, the FEMO model is very useful as it gives us a *qualitative* model of the structure, spectroscopy and photochemistry of these molecules. The FEMO model explains why, for this biologically and industrially important class of molecules, the absorption wavelength increases with conjugated chain length until it moves from the UV into the visible to give the pigments found in plants such as green chlorophyll, red lycopene in tomatoes and orange-yellow  $\beta$ -carotene in carrots and other vegetables. The  $\beta$ -carotene is converted to vitamin A in our livers.

No. of C=C bonds	molecule	expt $\lambda_{\text{max/nm}}$
1	ethene	171
2	1,3-butadiene	217
3	1,3,5-hexatriene	263
4	1,3,5,7-octatetraene	290
11	$\beta$ -carotene	451
15	lycopene	504

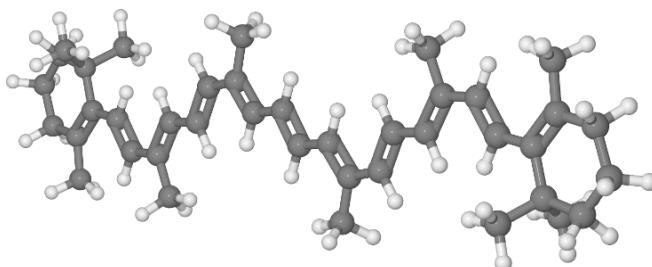


Figure 1.28:  $\beta$ -carotene.

### 1.7.3 Translational Motion of a Particle Confined to a Surface

A particle trapped on a two-dimensional surface is important in surface science, *e.g.* the chemistry and physics of catalysis and electronics. Again, inside the two-dimensional box there is a constant potential energy ( $V = 0$ ) and the walls have infinite potential energy. It is easy to generalize our one-dimensional results for two-dimensions. We make use of the *separation of variables method*, the idea is very simply, that the translational motion of the particle in the  $x$  direction is independent of its motion in the  $y$  direction. So each direction has its own wavefunction  $\psi_x$  and  $\psi_y$  and the overall wavefunction  $\psi_{x,y}$  is the *product* of the two wavefunctions. The total energy of these “two” motions is the *sum* of their energies  $E_x$  and  $E_y$ . The separation of variables method has another use (Parker 2013b, pp. 109 and 110). As there are two degrees of freedom ( $x$  and  $y$ ) there are two quantum numbers ( $n_x$  and  $n_y$ ).

$$\psi_{x,y} = \psi_x \times \psi_y \quad \text{the separation of variables method}$$

$$E_{x,y} = E_x + E_y$$

$$\psi_{x,y} = \sqrt{\frac{2}{L_x}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sqrt{\frac{2}{L_y}} \sin\left(\frac{n_y \pi y}{L_y}\right) \quad n_x = 1, 2, 3, 4, \dots \text{ and } n_y = 1, 2, 3, 4, \dots$$

$$\psi_{x,y} = \sqrt{\frac{4}{L_x L_y}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \quad \text{wavefunctions of a particle on a surface}$$

$$E_{x,y} = \left( \frac{n_x^2 h^2}{8 m L_x^2} \right) + \left( \frac{n_y^2 h^2}{8 m L_y^2} \right) \quad n_x = 1, 2, 3, 4, \dots \text{ and } n_y = 1, 2, 3, 4, \dots$$

$$E_{x,y} = \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right) \frac{h^2}{8 m} \quad \text{energies of a particle on a surface}$$

Consider a square box with  $L_x = L_y = 1$  unit. The ground state has one half-wavelength fitting in both the  $x$  and  $y$  sides of the surface, i.e.  $n_x = n_y = 1$ . Fig. 1.29 shows both  $\psi_{1,1}$  and  $|\psi_{1,1}|^2$  with only one maximum. Confirm for yourself that the energy would be  $E_{1,1} = 2(h^2/8m)$  which is the zero point energy for the square surface with unit sides.

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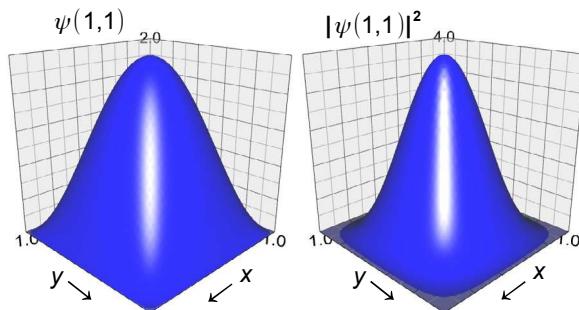
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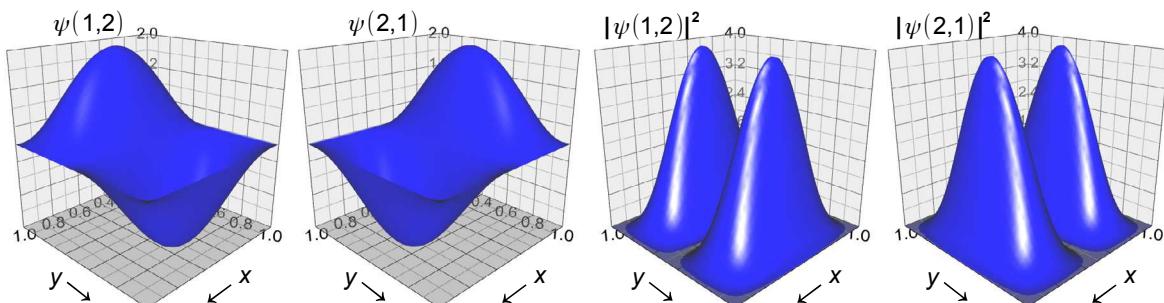


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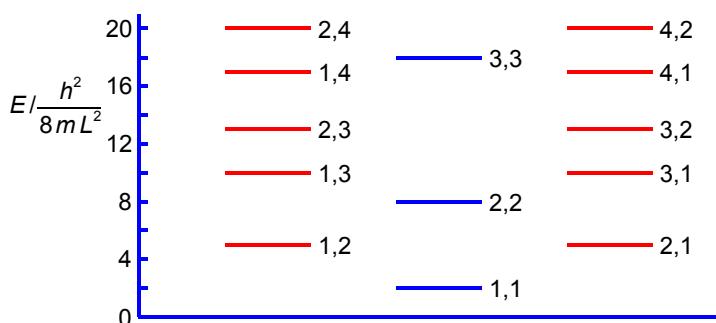


**Figure 1.29:**  $\psi$  and  $|\psi|^2$  with  $n_x = n_y = 1$  for a square surface.

What about a square surface with  $n_x = 1$  and  $n_y = 2$  and the similar state with  $n_x = 2$  and  $n_y = 1$ ? Fig.1.30 shows  $\psi(1,2)$  and  $\psi(2,1)$ . Clearly  $\psi(1,2)$  and  $\psi(2,1)$  are different from one another. Show for yourself that the energies are  $E(1,2) = E(2,1) = 5(h^2/8m)$ . An energy level which corresponds to two or more different states is called a *degenerate energy level*. The degree of degeneracy of an energy level is the number of these different states, e.g. we say that  $E(1,2)$  is doubly degenerate and the degree of degeneracy arises from the number of degrees of freedom (the number of dimensions) of the confining box, two for a two-dimensional surface, Fig.1.30.



**Figure 1.30:** example of degenerate wavefunctions and probability densities for a square surface.



**Figure 1.31:** the lower energy levels for a square surface with  $L_x = L_y = 1$ .

The energies of the lower states of a unit sided square surface are shown in Fig. 1.31. The non-degenerate levels are (1,1), (2,2) and (3,3) ... in blue, all the other levels are doubly degenerate. If the particle is trapped in a rectangular rather than a square surface, say with  $L_x = 1$  unit and  $L_y = 2$  units, show for yourself that the eigenvalues are  $E_{1,2} = 2(h^2/8m)$  and  $E_{2,1} = 4.25(h^2/8m)$  clearly the states are non-degenerate. So the degeneracy is lifted when the symmetry of the box is lowered.

#### 1.7.4 Translational Motion of a Particle Confined in a 3-Dimensional Box

Again the three-dimensional box has a constant potential energy ( $V = 0$ ) inside it and the walls have infinite potential energy. We can use the separation of variables method to find the wavefunctions  $\psi$  and allowed energies  $E$  as the translational motion is independent in the three Cartesian coordinates, where  $L_x$ ,  $L_y$  and  $L_z$  are the lengths of the three sides, we have

$$\psi_{x,y,z} = \sqrt{\frac{8}{L_x L_y L_z}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right) \quad \text{wavefunctions of a particle in a 3-D box}$$

$$E_{x,y,z} = \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) \frac{h^2}{8m} \quad \text{energies of a particle in a 3-D box}$$



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Sources: Keuzegids Master ranking 2013; Elsevier 'Beste Studies' ranking 2012;  
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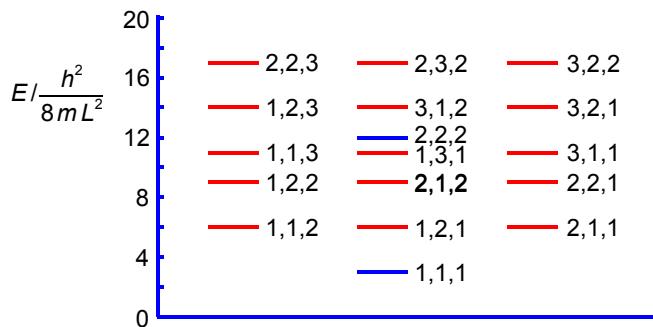
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The particle in a 3-dimensional box models the translational motion of a molecule inside a container, *i.e.* the translational motion of a gas. If the sides of the container are macroscopic then the energy levels are so closely spaced that the gas's translational motion may be treated as classical (Maxwell-Boltzmann equation), another example of the Correspondence Principle. Note that for the *cubic* box we have three-fold degenerate energy levels with only the 1,1,1 and 2,2,2 ... in blue being non-degenerate. Again the degeneracy is lifted if the symmetry is lowered from a cubic box to a box with sides of three different lengths.



**Figure 1.32:** the lower energy levels for a cubic box with  $L_x = L_y = L_z = 1$ .

To summarizing the particle in a box where the box is of one-, two-, or three-dimensions we have found,

1-D	ZPE $\neq 0$	non-degenerate	1 degree of freedom	1 quantum number
2-D	ZPE $\neq 0$	square maybe degenerate	2 degrees of freedom	2 quantum numbers
3-D	ZPE $\neq 0$	cube maybe degenerate	3 degrees of freedom	3 quantum numbers

### 1.7.5 Particle Tunnelling Through a Thin Finite Wall

So far our confining boxes have had walls with potential energy which was *infinite* and so the particle could not possibly escape from the box. What happens if the walls are not infinite but they still have potential energies  $V$  higher than the energy  $E$  of the particle? The wavefunction in the box when it meets the wall will decay exponentially as it passes through the wall and if the wall is thin  $\psi$  will still have a small but finite value when it exits the wall and  $\psi$  will then carry on oscillating *outside* the box. So the particle has quantum mechanically tunnelled through the barrier. Such “leakage” of particles is forbidden classically and it is only important for *thin* barriers and *light* mass particles such as electrons, protons and hydrogen atoms. Electron tunnelling is used in the scanning tunnelling microscope (STM) which allows us to “see” single atoms on a solid surface. Electron tunnelling is the cause of the leakage of current in large scale integrated chips and causes heating. Mutations of DNA can arise by proton tunnelling of an important and structurally significant proton and may lead to cancer and it is one possible cause of ageing. Radioactive decay involves either tunnelling of protons or neutrons out of the nucleus or the tunnelling of electrons into the nucleus. Chemical reactions involving H-atoms may have faster rates by a factor of 3–4 at low temperatures due to tunnelling than predicted from the higher temperature data. At the low temperatures the molecules no longer have enough energy to go over the activation energy barrier but can still “leak” through the barrier by tunnelling. There are several other applications in chemistry and physics which make use of tunnelling.

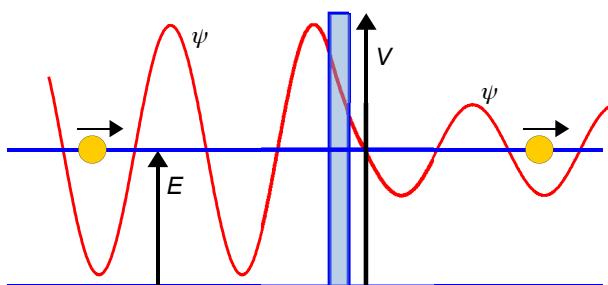


Figure 1.33: wavefunction for a particle travelling to the right encountering a thin wall of  $V > E$ .

### 1.7.6 Rotational Motion of a Particle on a Ring and Angular Momentum

The translational motion of a particle is clearly important. The other crucial motion that a particle has is rotation. Rotation (also called orbital motion) is the circular movement of a particle around a centre of rotation and the circular plane of rotation is at right angles to the axis of rotation. The particle will change at least *two* of its  $x$ ,  $y$ ,  $z$  coordinates in a periodic fashion. If the axis of rotation passes through the particle's *centre of mass* (also called centre of gravity) the motion is called *spin* and the particle will not change any of its  $x$ ,  $y$ ,  $z$  coordinates. A particle may well be both spinning and rotating.



Figure 1.34: the difference between rotation and spin.

The simplest case is the rotation of a particle on a ring at a distance  $r$  from the centre of rotation. In order for the wavefunction to persist through time and not interfere and cancel itself out on subsequent rotations, there must be an integral number of *whole* wavelengths fitting into the circumference of the circle, Fig 1.35, where  $n$  is the quantum number for the number of whole wavelengths fitting into the circumference.

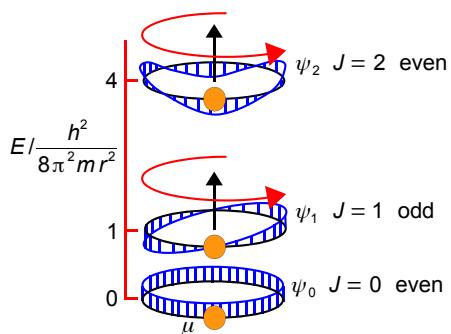


Figure 1.35: wavefunctions for a particle on a ring.

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Let us look at *angular momentum* which is important for electron orbital motion around nuclei and for electron or nuclear spin and also for the end-over-end rotation of a molecule in the gas phase. When we were dealing with translational motion of a particle in the sections on de Broglie's equation and Heisenberg's uncertainty principle we used linear momentum  $p = mv$  to quantify the translational motion. A particle rotating on a ring has an *angular velocity*  $\omega$  (Greek italic omega) the number of radians per second it travels round the ring ( $\text{rad s}^{-1}$ ). The angular momentum points in the  $z$  direction assuming the ring is in the  $xy$  plane and by analogy with translation motion the angular momentum is  $I\omega$  and is equal to the *moment of inertia*  $I$  times the angular velocity  $\omega$ .

$$I\omega \quad \text{angular momentum}$$

The moment of inertia  $I$  is the resistance to change for rotational motion and is equivalent to the resistance to change for translational motion, the mass  $m$  of the particle. The moment of inertia of a rotating system depends not only on the mass of the particle  $m$  but also the square of the radius of rotation  $r^2$ . Think about a playground roundabout or merry-go-round and the increased effort required to push it when somebody changes their position from the centre to the edge of the roundabout.

$$I = mr^2 \quad \text{moment of inertia}$$

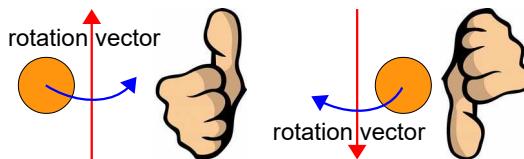
As the potential energy is constant around the ring, let's make it  $V = 0$ , and by analogy with translational motion where the total kinetic energy is  $E = \frac{1}{2}mv^2$  then the total rotational energy, equal to the rotational kinetic energy, is

$$E_{\text{rot}} = \frac{1}{2} I\omega^2$$

Returning to our quantized particle on a ring, we need a whole number of complete wavelengths fitting into the circumference of the ring in order to have a standing wave.

$$n\lambda = 2\pi r \quad n = 0, 1, 2, 3, 4, \dots$$

The rotational quantum number  $n$  can be  $n = 0$  where there is no rotation (the particle is stationary) with equal probability amplitude  $\psi$  for the stationary particle being *anywhere* around the ring. This situation agrees with Heisenberg's uncertainty principle in that the particle has zero rotational momentum, hence zero uncertainty in its rotational momentum, thus it has infinite uncertainty in its rotational position *i.e.* it may lie anywhere on the ring and we cannot tell where it is, even in principle! A particle on a ring with  $n = 0$  has a zero-point energy of zero (ZPE = 0) and is non-degenerate. When  $n \neq 0$  then the particle may rotate either clockwise or anti-clockwise around the ring with positive and negative values for  $n$  and the energy levels are all doubly degenerate for  $n \neq 0$ . The rotation axis is a vector and points in the direction of the right hand rule, Fig. 1.36 where the fingers of the right hand are curled in the direction of rotation and then the thumb points in the direction of the rotation or spin vector (axis).



**Figure 1.36:** right hand rule for the direction of the rotation vector or spin vector.

The potential energy around the ring is constant, let  $V = 0$  and the total rotational energy is then  $E$ . Firstly, using the analogy with translation motion and de Broglie's equation.

$$E = \frac{1}{2} m v^2 \quad E = \frac{(m v)^2}{2 m} \quad \lambda = \frac{h}{m v} \quad E = \frac{h^2}{\lambda^2 2 m}$$

The boundary condition of an integral number of complete wavelengths fitting the circumference gives the quantized rotational energy for a particle on a ring by substituting for lambda.

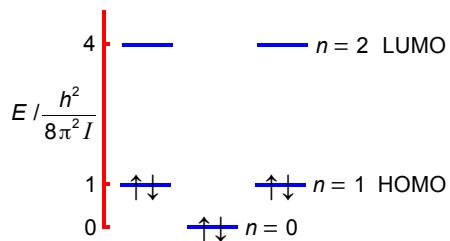
$$E = \frac{h^2}{\lambda^2 2 m} \quad n \lambda = 2 \pi r \quad E = \frac{n^2 h^2}{8 \pi^2 m r^2}$$

Moment of inertia  $I = mr^2$  and we obtain the quantized energy for a particle rotating on a ring.

$$E_{\text{rot}} = \frac{n^2 h^2}{8 \pi^2 I} \quad n = 0, 1, 2, \dots \quad \text{quantized energy for a particle on a ring}$$

Note that the quantum number  $n$  is squared and so states with  $\pm n$  values, positive or negative rotation directions, have the same energy and they are doubly degenerate. Rotation of a particle on a ring, although it is in two-dimensions has one degree of freedom, *i.e.* the position on the ring circumference, so the wavefunction has only one quantum number,  $n$ .

*Worked Example:* assuming that we can approximately treat the  $6 \pi$ -electrons in benzene as particles of mass  $9.109 \times 10^{-31}$  kg on a ring of radius corresponding to a C–C bond, 1.39 Å, what is the wavelength of the  $\pi$  to  $\pi^*$  absorption in benzene? The  $n = 0$  singly degenerate level contains 2  $\pi$ -electrons, the HOMO doubly degenerate  $n = 1$  levels contains the remaining 4  $\pi$ -electrons and the empty LUMO are the doubly degenerate  $n = 2$  levels, Fig. 1.37.



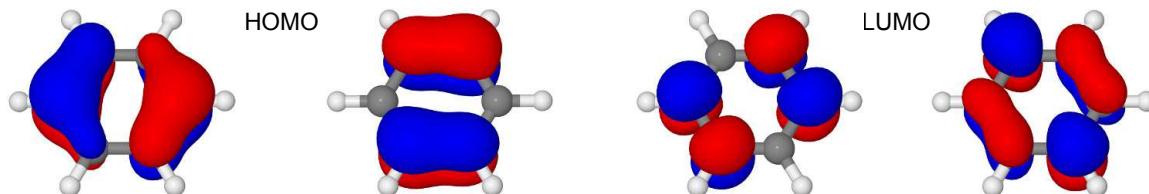
**Figure 1.37:** energy levels for benzene using the particle on a ring model.

$$\text{HOMO } E_1 = \frac{h^2}{8\pi^2 I} \quad \text{LUMO } E_2 = \frac{4h^2}{8\pi^2 I}$$

$$\Delta E_{2,1} = \frac{3h^2}{8\pi^2 I} = \frac{3(6.626 \times 10^{-34} \text{ J s})^2}{8\pi^2 (9.109 \times 10^{-31} \text{ kg})(1.39 \times 10^{-10} \text{ m})^2} = 9.479 \times 10^{-19} \text{ J}$$

$$E = h\nu \quad c = \lambda\nu$$

$$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})}{9.479 \times 10^{-19} \text{ J}} = 209.6 \text{ nm}$$



**Figure 1.38:** wavefunctions, left, the two degenerate HOMOs, right, the two degenerate LUMOs.

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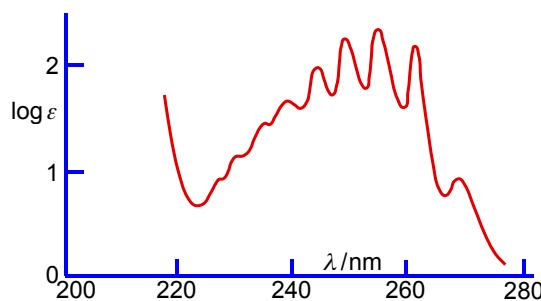
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Because flame and electric discharge *emission* spectra were historically the first to be studied, the convention is that we label any change in quantum number as “higher energy then lower energy” as is  $\Delta E_{2,1}$  above, whether it be an emission or an absorption process. The direction of the process of absorption or emission may be indicated by an arrow pointing to the left or right, respectively. Experimentally the  $\lambda_{\max}$  (the wavelength of maximum absorption) for the  $\pi^* \leftarrow \pi$  absorption in benzene dissolved in cyclohexane is around 255 nm in the UV, Fig. 1.39. Clearly we need a better model for the MOs of benzene but nevertheless the particle on a ring is a good starting point as it models the correct order of the levels and their degeneracies. The particle on a ring model explains Hückel’s ( $4n+2$ ) rule that aromatic molecules have extra stability compared with non-aromatic ring compounds. Hückel’s rule is that to fill all the energy levels up to  $n$  requires  $(4n+2)$  electrons so for benzene we fill up to  $n = 1$  which requires  $(4n+2) = 6$   $\pi$ -electrons in a ring in order to have aromatic stability. Quantum mechanically ( $4n+2$ ) arises from two electrons in each orbital  $2 \times (2n+1)$  along with the particle on a ring result that  $n = 0$  is non-degenerate but for  $n \neq 0$  the orbitals are doubly degenerate. The next level of sophistication from the particle on a ring is the Hückel MO treatment of molecules (Parker 2013a, pp. 105–111) and then semi-empirical and finally ab initio and DFT calculations.



**Figure 1.39:** absorption spectrum of benzene dissolved in cyclohexane.

## 1.8 Comparison of Matter and Light

Spectroscopy is the interaction of light with matter, so let’s summarize some of their various properties.

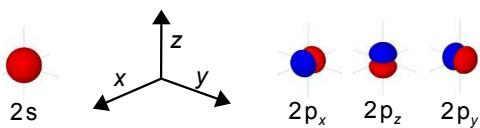
Property	Matter	Light
mass:	matter has mass	zero mass
velocity:	variable velocity	fixed velocity within a medium
volume:	occupies a volume in space	passes through space
wave:	probability amplitude $\psi$	$c = \lambda \nu$
particle:	$E_{\text{KE}} = \frac{1}{2}mv^2$	photon
momentum:	$p = mv$	$p = \frac{h\nu}{c} = \frac{h}{\lambda}$
spin:	nuclei: integer or half-integer electron: $\frac{1}{2}$	photon: 1
duality:	$\lambda = \frac{h}{mv}$	$E = h\nu$

## 1.9 Spectroscopy and Specific Selection Rules

This section may look like fierce Maths, but hang on in there and you will see it is simply looking at the shapes (or symmetries) of wavefunctions. When a molecule absorbs or emits a photon then it changes its quantum number, a specific selection rule tells us the transitions which are “allowed” (high intensity) and those which are “forbidden” (low intensity). The intensity of the spectral line when the molecule jumps from a wavefunction ( $\psi_n$ ) to different wavefunction ( $\psi_m$ ) is given by the square of the *transition moment*  $\mu_{mn}$  (also called the transition dipole moment).

$$\mu_{mn} = \int_{-\infty}^{\infty} \psi_m^* \hat{\mu} \psi_n d\tau \quad \text{transition moment}$$

If the wavefunctions are written as complex numbers (Parker 2013a, p. 52) then the star indicates that the complex conjugate must be used. The magnitude of the transition moment  $\mu_{mn}$  is a measure of the redistribution of charge that accompanies the transition. For example, an electron jump from a 2s atomic orbital to a 2p<sub>x</sub> or 2p<sub>y</sub> or 2p<sub>z</sub> atomic orbital, there is an obvious change in the charge distribution of the atom.



**Figure 1.40:** changes in electronic charge distribution.

The symbol “hat mu” (the electric dipole operator) describes how the electric vector of the light distorts, or operates on, the charges on the molecules and moves the charges from their original distribution to their final distribution (Parker 2013a, p 128). The term  $d\tau$  means integrate over all relevant space. The transition moment  $\mu_{mn}$  can be resolved into the three Cartesian coordinates, so for the *x* component of the transition moment we have

$$(\mu_{mn})_x = e \int_{-\infty}^{\infty} \psi_m^* \hat{x} \psi_n d\tau$$

where “hat x” is the *x* component of the electric dipole operator and *e* is the elementary charge. The intensity of the spectral line is the overall square of the transition moment.

$$(\mu_{mn})^2 = (\mu_{mn})_x^2 + (\mu_{mn})_y^2 + (\mu_{mn})_z^2$$

*Don't panic* if we only want to know whether the transition is allowed or forbidden we can get rid of the maths and use symmetry or shapes. The transition is forbidden if the transition moment  $\mu_{mn} = 0$  and is allowed if  $\mu_{mn} \neq 0$ . It is only if you need the actual intensities of the lines in a spectrum that the integral would need calculating. So to find whether  $\mu_{mn}$  is non-zero, allowed, we only need a minimum of *one* of its three components to be non-zero and that component tells us the polarization of the light which drives the transition dipole change and the quantum jump.

For an electron in a one-dimensional box, the specific selection rule is  $\Delta n = \pm 1$ , but why is it? Let's look at the shapes of the three terms in the integral of a component, *e.g.*  $(\mu_{mn})_x$  for the particle, an electron in this example. From Fig. 1.24 we haven't yet made any use of the symmetry of the wavefunctions, *i.e.* whether they are odd or even functions to the flipping the axis from say  $x$  to  $-x$ .

$$\begin{array}{ll} f(x) \text{ is an even function if} & f(x) = f(-x) \\ f(x) \text{ is an odd function if} & f(x) = -f(-x) \end{array}$$

When we flip the  $x$  axis in Fig. 1.24 we see that the  $n = 1, 3, 5 \dots$  are even (symmetric) and the  $n = 2, 4, 6 \dots$  are odd (antisymmetric). The  $x$  component of the electric dipole operator “hat x” is an odd function as the original and final electric dipole operators are related as in Fig. 1.41 and similarly for the  $y$  and  $z$  components which are also odd functions.

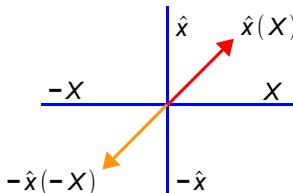


Figure 1.41: the  $x$ -component of the dipole moment operator.

The rules for multiplying even and odd symmetries are the same as multiplying plus and minus, *i.e.* even  $\times$  even = even, odd  $\times$  odd = even and even  $\times$  odd = odd. So for the transition  $\Delta n = \pm 1$  whether the particle starts in an odd level or an even level we have the transition moment is even *i.e.* symmetric and the transition is *symmetry allowed*.

$$(\mu_{mn})_x = e \int_{-\infty}^{\infty} \psi_m^* \hat{x} \psi_n dx$$

$$\mu_{\text{even,odd}} = \text{even} \times \text{odd} \times \text{odd} = \text{even} \quad \text{or} \quad \mu_{\text{odd,even}} = \text{odd} \times \text{odd} \times \text{even} = \text{even}$$

On the other hand, a transition with  $\Delta n = \pm 2$  then the transition moment is odd and the transition is *symmetry forbidden*.

$$(\mu_{mn})_x = e \int_{-\infty}^{\infty} \psi_m^* \hat{x} \psi_n dx$$
$$\mu_{\text{odd,odd}} = \text{odd} \times \text{odd} \times \text{odd} = \text{odd} \quad \text{or} \quad \mu_{\text{even,even}} = \text{even} \times \text{odd} \times \text{even} = \text{odd}$$

We can generalize this results to not just a particle in a box but to *all* electric dipole spectroscopies because the dipole moment operator is an odd function (but not for *magnetic* dipole spectroscopies of NMR and ESR).

$\psi(\text{even}) \leftrightarrow \psi(\text{odd})$  symmetry allowed electric dipole transitions

Note that we have not said anything about whether a transition is *spin allowed* or *spin forbidden*. The dipole changes we have been discussing involve the movement of at least one the  $x, y, z$  coordinates of the dipole charge. For spin, however, when spin-orbit coupling (section 6.2.1) is unimportant then the electric vector of light cannot affect a spin where the  $x, y, z$  positions are not altered. This applies for both an electron or a nuclear spin. A spinning electron or nucleus has a *magnetic* dipole and can undergo magnetic dipole transitions when the magnetic dipole (electron or nucleus) is aligned by an external magnetic field as in ESR and NMR apparatus.

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## 2 Pure Rotational Spectroscopy

The following approximate time and energy scales help to understand why microwave (MW) spectra are taken in the gas phase and why they are called “pure”.

motion	timescale/s	energy/cm <sup>-1</sup>
valence electron transition	$\sim 10^{-15}$	$\sim 14,000$ to $\sim 100,000$
vibration of bond or angle	$\sim 10^{-13}$	$\sim 300$ to $\sim 4400$
rotation of a molecule	$\sim 10^{-11}$	$\sim 0.2$ to $\sim 60$
molecular collisions, gas 1 atm 25°C	$\sim 10^{-10}$	$310.83 = \frac{3}{2}RT$
fluorescence	$\sim 10^{-8}$	$\sim 14,000$ to $\sim 40,000$
phosphorescence	$\sim 1$ to $\sim 10^3$	$\sim 14,000$ to $\sim 25,000$

The period of rotation for a typical molecule is about  $10^{-11}$  s and the time *between* collisions at one atmosphere pressure is about  $10^{-10}$  s so a molecule will on average undergo several full rotations before it is disturbed by a collision. The rotational state of the molecule is thus “well defined”, particularly at pressures of less than one atmosphere in the gas phase when the time between collisions will increase. In the liquid or solid phases the time between collisions is much smaller than  $10^{-10}$  s and the rotational states of molecules are not well defined so MW spectra must be taken in the gas phase. The rotations are “pure” in the sense that MW photons of an energy of  $\sim 0.2$  to  $\sim 60$  cm<sup>-1</sup> are *not* energetic enough to excite either the vibrations of chemical bonds (IR) or the electrons in their molecular orbitals (UV-visible). Fig. 2.1 shows the potential energy plot of the ground and excited electronic states of a diatomic molecule as a function of the internuclear distance, this is called a potential energy diagram, with superimposed energy levels of the vibrational and rotational energies. Note the convention that the upper quantum states are indicated with a single prime ( $\varepsilon'$ ,  $v'$  and  $J'$ ) and the lower quantum states with a double prime ( $\varepsilon''$ ,  $v''$  and  $J''$ ).

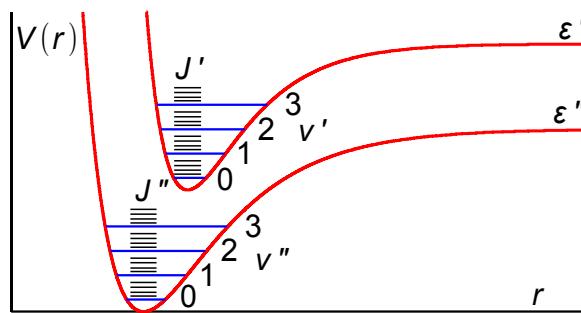


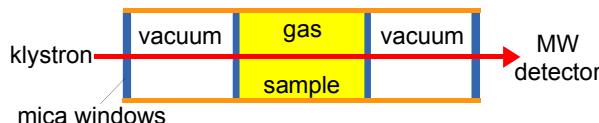
Figure 2.1: PE curve for a diatomic molecule, not to scale.

Considering the masses and velocities of the various species involved in the different motions of a molecule we find that the coupling or interaction of the motions is small and to a first approximation the different types of motion may be treated separately (the Born-Oppenheimer approximation).

$$\begin{aligned} m_{\text{electron}} &\ll m_{\text{nuclei}} < m_{\text{CM}} \\ v_{\text{electron}} &\gg v_{\text{nuclei}} > v_{\text{CM}} \\ E_{\text{total}} \approx E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{el}} &\quad \text{Born-Oppenheimer Approximation} \end{aligned}$$

I will mention later where the Born-Oppenheimer approximation breaks down. Translational motion is the motion of the centre of mass (CM) of the whole molecule and has already been discussed in the allowed levels for a particle in a three-dimensional box in which the gas is contained (section 1.7.4).

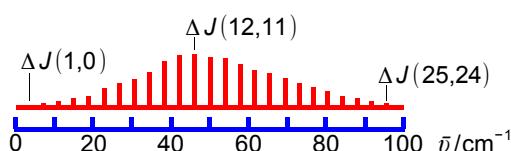
Let's first look at the rotations of molecules with MW spectroscopy which allows us to measure very precise bond lengths and bond angles, *i.e.* to obtain accurate chemical structures for molecules. Fig. 2.2 shows a simple absorption spectrometer, which can be used for stable molecules. A klystron (similar to the one in your MW oven) emits a narrow range of wavelengths and it can be tuned to give monochromatic MW of variable wavelength, so the klystron acts as its own monochromator. The MW radiation is focussed by an evacuated copper, or silver, rectangular tube *waveguide* which is under vacuum. A low pressure of gas or the vapour above a solid or liquid is held inside the waveguide between two thin mica windows as mica is MW transparent. A solid state detector has its signal amplified, processed and stored. Increasingly, however, Fourier transform MW (FTMW) spectrometers are being used to study at low temperatures the weakly bound complexes of molecules. FTMW gives measurements at high resolution and at high sensitivity. An introduction to the Maths behind the FT process is available (Parker 2012, pp. 60 and 69).



**Figure 2.2:** a MW absorption spectrometer.

## 2.1 Rigid Rotor Model for a Diatomic Molecule

Fig. 2.3 shows a simulation of the pure MW spectrum of carbon monoxide. The spectrum has *approximately* equally spaced absorption (or emission) lines when plotted on an energy scale of wavenumbers or frequency. The intensities of the lines initially increase, pass through a maximum and then decrease slowly. Let's firstly look at the positions of the spectral lines.



**Figure 2.3:** simulation of the MW absorption spectrum of  $^{12}\text{C}^{16}\text{O}$ .

The term “rigid-rotor” means that the bond length does not vary as the molecule rotates faster, *i.e.* there is no centrifugal distortion (stretching) of the bond length. Of course the bond is still vibrating, so the measured bond distance  $r$  is the bond length averaged over  $\sim 100$  vibrational periods. The rigid-rotor model is a *good* approximation to the true situation.

If the diatomic molecule was only rotating in two-dimensional space (like the particle on a ring) it would have only one degree of freedom and one quantum number  $J$ . However, the molecule is rotating in three-dimensional space,  $x$   $y$   $z$ , and it is equivalent to the reduced mass (defined below) confined on the surface of a sphere. So the diatomic molecule has *two* degrees of freedom, equivalent to our position east-west and north-south on the surface of the earth, with two quantum numbers  $J$  and  $M_J$ . Solving the Schrödinger equation for the allowed wavefunctions of these spherical harmonics (Atkins & de Paula 2006, p. 301) gives functions for the angular momentum  $I\omega$  in terms of the angular momentum quantum number  $J$  and the components of the angular momentum quantum number  $M_J$  along the rotation axis.

$$I\omega = \sqrt{J(J+1)} \frac{\hbar}{2\pi} \quad J = 0, 1, 2, 3, \dots$$
$$M_J = 0, \pm 1, \pm 2, \pm 3, \dots, \pm J$$

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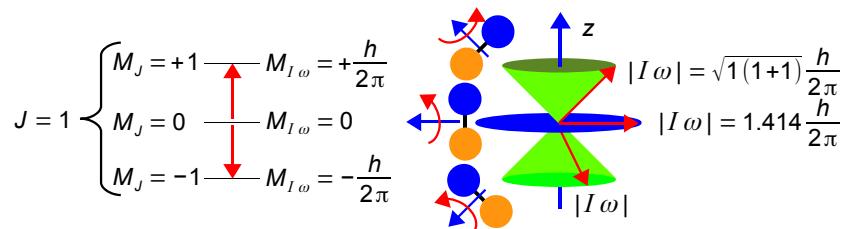
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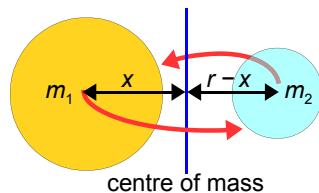
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Let's look at  $J = 1$  and its three components.



