The interaction of photons with matter
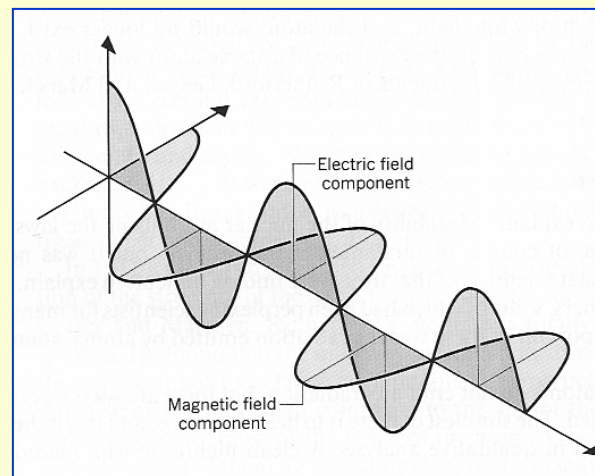
1. The electromagnetic spectrum – all electromagnetic waves share a common set of properties

    a) dual wave-like and particle-like behavior

    b) travel at the speed of light

    c) energy determined by frequency

    d) orientation of electrical and magnetic field

    e) phase – the waves vary with time.

2. Transitions of electrons in atoms and molecules are responsible for their chemical, electrical and magnetic behavior. All transitions involve exchanges of photons.

    a) In the ground state, the electrons occupy orbitals that represent the lowest energy level as determined by the Schrödinger equation, and the four quantum numbers, n, l, m_l and m_s, as we discussed in the previous lecture.

    b) Transitions can occur from the ground state to higher energy orbits through direct excitation, or within an energy level, by vibrational interaction, or through the effects of electrical and magnetic fields, etc.

    c) All transitions are quantized, and have a characteristic frequency, and hence energy, and all are therefore perturbed by photons of appropriate energy.

Electromagnetic Spectrum

Electronic Transitions   Molecular Vibrations   Molecular Rotations   ESR, NMR

UV	VIS	near IR	mid IR	far IR	Microwave		Radio

	UV	VIS	near IR	mid IR	far IR	Microwave		Radio
λ(nm)	400	700						
λ(cm)		10^{-4}	10^{-3}	10^{-2}	0.1	1	10	
λ(m)		10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	
$\widetilde{\nu}$(cm^{-1})	10,000		1,000	100	10	1	0.1	
ν(Hz)	3×10^{14}		3×10^{13}	3×10^{12}	3×10^{11}	3×10^{10}	3×10^{9}	
ΔE (kcal/mol)	~30		3	0.3	0.03	0.003	0.0003	
ΔE (eV)	1.3 V		130 mV	13 mV	1.3 mV	130 μV	13 μV	

$$N_{excited} / N_{ground} = e^{\Delta E / RT}$$

RT=0.593 kcal/mol at 298°K

RT=0.002 kcal/mol at 10°K

On the nature of electromagnetic waves, and the transitions that absorb or generate them

All that we know about electromagnetic waves comes from their interactions with matter. We **measure them by looking at the transitions they generate** in atoms, molecules, and other antennae. They are **generated by transitions that decay** by emitting a photon. They are called electromagnetic, not because they are either electrical or magnetic entities, but because they generate or are generated by electrical transitions, which have a linked magnetic component.

The energy of photons is expressed in terms of eV, J mol^{-1}, or of frequency, wavenumber, or wavelength, all of which are related to energy through the Planck constant. All photons move at the speed of light (~1ft/ns), - this relates frequency to wavelength.

The frequency is related to the timescale of the transition associated with absorption or generation of the photon.

Energy of transition

$$E = h\nu = hc/\lambda$$

$$\nu = E/h$$

ν - frequency (Hz)

$\widetilde{\nu}$ - wavenumber (cm^{-1})

λ - wavelength (nm)

$$\widetilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$$

Photons have a "memory" based on the transition that generated them. They "remember":
1. The energy of the transition that generated them, and hence frequency.
2. The orientation of the transition, - and hence polarity.
3. The phase of the transition, - the point in time at which they were generated.

The interactions of photons with atoms and molecules depend on the fact that photons are looking for a "home", - a transition that matches that which generated them. However, photons are just packets of energy. They are not particular about the transition, but rather promiscuous in a very selective way. Any transition will be "home" if it matches: (1) the energy (frequency); (2) the orientation (polarity); and (3) the phase of the photon.
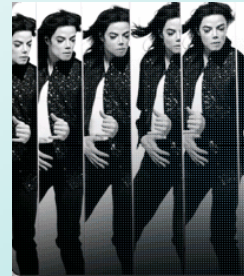
Excited state

e⁻

E

Ground state

λ
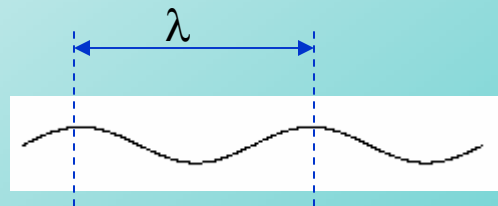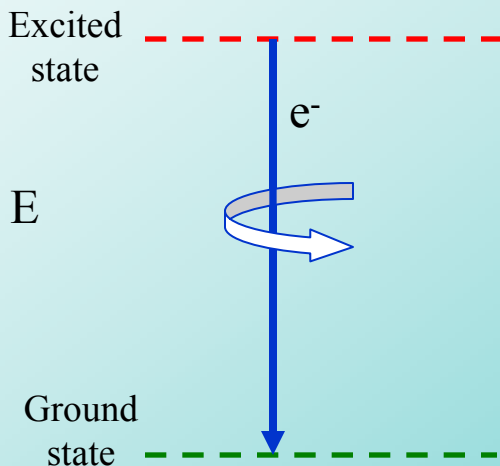
$E = h\nu = hc/\lambda$

Matching of phase, frequency and orientation

z

wrong phase

wrong frequency

wrong phase

wrong frequency

wrong polarity

x

Madonna is looking for Mr. Right

y

right phase

right frequency

wrong polarity

Mr. Right

Absorption of light by molecules

Transitions within molecules

Examples:

absorbance measurements

molecular spectroscopy

fluorescence

Determined by absorption of photons with energy equivalent to the energy difference between transition states. Transitions have a small energy range, so bands are narrow and specific.

Treated using quantum mechanical view point, because energy levels are well defined

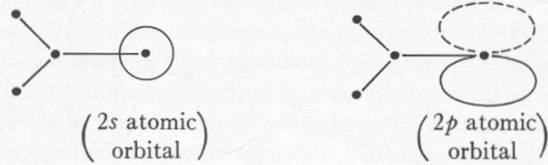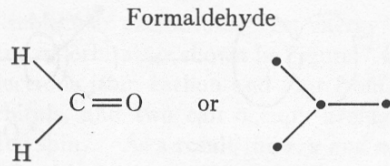## Transitions due to interactions between many molecules

Examples:

refraction

optical rotation

Determined by transitions arising from induced dipoles coming from interactions