**Figure 2.4:**  $J = 1$  and the  $M_J = 0, \pm 1$  components.

On the left of Fig. 2.4 are the components of the angular momenta and on the right are the angular momenta. Each of the angular momenta (the sides of the cones) are of length  $|I\omega| = 1.414(h/2\pi)$  and the heights of the cones are the components  $M_J = 0$  or  $\pm 1(h/2\pi)$ . What are these cones? We know both the angular momentum  $I\omega$  and its  $z$ -component exactly so from Heisenberg's uncertainty principle the position of the angular momentum vector has infinite  $x$  and  $y$  uncertainty, *i.e.* the angular momentum vector is pointing somewhere to the tip of the cone but we don't know where, so these are "cones of uncertainty".



**Figure 2.5:** a diatomic molecule rotating around its centre of mass.

We can now calculate the quantized energy levels of our rotating diatomic, Fig. 2.5 shows the rotation of a diatomic molecule of bond length  $r$  around its centre of mass (or centre of gravity). From the analogy of a *single* particle's moment of inertia,  $I = mr^2$  (section 1.7.6) the diatomic molecule's moment of inertia will be.

$$I = \sum m_i r_i^2 \quad r_i \text{ is the perpendicular distance from atom } i \text{ to the rotation axis}$$

The moment of inertia  $I$  is the sum of the separate atoms' moment of inertia.

$$I = m_1 x^2 + m_2 (r-x)^2 \quad \text{also we have the lever rule} \quad m_1 x = m_2 (r-x)$$

The moment of inertia  $I$  with the level rule (as in a child's see-saw) allows us to eliminate the unknown  $x$ .

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2 \text{ kg m}^2 \quad \text{reduced mass } \mu = \frac{m_1 m_2}{m_1 + m_2} \text{ kg molecule}^{-1} \quad I = \mu r^2 \text{ kg m}^2$$

From the moment of inertia  $I$  and the quantized angular momentum we can find the allowed rotational energy levels  $E_J$  which are equal to the rotational kinetic energies as the potential energy  $V_{\text{rot}} = 0$ . The analogy with translational energy  $E_{\text{trans}} = \frac{1}{2}mv^2$  gives us the rotational equivalent.

$$\boxed{E_J = \frac{1}{2}I\omega^2 \quad E_J = \frac{(I\omega)^2}{2I} \quad I\omega = \sqrt{J(J+1)}\frac{\hbar}{2\pi} \\ E_J = J(J+1)\frac{\hbar^2}{8\pi^2 I} \text{ J} \quad \text{diatomic molecule rigid-rotor energies}}$$

$E_J$  is in joules, a unit with a symbol J (symbols are in roman type), don't confuse this unit with the quantum number  $J$  (a variable in italic type). Help with physical quantities, variables, units, symbols, labels and equations see (Parker 2013b, p. 9). In the absence of any external electrical or magnetic fields the rotational energy depends only on  $J$  and the molecular property  $I$  but the rotational energy does *not* depend upon the component of the angular momentum along the rotation axis  $M_J$ . So each rotational energy level  $J$  has a degeneracy of  $(2J+1)$ .

The rotational energy are conventionally measured in wavenumbers (symbol  $F_J$ ) which comes by dividing  $E_J$  in joules by  $hc$  with  $c$  in  $\text{cm s}^{-1}$  rather than  $\text{m s}^{-1}$ .

$$\boxed{F_J = J(J+1)\frac{\hbar}{8\pi^2 I c} \text{ cm}^{-1} \quad \text{diatomic molecule rigid-rotor energies}}$$

Note the difference between the equations for  $E_J$  and  $F_J$ . In  $F_J$  the  $h$  is not squared and it is divided by the speed of light in  $\text{cm s}^{-1}$ . We define the rotational constant  $B \text{ cm}^{-1}$  below which is characteristic of the molecule as it depends upon the masses of the atoms and the geometry of the molecule through the molecular variable, the moment of inertia  $I$ .

$$\boxed{B = \frac{\hbar}{8\pi^2 I c} \text{ cm}^{-1} \quad \text{rotational constant of a diatomic molecule}}$$

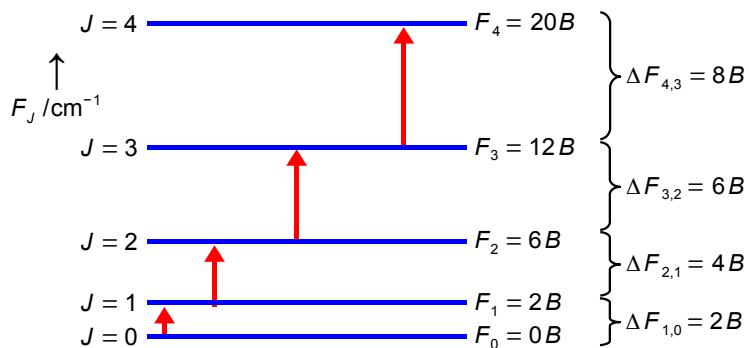
The  $F_J$  is usually written as shown below.

$$\boxed{F_J = J(J+1)B \text{ cm}^{-1}}$$

*Worked example:* calculate the reduced mass and moment of inertia of D<sup>35</sup>Cl given  $m(\text{D}) = 2.01410 \text{ g mol}^{-1}$ ,  $m(^{35}\text{Cl}) = 34.96885 \text{ g mol}^{-1}$  and  $r_0 = 1.275 \text{ \AA}$ .

$$\begin{aligned} \mu &= \frac{m_{\text{D}} m_{\text{Cl}}}{m_{\text{D}} + m_{\text{Cl}}} = \frac{2.01410 \times 34.96885}{2.01410 + 34.96885} \text{ g mol}^{-1} \frac{10^{-3} \text{ kg g}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 3.1624 \times 10^{-27} \text{ kg molecule}^{-1} \\ I &= \mu r^2 = (3.1624 \times 10^{-27} \text{ kg molecule}^{-1})(1.275 \times 10^{-10} \text{ m})^2 = 5.1409 \times 10^{-47} \text{ kg m}^2 \end{aligned}$$

“Molecule” is not an SI unit but nevertheless it is still a very useful reminder of exactly what we are doing. Also the SI base unit of mass is the kg not the g (Parker 2013b p. 9). The orders of magnitude for reduced masses of many simple molecules is  $10^{-27}$  kg with the order of magnitude for moments of inertia of  $10^{-47}$  kg m<sup>2</sup>. The quantized rotational energy levels for a rigid-rotor diatomic molecule are shown in Fig. 2.6.



**Figure 2.6:** rigid-rotor energy levels and transitions between neighbouring levels.

We note the energies of the spectral lines are at  $2B$ ,  $4B$ ,  $6B$ ,  $8B$  ... and so the rigid-rotor model gives the spacings between spectrum lines as a constant  $2B$  agreeing with experiment.

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*Worked example:* if a rotational absorption occurs at  $220\text{ cm}^{-1}$  for a molecule with  $B = 10\text{ cm}^{-1}$  what are the quantum states involved in the transition?

$$\begin{aligned}\Delta F(J+1, J) &= (J+1)(J+2)B - J(J+1)B = 2(J+1)B \\ 220\text{ cm}^{-1} &= 2(J+1)(10\text{ cm}^{-1}) \\ J+1 &= \frac{220\text{ cm}^{-1}}{2 \times 10\text{ cm}^{-1}} = 11 \text{ and so } J = 10 \\ \Delta J &= 11 \leftarrow 10 \quad \text{or} \quad \Delta J = 11, 10\end{aligned}$$

### 2.1.1 Centrifugal Distortion and the Non-Rigid Rotor

The rigid rotor model is a *good* approximation and centrifugal distortion is only normally significant for light molecules or when spectra are taken at high resolution then the spectrum lines close up slightly as  $J$  increases, the gap becomes less than the constant  $2B$ . This is due to centrifugal distortion of both the bond lengths and angles at high rotational velocities. We need to modify our quantum energies to allow for the effect at high  $J$  values.

$$F_J = J(J+1)B - J^2(J+1)^2 D \text{ cm}^{-1} \quad \text{non-rigid rotor energy levels}$$

Note that the negative centrifugal distortion term increases faster than  $J^4$  compared with the rigid rotor term increasing faster than  $J^2$  and hence centrifugal distortion is important at high values of  $J$ . The centrifugal constant  $D$  is characteristic for a given molecule and depends upon the flexibility of the chemical bond.

$$D = \frac{4B^3}{\bar{\nu}_e^2} \text{ cm}^{-1}$$

Where  $\bar{\nu}_e$  (nu “e” bar) is the equilibrium *vibration* wavenumber which measures the flexibility of the bond and  $D$  is typically about 1/1000 of the magnitude of  $B$ , *i.e.* centrifugal distortion is generally only a small second order effect. For example,  $B$  and  $D$  for  ${}^1\text{H}_2$  are  $B = 60.85\text{ cm}^{-1}$  and  $D = 0.046\text{ cm}^{-1}$  but for  ${}^{12}\text{C}{}^{16}\text{O}$  we have  $B = 1.931\text{ cm}^{-1}$  and  $D = 6.1 \times 10^{-6}\text{ cm}^{-1}$ . If anharmonicity (see section 3.2) is to be taken into account for the flexibility of the bonds then terms in higher powers of  $J(J+1)$  should be added to the expressions for the energy levels and line positions.

$$F(J) = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 - LJ^4(J+1)^4 + MJ^5(J+1)^5$$

Most of the terms are negligible compared with  $D$  except at high rotational levels and for measurements at very high resolution. A striking example is the rotational energy of hydrogen fluoride which has been fitted to the fifth-order polynomial in  $J(J+1)$  for transitions up to  $\Delta J(33,32)$  (Jennings *et al.* 1987).

	MHz	$\text{cm}^{-1}$
<i>B</i>	616365.2	20.55973
<i>D</i>	63.55	$2.12 \times 10^{-3}$
<i>H</i>	$4.9 \times 10^{-3}$	$0.163 \times 10^{-6}$
<i>L</i>	$4.4 \times 10^{-7}$	$0.15 \times 10^{-10}$
<i>M</i>	$2.8 \times 10^{-11}$	$0.9 \times 10^{-15}$

**Table 2.1:** HF rotational constants for the ground vibrational level.

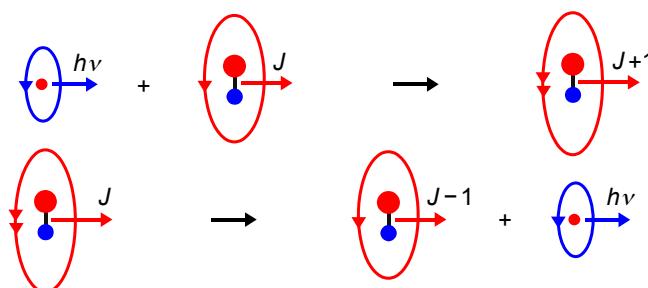
For most molecules at normal resolution the quadratic polynomial is an excellent fit to the experimental microwave data. The positions of the  $(J+1) \leftarrow J$  transitions between neighbouring levels are then

$$\begin{aligned} F_J &= J(J+1)B - J^2(J+1)^2D \text{ cm}^{-1} \\ F_{J+1} &= (J+1)(J+2)B - (J+1)^2(J+2)^2D \text{ cm}^{-1} \\ \Delta F_{J+1,J} &= (J+1)(J+2-J)B - (J+1)^2(J^2+4J+4-J^2)D \text{ cm}^{-1} \\ \Delta F_{(J+1,J)} &= 2(J+1)B - 4(J+1)^3D \text{ cm}^{-1} \end{aligned}$$

As there are three unknowns in this equation,  $J$ ,  $B$  and  $D$  we need to use three *consecutive* lines in the spectrum with this equation to find  $B$  (gives  $r_0$ ),  $D$  (gives  $\bar{v}_e$ ) and  $J$  which assigns the  $J$  values to the three consecutive lines in the spectrum.

## 2.2 Specific Selection Rule for Pure Rotational Spectroscopy

A specific selection rule deals with the changes in quantum numbers that are experimentally observed. Observed transitions are called “allowed” and those not observed or only weakly observed are called “forbidden”. In the MW spectrum we only see absorption or emission between neighbouring energy levels, why? We have to consider angular momentum both of the molecule and of the photon. Angular momentum is a conserved quantity in any process (in the same way as energy is conserved in a process). Fig. 2.7 shows absorption (top) and emission (bottom) of a photon by a rotating molecule.



**Figure 2.7:** rotational spectroscopy specific selection rule and angular momentum.

For a linear molecule the specific selection rule for the component of  $J$  along an external axis  $M_J$  can be visualized by considering the standing waves of a sphere, the spherical harmonics. For a linear molecule,

$$\Delta J = \pm 1 \text{ and } \Delta M_J = 0, \pm 1 \quad \text{linear molecule rotational specific selection rule}$$

$\Delta M_J = 0, \pm 1$  selection rule is important if the molecule is in an *external* electric field where the  $(2J+1)$  fold-degeneracy is then lifted (Atkins & de Paula 2006, p. 445). The  $(2J+1)$  degeneracy is important for the intensity of the microwave lines.

The second way of looking at  $\Delta J = \pm 1$  is to consider the symmetry of the rotational wavefunctions? From our particle on a ring discussion we can extend this to our diatomic rotor if we consider the particle to be the *reduced mass*  $\mu$  of our diatomic molecule rotating around the centre of mass, Fig. 2.8. The symmetry of the wavefunctions  $J = 0, 2, 4, \dots$  is even (symmetric) and for  $J = 1, 3, 5, \dots$  is odd (antisymmetric) with respect to  $180^\circ$  rotation around the axis.

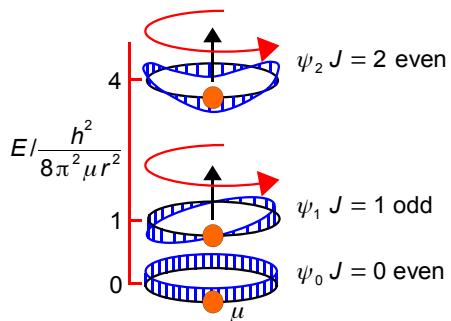


Figure 2.8: symmetry of diatomic molecule's rotational wavefunctions.



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We have previously seen that the transition moment  $\mu_{mn}$  is non-zero, even or symmetric, and hence allowed for jumps between even  $\leftrightarrow$  odd wavefunctions as the component of the molecule's dipole moment operator ("hat" mu) is odd in the direction of the light's electric vector (section 1.9).

$$\begin{aligned}\mu_{mn} &= \int_{-\infty}^{\infty} \psi_m^* \hat{\mu} \psi_n d\tau \\ \mu_{mn} &= \text{even} \times \text{odd} \times \text{odd} = \text{even} \\ \mu_{mn} &= \text{odd} \times \text{odd} \times \text{even} = \text{even}\end{aligned}$$

So symmetry would potentially allow transitions of  $\Delta J = \pm 1, \pm 3, \pm 5 \dots$  but the angular momentum of the photon restricts the allowed transitions to only  $\Delta J = \pm 1$  for pure rotational spectroscopy. In microwave absorption spectra the molecule is excited and they jump up a level  $\Delta J = +1$ . Rotationally excited molecules emit microwave dropping down a level with  $\Delta J = -1$ .

*Worked Example:* what is the bond length of  ${}^1\text{H}{}^{79}\text{Br}$  if its rotational spectrum has peaks separated by  $16.72 \text{ cm}^{-1}$  given  $m({}^1\text{H}) = 1.0008 \text{ g mol}^{-1}$  and  $m({}^{79}\text{Br}) = 78.92 \text{ g mol}^{-1}$ ? Spectrum line spacing is  $2B$  so  $B = 8.36 \text{ cm}^{-1}$  and the rotational constant  $B = h/8\pi^2 I c$ .

$$\begin{aligned}I &= \frac{6.626 \times 10^{-34} \text{ J s}}{8\pi^2 (8.36 \text{ cm}^{-1})(2.998 \times 10^{10} \text{ cm s}^{-1})} = 3.348 \times 10^{-47} \text{ kg m}^2 \\ \mu &= \frac{1.008 \times 78.92}{1.008 + 78.92} \text{ g mol}^{-1} \times \frac{10^{-3} \text{ kg g}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 1.6527 \times 10^{-27} \text{ kg} \\ I &= \mu r^2 \quad r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{3.348 \times 10^{-47} \text{ kg m}^2}{1.6527 \times 10^{-27} \text{ kg}}} = 1.423 \times 10^{-10} \text{ m} = 1.423 \text{ \AA}\end{aligned}$$

Notice the use of physical quantities and units (Parker 2013b, p. 9) and we also use Newton's laws of motion for the units conversion of joule =  $\text{kg m}^2 \text{ s}^{-2}$ .

There are a couple of points to note. Firstly, that chemical bond lengths don't vary very much for small molecules they are generally 1-2.5 Å, e.g.  $\text{H}_2$  is 0.74 Å and  $\text{Cl}_2$  is 1.99 Å. Secondly, a simple spectroscopic measurement has led to an *accurate* value for the *average* internuclear distance of the molecule in the  $v = 0$  vibrational level. So the bond length is normally written as  $r_0 = 1.423 \text{ \AA}$ .

## 2.3 Gross Selection Rule for Pure Rotational Spectroscopy

A gross selection rule deals with the *physical property* that a molecule must possess in order to undergo a given type of spectroscopic transition.

The molecule must have a *permanent* dipole moment      MW gross selection rule

So homonuclear diatomic molecules *e.g.* N<sub>2</sub> or O<sub>2</sub> and molecules with a centre of symmetry *e.g.* CH<sub>4</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>2</sub> are transparent to MW radiation. Molecules without a centre of symmetry, *e.g.* heteronuclear diatomics such as HCl or CO and molecules such as CHCl<sub>3</sub> or HCCBr, absorb in the microwave region.

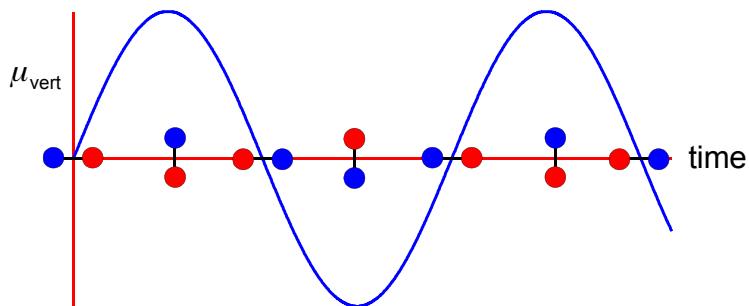


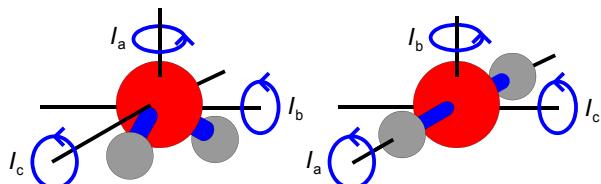
Figure 2.9: vertical component of the dipole moment of a rotating polar molecule.

A rotating molecule with a *permanent* dipole moment produces an oscillating electric field along a chosen direction, Fig. 2.9. Classically this oscillating electric field can exchange energy with the oscillating electric field of the MW radiation. A rotating molecule without a permanent dipole does not produce an oscillating electric field although it is still rotating with a quantum number  $J$ . Such non-polar molecules may still change their value of  $J$  by collisional energy transfer with other molecules but not by photon absorption or emission.

So in the Earth's atmosphere the major constituent gases N<sub>2</sub>, O<sub>2</sub>, Ar, CH<sub>4</sub>, CO<sub>2</sub> are transparent to MW but H<sub>2</sub>O and N<sub>2</sub>O are MW absorbers. This allows us to observe from the Earth's surface using MW telescopes, *e.g.* the cosmic microwave background radiation which corresponds to a blackbody temperature of about 2.7 K. Also, from the Earth's surface, around 210 different molecules in interstellar gas clouds have been detected using microwave spectroscopy, the largest being C<sub>70</sub> a 70-fullerene, and the molecules' temperatures have also been measured from their line intensities giving the various gas clouds' temperatures.

## 2.4 Rotational Motion of Polyatomic Molecules

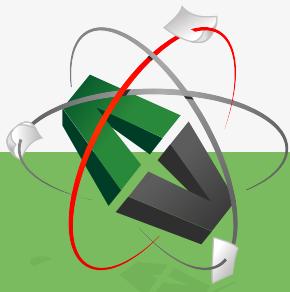
A molecule's random rotation may be resolved into three components of independent rotation around the  $x$ ,  $y$ , and  $z$  axes.



**Figure 2.10:** independent rotations for some polyatomic molecules.

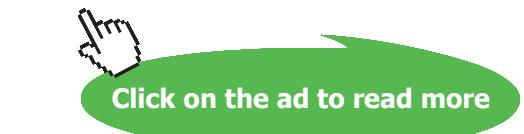
Any molecule has three moments of inertia which are conventionally defined in terms of their magnitudes as  $I_a \leq I_b \leq I_c$ . Remember, the difference between rotation and spin (section 1.7.6) that a rotating molecule must change at least two of its three coordinates and a spinning molecule does not change any of its coordinates. We can then classify molecules into five different shapes or symmetries with the following moments of inertia.

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linear	$I_a = 0 < (I_b = I_c)$	CO, OCS, N <sub>2</sub> , HCl, O <sub>2</sub>
oblate symmetric top (pancake)	$(I_a = I_b) < I_c$	C <sub>6</sub> H <sub>6</sub> , NH <sub>3</sub>
prolate symmetric top (rugby ball)	$I_a < (I_b = I_c)$	CH <sub>3</sub> Cl,
spherical top	$I_a = I_b = I_c$	CH <sub>4</sub> , SF <sub>4</sub> , SF <sub>6</sub>
asymmetric top	$I_a \neq I_b \neq I_c$	H <sub>2</sub> O, NO <sub>2</sub>

Non-linear molecule are said to have 3 degrees of rotational freedom but linear molecules only have 2 degrees of rotational freedom as  $I_a$  is zero and it is a *spin* not a rotation as none of the  $x$ ,  $y$ ,  $z$  coordinates change.

The moments of inertia of non-linear polyatomic molecules are summarized in Atkins and de Paula (Atkins & de Paula 2013, p 480). Although spherical top molecules such CH<sub>4</sub> or SiH<sub>4</sub> have no permanent dipole moment, rotations around any of the C-H bonds will centrifugally distort the remaining three C-H bonds and give a small dipole moment. An extremely weak rotational spectrum which may be observed with Fourier transform instruments using long path length cells of 10s metres, but for ordinary purposes such spherical top molecules may be considered transparent to MW.

## 2.5 Intensities of Rotational Lines

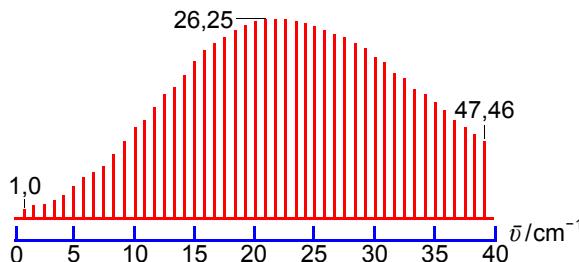


Figure 2.11: simulation of the microwave absorption spectrum of N<sub>2</sub>O.

The intensities of the lines  $I(J+1,J)$  are normally all measured relative to the intensity of the lowest transition  $I(1,0)$ . In Fig. 2.11 the relative intensities of the lines increase with  $J$  then pass through a maximum before a slow decrease.

$$\frac{I(J+1,J)}{I(1,0)} = \frac{P(J+1,J)}{P(1,0)} \frac{g_J}{g_0} \frac{n_J}{n_0}$$

The quantum mechanical probabilities of the transitions  $P(J+1,J)$  all have  $\Delta J = +1$  are equal to one another, so the ratio of  $P(J+1,J)/P(1,0)$  is unity or one. The degeneracy  $g_J$  of level  $J$  (the number of states  $M_J$  with the same energy) is  $2J+1$  and  $g_0$  is unity so the ratio of degeneracies is  $2J+1$ , see Fig. 2.4. The ratio of the populations of molecules in two quantum energy levels,  $E_i$  and  $E_p$  is given by Boltzmann's distribution law. Notice the difference (due to degeneracies) between counting states and counting energy levels.

$$\frac{n_f}{n_i} = \frac{g_f}{g_i} \exp\left(-\frac{E_f - E_i}{k_B T}\right) \quad \text{Boltzmann distribution law of energy levels}$$

$$\frac{n_f}{n_i} = \exp\left(-\frac{E_f - E_i}{k_B T}\right) \quad \text{Boltzmann distribution law of states}$$

Don't confuse the distribution law with the non-quantized (classical) Maxwell-Boltzmann equation for translational motion. The Boltzmann distribution law is true for any quantized motion not just rotations. In our case the rotational energy terms in the exponential are  $F(J) = BJ(J+1)$  cm<sup>-1</sup> and  $F(0) = 0$  cm<sup>-1</sup>. Converting  $k_B T$  from joules to wavenumbers it becomes  $k_B T/hc$  with the speed of light in cm s<sup>-1</sup>. The ratio of rotational spectrum lines is then

$$\frac{I(J+1, J)}{I(1, 0)} = (2J+1) \exp\left(-\frac{hcBJ(J+1)}{k_B T}\right) \quad \text{rotational spectrum line intensities}$$

The pre-exponential term increases linearly with  $J$  and the exponential term decreases slowly with  $J(J+1)$  and the product of the two terms models the intensities of the rotational spectrum.

*Worked example:* what is the ratio of the populations of rotational energy levels  $J = 3$  to  $J = 0$  for  $^1\text{H}^{35}\text{Cl}$  at 25°C if  $B = 10.59$  cm<sup>-1</sup> for  $^1\text{H}^{35}\text{Cl}$ ? Note that the useful conversion factor  $k_B T/hc = 207.23$  cm<sup>-1</sup> at 298.15 K with  $c$  in cm s<sup>-1</sup> this factor also allows us to easily calculate the  $k_B T/hc$  at any other temperature.



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$$\frac{n_{J=3}}{n_{J=0}} = (2J+1) \exp\left(-\frac{hcB(J+1)}{k_B T}\right) = (2 \times 3 + 1) \exp\left(-\frac{10.59 \text{ cm}^{-1} \times 3 \times 4}{207.23 \text{ cm}^{-1}}\right) = 3.791$$

Fig. 2.12 shows the populations of rotational quantum level populations for  $^{12}\text{C}^{16}\text{O}$  with a rotational constant of  $B$  of  $1.9313 \text{ cm}^{-1}$  at three temperatures. The highest populated  $J$  level at 100 K is  $J = 4$ , at 300 K  $J = 7$  and at 500 K  $J = 9$ .

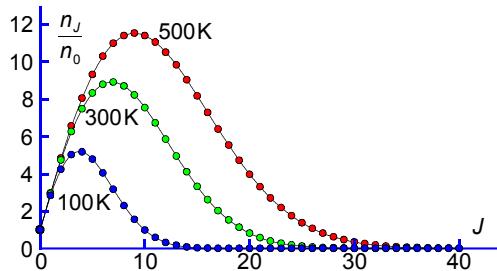


Figure 2.12:  $^{12}\text{C}^{16}\text{O}$  relative rotational populations.

*Worked example:* if the maximum intensity of the CO spectrum is  $\Delta J = (12,11)$  what is the temperature, assuming it is a rigid-rotor?  $B = 1.931 \text{ cm}^{-1}$  for CO, use the differential of a product (Parker 2013b, p. 89).

$$I = \frac{I_{J+1,J}}{I_{1,0}} = (2J+1) \exp\left(-\frac{hcB(J^2+J)}{k_B T}\right)$$

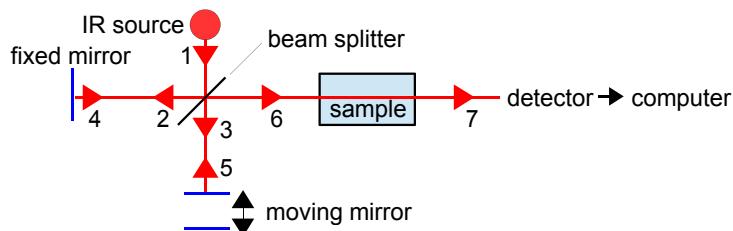
$$\frac{dI}{dJ} = 2 \exp\left(-\frac{hcB(J^2+J)}{k_B T}\right) - (2J+1) \frac{hcB}{k_B T} (2J+1) \exp\left(-\frac{hcB(J^2+J)}{k_B T}\right) = 0$$

$$\frac{k_B T}{hc} = \frac{B}{2} (2J_{\max}+1)^2 = \frac{1.931 \text{ cm}^{-1}}{2} (2 \times 11 + 1)^2 = 510.7 \text{ cm}^{-1}$$

$$k_B T / hc = 207.2 \text{ cm}^{-1} \text{ at } 298.15 \text{ K} \quad T = 735 \text{ K}$$

The Boltzmann distribution law applies what is called Boltzmann statistics, *i.e.* the effect of any nuclear spin is ignored. This is valid for most molecules but we will return to the effect of nuclear spin on rotational populations and spectra later on (section 4.2).

# 3 Pure Vibrational Spectroscopy



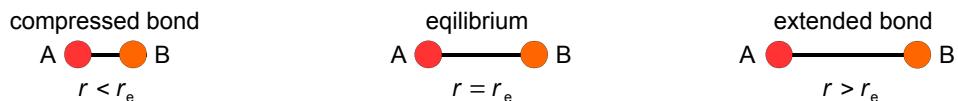
**Figure 3.1:** schematic FTIR Michelson interferometer.

The Fourier transform FTIR based on the Michelson interferometer is the normal instrument for measuring IR spectra. The non-dispersed IR (1) hits a beam splitter which is a partially reflective/transmissive plate. Half of (1) is reflected as (2) to a fixed mirror and half is transmitted as (3) to the moving mirror, which is motor driven to move at a constant speed perpendicular to the light. The reflected light from the mirrors (4) and (5) hit the beam splitter a second time. The beam splitter transmits half of (4) and reflects half of (5) which are combined as (6) but since there is a difference in path length of (4) and (5) they interfere. The interfered light intensity of (6) passes through the sample chamber, which may contain a solid, liquid or gas. The partially absorbed light passes from the sample chamber as (7) into the detector and then computer for FT processing. Experimental details may be found in (Harris 2007, p. 442) and (Levine 2009, p. 770), a gentle introduction to the underlying maths of the Fourier transform (FT) process may be found in Parker (Parker 2012, pp. 60 and 69).

motion	timescale/s	energy/cm <sup>-1</sup>
valence electron transition	$\sim 10^{-15}$	$\sim 14,000$ to $\sim 100,000$
vibration of bond or angle	$\sim 10^{-13}$	$\sim 300$ to $\sim 4400$
rotation of a molecule	$\sim 10^{-11}$	$\sim 0.2$ to $\sim 60$
molecular collisions, gas 1 atm 25°C	$\sim 10^{-10}$	$310.83 = \frac{3}{2}RT$
fluorescence	$\sim 10^{-8}$	$\sim 14,000$ to $\sim 40,000$
phosphorescence	$\sim 1$ to $\sim 10^3$	$\sim 14,000$ to $\sim 25,000$

Consider the above approximate time and energy scales. In the gas phase the time *between* collisions is about  $10^{-10}$  s, so a vibrating chemical bond or a bending bond angle will have completed  $\sim 1000$  vibrations between collisions, however, the molecule would also undergo about 10 rotations between collisions. So to observe a *pure* vibrational spectrum the molecule must be in the *liquid* or *solid phase* to dampen out the molecular rotations. Using IR radiation of 300-4000 cm<sup>-1</sup> the photon will not be energetic enough to excite electrons in the molecular orbitals.

### 3.1 Simple Harmonic Oscillator (SHO) Model for a Vibrating Bond



**Figure 3.2:** a vibrating diatomic molecule.

In Fig.3.2 the diatomic molecule A-B has a natural vibration frequency (or wavenumber  $\bar{v}_e \text{ cm}^{-1}$ ) with the bond length  $r$  varying from fully compressed to fully extended and passing through the equilibrium bond length  $r_e$ . To a first approximation the vibrations of a chemical bond, or the bending of a bond angle between three atoms, behaves similarly to an elastic mechanical spring which was studied by Robert Hooke in 1660.

$$F(r) = -k(r - r_e) \quad \text{Hooke's Law}$$

The restoring force  $F(r)$  between the atoms is proportional to the change in the bond length  $r$  from its equilibrium value  $r_e$ . The negative sign is because the restoring force is in the *opposite* direction to the bond extension or compression, *i.e.* when the bond is fully extended  $F(r)$  will try and shorten the bond. The force constant  $k$  measures the stiffness of the bond and its resistance to changing its length.



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molecule	$k/\text{N m}^{-1}$	comment
HI	314	flexible bond
HCl	516	
$\text{H}_2$	575	
$\text{O}_2$	1177	
$\text{N}_2$	2294	inflexible bond

The vibrational potential energy  $V(r)$  is found by taking the negative of the integral of the force  $F(r)$  with respect to  $r$  in Hooke's law and choosing the potential energy to be zero at the equilibrium distance,  $V(r_e) = 0$ .

$$V(r) = \frac{1}{2}k(r - r_e)^2 \quad \text{simple harmonic vibrational potential energy}$$

In Fig. 3.3 the potential energy  $V(r)$  is the curve in red, a parabola, also shown are the lower quantized vibrational energy levels in blue *i.e.* Fig. 3.3 is an expanded version of Fig. 2.1.

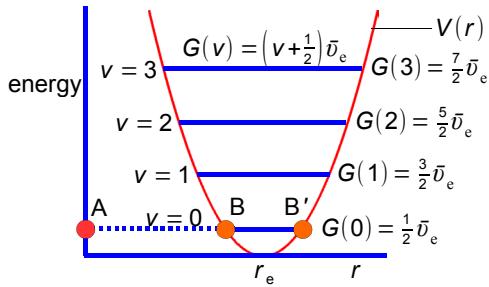


Figure 3.3: SHO model for a diatomic molecule's vibrations.

In the vibrational quantum level  $v = 0$  let us start from the fully compressed chemical bond A-B, the bond distance  $r$  has one atom A at zero distance and the other atom B is on the left hand side of the red PE curve  $V(r)$ . The bond lengthens and the molecule's PE follows the red curve  $V(r)$  down and passes through the equilibrium bond distance at  $r_e$  when  $V(r) = 0$  and then the molecule's PE  $V(r)$  moves up to the fully extended distance with atom B' now on the right hand side of the red PE curve  $V(r)$ . The vibration is completed by atom B' returning to its "starting" position at the left hand side of the vibrational PE curve  $V(r)$  at B again passing through  $V(r) = 0$  at  $r_e$ . During this vibration the  $V(r)$  has decreased from its maximum value at the start on the left hand end and followed the red curve downwards through a zero value at  $r_e$  and then upwards to the right hand side to reach the same maximum value of  $V(r)$  as it started with. Although the  $V(r)$  varies, the total vibration energy  $E(v)$  does *not* vary with bond distance, the blue horizontal lines.  $E(v)$  is in joules but it is more convenient to work in wavenumbers when we use the symbol  $G(v)$  in  $\text{cm}^{-1}$  as shown in Fig. 3.3. This constant vibrational energy  $G(v)$  implies that the vibrational kinetic energy KE is a vertical mirror image of  $V(r)$  with the KE increasing and the decreasing back down to the horizontal energy level  $G(v)$ . For clarity, only the potential and total energies are shown, not the KE.

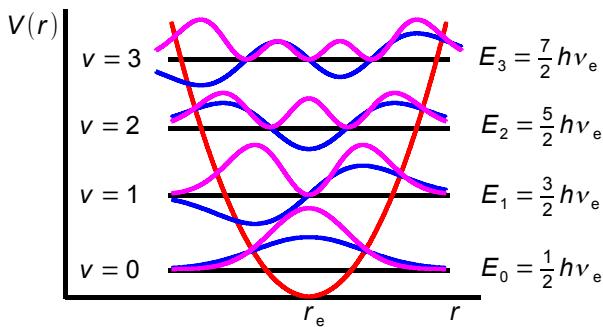
The vibrational potential energy  $V(r)$ , the red curve in Fig.3.3, is always positive due to the square term in  $V(r) = \frac{1}{2}k(r - r_e)^2$  so  $V(r)$  is a parabola centred at  $r_e$ .  $V(r)$  for the SHO rises to infinity, which cannot be physically correct (we will correct this soon) but the SHO is a reasonable *first* approximation for the *lower* vibrational levels.

Solving the Schrödinger equation with  $V(r) = \frac{1}{2}k(r - r_e)^2$  substituted for the PE gives the allowed vibrational energy levels  $E(v)$  or  $G(v)$  or eigenvalues. The mass  $m$  is replaced by the reduced mass  $\mu$  of the vibrating diatomic molecule.

$$-\frac{\hbar^2}{8\pi^2\mu} \frac{d^2\psi(r)}{dr^2} + \frac{1}{2}k(r-r_e)^2\psi(r) = E\psi(r) \quad \text{the SHO Schrödinger equation}$$

$$\begin{aligned} E(v) &= (v+\frac{1}{2})\hbar\nu_e \text{ J} & v = 0, 1, 2, 3, 4, \dots \\ G(v) &= (v+\frac{1}{2})\bar{\nu}_e \text{ cm}^{-1} & v = 0, 1, 2, 3, 4, \dots \end{aligned} \quad \text{SHO energy levels}$$

We need to distinguish between the vibrational quantum number  $v$  (Roman italic “vee”) from the equilibrium vibrational frequency  $\nu_e$  (Greek italic “nu” “ee”) and the wavenumber  $\bar{\nu}_e$  (Greek italic “nu” “ee” bar). When the vibrational quantum number is  $v = 0$  then  $E(0) = \frac{1}{2}\hbar\nu_e$  which is the vibrational *zero point energy* (ZPE). So even at zero kelvin the bonds of all molecules are still vibrating in their lowest level. Above the level  $v = 0$  there are a series of *equally* spaced energy levels. Note that the equally spaced levels are different from the situation of a particle in a one-dimensional box whose walls rise immediately from zero to infinity (section 1.7.2) unlike the parabolic increase of the SHO model.



**Figure 3.4:** sketch of  $\psi$  (blue) and  $\psi^2$  (magenta) for a SHO.

The vibrational ZPE satisfies Heisenberg's uncertainty principle. Although the total vibrational energy is known exactly,  $E_0 = \frac{1}{2}\hbar\nu_e$  the uncertainties in the vibrational kinetic energies is  $\Delta KE \approx \frac{1}{2}\hbar\nu_e \approx \Delta p^2/2\mu$  so the uncertainty in the momentum is  $\Delta p \approx (\hbar\mu\nu_e)^{\frac{1}{2}}$ . The uncertainty in the vibrational position is  $\Delta r \approx 2 \times$  vibrational amplitude and so  $\Delta p \times \Delta r \geq \hbar/4\pi$ . If hypothetically the molecule could be permanently at the minimum of the curve then simultaneously both  $\Delta r = 0$  and  $\Delta p = 0$  which is not allowed by the Heisenberg uncertainty principle.

The probability density distributions  $\psi^2$  is shown Fig. 3.4. There is a small probability, dependent upon  $\exp(-(r - r_e)^2)$  of finding the bond length outside the two classical turning points. For clarity this is exaggerated in Fig. 3.4. This arises because the potential energy does not rise to infinity as vertical walls as it did in the particle in a one-dimensional box (section 1.7.2) but rises more slowly as  $V(r) = \frac{1}{2}k(r - r_e)^2$ .

Classically you would expect the atoms to spend most time where they have zero kinetic energy *i.e.* at the turning points. In the  $v = 0$  level, however, the most probable bond length is  $r_e$  where they have the maximum velocity! But as  $v$  increases and the vibrational energy increases and the amplitude of the vibrations increase the two wings of the probability density distribution start to become more important and they dominate from  $v \sim 15$  onwards. This is another example of the correspondence principle (section 1.7.1). Note that in the simple harmonic oscillator model the frequency of vibration  $\nu_e$  is constant but as the amplitude increases and as the atoms have to travel a greater distance in the same time they have a higher average kinetic energy thus  $E(v)$  increases. The frequency of vibration is

$$\nu_e = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{ Hz or s}^{-1} \quad \text{equilibrium vibration frequency}$$
$$\bar{\nu}_e = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \text{ cm}^{-1} \quad \text{equilibrium vibration wavenumber}$$

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Where  $c = 2.9979 \times 10^{10} \text{ cm s}^{-1}$ ,  $k$  is the force constant and  $\mu$  is the reduced mass of the diatomic molecule. If one is dealing with a polyatomic molecule then the reduced mass should be replaced by the effective mass  $m_{\text{eff}}$  as not all of a large molecule is involved in a given vibrational mode.

*Worked example:* for an IR photon of  $\bar{\nu} = 1000 \text{ cm}^{-1}$  determine the frequency  $\nu$  and the period of rotation  $\tau_{\text{vib}}$  (Greek italic tau) assuming it is equal to the reciprocal of the frequency.

$$c = \lambda \nu \quad \nu = c/\lambda = c \bar{\nu} = (2.998 \times 10^{10} \text{ cm s}^{-1})(1000 \text{ cm}^{-1}) = 2.998 \times 10^{13} \text{ s}^{-1}$$

$$\tau_{\text{vib}} = 1/\nu = 3.336 \times 10^{-14} \text{ s}^{-1}$$

### 3.1.1 Specific Selection Rule for SHO Transitions

I am going to leave discussing the gross selection rule for vibrational transitions until we have a look at polyatomic molecules. In the meantime let's concentrate on the specific selections rule.

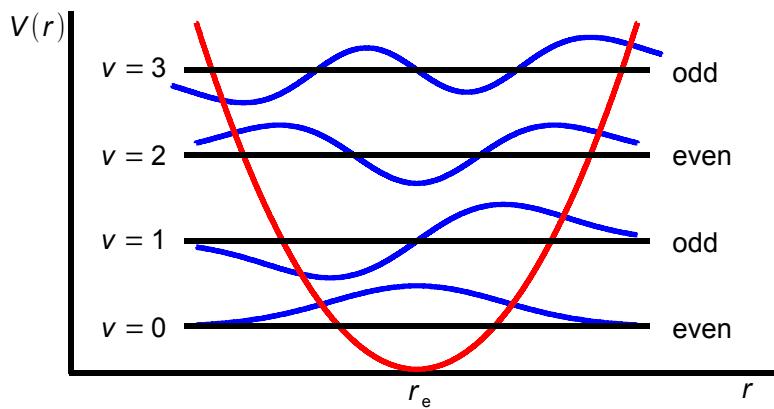


Figure 3.5: symmetry of the SHO vibrational wavefunctions.

The simple harmonic oscillator wavefunctions alternate even and odd or symmetric and antisymmetric around the  $r_e$  position. The transition moment  $\mu_{mn}$  (section 1.9) is only even or symmetric (transition is allowed) for jumps between even  $\leftrightarrow$  odd wavefunctions as the component of the molecule's dipole moment operator ("hat mu") is odd in the direction of the light's electric vector.

$$\mu_{mn} = \int_{-\infty}^{\infty} \psi_m^* \hat{\mu} \psi_n d\tau$$

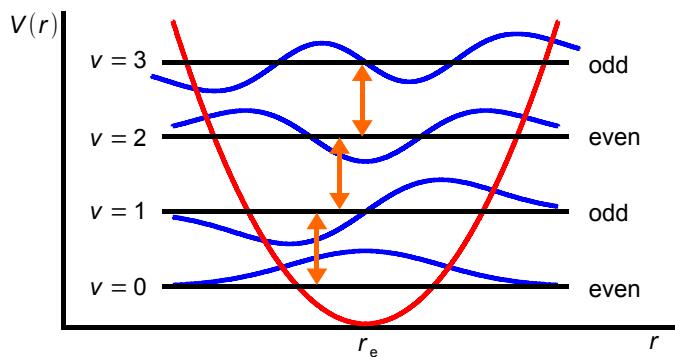
$$\mu_{mn} = \text{even} \times \text{odd} \times \text{odd} = \text{even}$$

$$\mu_{mn} = \text{odd} \times \text{odd} \times \text{even} = \text{even}$$

The specific selection rule for the simple harmonic oscillator model vibrational transitions is

$$\Delta \nu = \pm 1 \quad \text{SHO specific selection rule}$$

Transitions with  $\Delta\nu = +1$  are absorptions and  $\Delta\nu = -1$  are emissions. The simple harmonic transitions would be as in Fig. 3.6 and they would all appear at the same wavenumber in the spectrum.



**Figure 3.6:** simple harmonic oscillator allowed transitions.

### 3.2 Anharmonic Model for a Vibrating Molecule

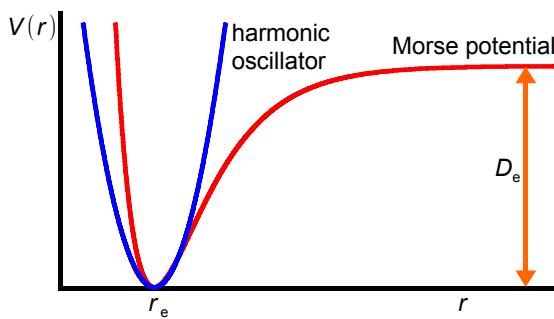
Although the simple harmonic oscillator model is a useful first approximation for the lower vibrational levels, we know it is physically unrealistic at high vibrational quantum numbers. A parabola rises to infinity so the molecule would not dissociate by bond breaking. A better model, firstly, needs to rise more steeply as  $r$  gets smaller on the left hand side on the PE curve due to electron-electron and nuclear-nuclear repulsion. Secondly, at large values of  $r$  it must eventually curve over and become horizontal (plateau off) as the bond dissociates into separate atoms moving apart from one another on the right hand side of the PE curve. The empirical Morse potential satisfies these requirements.

$$V(r) = D_e \left(1 - e^{-\alpha(r - r_e)}\right)^2 \quad \text{Morse potential}$$

Where  $\alpha$  is the width or the steepness of the curve,

$$\alpha = \sqrt{\frac{k_e}{2D_e}}$$

$k_e$  is the force constant at the bottom of the well and  $D_e$  is the well depth from the minimum to the plateau of the Morse curve.



**Figure 3.7:** Morse potential (red) and SHO potential (blue).

Solving the Schrödinger equation with the Morse function used for the potential energy gives the vibrational energies or eigenvalues  $E(v)$  for the anharmonic oscillator (AHO).

$$E(v) = (v + \frac{1}{2})h\nu_e - (v + \frac{1}{2})^2 x_e h\nu_e \text{ J}$$

$$G(v) = (v + \frac{1}{2})\bar{\nu}_e - (v + \frac{1}{2})^2 x_e \bar{\nu}_e \text{ cm}^{-1}$$

AHO energy levels

The second negative square term increases rapidly with increasing vibrational quantum number and causes the vibrational levels to close up. The amount of anharmonicity is determined by the anharmonicity constant  $x_e$ . Although the Morse potential and the above form of the vibrational energy levels is adequate for many purposes, at high resolution or near the dissociation limit an empirical polynomial equation is required.

$$E(v) = (v + \frac{1}{2})h\nu_e - (v + \frac{1}{2})^2 x_e h\nu_e + (v + \frac{1}{2})^3 y_e h\nu_e - (v + \frac{1}{2})^4 z_e h\nu_e + \dots \text{ J}$$

$$G(v) = (v + \frac{1}{2})\bar{\nu}_e - (v + \frac{1}{2})^2 x_e \bar{\nu}_e + (v + \frac{1}{2})^3 y_e \bar{\nu}_e - (v + \frac{1}{2})^4 z_e \bar{\nu}_e + \dots \text{ cm}^{-1}$$

The constants  $x_e$ ,  $y_e$  and  $z_e$  are dimensionless with  $x_e$  typically between 0.02 and 0.004 and  $y_e$  and  $z_e$  being even smaller. The anharmonic oscillator model still predicts a zero point energy but the vibrational energy levels close-up as  $v$  increases and become a continuum at the dissociation limit.

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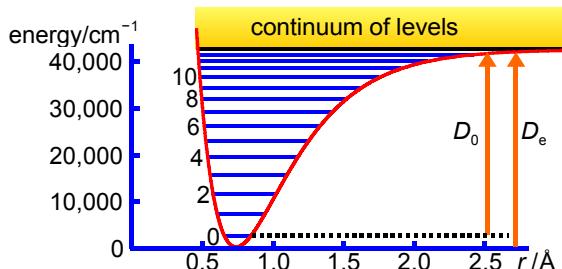
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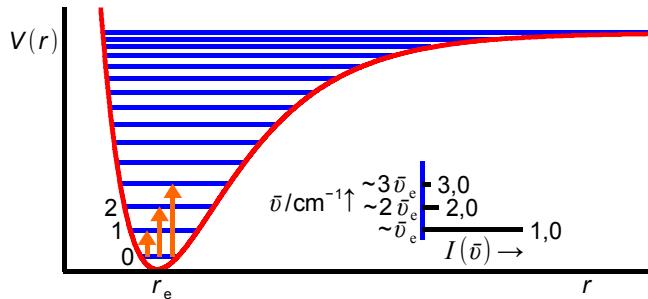
**Figure 3.8:** diatomic molecule anharmonic vibrational energy levels.

### 3.2.1 Specific Selection Rule for the Anharmonic Oscillator

There is an asymmetry in each of the vibrational wavefunctions for the AHO with the right hand side of them spread out over a greater bond distance than the corresponding left hand side. As a consequence the transition dipole  $\mu_{mn}$  when calculated gives the following specific selection rule.

$\Delta v = \pm 1$	fundamental	high intensity
$\Delta v = \pm 2$	first overtone	low intensity
$\Delta v = \pm 3$	second overtone	very low intensity

### 3.2.2 Overtone Transitions



**Figure 3.9:** overtone transitions.

The overtones are at approximate multiples of  $\bar{v}_e$  the fundamental wavenumber due to the closing up of the vibrational levels with increasing values of  $v$ . The intensities drop rapidly due to the decrease in the quantum mechanical probability as the transition moment  $\mu_{mn}$  decreasing with increasing  $v$ . To calculate the energies of the overtones we calculate the  $v = 0, 1, 2$  and  $3$  energy levels making use of fractions (for ease of subtraction) we then subtract the energies of the levels to find the energies of the transitions.

$G_1 = \frac{3}{2} \bar{v}_e - \frac{9}{4} x_e \bar{v}_e$	$\Delta G_{1,0} = \bar{v}_e - 2 x_e \bar{v}_e$	$\text{cm}^{-1}$	fundamental
$G_2 = \frac{5}{2} \bar{v}_e - \frac{25}{4} x_e \bar{v}_e$	$\Delta G_{2,0} = 2 \bar{v}_e - 6 x_e \bar{v}_e$	$\text{cm}^{-1}$	first overtone
$G_3 = \frac{7}{2} \bar{v}_e - \frac{49}{4} x_e \bar{v}_e$	$\Delta G_{3,0} = 3 \bar{v}_e - 12 x_e \bar{v}_e$	$\text{cm}^{-1}$	second overtone

There is another consequence of anharmonicity which we will leave until we consider polyatomic molecules.

### 3.3 Hot Band Transitions

Hot bands involve only  $\Delta\nu = +1$  absorptions, unlike overtone transitions. The intensity ratio of any  $\Delta\nu = +1$  hot band transition compared to the fundamental is given by

$$\frac{I(\nu+1,\nu)}{I(1,0)} = \frac{\mu(\nu+1,\nu)}{\mu(1,0)} \frac{g_\nu}{g_0} \frac{n_\nu}{n_0}$$

The transition moments  $\mu_{mn}$  are identical for all  $\Delta\nu = \pm 1$ , so the ratio of the transition moments (the  $\mu$  term) is unity. Each of the vibrational levels are non-degenerate so the ratio of degeneracies (the  $g$  term) is also unity. The thermal population of the *initial* vibrational energy levels (the  $n$  term) is given by the Boltzmann distribution law for the vibrational levels and for simplicity we will use the simple harmonic energies.

$$\frac{n_\nu}{n_0} = \exp\left(-\frac{E_\nu - E_0}{k_B T}\right) \quad \text{Boltzmann distribution law for vibrational levels}$$

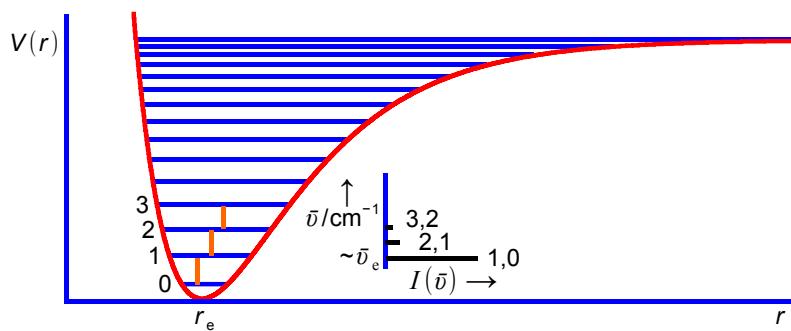
The exponential energy terms is  $G(\nu) = (\nu + \frac{1}{2})\bar{v}_e$  and  $G(0) = \frac{1}{2}\bar{v}_e$  and so  $G(\nu) - G(0) = \nu \bar{v}_e \text{ cm}^{-1}$ .

$$\frac{I(\nu+1,\nu)}{I(1,0)} = \frac{n_\nu}{n_0} = \exp\left(-\frac{\nu \bar{v}_e}{k_B T / h c}\right) \quad \text{intensities of vibrational hot bands}$$

As the name implies the hot bands intensities are altered by temperature whereas the overtone intensities are independent of temperature as it is the transition moment  $\mu_{mn}$  which is their determining factor.

$G_0 = \frac{1}{2}\bar{v}_e - \frac{1}{4}x_e\bar{v}_e$		
$G_1 = \frac{3}{2}\bar{v}_e - \frac{9}{4}x_e\bar{v}_e$	$\Delta G_{1,0} = \bar{v}_e - 2x_e\bar{v}_e \text{ cm}^{-1}$	fundamental
$G_2 = \frac{5}{2}\bar{v}_e - \frac{25}{4}x_e\bar{v}_e$	$\Delta G_{2,1} = \bar{v}_e - 4x_e\bar{v}_e \text{ cm}^{-1}$	first hot band
$G_3 = \frac{7}{2}\bar{v}_e - \frac{49}{4}x_e\bar{v}_e$	$\Delta G_{3,2} = \bar{v}_e - 6x_e\bar{v}_e \text{ cm}^{-1}$	second hot band

Hot bands are all very close to the fundamental, but at slightly *lower* wavenumbers.



**Figure 3.10:** simulation of hot bands.

The thermal population of vibrational levels *always* has  $\nu = 0$  as the most populated level and there is an exponential decrease in population of higher levels. Of course a real spectrum may have both overtones and hot bands present depending upon the equilibrium vibration wavenumber and the temperature.

*Worked example:* a molecule has  $\bar{v}_e = 2000 \text{ cm}^{-1}$  what are the relative intensities of the fundamental, and the first and second hot bands at 298 K, and in an electrical discharge at 2000 K? Treat the molecule as a harmonic oscillator for simplicity.

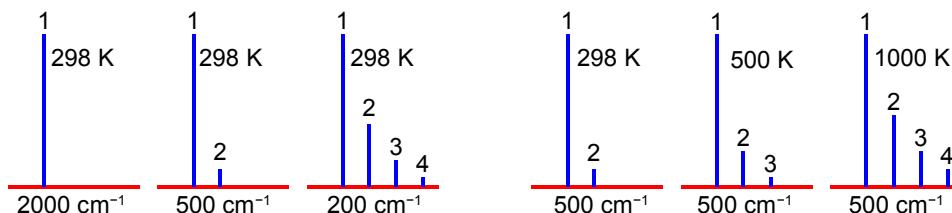
$$(a) k_B T / hc = 207.23 \text{ cm}^{-1} \text{ at } 298.15 \text{ K}$$

$$\frac{I(2,1)}{I(1,0)} = \exp\left(-\frac{1 \times 2000 \text{ cm}^{-1}}{207.2 \text{ cm}^{-1}}\right) = 6.4 \times 10^{-5} \quad \frac{I(3,2)}{I(1,0)} = \exp\left(-\frac{2 \times 2000 \text{ cm}^{-1}}{207.2 \text{ cm}^{-1}}\right) = 4.1 \times 10^{-9}$$

$$(b) k_B T / hc = 1390 \text{ cm}^{-1} \text{ at } 2000 \text{ K}$$

$$\frac{I(2,1)}{I(1,0)} = \exp\left(-\frac{1 \times 2000 \text{ cm}^{-1}}{1390 \text{ cm}^{-1}}\right) = 0.24 \quad \frac{I(3,2)}{I(1,0)} = \exp\left(-\frac{2 \times 2000 \text{ cm}^{-1}}{1390 \text{ cm}^{-1}}\right) = 0.06$$

Fig. 3.11 shows how the populations in the various vibrational levels vary with both the  $\bar{v}_e$  and  $T$ . Most small molecules with a large  $\bar{v}_e$  e.g.  $^1\text{H}^{81}\text{Br}$   $\bar{v}_e = 2649 \text{ cm}^{-1}$ , essentially populate only the  $\nu = 0$  at normal temperatures around 298 K. Molecules with small  $\bar{v}_e$  due to very flexible/weak bonds with a small  $k$  and/or large  $\mu$  may have significant populations of  $\nu = 1$ , and sometimes higher  $\nu$  as well, e.g.  $^{79}\text{Br}^{81}\text{Br}$   $\bar{v}_e = 323 \text{ cm}^{-1}$ .



**Figure 3.11:** vibrational populations relative to  $\nu = 1$ .

### 3.4 Vibrational Spectra of Polyatomic Molecules

If a molecule contains  $N$  atoms and then each atom requires three coordinates ( $x, y, z$ ) to specify its position and the molecule needs a total of  $3N$  coordinates to describe the positions of all its atoms. We say the molecule has  $3N$  degrees of freedom. These  $3N$  degrees of freedom describe the translational, rotational and vibrational motions of the molecule. The translation of the whole molecule accounts for three degrees of freedom. A linear molecule has two rotational degrees of freedom (section 2.4) and so a linear molecule has  $(3N - 5)$  degrees of freedom left to describe its vibrations, we say it has  $(3N - 5)$  modes of vibration or ways of vibrating

$(3N - 5)$  modes of vibration for a linear molecule

A non-linear molecule has three rotational degrees of freedom and so it has one less vibrational mode than a linear molecule.

$(3N - 6)$  modes of vibration for a non-linear molecule

In the simple harmonic approximation these modes of vibration are independent of one another and don't interact. In the anharmonic treatment different modes of vibration may interact weakly and give mixed mode vibrations, *combination bands*.

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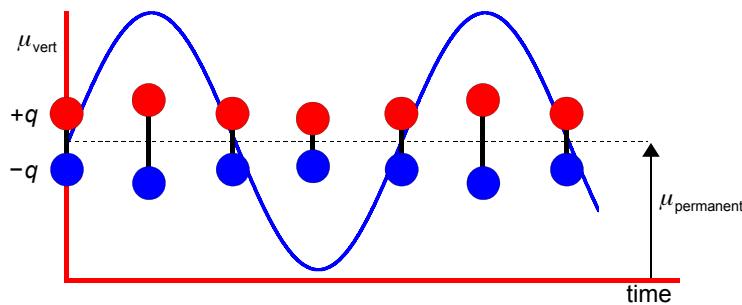
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### 3.4.1 Gross Selection Rule for Pure Vibrational Spectroscopy

The gross selection rule applies to *each* of the vibration modes rather than to the molecule as a whole, of course for a diatomic molecule only has one vibration mode as  $N = 2$  so  $(3N - 5) = 1$ .

A vibrational mode is IR active if the dipole moment of the molecule changes      IR gross selection rule



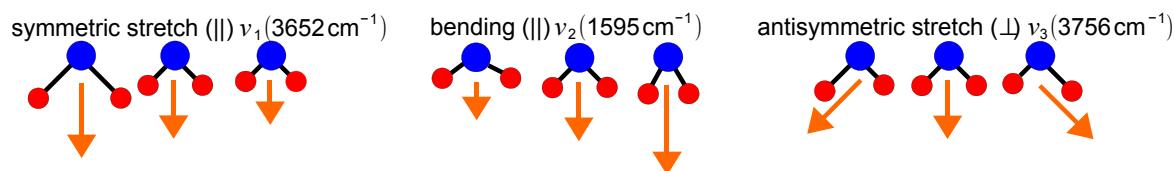
**Figure 3.12:** vertical component of the dipole moment of a vibrating heteronuclear diatomic.

Remember, a dipole moment  $\mu$  (strictly an electric dipole moment as there are also magnetic dipole moments) is the partial charge separation ( $+q$  and  $-q$ ) multiplied by the distance between them  $r$ .

$$\mu = qr \quad \text{C m}$$

The coulomb metre (C m) is too large a unit for molecular dipoles which are measured, so the non-SI unit of debye is used (symbol D) where  $1 \text{ D} = 3.33564 \times 10^{-30} \text{ C} \cdot \text{m}$ . Fig. 3.12 shows a diatomic molecule's vertical component of its dipole moment varying as it vibrates. This oscillating electric field can interact with the electric field of light. A heteronuclear diatomic will be IR active, *i.e.* it will have an IR spectrum. A homonuclear diatomic molecule (as well as not having a permanent dipole moment) does not have a *change* in dipole moment as it vibrates and is IR inactive, *i.e.* does not absorb in the IR. Homonuclear diatomics are both IR and MW inactive but for different reasons. So thinking about the Earth's major atmospheric constituents  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{Ar}$  are IR inactive and allow IR from the Sun to reach us and warm the Earth where the IR is absorbed mainly at the surface by the ground, clouds, ice and water. Of the minor constituents,  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{O}_3$ ,  $\text{CH}_4$  and  $\text{CO}_2$  they are all IR active and are IR absorbers. Let's have a look at  $\text{H}_2\text{O}$  and  $\text{CO}_2$  in detail.

### 3.4.2 Water IR Spectrum



**Figure 3.13:** vibrational modes of  $\text{H}_2\text{O}$ .

Water is a triatomic non-linear molecule with  $N = 3$  and  $(3N - 6) = 3$ , so water has three vibrational modes (also called normal modes). In the simple harmonic approximation these modes are independent in that you can excite one of them and not excite any others, they are quantum mechanically *orthogonal* to one another. Fig. 3.13 shows the three fundamental vibration modes for  $\text{H}_2\text{O}$  with exaggerated movements. Each mode shows the two classical turning points and the equilibrium position. The dipole vector points towards the *positive* end of the molecule, see Parker for the convention with dipoles (Parker 2013a, p. 129) with the O-atom partially negative and the H-atoms carrying a partial positive charge. Two of the modes involve stretching of the OH bond and the third does not alter the OH bonds lengths but instead alters the HOH bond angle.

In the symmetric stretching mode the two bonds extend and contract in phase with one another and the molecule's dipole moment vector increases and decrease in unison with them and always points along the main symmetry axis of the molecule, called a *parallel* vibration, symbol  $\parallel$ , and is IR active. In the  $C_{2v}$  point group for water the symmetric stretching mode has  $a_1$  symmetry.

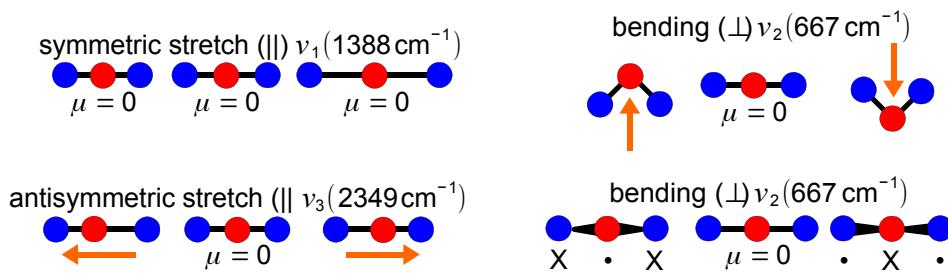
In the antisymmetric stretching mode the two OH bond lengths expand and contact out of phase and the water molecule's dipole moment vector alters perpendicular to the main symmetry axis of the molecule, called a perpendicular mode, symbol  $\perp$ , and is IR active with  $b_2$  symmetry with  $yz$ -plane is the plane of the molecule.

The bending mode alters predominantly the HOH bond angle (although there is also a small change in bond lengths), the molecule's dipole moment changes in magnitude but continues to point along the symmetry axis, a parallel vibration  $\parallel$ , and is IR active with  $a_1$  symmetry.

The vibrations are also labelled as  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$  by decreasing wavenumber within their symmetry type. The parallel symmetric vibrations (symmetric stretch and bending) are of  $a_1$  symmetry and are labelled  $\nu_1$  for the highest symmetric wavenumber and  $\nu_2$  for the next highest symmetric wavenumber also of  $a_1$  symmetry. The antisymmetric stretch which is  $b_2$  is then labelled  $\nu_3$ .

From the values of the wavenumbers we see that it is easier to bend chemical bonds compared with altering their lengths and symmetric stretching always occur at lower wavenumbers than the corresponding antisymmetric stretch. The heavy atoms move shorter distances than the light atoms such as hydrogen (although this is not apparent from Fig. 3.13).

### 3.4.3 Carbon Dioxide IR Spectrum



**Figure 3.14:** vibrational modes of  $\text{CO}_2$ .

Carbon dioxide is a triatomic linear molecule,  $N = 3$  and  $(3N - 5) = 4$ , so  $\text{CO}_2$  has four vibrational modes. The C-atom carries a partial positive charge and the O-atom carries a partial negative charge. The modes are shown in Fig. 3.14 with exaggerated movements. For historical reasons, the degenerate bending modes of linear triatomics such as  $\text{CO}_2$  are always labelled as  $\nu_2$ . The symmetric stretching mode does not have any change in dipole moment ( $\sigma_g^+$  in the  $D_{\infty h}$  point group) and is IR inactive and transparent to IR, so this mode's fundamental wavenumber was obtained from its Raman spectrum. Remember, although this mode is IR inactive the  $\text{CO}_2$  molecules will still vibrate symmetrically but will only change their  $\nu_1$  quantum number by collisional energy transfer rather than by IR photon absorption or emission.

The antisymmetric stretching mode is IR active the dipole moment changes are along the molecule's symmetry axis ( $\sigma_u^+$  in the  $D_{\infty h}$  point group) and it is a parallel vibration.

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The other two modes involve bending vibrations where the OCO bond angle changes. Any arbitrary bending of the molecule can be resolved into two components of mutually perpendicular bending modes one in the plane of the page (left) and the other coming into and out of the page (right). The latter is indicated by the arrow convention with the point of the arrow (dot) coming towards you and the flight feathers (cross) moving away from you. Both of the bending modes are IR active but they require the same amount of energy and are degenerate with one another ( $\pi_u$  in the  $D_{\infty h}$  point group) but each of the four modes are themselves non-degenerate. The bending modes are perpendicular modes as the dipole change is at right angles to the symmetry axis of the CO<sub>2</sub> molecule.

Although there are four modes for CO<sub>2</sub> we observe only two fundamental peaks in the IR, these are important as CO<sub>2</sub> is a greenhouse gas, indeed H<sub>2</sub>O is also an important greenhouse gas with its three active modes. Again we note that bending the bond angles is easier than stretching the bonds and symmetric stretching always occur at lower wavenumbers than the corresponding antisymmetric stretch.

### 3.4.4 Combination Bands

Anharmonic modes interact weakly with one another due to the asymmetry of the vibrational wavefunctions and so we can observe *low* intensity absorptions due to combinations of two different modes. These are at slightly *less* than the sum of the fundamentals due to the different anharmonicities of the upper states of the different modes. The quantum numbers  $\nu_1' \nu_2' \nu_3'$  of the upper level of the modes are given below for the combination bands of water as they all start from the 000 ground state.

$\bar{\nu} \text{ cm}^{-1}$	intensity	$\nu_1' \nu_2' \nu_3'$	vibration mode
1595	very strong	010	bend fundamental
3152	medium	020	bend first overtone
3652	strong	100	sym. stretch fundamental
3756	very strong	001	antisym. stretch fundamental
5331	medium	011	combination
6872	weak	021	combination

# 4 Vibration-Rotation Spectroscopy

motion	timescale/s	energy/cm <sup>-1</sup>
valence electron transition	$\sim 10^{-15}$	$\sim 14,000$ to $\sim 100,000$
vibration of bond or angle	$\sim 10^{-13}$	$\sim 300$ to $\sim 4400$
rotation of a molecule	$\sim 10^{-11}$	$\sim 0.2$ to $\sim 60$
molecular collisions, gas 1 atm 25°C	$\sim 10^{-10}$	$310.83 = \frac{3}{2}RT$
fluorescence	$\sim 10^{-8}$	$\sim 14,000$ to $\sim 40,000$
phosphorescence	$\sim 1$ to $\sim 10^3$	$\sim 14,000$ to $\sim 25,000$

From the time scales above, gas phase molecules can rotate freely and undergo about 100 rotations during one vibration, so the rotational levels are well defined in the gas-phase. A gas-phase IR spectrum shows both a vibrational peak and many closely spaced peaks due to simultaneous changes in the rotational level. Expanding the scale of Fig. 2.1 to cover just the  $\nu'' = 0$  and  $\nu' = 1$  and their associated rotational levels we have Fig. 4.1 with  $(\nu, J)$  vibration-rotation levels. The energy scale in Fig. 4.1 is not continuous as the gap between  $J$  levels is 10s of cm<sup>-1</sup> but the gap between  $\nu$  levels is 1000s cm<sup>-1</sup> and we may ignore the small amount of centrifugal distortion but we must take account of anharmonicity of the vibrations. The energy term in cm<sup>-1</sup> for a vibration-rotation level has the symbol  $S(\nu, J)$ .

$$S(\nu, J) = G(\nu) + F(J)$$

Ignoring centrifugal distortion but not vibrational anharmonicity we have for a vibration-rotation term.

$$S(\nu, J) = \left(\nu + \frac{1}{2}\right)\bar{\nu}_e - \left(\nu + \frac{1}{2}\right)^2 x_e \bar{\nu}_e + BJ(J+1) \quad \text{cm}^{-1} \quad \text{vibration-rotation term}$$

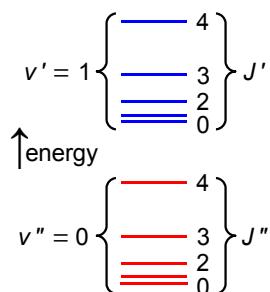


Figure 4.1: low vibration-rotation levels.

## 4.1 Selection Rules for Vibration-Rotation Transitions

The gross selection rule for vibration-rotation transitions is the same as for pure vibrational transitions,

A mode is IR active if the dipole moment of the molecule changes      IR gross selection rule

For the specific selection rule for vibration-rotation transitions we must take into account the two symmetry types of vibrational mode to be considered, parallel  $\parallel$  modes and perpendicular  $\perp$  modes.

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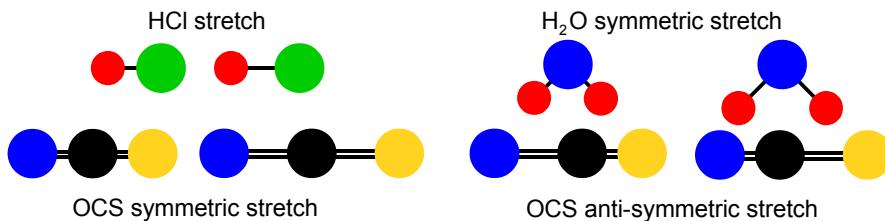
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## 4.1.1 Parallel Vibration-Rotation Specific Selection Rule

In heteronuclear diatomics there is only one mode and it is a parallel mode. In a polyatomic linear molecule the symmetric and antisymmetric stretching modes are both parallel modes. In non-linear polyatomic molecules *e.g.* water, the symmetric stretch and bending mode are parallel modes.



**Figure 4.2:** parallel (||) vibrational modes, amplitudes are exaggerated.

$$\Delta v = \pm 1, \pm 2, \pm 3, \dots \text{ and } \Delta J = \pm 1 \quad \text{parallel vibration-rotation selection rule}$$

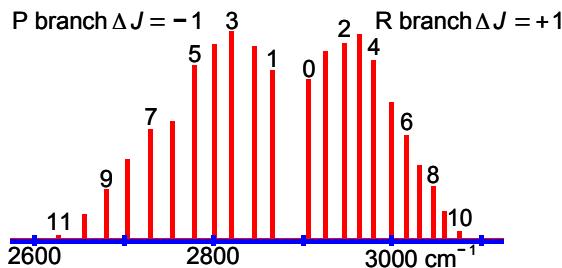
At ambient temperatures the vibration modes with equilibrium vibration wavenumbers greater than about  $700 \text{ cm}^{-1}$  are predominantly in the  $v = 0$  level but the molecules occupy a large range of rotational levels. In *most* cases we can consider absorption in a parallel vibration to follow the rule.

$$\Delta v = 1 \leftarrow 0 \text{ and } \Delta J = \pm 1$$

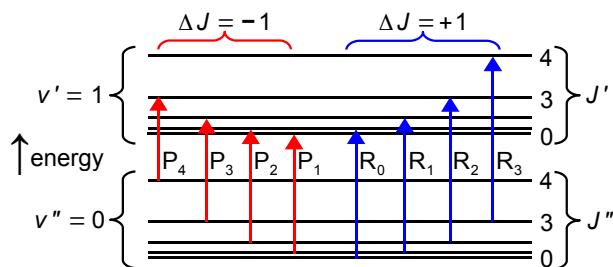
A parallel vibration-rotation spectrum has a series of lines  $2B$  apart, but the central  $\Delta J = 0$  line is absent. So remember, the parallel bands with PR branches look similar to the parallel symbol ||. Fig. 4.3 shows the HCl spectrum with the  $\Delta J = -1$  lines are called the P branch. The missing  $\Delta J = 0$  lines are called the Q branch (in the middle of the alphabet). The  $\Delta J = +1$  lines are called the R branch. Note the consistency in the spectrum. From left to right: wavenumber is increasing,  $\Delta J$  is increasing, finally P, Q, R are increasing alphabetically. The number next to each of the lines is the value of  $J''$ , the initial rotational level. In Fig. 4.3 the intensities of the lines reflects the thermal populations of the molecules in their initial rotational states  $J''$  as determined by the Boltzmann distribution law, section 2.5. We see that although the separation between the vibration-rotation lines is *roughly*  $2B$  the spectrum in fact closes up at high R branch transitions. This is due to anharmonicity, the average bond length ( $r_1$ ) of the molecule in the  $v = 1$  vibrational level is larger than in the  $v = 0$  level ( $r_0$ ) as  $B = h/8\pi Ic$  we have the following.

$$r_0 < r_1 \quad \text{then} \quad B_0 > B_1$$

Which causes the R branch to close-up relative to the P branch. So for example for  $^1\text{H}^{35}\text{Cl}$  we have the following bond lengths  $r_e = 1.275 \text{ \AA}$  with  $r_0 = 1.294 \text{ \AA}$  and  $r_1 = 1.314 \text{ \AA}$ .



**Figure 4.3:** simulation of the HCl vibration-rotation spectrum.



**Figure 4.4:** parallel vibrational energy level and transitions, energy not to scale.

In Fig. 4.4. the energy scale is not continuous as the gap between  $J$  levels is 10s of  $\text{cm}^{-1}$  but the gap between  $v$  levels is 1000s  $\text{cm}^{-1}$ .

#### 4.1.2 Perpendicular Vibration-Rotation Specific Section Rule

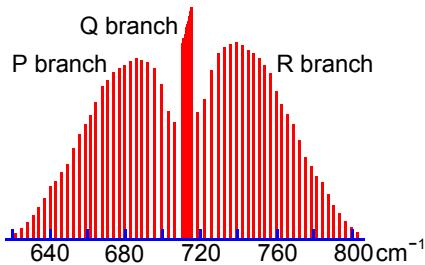
Vibrational modes which change the dipole moment of the molecule perpendicular to the main symmetry axis are perpendicular modes. Bending modes of linear molecules are perpendicular vibrations and perpendicular bands can put angular momentum into degenerate bending vibrations. This allows the molecule to have a vibration-rotation spectrum with no simultaneous change in the rotational level.

$\Delta v = \pm 1, \pm 2, \pm 3, \dots$  and  $\Delta J = 0, \pm 1$       perpendicular vibration-rotation selection rule

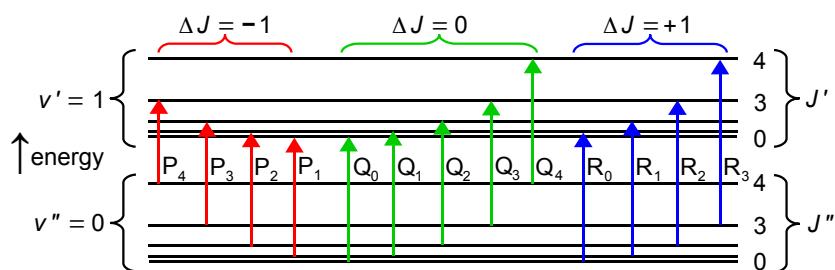
In most cases for equilibrium vibration wavenumbers above about  $700 \text{ cm}^{-1}$  and at room temperature we can consider absorption in a perpendicular vibration to follow the rule.

$\Delta v = 1 \leftarrow 0$  and  $\Delta J = 0, \pm 1$

Fig. 4.5 shows the PQR structure typical of a perpendicular mode with again the P and R branch lines roughly  $2B$  apart. The Q branch peaks with  $\Delta J = 0$  are not coincident due to  $B_0 > B_1$  from the anharmonic vibrations with the Q branch partially overlapping on the low wavenumber side of the  $\Delta J = 0,0$  transition hence the Q branch appears more intense than the P and R branches. The perpendicular vibration-rotation spectrum with its intense Q-branch in the middle looks a little like the perpendicular symbol  $\perp$ .



**Figure 4.5:** simulation of the HCN bending mode spectrum.



**Figure 4.6:** perpendicular vibration-rotation energy levels and transitions, energy not to scale.

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In Fig. 4.6. the energy scale is not continuous as the gap between  $J$  levels is 10s of  $\text{cm}^{-1}$  but the gap between  $v$  levels is 1000s  $\text{cm}^{-1}$ . Although pure rotation spectroscopy in the MW region gives high precision measurements for bond lengths and angles, this is not possible for those molecules which have a centre of symmetry and are MW inactive. Vibration-rotation spectroscopy allows molecules without permanent dipole moments, e.g.  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{HCCH}$  and benzene, to have their rotational constants and hence their structures determined.

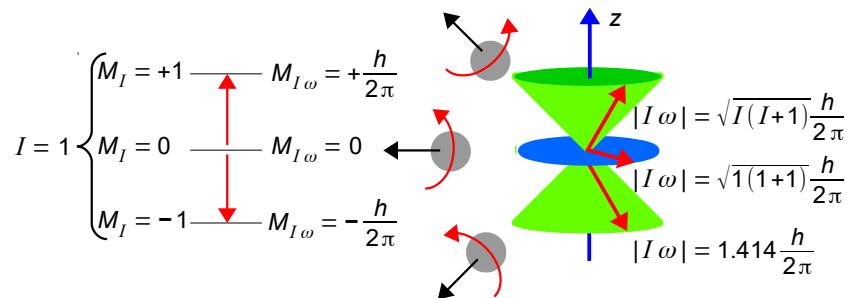
## 4.2 Rotations and Nuclear Statistics

In section 2.5 we looked at the Boltzmann distribution law and its effect on rotational populations and consequently its effect on both pure rotational spectroscopy and vibration-rotation spectroscopy. Boltzmann statistics, where the effect of nuclear spin is ignored, applies to most molecules but not to molecules with a centre of symmetry.

Individual neutrons and protons have spin quantum numbers  $I$  equal to  $\frac{1}{2}$  (as do electrons with  $s = \frac{1}{2}$ ) and so the nuclei of atoms have spin quantum numbers  $I$ , see below. Particles with *half-integral* values of  $I$  are called *fermions* (pronounced “fermi-ons” after the Italian physicist Enrico Fermi). Particles with *integral* values of  $I$  including 0 are called *bosons* (pronounced “bose-ons” named after the Indian physicist SN Bose). As we discussed in section 1.2.2 the photon it has a spin quantum number of 1 and is a boson.

particle	$e^-$	$h\nu$	$^1\text{H}$	$^2\text{H}$	$^{12}\text{C}$	$^{13}\text{C}$	$^{16}\text{O}$	$^{17}\text{O}$	$^{19}\text{F}$	$^{35}\text{Cl}$	$^{37}\text{Cl}$
spin quantum number	$\frac{1}{2}$	1	$\frac{1}{2}$	1	0	$\frac{1}{2}$	0	$\frac{5}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$
fermion/boson	f	b	f	b	b	f	b	f	f	f	f

Fig. 4.7 shows the example for a nuclear spin quantum number of  $I = 1$ , the magnitude of the nuclear spin angular momentum (the length of the side of the cones of uncertainty) is the modulus  $|I\omega|$ . The component in a given direction (the  $z$  direction) of the nuclear spin angular momentum  $M_{I\omega}$  is the height of the cone and it is also quantized.



**Figure 4.7:** nuclear spin quantum number  $I = 1$  and nuclear spin angular momentum.

All particles have to obey the Pauli Principle which describes the different effects of symmetry on the two types of particle.

When two indistinguishable *fermions* are interchanged  
the *overall* wavefunction must *change sign* (antisymmetric)

Pauli's principle

When two indistinguishable *bosons* are interchanged  
the *overall* wavefunction must stay the *same* (symmetric)

The Pauli *exclusion* principle is the application of the more general Pauli principle to the specific case of the antiparallel spins of a pair of electrons (fermions) occupying the same atomic or molecular orbital.

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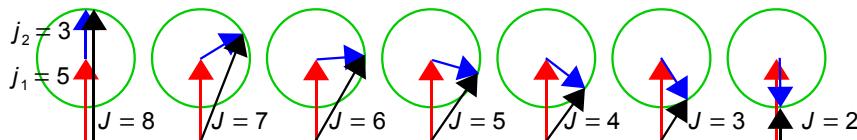


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#### 4.2.1 Clebsch-Gordon Series

Angular momentum is a vector and when we consider the *coupling* between *two* angular momentum vectors then the possible values of the total angular momentum is summarized by the Clebsch-Gordon series. If our individual angular momentum quantum numbers are in general  $j_1$  and  $j_2$  then the total angular momentum quantum number is symbolized by a capital letter  $J$ . Angular momentum quantum numbers  $j_1$  and  $j_2$  as well as the total  $J$  are all *positive* numbers as is implied by the absolute sign in the Clebsch-Gordon series, it is *only* their components along a given direction that may be positive or negative. If  $j_1$  and  $j_2$  are both integers then  $J$  is also an integer but if either  $j_1$  or  $j_2$  are half-integers then  $J$  may also be a half-integer. Remember that each of the quantum numbers  $j_1$  and  $j_2$  as well as the total  $J$  tells us the how many  $h/2\pi$  units of angular momentum we have, but normally the multiplier  $h/2\pi$  is assumed and only the quantum numbers are explicitly considered. The Clebsch-Gordon series is a summary of the vector additions and subtractions shown pictorially in Fig. 4.8 where a circle is drawn centred at the junction of  $j_1$  and  $j_2$  and of radius of the smaller vector,  $j_2$ . The sum of these vectors  $J$  has to start at the tail of  $j_1$  and meet the head of  $j_2$  at the circumference of the circle.

$$J = j_1 + j_2, \quad j_1 + j_2 - 1, \quad j_1 + j_2 - 2, \quad j_1 + j_2 - 3, \quad \dots, \quad |j_1 - j_2| \quad \text{Clebsch-Gordon series}$$



**Figure 4.8:** the triangle rule for coupling two angular momenta.

We will be using the Clebsch-Gordon series at various times from now on for spin and orbital angular momenta of molecules, nuclei and electrons. The various conventional symbols used for these different types of angular momenta will introduce as we meet them, we have already met rotational and nuclear angular momentum  $J$  and  $I$  quantum number symbols.

#### 4.2.2 CO<sub>2</sub> Rotational Populations and Spectrum

If a CO<sub>2</sub> molecule has two identical <sup>16</sup>O nuclei at each end, *i.e.* <sup>16</sup>OC<sup>16</sup>O then the molecule has a centre of symmetry at the C-atom nucleus. The two <sup>16</sup>O nuclei have spin quantum numbers  $I_1 = I_2 = 0$  and they are bosons. From the Clebsch-Gordon series the total nuclear spin quantum number  $I$  for the two <sup>16</sup>O atoms has a maximum value of  $I = 0$  and a minimum value of  $I = 0$ , *i.e.* there is only one value  $I = 0$ .

When  $^{16}\text{OC}^{16}\text{O}$  undergoes half a rotation ( $180^\circ$ ) the two identical boson  $^{16}\text{O}$  atoms have interchanged position and the overall wavefunction  $\psi_{\text{overall}}$  for this interchange of bosons must be symmetric. Now the overall wavefunction  $\psi_{\text{overall}}$  for the interchange is the product of the rotational wavefunction  $\psi_{\text{rot}}$  and the nuclear spin wavefunction  $\psi_{\text{ns}}$  as these are the only wavefunctions that are changed by the  $180^\circ$  rotation. The maths of multiplying symmetric and antisymmetric wavefunctions is the same as multiplying plus and minus.

$$\psi_{\text{overall}} = \psi_{\text{rot}} \times \psi_{\text{ns}}$$

The  $\psi_{\text{overall}}$  wavefunction for exchanging the two  $^{16}\text{O}$  bosons must be symmetric and the  $\psi_{\text{ns}}$  for the exchange of the two zero nuclear spins  $I_1 = 0$  and  $I_2 = 0$  is also symmetric.

$$\psi_{\text{overall}} = \psi_{\text{rot}} \times \psi_{\text{ns}} \quad \text{symmetric} = \psi_{\text{rot}} \times \text{symmetric}$$

This means that the rotational wavefunction  $\psi_{\text{rot}}$  must be symmetric, *i.e.*  $J = 0, 2, 4, \dots$  levels are occupied by  $^{16}\text{OC}^{16}\text{O}$  molecules as the rotational quantum levels  $J = 0, 2, 4, \dots$  are symmetric (or even) to a rotation of  $180^\circ$  as in Fig. 4.9. On the other hand, the rotational quantum levels  $J = 1, 3, 5, \dots$  are antisymmetric to an  $180^\circ$  rotation and they do *not exist* for the  $^{16}\text{OC}^{16}\text{O}$  molecule and the transitions are between even  $J$  levels.

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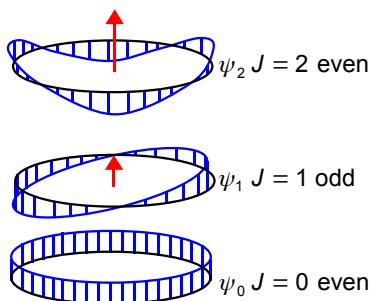
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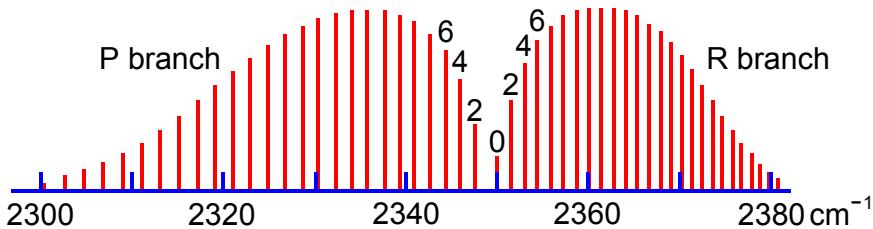


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**Figure 4.9:** symmetries of the lower rotational quantum levels.

The gap between the lines within the P and R branches for  $^{16}\text{OC}^{16}\text{O}$  is approximately  $4B$  rather than the usual  $2B$  (where the numbers are the  $J''$  values) and from Fig. 4.10 this gives  $B = 0.3902 \text{ cm}^{-1}$ . This nuclear spin interpretation is shown to be correct when we look at the vibration-rotation spectrum of  $^{18}\text{OC}^{16}\text{O}$  there is no centre of symmetry in the molecule and the PR spacings are the expected  $2B$  with twice as many lines in the PR branches as in the  $^{16}\text{OC}^{16}\text{O}$  spectrum.



**Figure 4.10:** simulation of the antisymmetric stretching (parallel) band for  $^{12}\text{C}^{16}\text{O}_2$ .

#### 4.2.3 $\text{C}_2\text{H}_2$ Rotational Populations and Spectrum

The obvious molecule that might spring to mind to examine for nuclei spin is  $^1\text{H}_2$  but as it is a homonuclear diatomic it has zero dipole moment (MW inactive) and zero change in dipole moment when it vibrates (IR inactive) and so does not have a vibration-rotation spectrum. Instead we will concentrate on acetylene (ethyne)  $^1\text{H}^{12}\text{C}^{12}\text{C}^1\text{H}$  which has the same symmetry and has the same two fermions with  $I_1 = I_2 = \frac{1}{2}$  at each end (the  $^{12}\text{C}$ -atoms are bosons  $I = 0$  and symmetric to interchange). From the Clebsch-Gordon series the maximum value for  $I = \frac{1}{2} + \frac{1}{2} = 1$  and the minimum is  $I = \frac{1}{2} - \frac{1}{2} = 0$  with the two H-atom nuclear spins respectively, either parallel  $\uparrow\uparrow$  and antiparallel  $\uparrow\downarrow$  to one another.

For acetylene molecules with the two proton spins parallel  $\uparrow\uparrow$ ,  $I = 1$  the components are  $M_I = 1, 0, -1$  so this arrangement has a degeneracy of  $(2I + 1) = 3$  i.e. it is 3-fold degenerate. The overall wavefunction  $\psi_{\text{overall}}$  must be antisymmetric to the exchange of two fermions by an  $180^\circ$  rotation. The nuclear spin wavefunction  $\psi_{\text{ns}}$  for the exchange of spin  $\uparrow$  for  $\uparrow$  is symmetric.

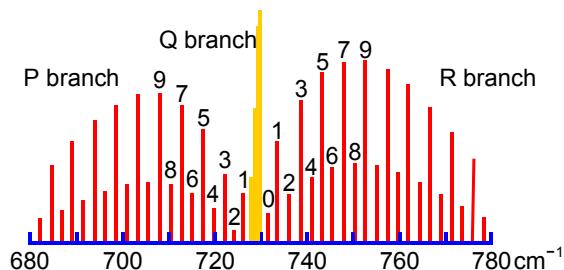
$$\psi_{\text{overall}} = \psi_{\text{rot}} \times \psi_{\text{ns}} \quad \text{antisymmetric} = \psi_{\text{rot}} \times \text{symmetric}$$

This means that the rotational wavefunction  $\psi_{\text{rot}}$  must be antisymmetric, *i.e.*  $J = 1, 3, 5 \dots$  levels are occupied by the parallel nuclear spin acetylene molecules with three times the population of acetylene molecules with non-degenerate levels.

For the acetylene with the two H-atom proton spins antiparallel  $\uparrow\downarrow$ ,  $I = 0$  and the component is  $M_I = 0$  so this arrangement has a degeneracy of  $(2I + 1) = 1$  *i.e.* it is non-degenerate. The overall wavefunction  $\psi_{\text{overall}}$  must be antisymmetric to the exchange of the two fermions by an  $180^\circ$  rotation. However, the wavefunction  $\psi_{\text{ns}}$  for the exchange of the two nuclear spins  $\uparrow$  and  $\downarrow$  is also antisymmetric.

$$\psi_{\text{overall}} = \psi_{\text{rot}} \times \psi_{\text{ns}} \quad \text{antisymmetric} = \psi_{\text{rot}} \times \text{antisymmetric}$$

This means that the rotational wavefunction  $\psi_{\text{rot}}$  must be symmetric, *i.e.*  $J = 0, 2, 4 \dots$  levels are occupied by the non-degenerate antiparallel nuclear spin acetylene molecules. The vibration-rotation spectrum of acetylene has a 3 to 1 alternation in the intensities of the lines in the PR branches. Fig. 4.11 is for one of the perpendicular bending modes of acetylene where the numbers are the  $J''$  values with the Q branch is shown in yellow. This alternating intensity disappears for the vibration-rotation spectrum of mono-deuterated acetylene HCCD as the symmetry is then lifted.



**Figure 4.11:** simulation of an acetylene bending band for  ${}^1\text{HCC}'\text{H}$ .

# 5 Raman Spectroscopy

Raman spectroscopy is named after the Indian physicist CV Raman. Monochromatic light (from a IR laser for example a Nd-YAG laser at 1064 nm or alternatively a UV-visible laser such as a dye laser) is shone on a material and the *scattered* light is examined, *not* the absorbed light. About 0.001% of the incident is scattered and about 99% of that is at the same wavelength as the incident light and is called Rayleigh scattering (elastic photon scattering). The intensity of the Rayleigh scattering depends inversely on the fourth power of the wavelength of the incident light with the blue end of the visible spectrum being scattered much more than the red end of the spectrum. Thus Rayleigh scattering of the Sun's white light by the molecules, microscopic dust and water droplets in the atmosphere is responsible for the blue sky on a summer day, the slightly reddish-yellowish colour of the Sun itself and the red sky at sunset.

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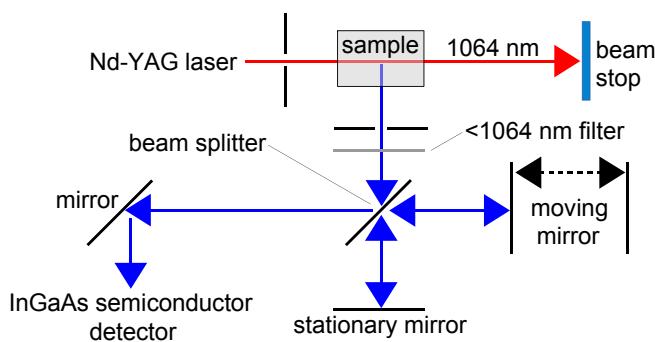
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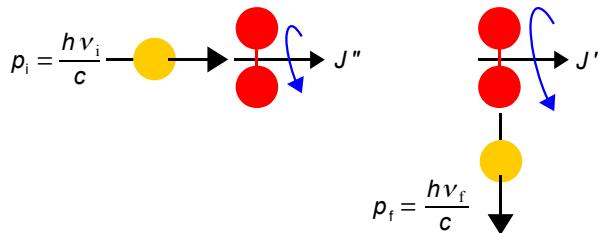
Around 1% of the scattered light has its wavelength shifted to either a lower or higher wavelength (inelastically scattered photons). A photon may collide with a molecule and there is a transfer of energy to the molecule and the scattered photon has a lower frequency than initially, this is Stokes Raman scattering. On the other hand if a photon collides with an already excited molecule then the scattered photon may gain that excitation energy and leave with a higher frequency than the incident photon, this is anti-Stokes Raman scattering. The Stokes scattering is more intense than the anti-Stokes scattering but both are very weak. In order to observe the Raman shifted lines (Stokes and anti-Stokes) and not have the analysing spectrometer swamped by the incident laser light the scattered light is analyzed at right angles to the incident laser light which is trapped by a matt black absorbing material. Filters may also be used to reduce the Rayleigh photons intensity being detected. Normally the Raman spectrometer is a Fourier transform spectrometer which gives greater sensitivity and resolution.



**Figure 5.1:** schematic Fourier transform Raman spectrometer.

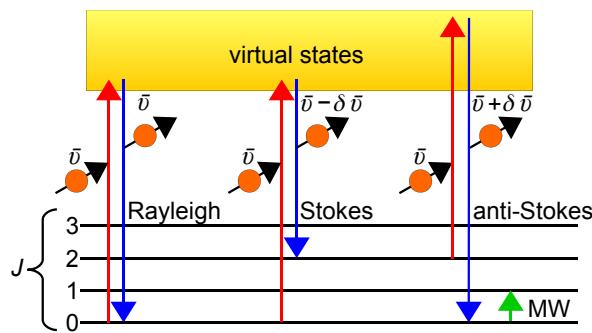
Raman scattering is used to obtain structural data for molecules with no permanent dipole moment, e.g. homonuclear diatomics H<sub>2</sub>, O<sub>2</sub> (MW inactive); or no change in dipole moment for a vibration mode, e.g. symmetric stretching mode of CO<sub>2</sub> (IR inactive mode). However, the main application of Raman spectroscopy is in chemical, biological and physical analysis for gases, liquids, solids, surfaces, human tissue, DNA and biological organisms for both stable molecules and transient species. Raman lidar (similar to radar but using shorter wavelength laser light) is used in atmospheric physics to measure the atmospheric turbulence and the water vapour vertical distribution.

The IR laser photons with initial frequency  $\nu_i$  interacts directly with the electron cloud and the bonding electrons of molecules. The incident photon has a linear momentum which is a vector and has direction as well as a magnitude of  $p_i = h\nu_i/c$ . Some of the photon's linear momentum is transferred to the molecule via its electrons to appear as rotational and vibrational changes to the molecule and after the energy transfer the photon moves off with a final linear momentum  $p_f = h\nu_f/c$  in a different direction. So generally there has been a change of both direction and frequency for the Raman scattered photon, Fig. 5.2.



**Figure 5.2:** Stokes rotational Raman scattering viewed as a photon-molecule collision.

Raman scattering may also be thought of as a two-photon process, as depicted in Fig. 5.3 where the incident photon causes the molecule to pass through a broad band of *non-stationary* electronic states. As they are non-stationary states (they are not eigenstates) they do *not* persist through time and are called virtual states, the virtual states emit the Rayleigh and Raman photons. Also shown for comparison is the MW *absorption* between two rotational eigenstates.

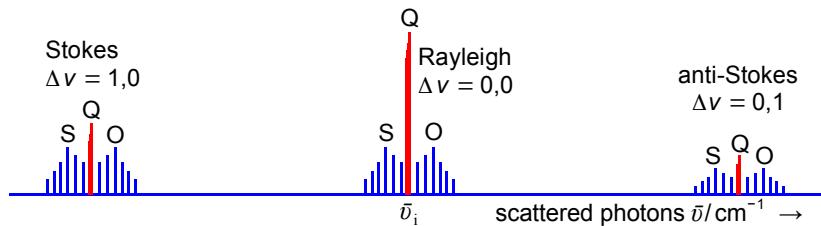


**Figure 5.3:** Rayleigh and Raman rotational scattering.

In molecules, Raman scattering excites vibrational or rotational levels, in solids or surfaces it can also excite phonons (collective excitation of lattice atoms or ions) or magnons (collective excitations of electrons spins in a crystal lattice). If the initial and final energies of the molecule are  $E_i$  and  $E_f$  then we have the following conservation of energy equation.

$$h\nu_i + E_i = h\nu_f + E_f \quad \Delta E = E_f - E_i = h(\nu_i - \nu_f) = h\Delta\nu \quad \text{Raman shift} = \Delta\nu$$

So the Raman shift gives us the molecule's energy level *difference*. Unlike absorption spectroscopy  $\nu_i$  does not have to match the molecule's energy level difference (a resonance process) but as the Raman scattering is a non-resonant process we can use any wavelength laser.



**Figure 5.4:** Raman spectrum of a gas phase diatomic molecule.

The three red lines in Fig. 5.4 are on the left the vibrational Stokes Raman line  $\nu = 1 \leftarrow 0$ ; the central red line is the Rayleigh scattered line  $\nu = 0 \leftarrow 0$ ; the right hand red line is the anti-Stokes vibrational Raman line  $\nu = 0 \leftarrow 1$ . Note the Stokes vibrational lines starting from  $\nu = 0$  are more intense than the anti-Stokes line starting from the excited vibrational level  $\nu = 1$ . The blue lines each side of the red lines are the vibration-rotation lines for the appropriate vibrational transitions. So the central blue lines surrounding the Rayleigh scattered line are the pure rotational Raman lines. Any rotationally Raman shifted lines with  $\Delta\nu$  from about 0 to 10  $\text{cm}^{-1}$  will be obscured as they are too close to the intense Rayleigh line. Those Raman shifted lines with  $\Delta\nu = 10\text{-}100 \text{ cm}^{-1}$  are easy to measure as they are away from the Rayleigh line, whereas in the IR absorption spectrum, any transitions in the 10-100  $\text{cm}^{-1}$  range are very difficult to measure. The lines on the left of the Rayleigh line with  $\bar{\nu}_f < \bar{\nu}_i$  are from the Stokes rotational Raman scattering with  $\Delta J$  positive. The lines on the right of the Rayleigh line with  $\bar{\nu}_f > \bar{\nu}_i$  are from the anti-Stokes Raman scattering with  $\Delta J$  negative.



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## 5.1 Rotational Raman Scattering

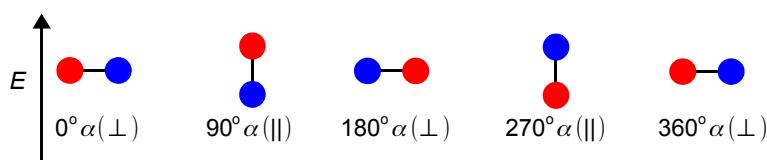
When a molecule is placed in an external electric field it becomes polarized, *i.e.* the electron density moves towards the positive part of the field to give the molecule an induced dipole. The size of the induced dipole ( $\mu_{\text{in}}$ ) is proportional to the electric field ( $E$ ) and the polarizability ( $\alpha$ ) of the molecule.

$$\mu_{\text{in}} = \alpha E \quad \text{polarization of a molecule}$$

The gross selection rule for rotational Raman activity is

There must be a change in polarizability of the molecule as the molecule rotates      rotational Raman gross selection rule

Note that this is a different requirement from pure rotational spectroscopy in the MW where the molecule needs a permanent dipole moment for a photon to be absorbed. Consider a linear molecule then the polarizability along the molecular axis will be different from that perpendicular to the axis,  $\alpha(\parallel) \neq \alpha(\perp)$  and as shown in Fig. 5.5 the polarizability will appear to be rotating twice as fast as the molecule itself.



**Figure 5.5:** rotational polarizability change for a gas phase linear molecule.

All linear molecules are rotationally Raman active molecules includes H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub> which are MW inactive. The polarizability changes twice in every rotation, so for a linear molecule we have the following rotational Raman selection rule.

$$\Delta J = 0, \pm 2, \pm 4, \dots \quad \text{linear rotor Raman selection rule}$$

Oblate and prolate symmetric molecules (section 2.4), *e.g.* C<sub>6</sub>H<sub>6</sub>, NH<sub>3</sub>, CH<sub>3</sub>Cl, have two Cartesian axes with equal polarizabilities which are different from the third Cartesian axis polarizability. They have the same polarizability only after a full 360° rotation.

$$\Delta J = 0, \pm 1, \pm 2, \pm 3, \pm 4, \dots \text{ and } \Delta K = 0 \quad \text{oblate \& prolate rotor Raman selection rule}$$

The quantum number  $K$  for the symmetric rotor is the component of  $J$  along the *molecule's* principal axis (we use  $M$ , for the component along an *externally* defined axis). As  $\Delta J = 0$  does not shift the wavenumber of the scattered photon it is at the same position as the Rayleigh scattered photons in a pure rotational Raman spectrum.

For a linear molecule the Stokes lines have  $\Delta J = +2$  and the Stokes lines start at  $J = 0$  with the following Stokes lines ignoring centrifugal distortion.

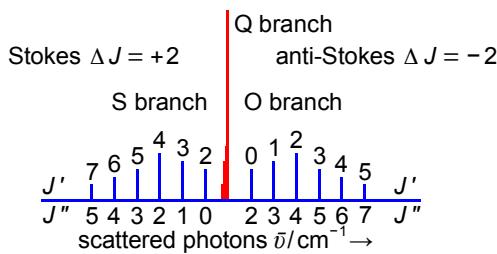
$$\begin{aligned}\bar{\nu}(J+2, J) &= \bar{\nu}_i - [F(J+2) - F(J)] = \bar{\nu}_i - B(J+2)(J+3) + BJ(J+1) \\ \bar{\nu}(J+2, J) &= \bar{\nu}_i - 2B(2J+3) \\ J &\quad 0 \quad 1 \quad 2 \quad 3 \quad \dots \\ \bar{\nu}(J+2, J) & \quad \bar{\nu}_i - 6B \quad \bar{\nu}_i - 10B \quad \bar{\nu}_i - 14B \quad \bar{\nu}_i - 18B \quad \dots\end{aligned}$$

The linear molecule anti-Stokes lines start at  $J = 2$  as  $\Delta J = -2$  with the following lines.

So the spacings in the spectrum for a linear molecule for both the Stokes and anti-Stokes rotational lines is  $4B$  with the initial lines at  $6B$  from the laser line. We can measure the rotational constant  $B$  which allows the moment of inertia to be found and hence bond lengths to be determined for linear molecules using isotopic variants for triatomic and larger linear molecule.

$$\begin{aligned}\bar{\nu}(J-2, J) &= \bar{\nu}_i - [F(J-2) - F(J)] = \bar{\nu}_i - B(J-2)(J-1) + BJ(J+1) \\ \bar{\nu}(J-2, J) &= \bar{\nu}_i + 2B(2J-1) \\ J &\quad 2 \quad 3 \quad 4 \quad 5 \quad \dots \\ \bar{\nu}(J-2, J) & \quad \bar{\nu}_i + 6B \quad \bar{\nu}_i + 10B \quad \bar{\nu}_i + 14B \quad \bar{\nu}_i + 18B \quad \dots\end{aligned}$$

Fig. 5.6 is for the  $\Delta\nu = 1,0$  transition with a Q branch for  $\Delta J = 0$ , the intensity of the Q branch is curtailed for reasons of clarity and the structure in the Q branch arises from the  $r_1 > r_0$  and so  $B_1 < B_0$ . Fig. 5.6 shows the initial and final rotational quantum numbers for the transitions. At lower wavenumbers are the Stokes rotational Raman lines with  $\Delta J = +2$  also called the S branch and to the right the anti-Stokes lines with  $\Delta J = -2$  called the O branch.



**Figure 5.6:** schematic rotational Raman spectrum in a vibrational Raman transition.

For a non-linear molecule the selection rule is complicated and we won't consider them but spherical top molecules (*e.g.* CH<sub>4</sub>) do not have a pure rotational Raman spectra whereas symmetric and asymmetric top molecules both have a pure rotational Raman spectrum. Nuclear statistics apply to rotational Raman spectra, *e.g.* C<sup>16</sup>O<sub>2</sub> only exists in  $J'' = 0, 2, 4, \dots$  so the Raman line spacings will be  $8B$  not  $4B$ . Also, in H<sub>2</sub> the odd  $J''$  lines are three times as intense as the even  $J''$  lines but in D<sub>2</sub> and <sup>14</sup>N<sub>2</sub> the even  $J''$  lines are twice as intense as the odd  $J''$  lines.

## 5.2 Vibrational Raman Scattering

The gross selection rule for vibrational Raman activity is

There must be a *change* in polarizability ( $\alpha$ ) of the molecule as the molecule vibrates in a given mode

vibrational Raman gross selection rule

Note that this is a different requirement from pure vibrational spectroscopy in the IR where the molecule needs a change in dipole moment for a photon to be absorbed. As a crude approximation this can be understood if the mode involves making the molecule *larger* then its polarizability will *increase*. So for example, the symmetric stretching mode of CO<sub>2</sub> is vibrationally Raman active but as we have seen it is IR inactive.

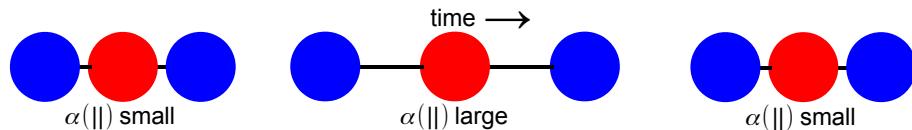
A woman with red hair and freckles is smiling. A red diagonal bar is positioned above her head. The background is a blurred outdoor scene.

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**Figure 5.7:** symmetric stretching mode of  $\text{CO}_2$ .

However, the anti-symmetric stretching and bending modes of  $\text{CO}_2$  are all vibrationally Raman inactive. As we previously saw the anti-symmetric stretching and bending modes of  $\text{CO}_2$  are IR active.. We use the group character table for a molecule and look at the vibrational mode's symmetry. The character table has entries on the right hand side with labels of either the form  $\alpha_{xy}$ ,  $\alpha_{xx}$ ,  $\alpha_{x^2-y^2}$  etc. (Hollas 2004) or just as  $x^2$ ,  $xy$ ,  $x^2-y^2$  etc. (Atkins & de Paula 2006). They are the symmetry elements of the polarizability there are six of them and they are called the “quadratic terms”.

If the symmetry of a vibrational mode is the same as a quadratic term then the mode is Raman active      Raman vibrational symmetry

$\text{CO}_2$  has  $D_{\infty h}$  symmetry and the symmetric stretching mode transforms as  $\sigma_g^+$  (lower case for vibrational labels and capitals for wavefunctions) which does *not* transform as any of the  $x$ ,  $y$  or  $z$  axes (labelled as  $T_x$ ,  $T_y$  or  $T_z$  in the character table) and so is IR inactive but is does transforms the same as the quadratic term  $\alpha_{zz}$  and is vibrationally Raman active. The anti-symmetric stretching mode of  $\text{CO}_2$  transforms as  $\sigma_u^+$  which is the same symmetry as  $T_z$  and it is IR active, but this does not correspond with any the quadratic terms and it is vibrationally Raman inactive. The degenerate bending modes are  $\pi_u$  symmetry which transforms as the pair  $T_x$  and  $T_y$  are they are IR active but they do not correspond to any of the quadratic terms so are vibrationally Raman inactive.  $\text{CO}_2$  is an example of the Raman exclusion rule as  $D_{\infty h}$  symmetry has a centre of inversion as one of its elements. For more details about polarizability see section 4.2 in Parker (Parker 2015).

For a molecule with a centre of inversion a vibrational mode cannot be both Raman and IR active      the vibrational Raman exclusion rule

### 5.3 Advantages and Applications of Raman Scattering

Overtone and combination bands in Raman spectra are often too weak to be observed and so the spectra are cleaner and generally easier to interpret than IR ones. Although gases have rotational Raman lines, liquids and solids do not (as in the IR) and again this keeps the liquid and solid spectra simpler. Perhaps the most important advantage is that liquid  $\text{H}_2\text{O}$  has only weak Raman vibrational peaks in  $\Delta\bar{\nu} = 300\text{-}3000 \text{ cm}^{-1}$  region but liquid water has strong IR absorptions in the  $\bar{\nu} = 300\text{-}3000 \text{ cm}^{-1}$  region. So aqueous, e.g. biological, samples can be investigated to look for H-bonding and molecular conformation information. For example, Raman spectroscopy has shown that dissolved  $\text{CO}_2$  exists mainly as  $\text{CO}_2$  solvated by water molecules and not primarily as carbonic acid  $\text{H}_3\text{CO}_3$  which may have physiological implications.

### 5.3.1 Resonance Raman Spectroscopy

If the excitation frequency  $\nu_i$  is chosen to be the same as an *electronic* absorption frequency of the molecule, usually with a tunable dye laser in the visible-UV, then there is a significant increase in the signal for the vibrational Raman modes which are located *near* to the site of absorption in the molecule, the chromophore, which absorbs the  $\nu_i$  photon. This increases the sensitivity allowing biological molecules, e.g. proteins, to be studied at high dilutions of  $10^{-3}$ - $10^{-6}$  mol L<sup>-1</sup> which are typical concentrations in organisms. A second advantage is that by enhancing the sensitivity near the chromophore resonance, Raman greatly simplified the vibrational Raman spectrum for large proteins such as haemoglobin or myoglobin.

### 5.3.2 Surface Enhanced Raman Spectroscopy (SERS)

If a roughened solid metal surface or the surface of a colloidal dispersion has molecules with lone pairs on or near to its surface; or a vacuum deposited thin film of Cu, Ag or Au is deposited onto a metal surface there is an enormous increase (up to  $\sim 10^{10}$ ) in Raman spectrum intensity. The incident photons interact with either the lone pair electrons of O, N, S or with the electrons of the Cu, Ag or Au to give an increase in electric field strength which increases the Raman scattering. SERS is used for a detecting single molecules or for studying surface reactions.

### 5.3.3 The Difference between Raman Scattering and Fluorescence

In our next chapter we start looking at electronic spectroscopy but before we do we should emphasize the difference between Raman and fluorescence. In fluorescence a photon of the correct frequency is absorbed or annihilated and its energy is used to excite a molecule from stationary state 1 to stationary state 2, so the absorption process is a resonance process obeying Planck's equation  $\Delta E_{2,1} = h\nu_{\text{abs}}$ . After a certain natural lifetime of the excited state typically  $10^{-7}$ - $10^{-9}$  s, the excited molecule in state 2 may move down to a lower energy level state 3 and emit a photon as fluorescence  $\Delta E_{3,2} = h\nu_{\text{fluor}}$ . In the Raman effect *any* frequency of light may be used, it is *not* a resonance process. The photon is scattered by interaction with the electrons of the molecule polarizing the molecule. In this interaction process energy can be transferred to the molecule (Stokes scattering) or gained from the molecule (anti-Stokes scattering) the scattered photon's momentum ( $p = h\nu/c$ ) changes in the scattering process with the frequency changing. As the Raman photon is not absorbed there is also no time delay as there is in fluorescence.

# 6 Atomic Spectroscopy

Atoms differ from molecules in that they can possess only electronic (and translational) energy, since they cannot rotate or vibrate. The energy diagram of atoms is much simpler than for molecules, the Grotrian or term diagram for the H-atom is shown in Fig. 6.1. The energy differences of electronic states are in the 10,000s of  $\text{cm}^{-1}$  and a much more convenient non-SI unit is the electronvolt (symbol eV). An electronvolt is the energy gained by an electron when it is accelerated by 1 volt.

$$1 \text{ eV} = 1.60219 \times 10^{-10} \text{ J} = 8065.5 \text{ cm}^{-1} = 96.485 \text{ kJ mol}^{-1}$$

conversion factors for eV

In section 1.3 we introduced the H-atom spectrum. We showed that the Rydberg equation was an accurate model for one-electron atoms, *i.e.* H,  $\text{He}^+$ ,  $\text{Li}^{2+}$  *etc.* with the Rydberg constant changing slightly for different nuclear charges of these one-electron atoms.

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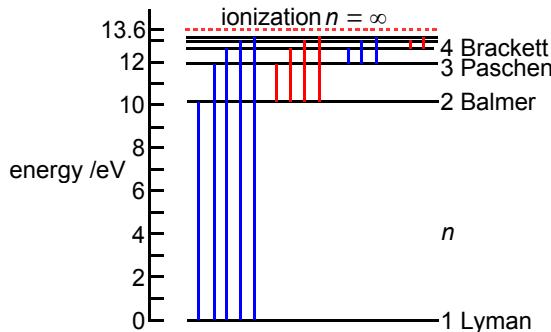
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**Figure 6.1:** H-atom Grotrian diagram.

$$\bar{v} = R_{\text{H}} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \text{the Rydberg equation}$$

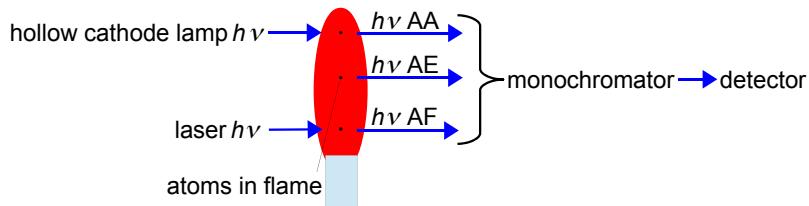
Where  $n_1$  is the lower and  $n_2$  is the upper *principal quantum number*  $R_{\text{H}} = 109737.3 \text{ cm}^{-1}$  is the Rydberg constant for the H-atom. The emissions of excited H-atoms are: the Lyman series of UV lines with quantum jumps down to  $n = 1$ ; the Balmer visible series with jumps down to  $n = 2$ ; the Paschen and Brackett series in the IR with jumps down to  $n = 3$  and  $4$ , respectively. Absorption arises when the H-atom converts the absorbed photon of the correct energy into electronic excitation energy and the electron makes a quantum jump up to a higher energy level with a higher principal quantum number  $n$ .

*Worked example:* calculate the wavelength of the  $n = 5$  line in the Balmer series.

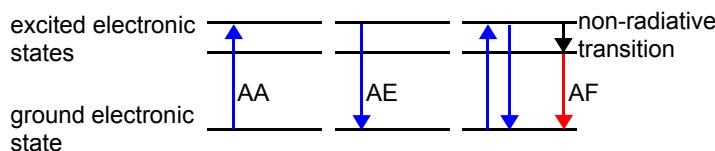
$$\begin{aligned}\bar{v} &= R_{\text{H}} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = 109737 \text{ cm}^{-1} \left( \frac{1}{2^2} - \frac{1}{5^2} \right) = 23045 \text{ cm}^{-1} \\ \lambda &= 1/(23045 \text{ cm}^{-1}) = 4.3393 \times 10^{-5} \text{ cm} \\ \lambda &= 4.3393 \times 10^{-5} \text{ cm} \left( \frac{1 \text{ m}}{100 \text{ cm}} \right) = 4.3393 \times 10^{-7} \text{ m} \\ \lambda &= 433.93 \text{ nm} \quad \text{the blue end of the visible}\end{aligned}$$

## 6.1 Analytical Applications of Atomic Spectroscopy

One common analytical technique that is widely used in a variety of labs is atomic spectroscopy. It is used for the quantitative analysis of the metallic elements in food, drinks, water supply, effluent, rivers, lakes, air, soil and also in forensic and clinical analysis. The sample may be a solid, liquid or gas but it is converted to its isolated atomic constituents by being passed either through a high temperature flame ( $\sim 3000 \text{ K}$ ) or an inductively coupled argon plasma, for details about analytical atomic spectroscopy see Harris (Harris 2007, p. 453). The three spectroscopic techniques used are atomic absorption (AA), atomic emission (AE) and atomic fluorescence (AF). Because the line widths of isolated atoms are so small  $\sim 0.001 \text{ nm}$  (compared with molecular spectra with line widths of  $\sim 100 \text{ nm}$ ) it is possible to simultaneously analyse 70 or more different elements in a sample.



**Figure 6.2:** high temperature flame AA, AE and AF.



**Figure 6.3:** transitions for AA, AE and AF.

Fig. 6.3 shows the transitions for AA, AE and AF but real atoms will have tens of excited electronic states so they have many lines at very specific wavelengths that can be used to characterize the atom concentrations.

## 6.2 Atomic Quantum Numbers

We are familiar from school or college with electron spin the quantum number  $s = \frac{1}{2}$  but what is the evidence that electrons have a spin? In 1922 Stern and Gerlach used a beam of silver atoms for convenience instead of free electrons, as silver atoms have one unpaired electron. The whole apparatus is under vacuum and the silver beam was formed by heating metallic silver in a furnace and letting the vapour escape through a small hole with the silver atoms collimated into a beam by a plate with a hole in it, at this stage the electron spins are pointing in random directions. The atomic beam of silver was passed through an *inhomogeneous* magnetic field made by machining the iron north pole to be a different shape from the iron south pole. The magnetic field (whether it is homogeneous or inhomogeneous) aligns the electron spins either with the field or against it, spin up  $\uparrow$  or spin down  $\downarrow$ . These spinning electrons are each a moving electric charge and act like a small bar magnet with their own N and S poles. Like magnetic poles repel one another and unlike magnetic poles attract one another. The inhomogeneous magnetic field as shown in Fig. 6.4 has a strong north pole and a weak south pole. The spin up electrons feel a stronger N-S attraction upwards than N-S attraction downwards and so the spin up electrons move upwards. The spin down electrons feel a stronger N-N repulsion downwards than the S-S repulsion upwards and so the spin down electrons move downwards. So it is the inhomogeneity which separates the beam in space into a spin up beam and a spin down beam. The final proof is that if you take a second Stern-Gerlach apparatus and you feed either a *pure* spin up or a *pure* spin down beam into the second inhomogeneous magnetic field, it does *not* separate the beam into two beams, the spin is an intrinsic (in-built) property of the electron.

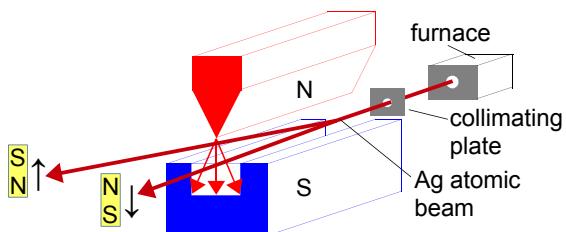


Figure 6.4: schematic Stern-Gerlach experiment.

Atoms have four quantum numbers  $n, l, s, j$  which all measure *magnitude* and which are always *positive*. They are written in lower case to signify that they apply to an individual electron or an individual atomic orbital. For multi-electron atoms the overall values of these quantum numbers is indicated by upper case symbols  $L, S, J$ . We are familiar with  $n$  and  $l$  quantum numbers from school with subshell symbols such as 1s, 2s, 2p, 3s, 3d, 4f and from the aufbau principle the subshells are filled in the order of the “diagonal rule” also called the Madelung rule or  $n+l$  rule. The aufbau principle is related to the number of nodes in the subshell ( $n+l$ ) which is related to the energy of the subshells, Fig. 6.5.

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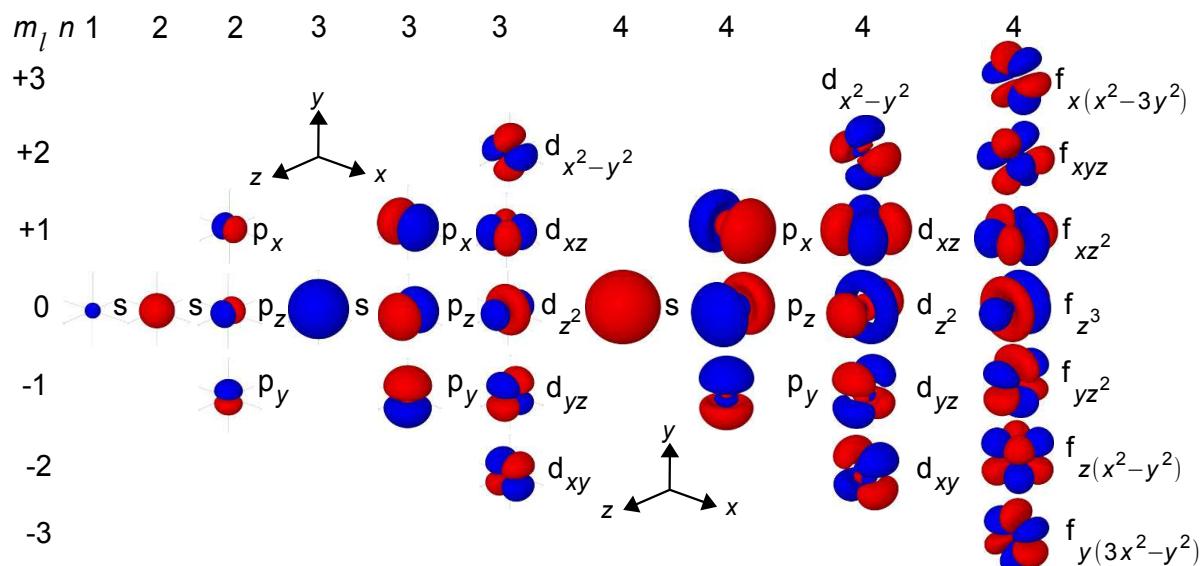
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**Figure 6.5:** diagonal, Madelung or  $n+l$  rule.

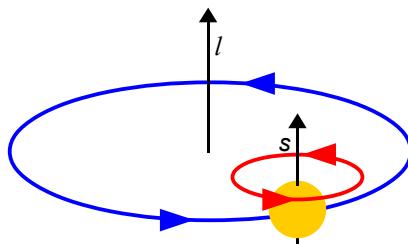
$n$	principal	$n = 1, 2, 3, 4, \dots$
$l$	orbital angular momentum, labelled as:	$l = 0, 1, 2, 3, \dots, n - 1$ $s, p, d, f,$ atomic quantum numbers
$s$	spin angular momentum	$s = \frac{1}{2}$
$j$	total angular momentum	$j = s + l$

The principal quantum number  $n$  is the main measure of the *size* of the atomic orbital (although the orbital angular momentum  $l$  also fine tunes the size). As  $n$  increases then the electrons are at a greater average distance from the nucleus and their energy is higher. However, remember the size of an AO is not well defined as the wavefunction for a particle in a spherical box with non-infinite potential walls (so called spherical harmonics) has a decreasing but non-zero probability at large distances. This is the reason for visualizing atomic orbitals as three-dimensional figures which enclose a fixed percentage (typically 90%) of the total probability density  $|\psi|^2$  of the electron giving the familiar spheres and “dumbbells”. The orbital angular momentum quantum number  $l$  tells us about the *shape* of the atomic orbital.



**Figure 6.6:** atomic orbitals with the different phases of  $\psi$  indicated by colour.

Fig. 6.6. shows the subshells ( $nl$ ) up to the end of the lanthanides, Lutetium. I will return to the  $j$  quantum number in a while. In the sections 1.7.6 and 2.1 we have met the idea of spin and orbital angular momentum, but an electron in an atom has both spin and orbital angular momentum.

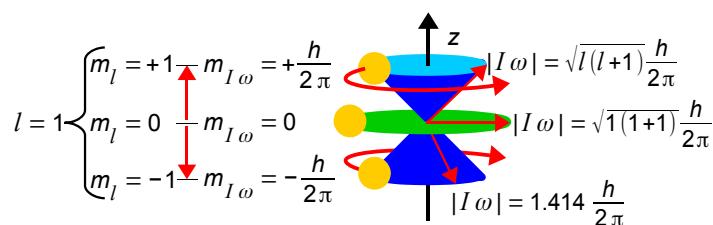


**Figure 6.7:** spin and orbital angular momentum.

Not only are angular momenta  $s$  and  $l$  quantized (positive numbers as they measure magnitudes) but also their *components* in a given direction are quantized (this is called *space quantization*). The possible values of the quantized components are given by the Clebsch-Gordon series. By convention the components have labels  $m_s$  and  $m_l$  and the components may be positive, zero or negative. For example, the d-atomic orbitals with  $l = 2$  have their five components as below.

$$\begin{aligned} m_l &= l, l-1, l-2, l-3, \dots && \text{this can also be written as below} \\ m_l &= 0, \pm 1, \pm 2, \pm 3, \dots, \pm l \\ m_l &= 0, \pm 1, \pm 2 && \text{magnetic quantum number } m_l \text{ for } l = 2 \end{aligned}$$

The electron spin quantum number  $s = \frac{1}{2}$  has from the Clebsch-Gordon series only two possible quantized orientations  $m_s = +\frac{1}{2}$  and  $m_s = -\frac{1}{2}$  (spin up and down) as we know from school. The degeneracies of  $s$  and  $l$  are  $(2s+1)$  and  $(2l+1)$  as in the above example for  $l = 2$ . As  $l$  determines the shape of the atomic orbital and something with a shape can also be oriented in space, so  $m_l$  determines the *orientation* in space of the angular momentum just as  $m_s$  determines the orientation in space of the electron spin  $s$ . The symbol  $m$  “magnetic” arose historically from studying the effects of external magnetic fields, the Zeeman effect. Our 2p electron has both spin and orbital angular momentum.

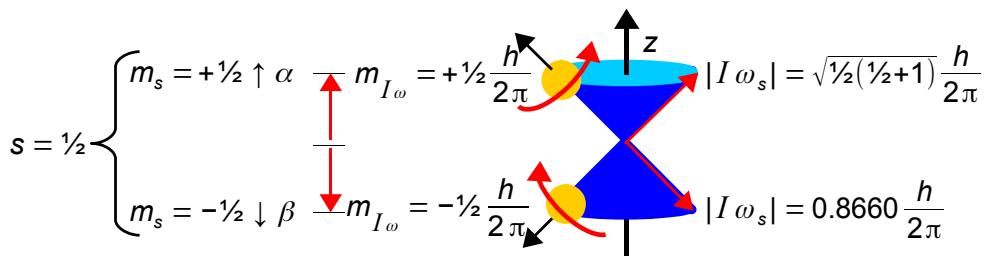


**Figure 6.8:** electron orbital angular momentum.

Fig.6.8 shows the three components for  $l = 1$ , i.e. the three p-atomic orbitals  $p_x$  ( $m_l = +1$ ),  $p_y$  ( $m_l = -1$ ) and  $p_z$  ( $m_l = 0$ ). As we know the z-component exactly then from Heisenberg's uncertainty principle it is impossible to know anything about the x- and y-components, all we know is the electron's angular momentum vector points to somewhere on the tip of the cone of uncertainty. The spin angular momentum is shown in Fig. 6.9 along with the conventional representation of the two components, the so-called spin up  $\uparrow$  or  $\alpha$  and spin down  $\downarrow$  or  $\beta$ . The heights of the cones (or circle for a zero height cone) are the z-components  $m_l$  or  $m_s$ . The length of sides of the cones are the magnitude (absolute value) of the angular momentum, shown below for a p-electron.

$$|I\omega_l| = \sqrt{l(l+1)} \frac{h}{2\pi} = \sqrt{1(1+1)} \frac{h}{2\pi} = \sqrt{2} \frac{h}{2\pi} = 1.414 \frac{h}{2\pi}$$

$$|I\omega_s| = \sqrt{s(s+1)} \frac{h}{2\pi} = \sqrt{\frac{1}{2}(\frac{1}{2}+1)} \frac{h}{2\pi} = \sqrt{\frac{3}{4}} \frac{h}{2\pi} = 0.8660 \frac{h}{2\pi}$$



**Figure 6.9:** electron spin angular momentum.

# Brain power



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*Self Test Question and Solution:* calculate both the  $m_s$  and  $m_l$  half-angles of the cones of uncertainty for an electron in a 2p atomic orbital (Parker 2013a, section 8.1.3).

### 6.2.1 Spin-Orbit coupling

The spin angular momentum of an electron ( $s$ ) is a moving electric charge and so produces a magnetic field similar to a small bar magnet with a north and a south pole. Also, the orbital angular momentum ( $l$ ) is a moving electric charge and so produces its own small magnetic field. The rule is that like magnetic poles repel one another ( $N \leftrightarrow N$  and  $S \leftrightarrow S$ ) and unlike poles attract one another ( $N \rightarrow S$ ) and so the total angular momentum quantum number  $j$  may have two or more values  $j_{\max} = l + s$  is the high energy spin-orbit coupling (interaction) level and  $j_{\min} = |l - s|$  is the low energy spin-orbit split level. The difference in energy between the spin-orbit levels is small since *magnetic* forces are much *weaker* than electric forces.

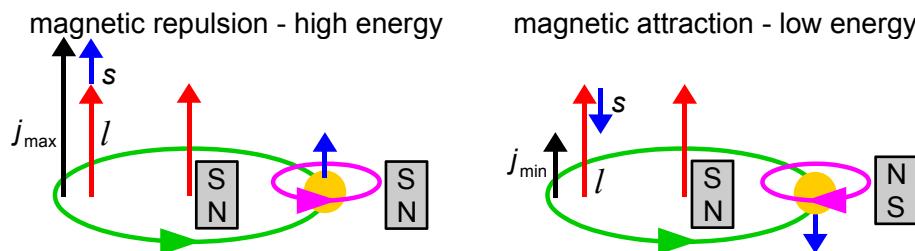


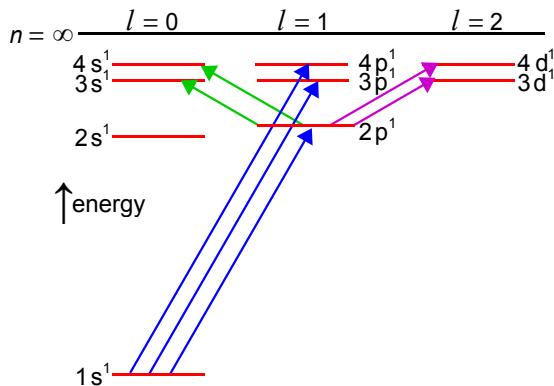
Figure 6.10: electron spin-orbit coupling.

The  $s$ ,  $l$  and  $j$  angular momentum quantum numbers are each given by their Clebsch-Gordon series. For atoms with several electrons the individual spin angular momenta ( $s$ ) couple to give an overall spin quantum number ( $S$ ) also the individual orbital angular momenta ( $l$ ) couple to give an overall orbital quantum number ( $L$ ). Then  $S$  and  $L$  couple to give the total angular momentum quantum number  $J$ . This process is called Russell-Saunders coupling (RS or sometimes LS coupling). We will return to other ways of coupling angular momenta later on. Note we use a capital letter for the whole atom and lower case letters for the individual electrons, individual orbitals or individual angular momenta.

$$\begin{aligned} S &= s_1 + s_2, \quad s_1 + s_2 - 1, \quad s_1 + s_2 - 2, \quad s_1 + s_2 - 3, \quad \dots, \quad |s_1 - s_2| \\ L &= l_1 + l_2, \quad l_1 + l_2 - 1, \quad l_1 + l_2 - 2, \quad l_1 + l_2 - 3, \quad \dots, \quad |l_1 - l_2| \quad \text{RS coupling} \\ J &= S + L, \quad S + L - 1, \quad S + L - 2, \quad S + L - 3, \quad \dots, \quad |S - L| \end{aligned}$$

### 6.3 Term Symbols, Selection Rules and Spectra of Atoms

At the beginning of Chapter 6 we looked at the line spectrum of the H-atom and its interpretation in terms of the principal quantum number  $n$  by the Rydberg equation. Fig. 6.11 shows some of the allowed transitions between the lower terms, for historical reasons, electronic energy levels are also called *terms* and hence we have term symbols. Only for the single electron H-atom are the s, p, d, and f orbitals degenerate. The symbols arose from the appearance of the lines as “sharp, principal, diffuse, fundamental” but are now just used as labels (hence roman text).

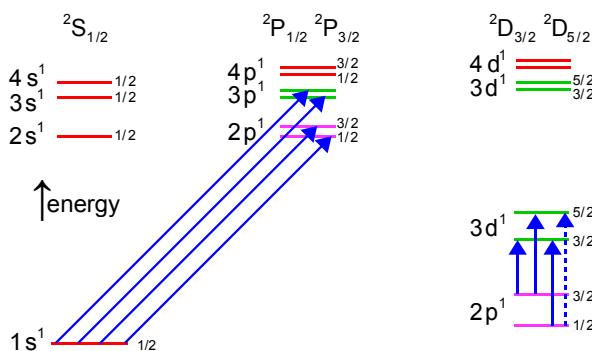


**Figure 6.11:** H-atom low resolution Grotrian diagram, not to scale.

The right hand superscript number is the number of electrons in that energy level. Experimentally it is found that the principal quantum number  $n$  may change ( $\Delta n$ ) by any integer amount as  $n$  measures the size and gross energy of an orbital. The photon has one unit of angular momentum and the total angular momentum of photon plus atom is conserved. The orbital angular momentum ( $l$ ) and its component along a given direction ( $m_l$ ) can only change as shown below.

$$\Delta n = \text{anything} \quad \Delta l = \pm 1 \quad \Delta m_l = 0, \pm 1 \quad \text{hydrogenic atoms selection rules}$$

Fig. 6.12 is a Grotrian diagram of a few lines of the high resolution spectrum of the H-atom including spin-orbit splitting with the  $j$  quantum number for the total angular momentum as the right hand subscript (exaggerated for clarity). The term symbols for the H-atom electronic states are along the top as  ${}^2S_{1/2}$ ,  ${}^2P_{3/2}$ , etc. Inserted on the right is the *compound doublet* of the possible  $2p \leftrightarrow 3d$  transitions. Of the possible four transitions one is forbidden due to the selection rule  $\Delta m_l = 0, \pm 1$  as  $\Delta m_l \neq 2$ .



**Figure 6.12:** H-atom high resolution Grotrian diagram, not to scale.

We have almost all our selection rules except for considering the total spin of the atom when more than one electron is present. In Fig. 6.13 the radial distribution functions for 2s and 2p orbitals shows that the 2s electrons spends more of its time between the nucleus and 1 Å than the 2p electron, the 2s electron has greater penetration in the core region. So the 2s electron partially shields the 2p electron from the nucleus, so the 2p spends more time at a greater distance from the nucleus and has a higher energy than with single electron hydrogenic atoms. The hydrogenic atom s-p-d-f degeneracy is lifted for multi-electron atoms and the energies of the atomic orbitals are then given by the diagonal rule, Fig. 6.5, with  $s < p < d < f$  for a given electronic shell, the same principal quantum number  $n$ . Fig. 6.14 is the Grotrian diagram for the helium atom which shows his effect and also that there are singlet and triplet states, the triplet splitting is exaggerated for clarity.

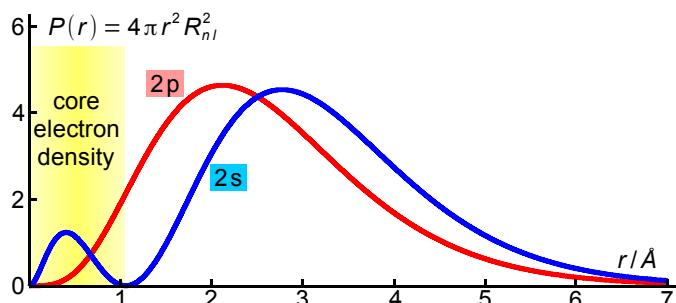


Figure 6.13: radial distribution functions for 2s and 2p electrons.



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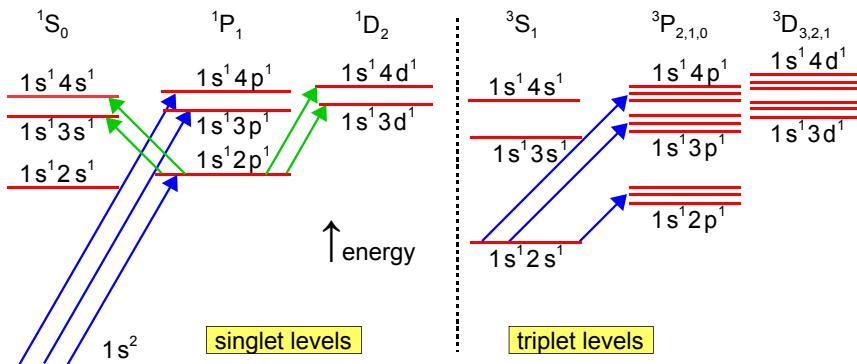


Figure 6.14: He-atom Grotrian diagram, not to scale.

The conclusions from the two-electron helium spectrum is that a photon absorption only excites *one* electron and secondly that there are two “families” of terms, the singlet and triplet, with no transitions between them. Singlet and triplet are the names of the *multiplicity* ( $2S+1$ ) which is the *number of orientations* of the total spin  $S$  and is the degeneracy of the total spin angular momentum quantum number  $S$  which arises from RS coupling of the two electrons’ spins (Figs. 6.15 and 6.16) and is summarized by the Clebsch-Gordon series.

$$\begin{aligned} S &= s_1 + s_2, s_1 + s_2 - 1, s_1 + s_2 - 2, s_1 + s_2 - 3, \dots, |s_1 - s_2| \\ S &= \frac{1}{2} + \frac{1}{2}, |\frac{1}{2} - \frac{1}{2}| = 1, 0 \\ (2S+1) &= 3(\text{triplet}), 1(\text{singlet}) \end{aligned} \quad \text{two-electron multiplicity}$$

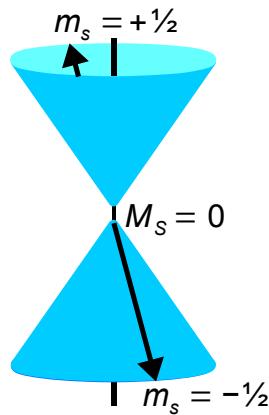
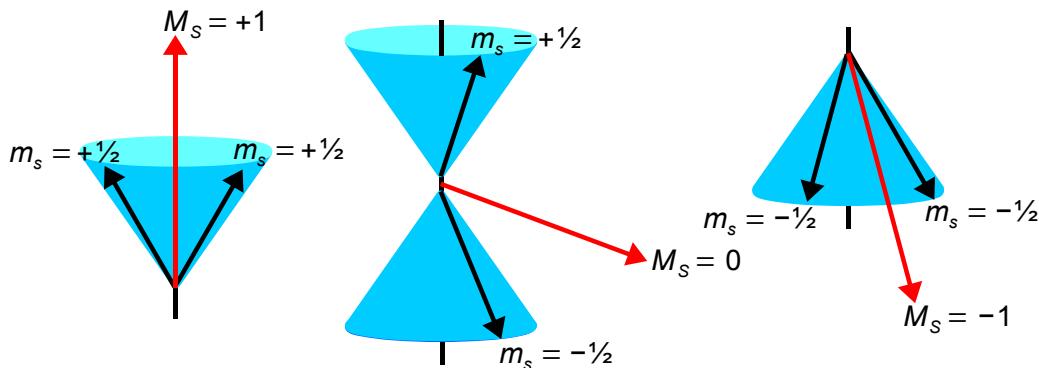


Figure 6.15: singlet coupling of two spin angular momenta.

The singlet term has the spins paired  $\uparrow\downarrow$  with them pointing *somewhere unknown* on the cones of uncertainty but at *exactly* 180° apart. The two spin vectors  $m_s = +\frac{1}{2}$  and  $-\frac{1}{2}$  then cancel one another out to give  $M_s = 0$ . Clearly there is only one arrangement for the singlet, that shown on Fig. 6.15.

The triplet term has the two spins “parallel”, symbolized by  $\uparrow\uparrow$ , as in Fig. 6.16 with three possible arrangements of the two spin vectors (none of which are strictly parallel to one another). The spin vectors point somewhere on the cones of uncertainty but the angle between them is the same in all three arrangements and so the magnitude of the  $M_s$  is the same but may be pointing in three possible directions, *i.e.* with three components of  $M_s = 1, 0, -1$  hence the term is triply degenerate.



**Figure 6.16:** triplet coupling of spin angular momenta.

The He-atom ground state electron configuration is  $1s^2$  and from Pauli's exclusion principle the spins must be paired  $\uparrow\downarrow$  and the ground state is a singlet  $1s^2 \ ^1S_0$  (pronounced “one es two, singlet es zero”). The excited electron configuration  $1s^1 2s^1$  can exist as two different terms; firstly,  $1s^1 2s^1 \ ^1S_0$  (pronounced “one es one, two es one, singlet es zero”) with spins paired  $\uparrow\downarrow$  or secondly,  $1s^1 2s^1 \ ^3S_1$  (pronounced “one es one, two es one, triplet es one”) with spins parallel  $\uparrow\uparrow$ . The lowest triplet term cannot lose a photon and drop down to the ground state, the triplet terms are formed in electric discharges. It is *metastable* with an energy of 19.8 eV, which is enough to collisionally ionize all molecules, and it has a collision-free lifetime of several milliseconds ( $\sim 10^{-3}$  s) compared with the natural lifetime of  $\sim 10^{-9}$  s for a singlet term which may lose energy by an allowed photon emission.

The term symbol, called the Russell-Saunders term symbol, neatly summarizes the quantum numbers of an atomic electronic state or term. When necessary to remove any ambiguity the term symbol should be preceded by the electron configuration.

${}^{2S+1}L_J$       Russell-Saunders term symbols

The total spin  $S$ , total orbital  $L$  and total spin-orbital angular momenta  $J$  may have the following values and symbols.

multiplicity	$2S+1 = 1, 2, 3, 4, 5, \dots$	singlet, doublet, triplet, quartet, quintet
	$L = 0, 1, 2, 3, 4, \dots$	
	$S, P, D, F, G, \dots$	
	$J = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, 3, \dots$	

If  $S \leq L$  then the number of  $J$  levels equals the multiplicity. Note the  $L$  symbols or labels are uppercase roman letters. The RS selection rules for electronic jumps in atoms involving photon absorption or emission arise from spin and symmetry considerations and also from the conservation of angular momentum with a photon having one unit of angular momentum.

- (1)  $\Delta n = \text{anything}$
- (2)  $\Delta(2S+1) = 0$
- (3)  $\Delta L = 0, \pm 1$  with active electron  $\Delta l = \pm 1$
- (4)  $\Delta J = 0, \pm 1$  but  $J = 0 \leftarrow \rightarrow J = 0$

Russell-Saunders selection rules

$\Delta n$  may be anything as  $n$  measures the size and the approximate energy of the atomic term but not its spin, symmetry or angular momentum. The multiplicity cannot change as light does not directly affect spin (NMR and ESR require the nucleus or electron to be in an external magnetic field).  $\Delta L$  and  $\Delta J$  arise from angular momentum conservation with the electron that actually makes the jump (the active electron) changing  $\Delta l$  by one unit. The symbol  $\leftarrow \rightarrow$  means a forbidden transition.

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We saw that spin-orbit splitting which is due to magnetic field interactions, is small. In a heavy atom with its large nuclear charge the spin-orbit interactions are larger than either spin-spin or orbit-orbit interactions. In this situation, *e.g.* iodine or mercury atoms, each orbital angular momentum  $l_i$  tends to combine with the corresponding individual spin angular momentum  $s_i$  giving an individual total angular momentum  $j_i$  for that individual electron. These  $j_i$  then couple together to form the total angular momentum  $J$ . This heavy atom interaction is known as  $jj$  coupling but we won't pursue it further at the moment.

$$J = j_1 + j_2, j_1 + j_2 - 1, j_1 + j_2 - 2, j_1 + j_2 - 3, \dots, |j_1 - j_2| \quad jj \text{ coupling}$$

## 6.4 Hund's Rules for Finding the Lower Energy Terms

In order to find the term symbols of an atom we ignore completely any closed shell (filled) orbitals as their contribution to  $S$ ,  $L$ , and  $J$  are all equal to zero. We only need to consider are the partially filled orbitals. Hund's rules only apply to *equivalent* electron configurations, *i.e.* where  $n$  and  $l$  are the same for the electrons of interest.

- |  |                             |
|--|-----------------------------|
| 1) A higher multiplicity ( $2S+1$ ) term has a lower energy  | Hund's 1 <sup>st</sup> rule |
| 2) A higher orbital angular momentum term $L$ has lower energy   | Hund's 2 <sup>nd</sup> rule |
| 3) If a subshell $\leq$ half-full then smaller $J$ has lower energy (normal order)<br>but if shell $>$ half-full then larger $J$ has lower energy (inverted order) | Hund's 3 <sup>rd</sup> rule |

Hund's first rule, also called Hund's rule of maximum multiplicity, is that the ground state has the largest number of *unpaired* equivalent electrons as possible, *e.g.* triplets are lower energy than equivalent singlets. Electrons with parallel spins quantum mechanically repel one another and so remain as far apart as possible (spin correlation) this will reduce the electrostatic Coulombic repulsion of the two negatively charged electrons. Hund's second rule implies that to find the ground state the atomic orbitals fill with the highest positive  $m_l$  values first, again reducing the electrostatics repulsion. Hund's third rule is due to the small energy difference arising from the magnetic interactions between the  $L$  and  $S$  magnetic dipoles.

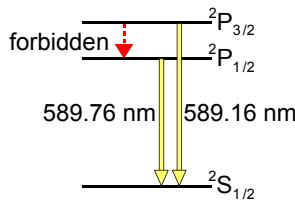
*Worked example:* (1) find the term symbol of the ground electron configuration of the Na-atom  $1s^2 2s^2 2p^6 3s^1$ .

$$\begin{aligned} S &= s = \frac{1}{2} \quad \text{multiplicity } (2S+1) = 2 \times \frac{1}{2} + 1 = 2 \quad \text{a doublet term} \\ L &= l = 0 \quad \text{an S term, } ^2\text{S term} \\ J_{\max} &= L+S = 0+\frac{1}{2} = \frac{1}{2} \\ J_{\min} &= |L-S| = |0-\frac{1}{2}| = \frac{1}{2} \quad \text{only one level} \\ &\text{Na } 1s^2 2s^2 2p^6 3s^1 \ ^2\text{S}_{1/2} \end{aligned}$$

*Worked example:* (2) find the term symbol for  $1s^2 2s^2 2p^6 3s^0 3p^1$  an *excited* electron configuration of Na.

$$\begin{aligned} S = s = \frac{1}{2} & \quad \text{multiplicity } (2S+1) = 2 \times \frac{1}{2} + 1 = 2 \quad \text{a doublet term} \\ L = l = 1 & \quad \text{a } ^2\text{P term} \\ J_{\max} = L+S & = 1 + \frac{1}{2} = \frac{3}{2} \\ J_{\min} = |L-S| & = |1 - \frac{1}{2}| = \frac{1}{2} \quad \text{two levels with the same configuration} \\ \text{Na } 1s^2 2s^2 2p^6 3s^0 3p^1 & ^2\text{P}_{1/2} \\ \text{Na } 1s^2 2s^2 2p^6 3s^0 3p^1 & ^2\text{P}_{3/2} \end{aligned}$$

Hund's third rule 3p subshell  $\leq$  half-full so the  ${}^2\text{P}_{1/2}$  level is the lower energy level.



**Figure 6.17:** Na doublet yellow emission spectrum.

The  ${}^2\text{P}_{1/2} \leftrightarrow {}^2\text{S}_{1/2}$  and  ${}^2\text{P}_{3/2} \leftrightarrow {}^2\text{S}_{1/2}$  transitions are allowed;  $P \rightarrow S \Delta L = -1$ , the active electron jumps  $3p \rightarrow 3s$  with  $\Delta l = -1$ , and  $\Delta J = 0$  and  $\Delta J = -1$ , respectively for the two transitions. The  ${}^2\text{P}_{3/2} \leftarrow {}^2\text{P}_{1/2}$  is forbidden; although  $P \rightarrow P \Delta L = 0$  is allowed and  $\Delta J = -1$  is allowed but the active electron jumps  $3p \rightarrow 3p$  with  $\Delta l = 0$  and is forbidden. The two allowed transitions are the yellow sodium doublet lines of street lamps.

*Worked example:* (3) find the lowest term for C-atoms in the *excited* electron configuration  $1s^2 2s^2 2p^1 3p^1$ .

$$\begin{aligned} s_1 = s_2 = \frac{1}{2} & \quad S = \frac{1}{2} + \frac{1}{2}, \frac{1}{2} + \frac{1}{2} - 1, \dots, \left| \frac{1}{2} - \frac{1}{2} \right| \quad S = 1, 0 \quad \text{triplet and singlet} \\ l_1 = l_2 = 1 & \quad L = 1+1, 1+1-1, \dots, |1-1| \quad L = 2, 1, 0 \quad \text{D, P and S terms} \\ & \quad {}^3\text{D}, {}^3\text{P}, {}^3\text{S}, {}^1\text{D}, {}^1\text{P}, {}^1\text{S} \text{ terms} \end{aligned}$$

From Hund's first and second rules  ${}^3\text{D}$  is the lowest energy term for which  $J = 3, 2, 1$  that is  ${}^3\text{D}_3$ ,  ${}^3\text{D}_2$  and  ${}^3\text{D}_1$  levels. The 2p and 3p subshells are less than half-full so from Hund's third rule the order is normal and for the excited electron configuration C  $1s^2 2s^2 2p^1 3p^1$  the lowest three levels are  ${}^3\text{D}_1 < {}^3\text{D}_2 < {}^3\text{D}_3$ . Flames and electric discharges produce excited C-atoms with the two p-electrons being non-equivalent as  $n$  is not the same so there are no restrictions from the Pauli exclusion principle. We see that just giving the electron configuration is not enough information to specify an electronic term as the  $1s^2 2s^2 2p^1 3p^1$  configuration has the following energy levels (not in energy order)  ${}^3\text{D}_1$ ,  ${}^3\text{D}_2$ ,  ${}^3\text{D}_3$ ,  ${}^3\text{P}_0$ ,  ${}^3\text{P}_1$ ,  ${}^3\text{P}_2$ ,  ${}^3\text{S}_1$ ,  ${}^1\text{D}_2$ ,  ${}^1\text{P}_1$ ,  ${}^1\text{S}_0$ .

# 7 Electronic Spectra

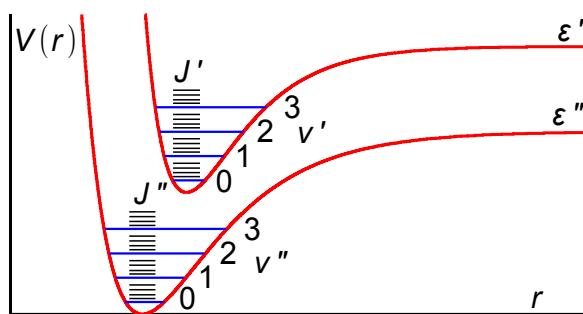


Figure 7.1: diatomic molecule's electronic, vibrational and rotational energies, not to scale.

Diatom and larger molecules possess electronic, vibrational, and rotational energy. The vibrational and rotational quantum levels may also change during an electronic transition in the visible-UV. The Born-Oppenheimer approximation assumes these motions behave completely independently. Electronic spectra are normally measured in the lab using a dual beam spectrophotometer.

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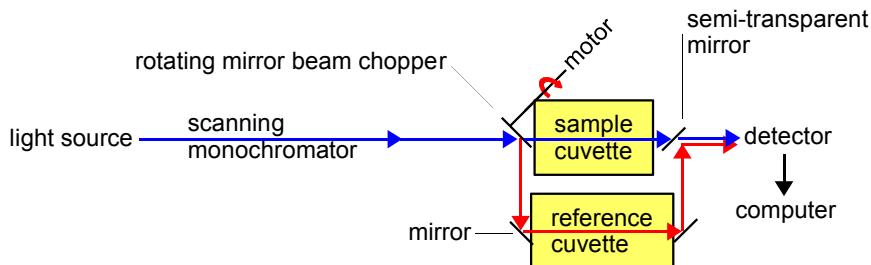


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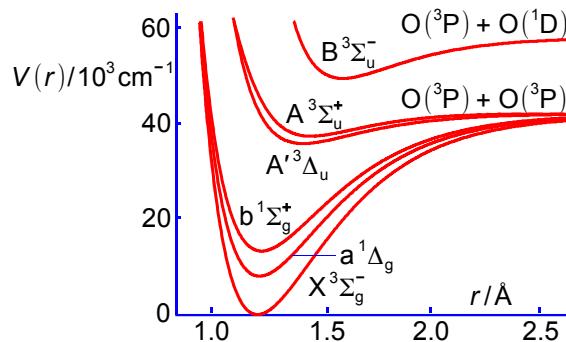
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**Figure 7.2:** schematic dual beam spectrophotometer.

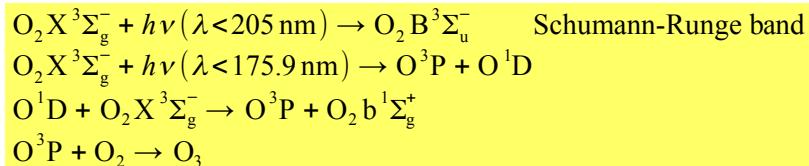
A beam chopper passes the monochromatic light alternatively through the sample solution and the reference of the pure solvent with the solvent signal being electronically subtracted from the solution signal. The solution and reference are held in a pair of optically matched cuvettes normally made of fused quartz as glass absorbs in the UV. Typically the optical path-length inside the cuvette is 1 cm.

We will start by examining diatomic electronic spectra as these are environmentally and biologically important and also teach us the fundamental ideas behind electronic spectroscopy and are easier to understand before looking (briefly) at polyatomic molecules.



**Figure 7.3:** schematic potential energy curves for some of the lower energy states of  $O_2$ .

Fig. 7.3 shows some of the many different electronic states that even a diatomic molecule has. Note that the energy gaps between electronic states are measured in  $10,000s\text{ cm}^{-1}$ . We will return to the term symbols used to label the states and the selection rules for transitions between them in a moment. The  $O_2$  absorption spectrum is important for the atmospheric absorption of harmful UV from the Sun's spectrum by the  $O_2$  itself and also by ozone  $O_3$ . There is a very strong  $O_2$  absorption starting at  $\sim 205$  nm due to the Schumann-Runge transitions to excited vibrational levels of the  $B^3\Sigma_u^-$  electronic excited state. Below 175.9 nm the absorption becomes a continuum with the  $B^3\Sigma_u^-$  dissociating into a ground and an excited state O-atom with the continuous absorption having a maximum intensity at 145 nm. This Schumann-Runge absorption protects the surface of the Earth from UV below  $\sim 200$  nm and also means that lab equipment has to be evacuated for experiments using light less than 200 nm (called the vacuum-UV range).



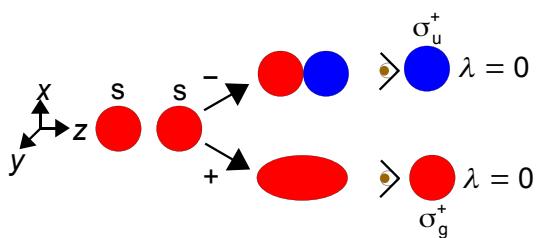
The excited O( $2^1\text{D}$ ) atom is metastable and is deactivated by an energy transfer collision with ground state O<sub>2</sub> to give a second O( $2^3\text{P}$ ) atom and both of these O( $2^3\text{P}$ ) atoms can form ozone. The ozone which has been formed by these photochemical reactions will itself absorbs virtually all the UV between 200 to 280 nm UV-C and most of the 280-315 nm UV-B. The remaining 280-315 nm UV-B along with the 315-400 nm UV-A is the remaining UV radiation which reaches the surface of the Earth. This UV reaching the surface is both dangerous (sunburn and DNA damage in plants and animals) and also necessary for vitamin-D synthesis to prevent rickets. This O<sub>2</sub> example shows how important it is to understand the various electronic states of atoms and diatomics as well as larger polyatomic molecules.

## 7.1 Term Symbols and Selection Rules for Diatomic Molecules

Firstly, we need to find the orbitals for the diatomic molecule, we will be using the *linear combination of atomic orbitals* (LCAO) approach to form our molecular orbitals. Compared with atoms the main difference is that diatomic molecules have an internal axis labelled *z*. The molecular axis has an electric field due to the nuclei whereas atoms don't have an *internal* axis. So atoms have an orbital angular momentum *l* and a total for the whole atom *L* which has components of *M<sub>L</sub>* along a chosen *external* axis. In contrast diatomic molecules have an orbital angular momentum for the whole molecule *Λ* (italic Greek uppercase lambda) but it is *not* the equivalent of *L* but it is the equivalent to *M<sub>L</sub>*. Conventionally, as Roman letters are used for atoms so the equivalent Greek letters are used for molecules. The symbolism is similar to atoms so that diatomic molecules' individual electrons or molecular orbitals have a roman *lowercase* Greek symbol and the overall electronic state has a roman *uppercase* Greek symbol. Here are the italic variables and their roman symbols.

atomic orbital	atomic state	molecular orbital	molecular state
<i>l</i> = 0 s	<i>L</i> = 0 S	$\lambda$ = 0 σ (sigma)	$\Lambda$ = 0 Σ (SIGMA)
<i>l</i> = 1 p	<i>L</i> = 1 P	$\lambda$ = ±1 π (pi)	$\Lambda$ = ±1 Π (PI)
<i>l</i> = 2 d	<i>L</i> = 2 D	$\lambda$ = ±2 δ (delta)	$\Lambda$ = ±2 Δ (DELTA)
<i>l</i> = 3 f	<i>L</i> = 3 F	$\lambda$ = ±3 φ (phi)	$\Lambda$ = ±3 Φ (PHI)

Let's look at the LCAO and see how the atomic orbitals of the two atoms combine to give the orbitals of the molecule. Two s atomic orbitals may be added to give a bonding orbitals or subtracted to give an antibonding orbitals.



**Figure 7.4:** schematic overlap of two s AO's for a centrosymmetric diatomic molecule.

In Fig. 7.4 the “end view” looking along the molecular axis (technically, the component  $\lambda$  along the molecular axis) looks like a sphere which has zero orbital angular momentum component along the axis,  $\lambda = 0$  and so these are labelled as  $\sigma$  orbitals. The bonding  $\sigma$  and antibonding  $\sigma^*$  orbitals also have two important symmetry properties. Any diatomic molecule orbitals will be either symmetric or antisymmetric (indicated with a superscript + or -) to *reflection* in a *mirror* plane lying along the molecular axis. A homonuclear diatomic molecule is also *centrosymmetric* the orbitals is either symmetric or antisymmetric to *inversion* through the centre of symmetry, this “parity” is indicated with subscript “g” or “u” (gerade is German for “even” and ungerade is “odd”).

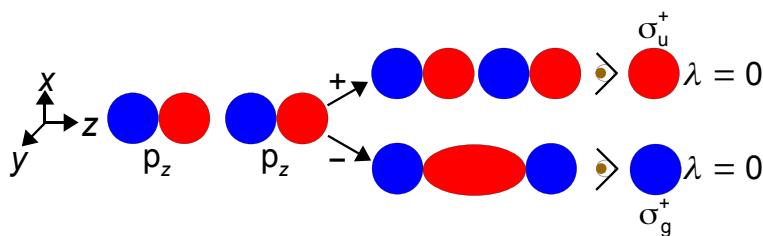
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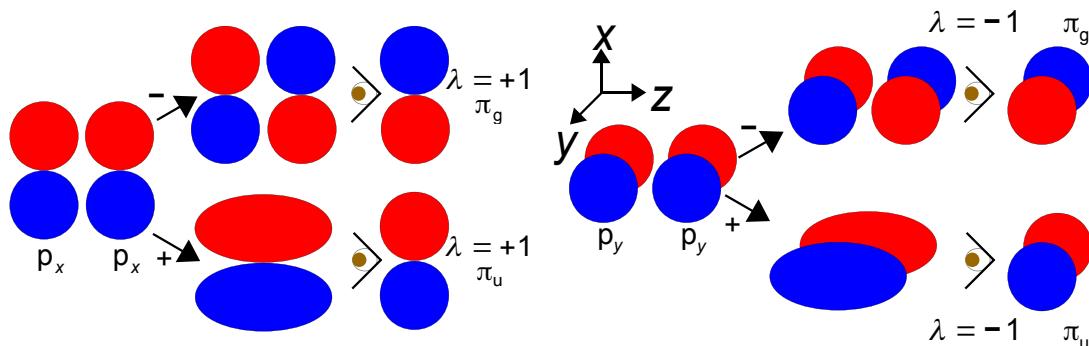
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**Figure 7.5:** schematic overlap of two  $p_z$  AOs for a centrosymmetric diatomic molecule.

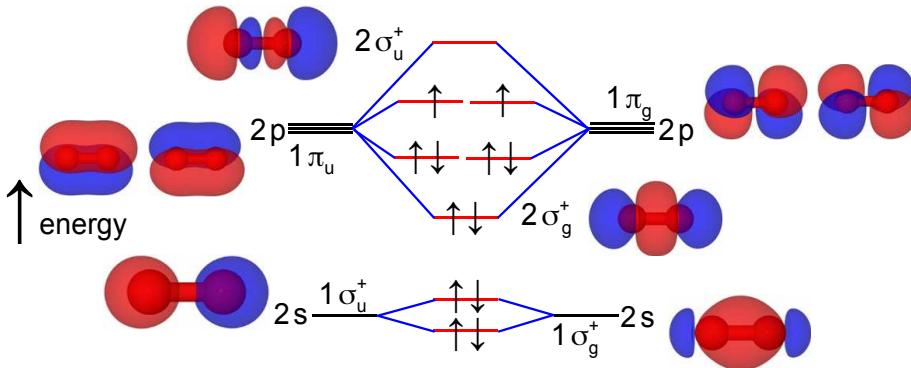
The overlap of a pair of  $p_z$  atomic orbitals is shown in Fig. 7.5, the end view shows the orbital angular momentum component along the molecular axis is zero so this overlap of two  $p_z$  atomic orbitals gives a  $\sigma$  and a  $\sigma^*$  orbital. Notice that the number of orbitals we obtain is always the same as the number of atomic orbitals that contribute to them.

Fig. 7.6 shows the overlap of a pair of  $p_x$  (in the plane of the paper) and a pair of  $p_y$  (at right angles to the plane of the paper). The overlap of the  $p_x$  atomic orbitals gives a  $\pi$  and a  $\pi^*$  orbital in the plane of the paper. The overlap of the two  $p_y$  atomic orbitals gives a  $\pi$  and a  $\pi^*$  orbital at right angles to the plane of the paper. The  $\pi_g(2p_x)$  and  $\pi_g(2p_y)$  anti-bonding orbitals are degenerate and the  $\pi_u(2p_x)$  and  $\pi_u(2p_y)$  bonding orbitals are also degenerate.

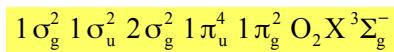


**Figure 7.6:** schematic overlap of two  $p_x$  and two  $p_y$  AOs for a centrosymmetric diatomic molecule.

The molecular orbitals of  $O_2$  are shown schematically in Fig. 7.7. The degenerate orbitals are shown slightly separated for clarity. A diagram similar to Fig. 7.7 applies to  $F_2$  but for the less electronegative second period elements  $Li_2$  to  $N_2$  the energy order of the  $2\sigma_g$  and  $1\pi_u$  orbitals is reversed. Heteronuclear diatomic molecules, due to the electronegativity differences of the atoms, have unequal energy gaps between the bonding and antibonding orbitals and their constituent atomic orbitals.

**Figure 7.7:** schematic of the valence MOs for the O<sub>2</sub> ground state.

MO theory predicts a bond order of two (explained later) and also that O<sub>2</sub> is paramagnetic (it has two unpaired electrons in the degenerate pair of  $\pi_g^*$  antibonding orbitals) the paramagnetism is experimentally proved when liquid O<sub>2</sub> is poured past a permanent magnet and the stream of liquid O<sub>2</sub> is deflected sideways. The valence shell electron configuration and ground state is below, note that the orbital reflection symmetry (superscript + or -) is only shown when necessary to distinguish between orbitals that may be confused but is always shown in the electronic state term symbol.



### 7.1.1 Term Symbols for Diatomic Molecules

Let's look in more detail at the term symbols for linear molecules, we have to consider the spin and orbital angular momentum and then the total from spin-orbit coupling. Each O-atom has 8 electrons so O<sub>2</sub> has 16 electrons in total which are fed into the orbitals in energy-order using Pauli's exclusion principle. Fourteen of the electrons completely fill all the orbitals up to and including the degenerate pair of  $1\pi_u$ . Hund's rule of maximum multiplicity has the remaining two electrons parallel as they quantum mechanically repel one another (spin correlation). From Pauli's exclusion principle they must occupy different orbitals, *i.e.* one in each of the pair of degenerate antibonding  $1\pi_g^*$ . The separate orbitals increases their average distance apart and so reduces the electrostatic repulsion between the two negative electrons and the triplet has lower energy than the corresponding singlet state.

Total spin angular momentum	$S = s_1 + s_2 + s_3 + \dots$
Components of $S$ along molecular axis	$\Sigma = S, S-1, S-2, \dots, -S$

So this ground electron configuration for O<sub>2</sub> has spin angular momentum  $S = 1$  from the two unpaired electrons in the  $1\pi_g^*$  antibonding orbitals. The components of the total spin orbital momentum ( $S = 1$ ) along the molecular axis are  $\Sigma = +1, 0, -1$  and it is a triplet state. Don't confuse the italic  $\Sigma$  (the variable for the total *spin* component) with the roman  $\Sigma$  which is the label for part of the term symbol for those states with a total *orbital* component  $\Lambda = 0$ .

The electronic orbital angular momentum (ignoring all electrons in closed shells just as we did for atoms) we only need to consider the two electrons in the degenerate pair of  $\pi^*$  orbitals. The  $1\pi_g^*$  arising from the overlap of the pair of  $2p_y$  AOs has  $\lambda = -1$  and the  $1\pi_g^*$  from overlap of the pair of  $2p_x$  AOs has  $\lambda = +1$ . For the  $O_2$  ground state  $\Lambda = -1 + 1 = 0$  and so the ground electronic state is a  $\Sigma$  state and we know it is a triplet so we have  ${}^3\Sigma$ . Below are the symbols for the *components* of the total orbital angular momentum along the molecular axis.

$$\begin{aligned}\Lambda &= \lambda_1 + \lambda_2 + \lambda_3 + \dots \\ \Lambda &= 0, \pm 1, \pm 2, \pm 3 \\ \Lambda &= \Sigma, \Pi, \Delta, \Phi\end{aligned}$$

The total *component* of the spin and orbital angular momentum along the molecular axis is  $\Omega$  which is written as a right hand subscript to the term symbol when it is required for clarity.

$$\Omega = \Lambda + \Sigma$$

The symmetry combinations of the two half-filled  $1\pi_g$  orbitals for the  $O_2$  ground state come from the rules.

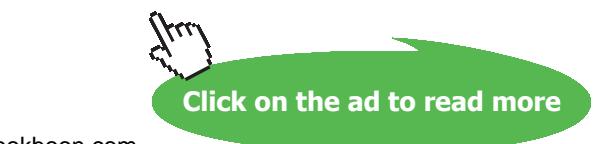
Parity	$g \times g = g$	$u \times u = g$	$g \times u = u$
Reflection	$(+) \times (+) = (+)$	$(-) \times (-) = (+)$	$(+) \times (-) = (-)$



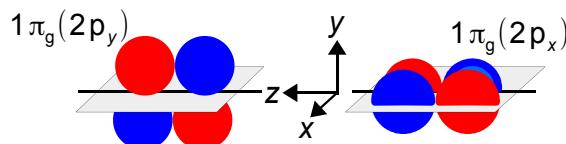
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As both of the antibonding  $1\pi_g$  orbitals are gerade the overall parity of  $^3\Sigma$  is gerade and so  ${}^3\Sigma_g$ .



**Figure 7.8:** mirror plane in the  $xz$  plane  $\sigma(xz)$ .

The reflection symmetry of the degenerate pair of  $1\pi_g$  orbitals are shown in Fig. 7.8. In the *same* mirror, let's choose it to be in the  $xz$  plane  $\sigma(xz)$ , the  $1\pi_g(2p_y)$  is antisymmetric to reflection but  $1\pi_g(2p_x)$  is symmetric to reflection, and so the overall reflection symmetry is antisymmetric (minus). So the ground electronic state has  ${}^3\Sigma_g^-$  as its term symbol. Clearly if we had chosen the mirror to be in the  $yz$  plane then  $\pi_g(2p_y)$  is symmetric and  $\pi_g(2p_x)$  antisymmetric to reflection and overall the reflection symmetry is again antisymmetric. The reflection symmetry is not normally shown on MOs other than  $\Sigma$  states. We highlight that this term is the ground state with a capital X that is  $X{}^3\Sigma_g^-$  as in Fig. 7.3. Conventionally, excited states which have the same multiplicity as the ground state are labelled A, B, C etc. in increasing energy order. Excited states which have different multiplicities from the ground state are labelled a, b, c, etc. This convention is sometimes modified for historical reasons, which I will point out where necessary.

The term symbols for the electronic states in Fig. 7.3 are best obtained using group theory character tables (Hollas 2004) and (Atkins & de Paula 2006). The lowest energy electron configuration is  $(1\pi_g)^1(1\pi_g)^1$  and using the  $D_{\infty h}$  character table for a homonuclear diatomic molecule the direct product of  $\Pi_g \times \Pi_g$  is the last line below where we have used the trigonometric identity  $4\cos^2\phi = 2 + 2\cos 2\phi$  (Stroud & Booth 2007, p. 271).

$D_{\infty h}$	$E$	$2C_\infty^\phi$	$\infty\sigma_v$	$i$	$2S_\infty^\phi$	$\infty C_2$
$\Pi_g$	2	$2\cos\phi$	0	2	$-2\cos\phi$	0
$\Pi_g$	2	$2\cos\phi$	0	2	$-2\cos\phi$	0
$\Pi_g \times \Pi_g$	4	$4\cos^2\phi$	0	4	$4\cos^2\phi$	0
$\Pi_g \times \Pi_g$	4	$2+2\cos 2\phi$	0	4	$2+2\cos 2\phi$	0

The  $D_{\infty h}$  character table shows the  $\Pi_g \times \Pi_g$  direct product is equal to the direct sum of  $\Sigma_g^- + \Sigma_g^+ + \Delta_g$ .

$D_{\infty h}$	$E$	$2C_\infty^\phi$	$\infty\sigma_v$	$i$	$2S_\infty^\phi$	$\infty C_2$
$\Sigma_g^-$	1	1	-1	1	1	-1
$\Sigma_g^+$	1	1	1	1	1	1
$\Delta_g$	2	$2\cos 2\phi$	0	2	$2\cos 2\phi$	0
$\Sigma_g^- + \Sigma_g^+ + \Delta_g$	4	$2+2\cos 2\phi$	0	4	$2+2\cos 2\phi$	0

That is our  $(1\pi_g)^1(1\pi_g)^1$  electron configuration corresponds to three different electronic states. The Pauli principle says that the interchange of our two electrons (fermions) must be overall antisymmetric. The characters for the  $\Sigma_g^-$  MO is antisymmetric (it has negative characters) so the spins of the two electrons must be symmetric, *i.e.* they must be parallel spins or a triplet, so it is a  $^3\Sigma_g^-$  state. The other two states  $\Sigma_g^+$  and  $\Delta_g$  are symmetric (all positive characters) states and so the electrons spins must be antisymmetric or spin-paired and the these two states are singlets  $^1\Sigma_g^+$  and  $^1\Delta_g$ . Applying Hund's rules, the energy ordering is  $^3\Sigma_g^- < ^1\Delta_g < ^1\Sigma_g^+$  and this is emphasized as the  $X^3\Sigma_g^-$  ground state, and the excited  $a^1\Delta_g$  often called “singlet” oxygen of atmospheric chemistry importance and  $b^1\Sigma_g^+$  states shown in Fig. 7.3. The angular momenta and parity for the three states are summarized below remembering that  $1\pi_g(2p_y)$  has  $\lambda = -1$  and  $1\pi_g(2p_x)$  has  $\lambda = +1$ .

$X^3\Sigma_g^-$	$a^1\Delta_g$	$b^1\Sigma_g^+$
$\uparrow 1\pi_g(2p_y) \quad \uparrow 1\pi_g(2p_x)$	$\uparrow\downarrow 1\pi_g(2p_y) \quad - 1\pi_g(2p_x)$	$\uparrow 1\pi_g(2p_y) \quad \downarrow 1\pi_g(2p_x)$
$S = +\frac{1}{2} + \frac{1}{2} = 1$	$S = +\frac{1}{2} - \frac{1}{2} = 0$	$S = +\frac{1}{2} - \frac{1}{2} = 0$
$A = -1 + 1 = 0$	$A = -1 - 1 = -2$	$A = -1 + 1 = 0$
$g \times g = g$	$g \times g = g$	$g \times g \times = g$

The *excited* electron configurations  $(1\pi_u)^3(1\pi_g)^3$  has the following direct product for  $D_{\infty h}$  symmetry.

$D_{\infty h}$	$E$	$2C_\infty^\phi$	$\infty\sigma_v$	$i$	$2S_\infty^\phi$	$\infty C_2$
$\Pi_u$	2	$2\cos\phi$	0	-2	$2\cos\phi$	0
$\Pi_g$	2	$2\cos\phi$	0	2	$-2\cos\phi$	0
$\Pi_u \times \Pi_g$	4	$4\cos^2\phi$	0	-4	$-4\cos^2\phi$	0
$\Pi_u \times \Pi_g$	4	$2+2\cos 2\phi$	0	-4	$-2-2\cos 2\phi$	0

The  $\Pi_u \times \Pi_g$  direct product is equal to the direct sum of the  $\Sigma_u^- + \Sigma_u^+ + \Delta_u$ .

$D_{\infty h}$	$E$	$2C_\infty^\phi$	$\infty\sigma_v$	$i$	$2S_\infty^\phi$	$\infty C_2$
$\Sigma_u^-$	1	1	-1	-1	-1	1
$\Sigma_u^+$	1	1	1	-1	-1	-1
$\Delta_u$	2	$2\cos 2\phi$	0	-2	$-2\cos 2\phi$	0
$\Sigma_u^- + \Sigma_u^+ + \Delta_u$	4	$2+2\cos 2\phi$	0	-4	$-2-2\cos 2\phi$	0

All three  $\Sigma_u^- \Sigma_u^+$  and  $\Delta_u$  states are antisymmetric as they have negative characters which means that the spins must be symmetric in order for these fermions to be overall antisymmetric to interchange and satisfy the Pauli principle. So the three states are triplets  ${}^3\Sigma_u^-$ ,  ${}^3\Sigma_u^+$  and  ${}^3\Delta_u$ . From Hund's rules they are in the following energy order  $A'{}^3\Delta_u$  then  $A{}^3\Sigma_u^+$  and then the Schumann-Runge upper state  $B{}^3\Sigma_u^-$  which is so important to terrestrial life on Earth. The  $A'{}^3\Delta_u$  state was discovered after the  $A{}^3\Sigma_u^+$  state's name was established in the literature and hence the prime was added to distinguish between them, Fig. 7.3. The angular momenta and parity for the three states are summarized below. The  $A'{}^3\Delta_u$  state could have its unpaired electrons in either  $(\pi_g 2p_y)^1(\pi_u 2p_y)^1$  or equivalently in  $(\pi_g 2p_x)^1(\pi_u 2p_x)^1$ .

$A'{}^3\Delta_u$	$A{}^3\Sigma_u^+$	$B{}^3\Sigma_u^-$
$\uparrow\downarrow 1\pi_g(2p_y) \quad \uparrow\downarrow 1\pi_g(2p_x)$	$\uparrow\downarrow 1\pi_g(2p_y) \quad \uparrow\downarrow 1\pi_g(2p_x)$	$\uparrow\downarrow 1\pi_g(2p_y) \quad \uparrow\downarrow 1\pi_g(2p_x)$
$\uparrow\downarrow 1\pi_u(2p_y) \quad \uparrow\downarrow 1\pi_u(2p_x)$	$\uparrow\downarrow 1\pi_u(2p_y) \quad \uparrow 1\pi_u(2p_x)$	$\uparrow 1\pi_u(2p_y) \quad \uparrow 1\pi_u(2p_x)$
$S = +\frac{1}{2} + \frac{1}{2} = 1$	$S = +\frac{1}{2} + \frac{1}{2} = 1$	$S = +\frac{1}{2} + \frac{1}{2} = 1$
$A = -1 - 1 = -2$	$A = -1 + 1 = 0$	$A = -1 + 1 = 0$
$g \times u = u$	$g \times u = u$	$g \times u = u$

## 7.1.2 Selection Rules for Diatomic Molecules

Summarizing the term symbol for a linear molecule.

$^{2S+1}\Lambda_{g \text{ or } u}^{+ \text{ or } -}$  term symbol for diatomic or linear molecules

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The multiplicity is  $2S+1$  and the components of the total spin  $S$  along the molecular axis are  $\Sigma$ .

$$\Sigma = S, S-1, S-2, S-3, \dots, -S$$

The component of the orbital angular momentum along the molecular axis is  $\Lambda$  (values and symbols below).

$$\begin{aligned} \Lambda &= 0, \pm 1, \pm 2, \pm 3, \dots \\ \Sigma, \Pi, \Delta, \Phi, \dots \end{aligned}$$

Be careful to distinguish between the symbol  $\Sigma$  (Greek roman) for zero component of orbital angular momentum and the multiplicity quantum number (Greek italic)  $\Sigma$ . The reflection symmetry (+ or  $-$ ) and centrosymmetric inversion symmetry or parity (g or u) we have already been described.

The first three selection rules arise from the conservation of angular momentum for which the photon has one unit. There is no change in multiplicity as a photon does not directly affect electron spin in the absence of an external magnetic field.

$$\Delta(2S+1) = 0 \quad \text{no change in multiplicity}$$

The component of orbital angular momentum either does not change or only changes by one unit, e.g. we have the allowed transitions  $\Sigma \leftrightarrow \Sigma$ ,  $\Sigma \leftrightarrow \Pi$  or  $\Pi \leftrightarrow \Delta$  but  $\Sigma \leftrightarrow \Delta$  is forbidden.

$$\Delta\Lambda = 0, \pm 1 \quad \text{change of component of orbital angular momentum}$$

The component of the total of the spin and orbital angular momenta is  $\Omega$  (Greek italic uppercase omega) which either does not change or only changes by one unit. The value of  $\Omega$  is indicated as a post-subscript.

$$\Omega = |\Lambda + \Sigma| \quad \Delta\Omega = 0, \pm 1 \quad \text{component of the total angular momentum}$$

The above angular momentum selection rules are for “normal” spin-orbit coupling and are called Hund’s case (a) (Hollas 2004, pp. 233–237). There are also two symmetry selection rules, firstly the reflection symmetry must *not* change.

$$+ \leftrightarrow + \quad - \leftrightarrow - \quad \text{but } \textit{not} \quad + \leftarrow | \rightarrow - \quad \text{reflection symmetry}$$

For centrosymmetric linear molecules the parity *must* change.

$$g \leftrightarrow u \quad \text{but not } g \leftarrow | \rightarrow g \text{ or } u \leftarrow | \rightarrow u \quad \text{parity selection rule}$$

These are exemplified by the very strong O<sub>2</sub> Schumann-Runge band system B<sup>3</sup>Σ<sub>u</sub><sup>-</sup> ← X<sup>3</sup>Σ<sub>g</sub><sup>-</sup> where the other transitions from the ground state are “forbidden”, *i.e.* weak or very weak.

### 7.1.3 Bond Order

The bond order  $b$  is equal to half the difference between  $N$  the number of electrons in bonding orbitals and  $N^*$  the number of electrons in antibonding orbitals. The ground electronic state of O<sub>2</sub> is a good example.

$$b = \frac{1}{2}(N - N^*) \quad \text{bond order}$$

$$b = \frac{1}{2}(2_{\sigma 1s} - 2_{\sigma^* 1s} + 2_{\sigma 2s} - 2_{\sigma^* 2s} + 2_{\sigma 2p} + 4_{\pi 2p} - 2_{\pi^* 2p}) = \frac{1}{2}(10 - 6) = 2$$

Molecular orbital theory has predicted a bond order of 2 exactly the same as in the Lewis dot picture we learned at school, of course excited states may have different bond orders. The MO theory has also given us all the different electronic states and the transitions between them which the Lewis dot ideas cannot!

## 7.2 Vibrational Progressions

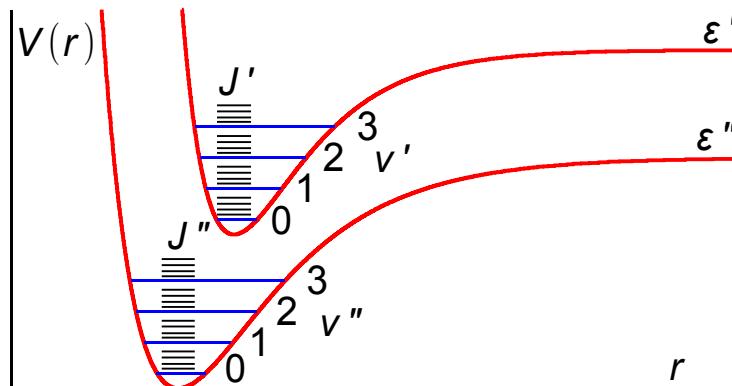


Figure 7.9: schematic diatomic electronic, vibrational and rotational energy levels.

A gas phase molecule will possess electronic, vibrational, and rotational energy, Fig. 7.9, but in condensed phases the rotations are “washed out” by collisions with neighbouring molecules and the molecules cannot rotate freely. When we use a medium resolution spectrophotometer to take the UV-visible spectrum we find there is a series of peaks called a *vibrational progression* which appears in most electronic spectra, Fig. 7.10.

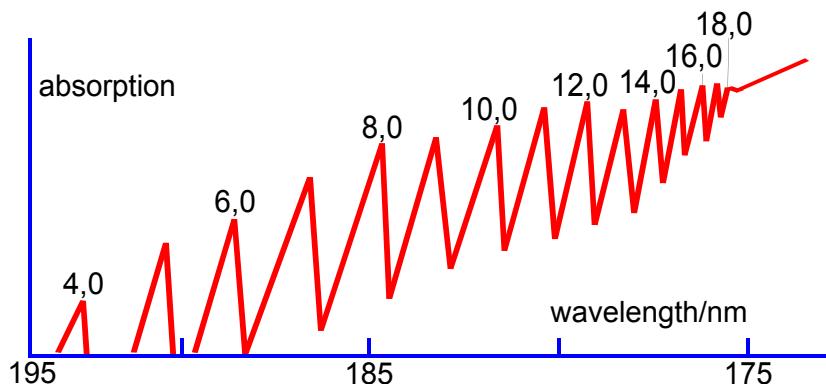


Figure 7.10: schematic O<sub>2</sub> Schumann-Runge vibrational progression.

Using a high resolution instrument (typically a laser based instrument) we find that each of these individual vibrational peaks has a rotational fine structure when the molecule is in the gas phase. The intensities of vibrational progression and the rotational fine structure of the electronic spectrum can be explained by the Franck-Condon principle.

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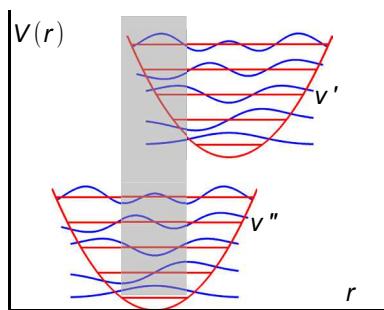
### 7.2.1 The Franck-Condon Principle

The mass that is moved during an electronic transition is an electron. Electron mass is much smaller than the effective mass  $m_{\text{eff}}$  (for a diatomic this is the reduced mass of the molecule) that is moving during a vibration. Finally, effective mass is much less than the moment of inertia  $I = \mu r^2$  (the rotational equivalent of mass) which moves during a rotation. These “mass” differences lead to the time scale differences for the three types of motion which each differ by roughly a couple of orders of magnitude from its neighbour.

<u>motion</u>	<u>timescale/s</u>	<u>energy/cm<sup>-1</sup></u>
valence electron transition	$\sim 10^{-15}$	$\sim 14,000$ to $\sim 100,000$
vibration of bond or angle	$\sim 10^{-13}$	$\sim 300$ to $\sim 4400$
rotation of a molecule	$\sim 10^{-11}$	$\sim 0.2$ to $\sim 60$
molecular collisions, gas 1 atm 25°C	$\sim 10^{-10}$	$310.83 = \frac{3}{2}RT$
fluorescence	$\sim 10^{-8}$	$\sim 14,000$ to $\sim 40,000$
phosphorescence	$\sim 1$ to $\sim 10^3$	$\sim 14,000$ to $\sim 25,000$

The molecule is initially in the ground electronic state in a vibrational level  $v''$  and a rotational level  $J''$ . During the electronic transition (during the electron jump) the molecular geometry is frozen and the electronic transition may be thought of as a *vertical* process on a potential energy diagram. The vibrational and rotational motion then *resume* from the “frozen” geometry but in the new electronic state, in a new vibrational level  $v'$  and a new rotational level  $J'$ . In general the excited state equilibrium bond length  $r_e'$  is expected to be different from the ground state  $r_e''$  also the potential energy curves are expected to have different well depths and width.

Most molecules occupy the  $v'' = 0$  level and from its vibrational wavefunction the highest probability bond length is in the middle of  $v'' = 0$  at about  $r_e''$ , so the highest intensity vibrational-electronic transition starts from the  $v'' = 0$  vibronic level and covers a region of bond lengths corresponding to the amplitude of the  $v'' = 0$  vibrational level. This *Franck-Condon region* vertically “cuts” a whole series of  $v'$  vibrational levels to give the *vibrational progression* scene in photon absorption e.g. Fig. 7.10 for the O<sub>2</sub> Schumann-Runge vibrational progression.



**Figure 7.11:** Franck-Condon region (grey) and vertical transitions.

In an electronic transition the vibrational change is

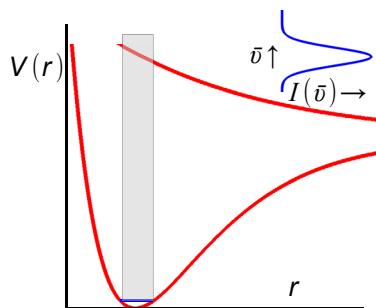
$$\Delta v = \text{anything} \quad \text{vibrational-electronic selection rule}$$

The peaks of the vibrational progression ( $v' \leftarrow v''$ ) vary in intensity determined by the square of the Franck-Condon factor  $S_{fi}$  (also called the square of the “overlap integral”).

$$S_{fi} = \int \psi_f^* \psi_i d\tau \quad \text{Franck-Condon factor or overlap integral}$$

Where  $\psi_i$  and  $\psi_f$  are the initial and final vibrational wavefunctions and if they are written as complex number (Parker 2013a, p. 52) then the star indicates that the complex conjugate must be used. The term  $d\tau$  (“dee tau”) means integrate over all relevant space, here it is the Franck-Condon region of bond length. You’ll be very pleased to know we don’t need to calculate the Franck-Condon factors but usually the most intense transitions are where the  $v'$  wavefunction within the Franck-Condon region most closely resembles the shape of the  $v'' = 0$  vibrational wavefunction. Thus in Fig. 7.11 the most intense peak of the progression is (4,0). Let us look at the shapes of the most common vibrational progressions.

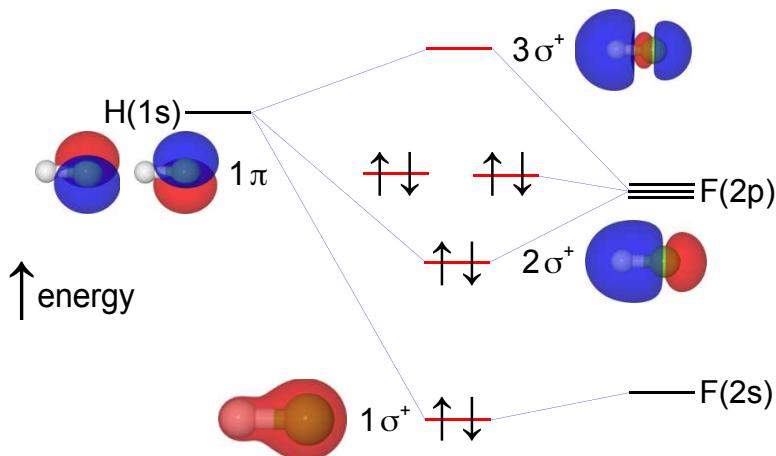
### 7.2.2 Vibrational Progression to a Repulsive Excited State



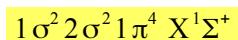
**Figure 7.12:** schematic PE curves for transitions to a repulsive electronic state.

If the upper electronic state is repulsive, there is no PE well, then the upper state does not have quantized vibrational or rotational levels. We observe a continuous absorption spectrum *without* any vibrational bands, insert of Fig. 7.12, which is a “reflection” of the  $v'' = 0$  wavefunction onto the repulsive curve. Examples are the hydrogen halides HF, HCl, HBr, and HI. The absorptions of HF lie completely in the vacuum-UV while HCl absorbs from 230 nm peaking in the vacuum-UV. HBr absorbs from 285 nm and peaking at 180 nm, HI absorbs from 360 nm and peaks at 218 nm.

Consider HF, the greater electronegativity of F compared to H means the F atomic orbitals have lower energies than the corresponding H atomic orbitals. The F(2s) orbital only has a small interaction with the H(1s) and so 1 $\sigma$  is largely on the F-atom. The H(1s) orbital is similar in energy to the F(2p<sub>z</sub>) orbital and interacts to form the 2 $\sigma$  and 3 $\sigma^*$  orbitals. The HF valence shell molecular orbitals have a lone pair fluorine 1 $\sigma$  and degenerate lone pairs of MOs which are the fluorine 1 $\pi$ (2p<sub>x</sub>) and 1 $\pi$ (2p<sub>y</sub>) and the single bonding orbital 2 $\sigma$  formed from the overlap of the H(1s) and the F(2p<sub>z</sub>).



**Figure 7.13:** schematic of the valence MOs for the HF ground state.



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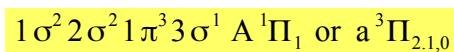
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As HF does not have a centre of symmetry the g and u symmetries do not apply. The excited electronic state involves one of the  $1\pi$  lone pair electrons being excited to the empty  $3\sigma^+$  orbital. The direct product of the two half-full orbitals  $1\pi$  and  $3\sigma^+$  for the  $C_{\infty v}$  point group is  $\Pi \times \Sigma^+ = \Pi$ .

$C_{\infty h}$	$E$	$2C_\phi$	$\infty\sigma_v$
$\Pi$	2	$2\cos\phi$	0
$\Sigma^+$	1	1	1
$\Pi \times \Sigma^+$	2	$2\cos\phi$	0
$= \Pi$	2	$2\cos\phi$	0



The active electron may come from either the  $1\pi(F2p_x)$  or the  $1\pi(F2p_y)$  lone pairs and the excited state may be either a singlet with spins paired or a triplet with spins parallel. Note the use of  $\Omega = \Sigma + \Lambda$  in the posterior subscript of the state symbols. The  $\text{a}^3\Pi_{2,1,0} \leftarrow \text{^1}\Sigma^+$  is a minor contributor to the spectrum as the transition involves a change in multiplicity.  $\text{A}^1\Pi_1$  dissociates to ground state atoms H( $^2S$ ) and F( $^2P_{3/2}$ ). The excited electronic  $\text{A}^1\Pi_1$  state has a zero bond order, *i.e.* it is a repulsive state with a continuous absorption spectrum and the excited H-F bond will break within half a “vibration”  $\sim 10^{-13}$  s to give isolated H and F atoms recoiling apart from another. The separate H and F atoms have a kinetic energy distribution determined by the difference between (a) where the HF was excited to on the repulsive curve after the vertical transition and (b) the dissociation asymptote energy of the repulsive curve.

### 7.2.3 Vibrational Progression to a Stronger Bonded Excited State $r_e' < r_e''$

This is a fairly rare situation and arises when the active electron in an antibonding orbital is promoted to a non-bonding orbital. Also it may occur in transitions between two excited states. The  $v''$  vibrational progression is fairly short with a maximum intensity at  $v' > 0$ .

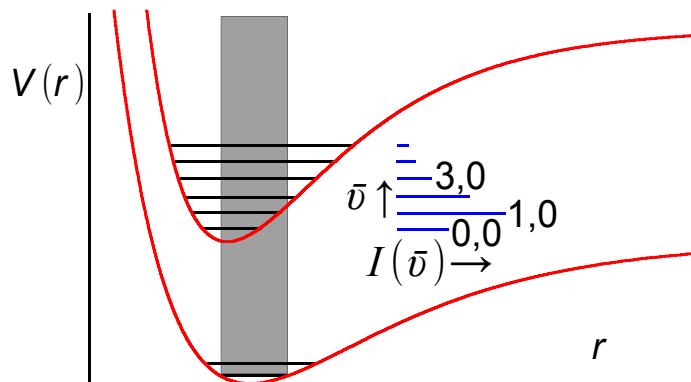
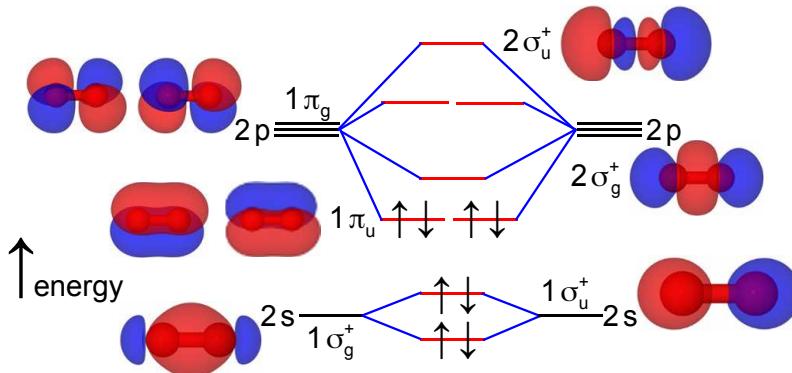


Figure 7.14: schematic PE curves for transitions with  $r_e' < r_e''$ .

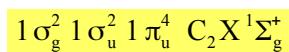
The Franck-Condon transition cuts the shallower side (the right hand side) of the upper electronic state and so the vibrational progression is short as relatively few  $v'$  levels are accessible.

#### 7.2.4 Vibrational Progression to an Equivalently Bonded Excited State $r_e' \approx r_e''$

An example of this situation comes from the transient  $C_2$  molecule which is found in electric discharges, hydrocarbons flames, comets and in stellar atmospheres.  $C_2$  has a double  $\pi$ -bond between the two C-atoms but without any  $\sigma$ -bond.

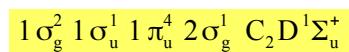


**Figure 7.15:** schematic of the valence MOs for the  $C_2$  ground state.



Excitation of a  $1\sigma_u^+$  electron to the  $2\sigma_g^+$  orbital gives a molecule with a bond length which only changes from 1.243 to 1.238 Å in jumping to this excited state. The direct product of the two half-full orbitals  $1\sigma_u^+$  and  $2\sigma_g^+$  for the  $D_{\infty h}$  point group is  $\Sigma_u^+ \times \Sigma_g^+ = \Sigma_u^+$  as shown below.

$D_{\infty h}$	$E$	$2C_\infty^\phi$	$\infty\sigma_v$	$i$	$2S_\infty^\phi$	$\infty C_2$
$\Sigma_u^+$	1	1	1	-1	-1	-1
$\Sigma_g^+$	1	1	1	1	1	1
$\Sigma_u^+ \times \Sigma_g^+$	1	1	1	-1	-1	-1
$= \Sigma_u^+$	1	1	1	-1	-1	-1



The Mulliken bands in the far-UV at 242–231 nm are transitions between  $D^1\Sigma_u^+ \leftrightarrow X^1\Sigma_g^+$  with  $r_e' \approx r_e''$ . Note that the blue visible colour of a Bunsen burner flame is due to a different transition, the Swan bands at 785–340 nm, which are from  $d^3\Pi_g$  down to the lower excited state  $a^3\Pi_u$  see Parker (Parker 2015, section 6.5).

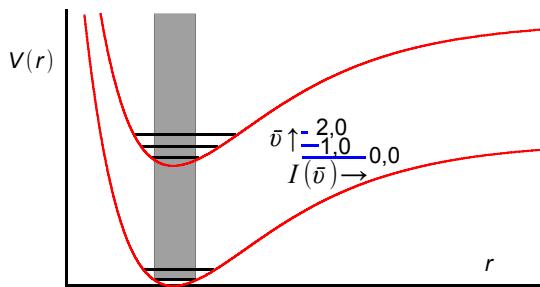


Figure 7.16: schematic PE curves for transitions with  $r_e' \approx r_e''$ .

As  $r_e' \approx r_e''$  the 0,0 transition dominates the vibrational progression which is very short with only a few peaks.

#### 7.2.5 Vibrational Progression to a Weaker Bonded Excited State $r_e' > r_e''$

This is the most common situation for the vibrational progression and arises when an electron in a bonding orbital is excited into an orbital which is less bonding or is antibonding. N<sub>2</sub> has a σ-bond and two π-bonds and has a bond order of three. As there are no partially filled orbitals in the N<sub>2</sub> ground configuration it's term symbol is X<sup>1</sup>Σ<sub>g</sub> state.

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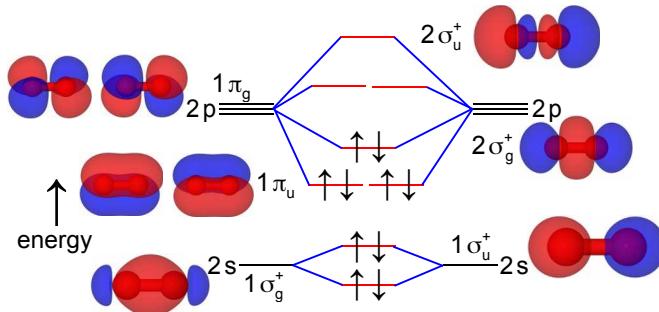
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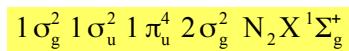
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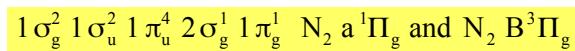
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**Figure 7.17:** schematic of the valence MOs for the N<sub>2</sub> ground state.



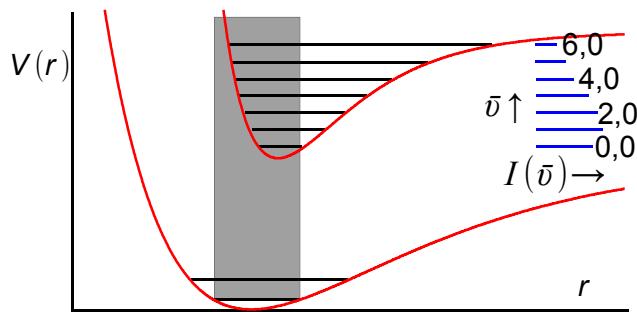
The N<sub>2</sub> ground state has  $r_e' = 1.098 \text{ \AA}$  and the excited singlet state and triplet states obtained by exciting an electron from the HOMO to the LUMO have  $r_e''$  of 1.220 and 1.213 Å, respectively, which are much longer bonds than the triple-bonded N<sub>2</sub> ground state. For historical reasons the A, B, C and a, b, c notation used for N<sub>2</sub> is not the standard notation.



This confirmed by from the direct product of  $\Sigma_g^+ \times \Pi_g$  which is equal to  $\Pi_g$  for the  $D_{\infty h}$  point group.

$D_{\infty h}$	$E$	$2C_\infty^\phi$	$\infty\sigma_v$	$i$	$2S_\infty^\phi$	$\infty C_2$
$\Sigma_g^+$	1	1	1	1	1	1
$\Pi_g$	2	$2\cos 2\phi$	0	2	$-2\cos 2\phi$	0
$\Sigma_g^+ \times \Pi_g$	2	$2\cos 2\phi$	0	2	$-2\cos 2\phi$	0
$= \Pi_g$	2	$2\cos 2\phi$	0	2	$-2\cos 2\phi$	0

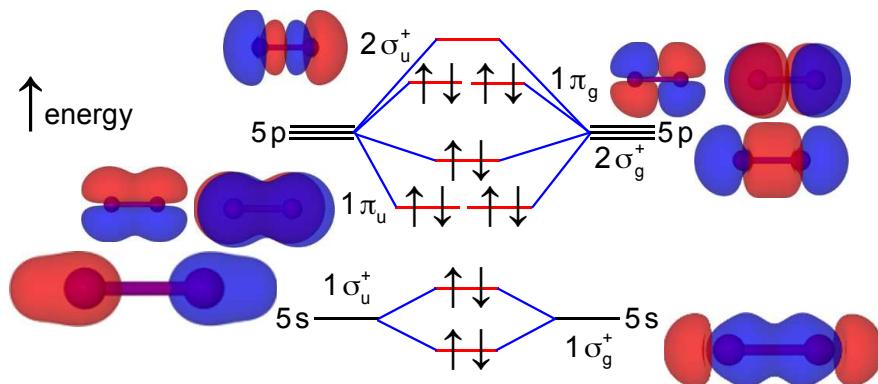
A vertical Franck-Condon transition will be to the steeper, repulsive, left hand side of the upper potential energy surface and so will cut many vibrational levels giving a broad vibrational progression. The commonly used nitrogen laser (337 nm) involves the  $C^3\Pi_u \rightarrow B^3\Pi_g$  emission with the  $C^3\Pi_u$  excited state formed by an electric discharge. A common use of the nitrogen laser is the excitation and ionization source for the analytical technique of matrix assisted laser desorption ionization (MALDI) mass spectrometry used for the analysis of solids, surfaces and large biological molecules.



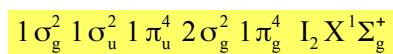
**Figure 7.18:** schematic PE curves for transitions with  $r_e' \gg r_e''$ .

### 7.2.6 Vibrational Progression to an Appreciably Weaker Bonded Excited State $r_e' \gg r_e''$

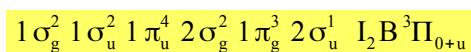
The halogens F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub> and I<sub>2</sub> absorb in the visible and near UV (F<sub>2</sub> is pale green, Cl<sub>2</sub> is yellow-green, Br<sub>2</sub> vapour is brown-red, and I<sub>2</sub> vapour is purple). Fig. 7.19, I<sub>2</sub> ground state configuration has a bond order of 1.



**Figure 7.19:** schematic of the valence MOs for the I<sub>2</sub> ground state.



Note that for F<sub>2</sub> the  $2\sigma_g^+$  and  $1\pi_u$  energies are inverted as they are for O<sub>2</sub> due to the high electronegativity of both F-atoms and O-atoms. The I<sub>2</sub> ground electronic state has  $r_e'' = 2.67 \text{ \AA}$ . Excitation of an electron from the antibonding  $1\pi_g$  HOMO, either the  $1\pi_g(p_x)$  or  $1\pi_g(p_y)$ , to the higher energy and even more antibonding  $2\sigma_u^+$  LUMO gives the excited B<sup>3</sup>Π<sub>0+u</sub> state.



The  $\Pi_u$  state is confirmed from the direct product of  $\Pi_g \times \Sigma_u^+$  which is equal to  $\Pi_u$  for the  $D_{\infty h}$  point group.

$D_{\infty h}$	$E$	$2C_\infty^\phi$	$\infty\sigma_v$	$i$	$2S_\infty^\phi$	$\infty C_2$
$\Pi_g$	2	$2\cos 2\phi$	0	2	$-2\cos 2\phi$	0
$\Sigma_u^+$	1	1	1	-1	-1	-1
$\Pi_g \times \Sigma_u^+$	2	$2\cos 2\phi$	0	-2	$2\cos 2\phi$	0
$= \Pi_u$	2	$2\cos 2\phi$	0	-2	$2\cos 2\phi$	0

The full term symbol for the excited state is  $B^3\Pi_{0+u}$  but for historical reasons with  $I_2$  and  $N_2$  the conventional labelling of states as A, B, C etc. is not followed. What about the  $0+$  part of the posterior subscript? Due to the high positive charge of the I-nuclei with 53 protons each, the spin-orbit coupling is very large. Analogously to the atomic case where one moves from LS coupling to JJ coupling, the  $I_2$  molecule moves from Hund's case (a) to Hund's case (c) coupling (Hollas 2004, p. 224).

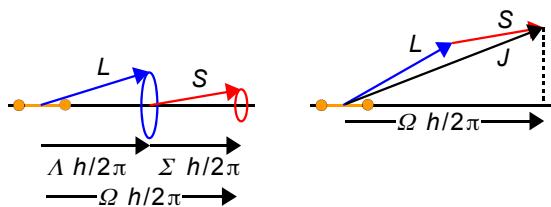
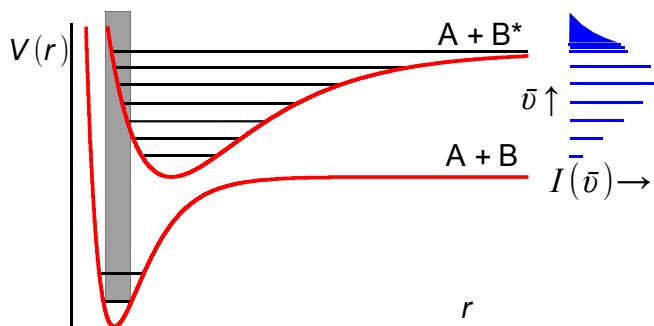


Figure 7.20: Hund's case (a) left; Hund's case (c) right.

The total orbital momentum of the electrons  $L$  has axial components  $\Lambda$ , the total spin angular momentum  $S$  with axial components  $\Sigma$  and the axial components of the total is  $\Omega = |\Lambda + \Sigma|$ . As we discussed in section 7.1.2 for Hund's case (a) with minimal spin-orbit coupling  $\Delta\Lambda = 0, \pm 1$  with  $\Delta(2S+1) = 0$  and  $\Delta\Omega = 0, \pm 1$  for the angular momentum selection rules (remember there are also the symmetry selection rules). However, with the high nuclear charges in the molecule then the individual electrons couple with the axial electrostatic field so that  $\Lambda$  and  $\Sigma$  are no longer good quantum numbers and only  $\Omega$  has any true meaning. This Hund's case (c) coupling means the  $\Delta\Lambda$  and  $\Delta(2S+1)$  no longer hold and the only angular momentum selection rule that applies is for  $\Delta\Omega$  where the plus and minus signs refer to reflection in the axial mirror plane for  $\Omega = 0$  and not  $\Lambda = 0$  which is for Hund's case (a).

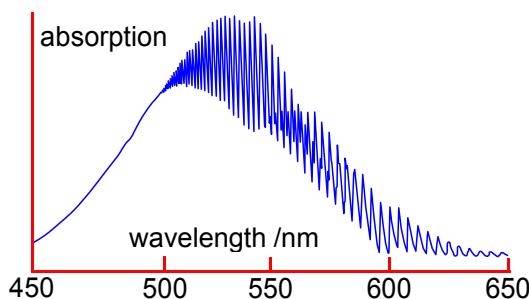
$$\Delta\Omega = 0^+ \leftrightarrow 0^+ \quad \Delta\Omega = 0^- \leftrightarrow 0^- \quad \Delta\Omega = 0^+ \leftarrow | \rightarrow 0^-$$

The transition  $B^3\Pi_{0+u} \leftarrow X^1\Sigma_g^+$  is allowed by  $\Omega = 0^+ \leftrightarrow 0^+$  selection rule. The transition is very intense and is responsible for the blue-violet colour of iodine vapour. The equilibrium bond lengths are  $r_e' = 3.03$  Å and  $r_e'' = 2.67$  Å and the  $B^3\Pi_{0+u} \leftarrow X^1\Sigma_g^+$  spectrum has a maximum intensity close to the continuum threshold. The  $B^3\Pi_{0+u}$  state dissociates to a ground state  ${}^3P_{3/2}$  and an excited state  ${}^2P_{1/2}$  I-atom.



**Figure 7.21:** schematic PE curves for transitions with  $r_e' \gg r_e''$ .

An undergraduate student's absorption spectrum of iodine vapour at room temperature obtained in the teaching labs at Heriot-Watt University Chemistry Department is shown in Fig. 7.22.



**Figure 7.22:** vibrational-electronic spectrum of iodine vapour.

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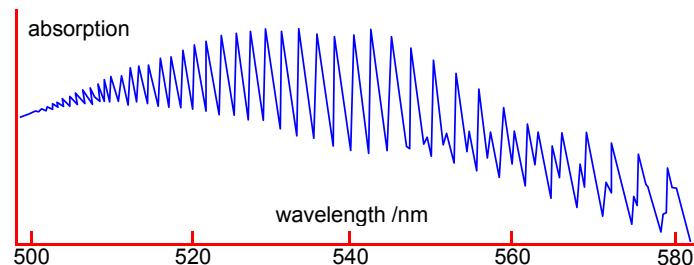


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The student's experimental data for the vibrational progression of iodine is treated in full using the Birge-Sponer extrapolation method (Parker 2013a, p19) to obtain the dissociation limit at  $\nu' = 69$  and the dissociation energy of the *excited* state as  $D_0' = 4500 \text{ cm}^{-1} = 54 \text{ kJ mol}^{-1}$ . The approximations involved in the Birge-Sponer extrapolation are discussed in Parker (Parker 2015, Question 6.2). In Fig. 7.22 we see both the intense  $\nu'' = 0$  vibrational progression and the weaker  $\nu'' = 1$  progression.

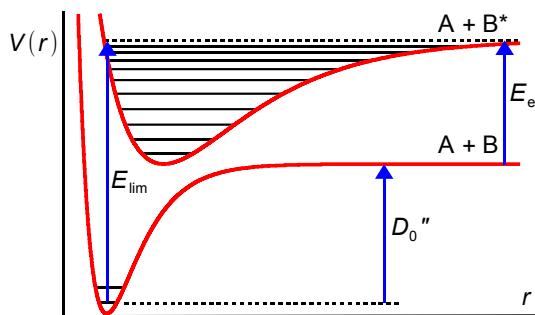


**Figure 7.23:** expanded vibrational-electronic spectrum of  $\text{I}_2$ .

The expanded spectrum of Fig.7.23 shows more clearly both the hot band vibrational progression and the approach to the dissociation limit and the continuum absorption.

### 7.2.7 Vibrational Progressions and Finding Bond Energies

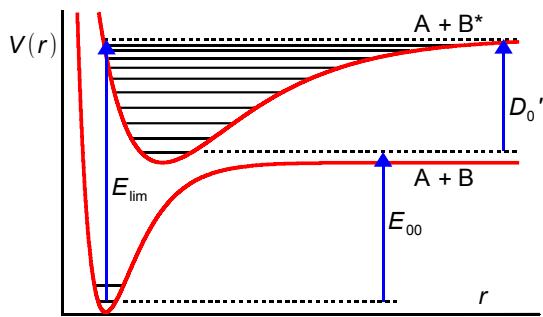
If we can determine the threshold wavelength for the dissociation limit  $E_{\text{lim}}$  and we know the energy of excitation of the products of dissociation  $E_{\text{ex}}$  then we can determine the bond dissociation energy of the *ground* state  $D_0''$  as in Fig. 24.



**Figure 7.24:** schematic for measuring  $D_0''$ .

$$E_{\text{lim}} = D_0'' + E_{\text{ex}} \quad D_0'' = E_{\text{lim}} - E_{\text{ex}}$$

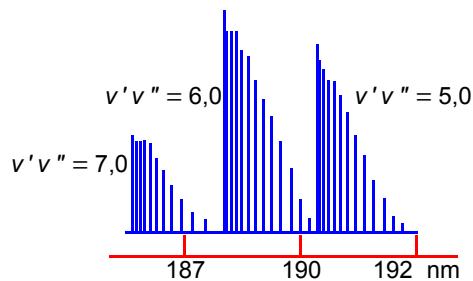
On the other hand if we can determine the threshold wavelength for dissociation  $E_{\text{lim}}$  and also we can determine the wavelength of the  $0 \leftarrow 0$  transition  $E_{00}$  then we can determine the bond dissociation energy of the *excited* state  $D_0'$  as in Fig. 7.25.



**Figure 7.25:** schematic for measuring  $D_0'$ .

$$E_{\text{lim}} = D_0' + E_{00} \quad D_0' = E_{\text{lim}} - E_{00}$$

### 7.2.8 Rotational Fine Structure in Vibrational-Electronic Spectra



**Figure 7.26:** schematic rotational fine structure of part of the Schumann-Runge band.

In the gas phase at high resolution, typically each of the vibrational-electronic peaks in a spectrum shows rotational fine structure. Any centrifugal distortion may be safely ignored and the rotational fine structure energy levels are given below.

$$E_{\text{rot}} = J(J+1) \frac{\hbar}{8\pi^2 I c} = J(J+1) B \text{ cm}^{-1}$$

Ignoring the translational energy of the molecule, the Born-Oppenheimer approximation gives the total energy as the sum of the individual energies.

$$E_{\text{total}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}}$$

So that transitions between rotational-vibrational-electronic levels  $\bar{v}_{\text{spect}}$  are equal to the vibrational-electronic plus the rotational transitions.

$$\bar{v}_{\text{spect}} = \bar{v}(v', v'') + \Delta(J(J+1)B) \text{ cm}^{-1}$$

The specific selection rule for the rotational change depends upon the electronic transition.

$$\begin{aligned}\Delta J &= \pm 1 && \text{for } ^1\Sigma \leftrightarrow ^1\Sigma \text{ transitions with PR branches} \\ \Delta J &= 0, \pm 1 && \text{for all other transitions with PQR branches, but } J' = 0 \leftarrow | \rightarrow J'' = 0\end{aligned}$$

The rotational constant  $B'$  of the upper electronic state may be very different from  $B''$  of the lower electronic state as their bond lengths may differ considerably. The P branch  $\Delta J = -1$  and R branch  $\Delta J = +1$  have the following general equation.

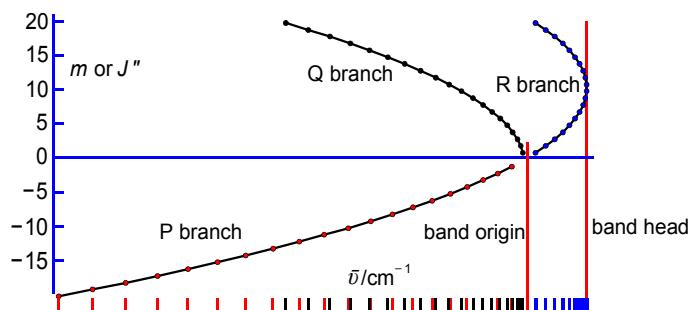
$$\bar{v}_{P,R} = \bar{v}(v', v'') + (B' + B'')m + (B' - B'')m^2 \text{ cm}^{-1} \quad \text{where } m = \pm 1, \pm 2, \pm 3, \dots$$

Where  $m$  has negative values for the P branch ( $\Delta J = -1$ ) and positive values for the R branch ( $\Delta J = +1$ ) and  $m \neq 0$ . None of the lines of the P and R branches are at the *band origin* which is  $\bar{v}(0,0)$ .

For the Q branch  $\Delta J = 0$  and  $J' = 0 \leftarrow | \rightarrow J'' = 0$ , no Q branch line appears at the band origin  $\bar{v}(0,0)$ .

$$\bar{v}_Q = \bar{v}(v', v'') + (B' - B'')J'' + (B' - B'')J''^2 \text{ cm}^{-1} \quad \text{where } J'' = 1, 2, 3, \dots$$

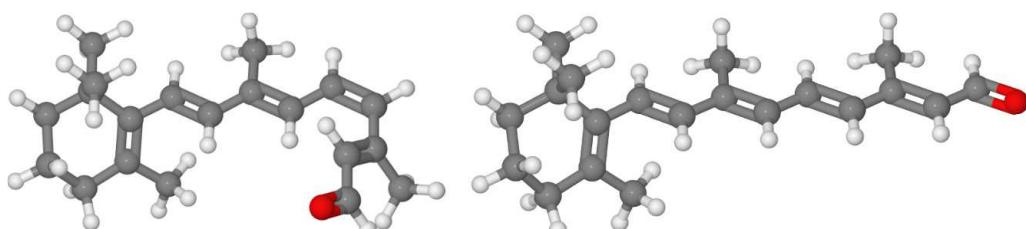
If  $r_e' > r_e''$  then we have  $B' < B''$  and if we let there be a 10% difference between the rotational constants we obtain the vibration-rotation-electronic spectrum in Fig. 7.27 which is described as *shaded to the red* (the spectrum is spaced out towards the red, low energy end). If a transition has  $r_e' < r_e''$  then we have  $B' > B''$  then the band would be shaded to the violet.



**Figure 7.27:** plot of  $m$  (PR branches) or  $J''$  (Q branch) for  $B' < B''$  with 10% difference.

### 7.3 Electronic Spectra of Polyatomic Molecules

I will only make a few general points about electronic spectra of polyatomics, for more details see Hollas (Hollas 2004, p. 260). Small inorganic molecules have very rich electronic spectra with a lot of detailed information about the energy levels and wavefunctions of the molecule. We have already looked at the basic quantum mechanics of large organic biological dye molecules such as  $\beta$ -carotene and chlorophyll (section 1.7.2). Another important biological example is vision which involves a  $\pi \rightarrow \pi^*$  transition in retinal when 11-cis-retinal absorbs light it isomerizes to all-trans-retinal with the absorption spectrum depending upon which particular opsin protein to which the retinal is bound. The all-trans-retinal opsin complex then triggers a series of chemical reactions which lead to an electrical signal in the optic nerve.



**Figure 7.28:** 11-cis-retinal (left) and all-trans-retinal (right).

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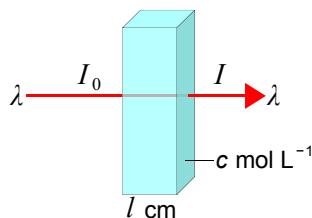
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## 7.3.1 Beer-Lambert Law

One of the commonest instruments in a chemical or analytical lab is a spectrophotometer which is used to measure not just the absorption spectrum and hence the identity of the compound (qualitative analysis) but also the concentration of compounds in solution (quantitative analysis). Quantitative analysis uses the Beer-Lambert law.

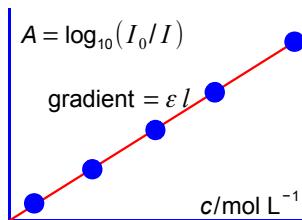
$$\log_{10} \frac{I_0}{I} = A = \varepsilon c l \quad \text{Beer-Lambert Law}$$

The sample holder (cuvette) is of path length  $l$  cm and the initial intensity is  $I_0$  of monochromatic light entering the solution of concentration  $c$  mol L<sup>-1</sup>. Some of the light will be absorbed and the remaining intensity  $I$  is transmitted through the cuvette and measured by the spectrophotometer.



**Figure 7.29:** Beer-Lambert measurements.

The absorbance  $A$  was formerly called the optical density. Note that the logs are to base 10 and the strength of the molecule's absorption  $\varepsilon$  (Greek italic epsilon) is called the molar decadic absorption coefficient and previously, the extinction coefficient. The absorption coefficient must be quoted at a particular wavelength as  $\varepsilon$  varies with  $\lambda$  hence the need for monochromatic light. The Beer-Lambert law applies to molecules of all sizes from atoms to proteins, and it applies to all the techniques we have met (MW, condensed phase IR, gas-phase IR and UV-visible). The plot of absorbance against concentration is linear for low concentrations and once the spectrophotometer has been calibrated with solutions of known concentration then the concentration of solutions of unknown may be measured. The Beer-Lambert plot may not be linear at high concentrations due to molecule-molecule interaction or chemical reactions.



**Figure 7.30:** Beer-Lambert calibration plot.

Typical values of absorption coefficients for allowed transitions are  $\epsilon \approx 10^3\text{-}10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$  and for forbidden transitions they are in the  $\epsilon \approx 1\text{-}100 \text{ L mol}^{-1} \text{ cm}^{-1}$  range.

*Worked Example:* A forensic/analytical lab needs to measure the concentration of benzene in a solution. At a wavelength of 256 nm in the UV, benzene has  $\epsilon = 15.144 \text{ L mol}^{-1} \text{ cm}^{-1}$ . If an optical cell of length 1 mm (the forensic lab only has a small amount of evidence) has 256 nm UV light reduced in intensity by 16%, what is the concentration of benzene in the solution?

$$\log_{10} \frac{I_0}{I} = A = \epsilon c l$$

$$\log_{10} \frac{100}{84} = (15.144 \text{ L mol}^{-1} \text{ cm}^{-1}) c (0.1 \text{ cm})$$

$$c = \frac{7.572 \times 10^{-2}}{(15.144 \text{ L mol}^{-1} \text{ cm}^{-1})(0.1 \text{ cm})} = 0.05 \text{ mol L}^{-1}$$

## 7.4 Decay of Electronically Excited Molecules

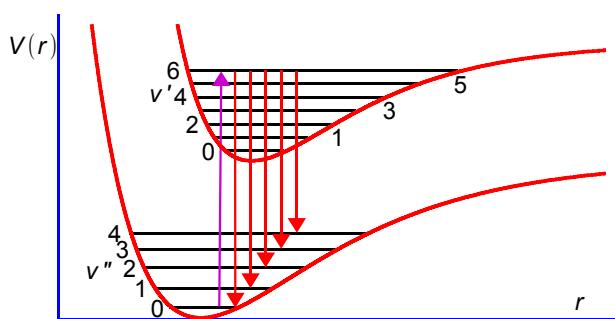
We will try to answer the question “what does an electronically excited molecule do?” The electronically excited molecule may lose its excitation energy by a photophysical process e.g. fluorescence or phosphorescence. Alternatively, it may undergo a photochemical change e.g. dissociation or some other chemical reaction involving the excited electronic state.

### 7.4.1 Resonance Fluorescence

A molecule may rapidly and spontaneously emit radiation following photon absorption, this is called fluorescence. Note that spontaneous means “on its own” and it does *not* imply anything about the speed of the process.

<u>motion</u>	<u>timescale/s</u>	<u>energy/cm<sup>-1</sup></u>
valence electron transition	$\sim 10^{-15}$	$\sim 14,000 \text{ to } \sim 100,000$
vibration of bond or angle	$\sim 10^{-13}$	$\sim 300 \text{ to } \sim 4400$
rotation of a molecule	$\sim 10^{-11}$	$\sim 0.2 \text{ to } \sim 60$
molecular collisions, gas 1 atm 25°C	$\sim 10^{-10}$	$310.83 = \frac{3}{2}RT$
fluorescence	$\sim 10^{-8}$	$\sim 14,000 \text{ to } \sim 40,000$
phosphorescence	$\sim 1 \text{ to } \sim 10^3$	$\sim 14,000 \text{ to } \sim 25,000$

A simpler short-hand notation is often used when discussing photophysical and photochemical processes particularly of large molecules, with  $S_0$ ,  $S_1$ ,  $S_2$  for singlet states and  $T_1$ ,  $T_2$ ,  $T_3$  for triplet states, assuming the ground state is a singlet. A singlet ground state molecule ( $S_0$ ) absorbs a photon to jump to the excited singlet state ( $S_1$ ) with a particular vibrational level  $v'$  in about  $10^{-15}$  s. The isolated  $S_1$  molecule has a natural radiative lifetime of around  $\tau_{\text{rad}} \approx 10^{-8}$  s. If the gas pressure is low with a long time between collisions, the  $S_1$  molecule will undergo direct, or resonance fluorescence,  $S_1 v' \rightarrow S_0 v''$ . This is a spin allowed process with a natural lifetime of  $\tau_{\text{fluor}} \approx 10^{-7}\text{--}10^{-9}$  s. Fluorescence is a *radiative* process and from the specific selection rules for electronic transitions we have  $\Delta v = \text{anything}$ .



**Figure 7.31:** resonance fluorescence.



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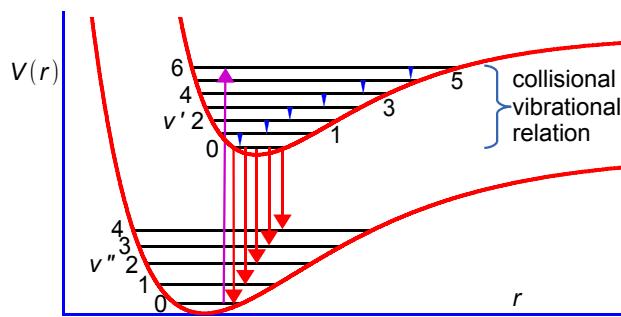
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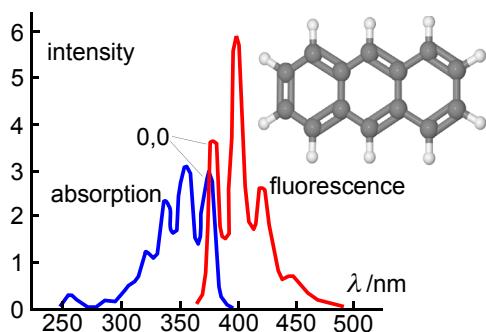
## 7.4.2 Relaxed Fluorescence

In the gas phase at pressures of  $\sim 1$  atmosphere the time between collisions  $\tau_{\text{collision}} \approx 10^{-10}$  s and the excited  $S_1$  state may undergo  $\sim 1000$  collisions before fluorescence occurs. The  $S_1$  excited state loses vibrational energy by molecular collisions with a conversion of vibrational into translation energy, known as *vibrational relaxation*, but it cannot lose the electronic energy by collision as the energy mismatch with translational energy is too large. The collisional vibrational relaxation is a *nonradiative* or *radiationless* process. In solutions or the pure liquid state the excited molecule always relaxes to  $v' = 0$  but in the gas phase the amount of relaxation is pressure dependent. The emission process is known as *relaxed* or *normal* or *delayed* fluorescence.



**Figure 7.32:** relaxed or normal fluorescence.

With relaxed fluorescence, the fluorescence spectrum is approximately a “mirror image” of the absorption spectrum. The fluorescence is at longer wavelengths compared with absorption and only the 0,0 transitions overlap. Fluorescence spectra give us experimental data about the  $S_0$  ground electronic state’s upper vibrational levels  $v''$ . Whereas we saw previously that absorption spectra give information about the  $S_1$  excited electronic state’s vibrational levels  $v'$ .



**Figure 7.33:** schematic absorption and fluorescence spectra of anthracene.

Note that the (0,0) transitions in absorption and in fluorescence usually do not coincide exactly, this is due to solvation effects, Fig. 7.34. Both the absorption and fluorescence are Franck-Condon vertical processes. When the photon is absorbed the  $S_1$  state formed has a non-optimized solvation shell as it still has the  $S_0$  geometry. It then relaxes to the stable  $S_1$  structure with the appropriate solvation shell which will then be lower in energy. When the photon is emitted the  $S_0$  state formed now has a non-optimized solvation as it still has the  $S_1$  geometry and so is higher in energy than when it relaxes back to the  $S_0$  geometry and solvation.

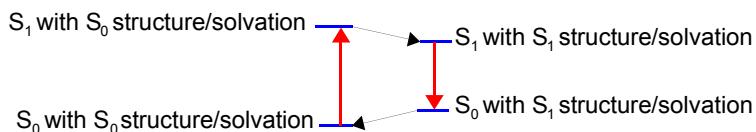


Figure 7.34: solvation effects in fluorescence spectra.

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Also solvent polarity can shift the fluorescence. In  $\pi$  to  $\pi^*$  transitions the  $S_1$  is more polar than  $S_0$ . A solvent that has stronger dipole-dipole interactions e.g. the polar solvent ethanol, will lower the energy of  $S_1$  more than for the less polar  $S_0$  state and the fluorescence will be  $\sim 10\text{-}20$  nm to longer wavelengths than when using a non-polar solvent e.g. hexane. In the  $n$  to  $\pi^*$  transitions in a carbonyl group the main solvent effect arises from hydrogen bonding the carbonyl group in the  $S_1$  state. In a hexane solution of acetone (2-propanone) the  $S_1$  state from the  $n$  to  $\pi^*$  transition is at a higher energy than when water is the solvent, so in hexane the fluorescence will shift to the blue compared to using water as the solvent. The position of the fluorescence peaks may thus be dependent upon which solvent is used which should always be quoted in your lab report.

Normally we observe emission at right angles to the exciting light to reduce the amount of scattered incident light. The light source is typically in the visible or UV with a monochromator used to select the excitation wavelength  $\lambda_{ex}$ . The emitted light is analysed with a second monochromator to select the fluorescence wavelength  $\lambda_{fl}$ . As well as the classic spectrofluorimeter of Fig. 7.35 which is used in analytical and forensic labs to identify samples ranging from oil pollution to tagged DNA and proteins, there is also the use of laser induced fluorescence, LIF, used for detailed study of the dynamics of chemical reactions particularly in the gas-phase.

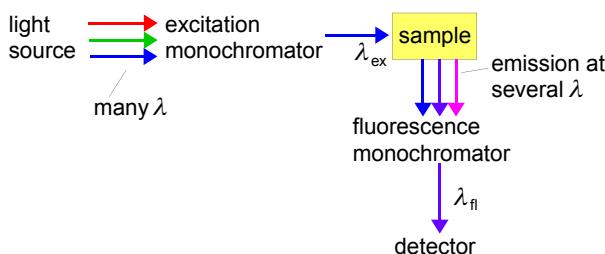
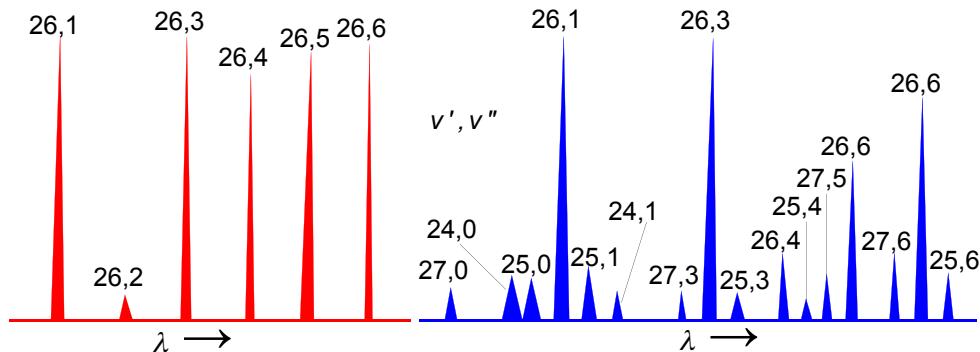


Figure 7.35: spectrofluorimeter.

By using a fixed excitation wavelength  $\lambda_{ex}$  and scanning the emitted light we obtain an *emission spectrum*. If alternatively we hold the emitted light wavelength constant and vary the excitation wavelength we obtain an *excitation spectrum*. A two-dimensional excitation-fluorescence spectrum (normally plotted as a contour diagram) can be obtained by varying both wavelengths in a controlled fashion. The effect of varying gas pressure on the fluorescence is shown below for  $I_2$  vapour. In Fig. 7.36 the experimental noise has been removed for clarity. On the left of Fig. 7.36 pure  $I_2$  vapour at 0.02 Torr total pressure shows resonance fluorescence from the  $v' = 26$  vibronic level following excitation at 546 nm from a mercury lamp (not shown). On the right, when 0.5 Torr of Ne is added there is partial collisional vibrational relaxation down to  $v' = 25$  and 24 and also a small amount of vibrational excitation to the  $v' = 27$  level.

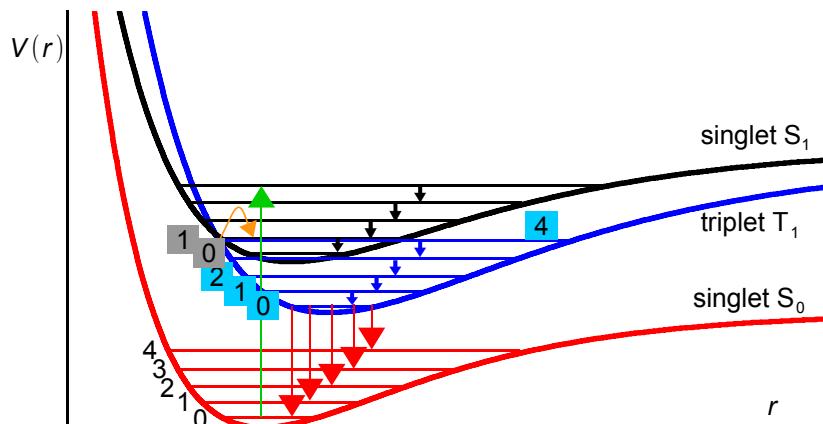


**Figure 7.36:** schematic of iodine vapour fluorescence at two pressure.

Using a laser as the excitation source has the added advantages that the light is polarized and pulsed. The excited molecules will be self-selected to those ground state molecules whose transition dipole was parallel to the excitation laser's polarization plane. The fluorescent light is polarized in the plane of the transition dipole moment of the emitting molecule. Laser induced fluorescence (LIF) is normally used to study a gas-phase and surface chemical or photochemical reaction and monitor the nascent state of the product(s) of reaction. The fluorescence will have some intensity of light both parallel and perpendicular to the laser polarization plane  $I_{\parallel}$  and  $I_{\perp}$  and the degree of polarization  $p$  carries information about the intrinsic rotational excitation of the reaction product being studied (Zare 2012).

$$p = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$$

#### 7.4.3 Phosphorescence



**Figure 7.37:** phosphorescence.

In phosphorescence, the absorption ( $S_1 < S_0$ ) and collisional vibrational relaxation stages (down to  $S_1 \nu = 1$  in the Fig. 7.37) are similar to those discussed with fluorescence. The excited singlet state  $S_1$  potential energy curve is crossed by the PE curve of an excited triplet state, e.g.  $T_1$ . At the crossing point the molecule's geometry and energy are identical in both the  $S_1$  and  $T_1$  states. There is a small probability of an *intersystem crossing* (a nonradiative change between two states of *different* multiplicity) where the excited electron spin-flips and the molecule goes from the  $S_1$  to the  $T_1$  state. In Fig. 7.37 this occurs from  $S_1 \nu = 1$  to  $T_1 \nu = 4$ . This nonradiative process is brought about by spin-orbit coupling helped by the presence of a heavy atoms, e.g. sulfur, in the molecule. For most molecules the triplet state is lower in energy than the corresponding singlet state. The  $T_1$  state relaxes down to its  $\nu = 0$  level and the molecule is then trapped as once vibrational relaxation has occurred within the triplet state the molecule cannot cross back from the  $T_1$  to the  $S_1$  singlet state as the molecule has different geometries and energies in the two states. Molecular collisions cannot remove the very large electronic energy difference between  $T_1$  and  $S_0$ . The only fate left to  $T_1$  in  $\nu = 0$  is to exist for seconds to minutes before it undergoes the low probability spin-forbidden radiative emission from  $T_1$  to  $S_0$  which is called phosphorescence. The phosphorescence is at longer wavelengths than both the absorption and the fluorescence of the molecule and occurs after the light source has been switched off for seconds-minutes. Safety signage such as exit signs are normally painted in the phosphor strontium aluminate. Ironically white phosphorous, from which the emission got its name, does not phosphoresce but instead undergoes a chemiluminescent oxidation reaction.

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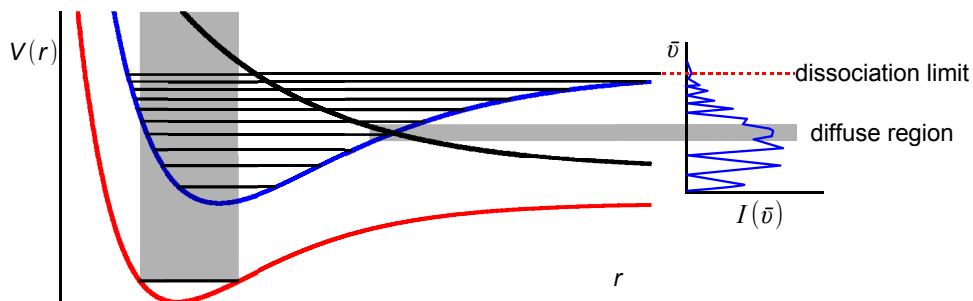
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## 7.4.4 Predissociation and Diffuse Spectra

For some molecules the absorption spectrum looks normal over most of its range with a vibrational progression leading to a continuous absorption at the dissociation limit of the excited state. But the sharp vibrational progression of the electronic spectrum may disappear and become diffuse at a certain  $v'$  level and then reappear as sharp structure again when higher energy photons are absorbed leading to higher energy  $v'$  levels. This region of diffuseness in the progression is due to the attractive excited electronic state being crossed at or near the critical  $v'$  level by a repulsive electronic state. An *internal conversion* (a nonradiative change between two states of the *same* multiplicity) occurs at the crossing point as the molecule has the same geometry and energy in both states. This will shorten the lifetime of the critical vibrational level at the crossing point because it is dissociating. From Heisenberg's uncertainty principle a shorter vibrational lifetime  $\tau_{\text{vib}}$  than the normal will increase the uncertainty of the vibrational energy  $\Delta E_{\text{vib}}$  of the  $v'$  level at the crossing point, *i.e.* there will be a broadening of the spectral structure in this region.

$$\tau_{\text{vib}} \times \Delta E_{\text{vib}} \geq \frac{\hbar}{4\pi}$$



**Figure 7.38:** predissociation and diffuse spectra.

Those transitions which are above the crossing point give a return to the sharp vibrational progression as the molecule no longer has the same geometry and energy in both  $v'$  and in the continuum of the repulsive state. We have seen the importance of time scales when looking at spectra so for convenience I am summarizing the most important ones below.

motion	timescale/s	energy/cm <sup>-1</sup>
valence electron transition	$\sim 10^{-15}$	$\sim 14,000$ to $\sim 100,000$
vibration of bond or angle	$\sim 10^{-13}$	$\sim 300$ to $\sim 4400$
rotation of a molecule	$\sim 10^{-11}$	$\sim 0.2$ to $\sim 60$
molecular collisions, gas 1 atm 25°C	$\sim 10^{-10}$	$310.83 = \frac{3}{2}RT$
fluorescence	$\sim 10^{-8}$	$\sim 14,000$ to $\sim 40,000$
phosphorescence	$\sim 1$ to $\sim 10^3$	$\sim 14,000$ to $\sim 25,000$

Remember, excited states may also lose energy and react chemically by dissociating directly from a repulsive state (section 7.2.2) or dissociating from above the dissociation limit of an attractive state (section 7.2.6). Also excited states can undergo chemical reactions that are not available to the ground state molecule, this is called photochemistry and is a book all on its own and can't be covered here.

For the second half of this book we have been using atomic orbitals and molecular orbitals. Spectroscopy is one of the main pieces of experimental evidence that MOs and quantum mechanics are real and not figments of the imagination. Are there any other experimental techniques that will allow us to "see" the orbitals? Yes there are and they use the ideas introduced by the photoelectric effect at the beginning of the quantum mechanics era (see section 1.1.2).

## 7.5 Ultraviolet Photoelectron Spectroscopy of Molecules

A fixed wavelength of light, typically 58.4 nm in the vacuum-UV (a photon energy of 21.2 eV) from a helium discharge lamp is passed through a gas sample and causes ionization of the valence electrons. The photoelectrons are energy analysed by a pair of hemispherical electrostatic plates the inner hemisphere with a positive and the outer one with a negative electric charge. The resulting spectrum of electron energies is related to the energies of the valence molecular orbitals. This is the technique called ultraviolet photoelectron spectroscopy (UPES).

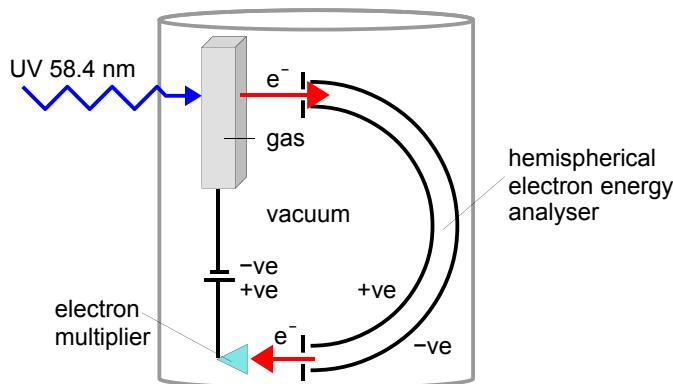
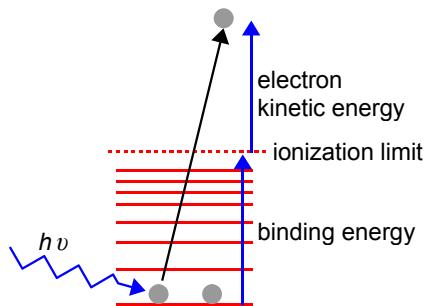


Figure 7.39: schematic UPES apparatus.

If even higher energy photons are used, *e.g.* the aluminium  $k_{\alpha}$  line at 1486.6 eV in the X-ray region (XPES), then the core 1s, 2s, 2p electrons are ionized. High intensity, pulsed, polarized photons are available using synchrotron radiation sources such as the Diamond Light Source in the UK. XPES can also be used on solids to look at the surface layer(s) and catalytic processes where the angle of the X-ray beam and angle of the ionized electrons are two other experimental variables.

The fundamental principle behind UPES is the same as discussed in the photoelectric effect of section 1.1.2.

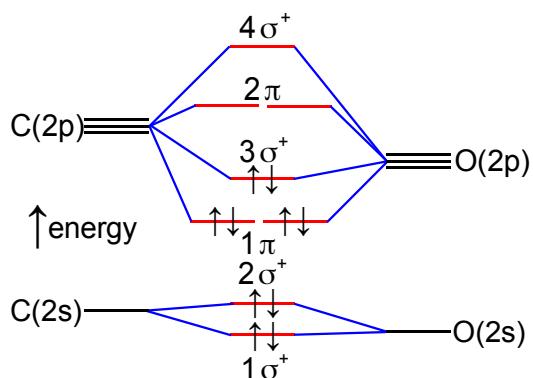


**Figure 7.40:** the principle of photoelectron spectroscopy.

$$h\nu = \text{binding energy} + \text{kinetic energy} \quad \text{binding energy} = h\nu - \text{kinetic energy}$$

Binding energy is the preferred term for an electron in a particular atomic or molecular orbital as ionization energy is reserved for the *minimum* energy required for ionization to occur, *i.e.* from the HOMO. So by using a fixed energy of photons and measuring the kinetic energy of the electrons released we measure the binding energy of the electron in a given atomic or molecular orbital.

Oxygen is more electronegative than carbon, so in carbon monoxide the molecular orbitals are asymmetric in energy terms as in Fig. 7.41 (Levine 2009, p. 691). Carbon monoxide has 10 valence electrons, 4 from C and 6 from O, with the valence shell configuration below. 21.2 eV photons have enough energy to ionize the valence electrons but not the core electrons.



**Figure 7.41:** schematic of the valence MOs for the CO ground state.

$$1\sigma^2 \ 2\sigma^2 \ 1\pi^4 \ 3\sigma^2$$

Carbon monoxide has a triple bond, one  $\sigma$ -sigma and a pair of  $\pi$ -bonds. All the electrons are paired in the CO ground state which is  $X^1\Sigma^+$  note that g/u symmetry does not exist for a molecule without a centre of symmetry of  $C_{\infty v}$  point group. One example will convince us that the molecular orbital view of bonding is not a figment of the imagination but is real, in Fig. 7.42 is the UPES for CO. The electronic transitions (ionizations) are Franck-Condon vertical ones from the  $\nu'' = 0$  of the CO molecule to the various  $\nu'$  vibronic levels of the  $CO^+$  cation and a free moving electron. The similar types of vibrational progressions which we covered in section 7.2.2–7.2.6 are also found in UPES. So we are seeing the vibrational structure of the *ion* and not the molecule, this is a similar situation to absorption spectra which gives us information about the excited electronic state.

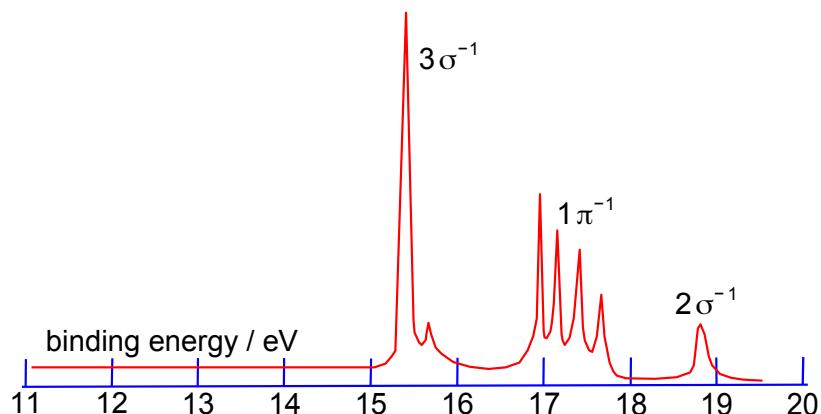


Figure 7.42: schematic UPES of CO.



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The peaks at a binding energy of 15–16 eV are for the loss of an electron from the  $3\sigma$  HOMO. The  $\text{CO}^+$  ionic state arising from this loss we label as  $3\sigma^{-1}$  and it is the  $\text{X}^2\Sigma^+$  of the  $\text{CO}^+$  cation. The  $3\sigma$  HOMO must be weakly bonding with the  $0\leftarrow 0$  transition dominant and the  $3\sigma$  energy is close to the energy of the O(2p) orbital. The short vibrational progression has a spacing of  $\sim 2200 \text{ cm}^{-1}$  which is similar to that of the neutral molecule at  $2157 \text{ cm}^{-1}$  confirming the weakly-bonding nature of the  $3\sigma$  MO, *i.e.* the geometry of the  $3\sigma^{-1}$  cation is similar to that of the neutral molecule.

The peaks at a binding energy of 17–18 eV are for the  $\text{CO}^+$  ionic state  $1\pi^{-1}$  formed by the loss of one of the four electrons from the  $1\pi$  orbital. The  $\text{CO}^+$  cation state  $1\pi^{-1}$  (the  $\text{A}^2\Pi^+$  state of the  $\text{CO}^+$  cation) has a reasonably long vibrational progression and the  $1\pi$  orbitals are strongly bonding. The electron loss gives a weaker and longer bond in the ion with a spacing of  $\sim 1549 \text{ cm}^{-1}$  which is a significantly lower wavenumber than the neutral molecule at  $2157 \text{ cm}^{-1}$ .

The peaks at a binding energy of  $\sim 19$  eV are for the  $\text{CO}^+$  ionic state  $2\sigma^{-1}$  formed by the loss of an electron from the  $2\sigma$  orbital. The  $2\sigma^{-1}$  cation state (the  $\text{B}^2\Sigma^+$  state of the  $\text{CO}^+$  cation) is weakly antibonding with the  $2\sigma$  orbital energy is close to but above the C(2p) orbital with a short vibrational progression of  $\sim 1706 \text{ cm}^{-1}$  compared with the CO molecule at  $2157 \text{ cm}^{-1}$ .

Koopman's theorem states that the binding energy of an electron in the molecule is approximately equal to the negative of the one-electron energies of the molecule's orbitals. Koopman's theorem is only approximately true because the PES spectrum measures an energy *difference* between the molecule's electronic ground state and one of the ion's specific electronic states, the state which arises from the loss of an electron from a given MO of the molecule. Nevertheless Koopman's theorem is a very useful guide to help interpret the PES spectrum, as we have seen with the CO example.

We have now come to the end of our introduction to quantum mechanics and atomic and molecular spectroscopy and are in a position to build upon this foundation in the areas of physical, organic, inorganic and analytical chemistry, biochemistry, molecular biology and physics. The current textbook is accompanied by a companion book (Parker 2015) *Chemistry: Quantum Mechanics and Spectroscopy, Tutorial Questions and Solutions*, which should be used together with the current textbook. I wish you good luck with your future studies. If you have problems with Maths, remember at any time you can get help by downloading my free workbooks *Introductory Maths for Chemists* (Parker 2013b) *Intermediate Maths for Chemists* (Parker 2012), *Advanced Maths for Chemists* (Parker 2013a) by going to my web page at <http://johnericparker.wordpress.com/> which links to the publisher's website for the actual downloads.

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# 9 List of Formulae

These are a selection of *some* of the formulae from the book.

$c = \nu \lambda$	the wave nature of light
$E = h\nu$	energy of a photon
$\bar{v} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$	the Rydberg equation
$\lambda = \frac{h}{m\nu} = \frac{h}{p}$	the de Broglie equation
$\Delta x \Delta p \geq \frac{h}{4\pi}$ or $\Delta t \Delta E \geq \frac{h}{4\pi}$	Heisenberg's uncertainty principle
$P(x) =  \psi(x) ^2$ or $P(x) = \psi^*(x)\psi(x)$	Born's interpretation of a wavefunction
$-\frac{\hbar^2}{8\pi^2 m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$	the Schrödinger equation
$\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad n = 1, 2, 3, 4, \dots$	wavefunctions for a particle in a 1-D box
$E_n = \frac{n^2 \hbar^2}{8mL^2} \quad n = 1, 2, 3, 4, \dots$	energies for a particle in a 1-D box
$E_{\text{rot}} = \frac{n^2 \hbar^2}{8\pi^2 I}$	quantized energies for a particle on a ring
$\mu_{mn} = \int_{-\infty}^{\infty} \psi_m^* \hat{\mu} \psi_n d\tau$	transition moment
$E_J = J(J+1) \frac{\hbar^2}{8\pi^2 I} \quad J$	diatomic molecule rigid-rotor energies
$\frac{n_f}{n_i} = \exp\left(-\frac{E_f - E_i}{k_B T}\right)$	Boltzmann ratio of states
$E(v) = (v + \frac{1}{2})h\nu_e \quad J \quad v = 0, 1, 2, 3, 4, \dots$	SHO energy levels
$G(v) = (v + \frac{1}{2})\bar{v}_e \quad \text{cm}^{-1} \quad v = 0, 1, 2, 3, 4, \dots$	
$V(r) = D_e \left(1 - e^{-\alpha(r-r_e)}\right)^2$	Morse potential
$E(v) = (v + \frac{1}{2})h\nu_e - (v + \frac{1}{2})^2 x_e h\nu_e \quad J$	
$G(v) = (v + \frac{1}{2})\bar{v}_e - (v + \frac{1}{2})^2 x_e \bar{v}_e \quad \text{cm}^{-1}$	AHO energy levels
$S(v, J) = BJ(J+1) + (v + \frac{1}{2})\bar{v}_e - (v + \frac{1}{2})^2 x_e \bar{v}_e \quad \text{cm}^{-1}$	vibration-rotation energy term
$J = j_1 + j_2, \quad j_1 + j_2 - 1, \quad j_1 + j_2 - 2, \quad j_1 + j_2 - 3, \quad \dots, \quad  j_1 - j_2 $	Clebsch-Gordon series

$$h\nu_i + E_i = h\nu_f + E_f \quad \Delta E = E_f - E_i = h(\nu_i - \nu_f) = h\Delta\nu \text{ Raman shift} = \Delta\nu$$

$$S=s_1+s_2, \quad s_1+s_2-1, \quad s_1+s_2-2, \quad s_1+s_2-3, \quad \dots, \quad |s_1-s_2|$$

$$L=l_1+l_2, \quad l_1+l_2-1, \quad l_1+l_2-2, \quad l_1+l_2-3, \quad \dots, \quad |l_1-l_2| \quad \text{RS coupling}$$

$$J=S+L, \quad S+L-1, \quad S+L-2, \quad S+L-3, \quad \dots, \quad |S-L|$$

(1)  $\Delta n = \text{anything}$

(2)  $\Delta(2S+1) = 0$

(3)  $\Delta L = 0, \pm 1$  with active electron  $\Delta l = \pm 1$

(4)  $\Delta J = 0, \pm 1$  but  $J = 0 \leftarrow \rightarrow J = 0$

Russell-Saunders selection rules

$$2S+1 A_{g/u}^{\pm}$$

diatomic or linear molecule term symbol

$$S_{fi} = \int \psi_f^* \psi_i d\tau$$

Franck-Condon factor or overlap integral

$$\bar{v}_{p,R} = \bar{v}_{(v',v'')} + (B'+B'')m + (B'-B'')m^2 \text{ cm}^{-1} \quad \text{where } m = \pm 1, \pm 2, \pm 3, \dots$$

$$\log_{10} \frac{I_0}{I} = A = \epsilon cl$$

Beer-Lambert Law

$$p = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$$

degree of polarization

binding energy =  $h\nu - \text{kinetic energy}$

photoelectron spectroscopy

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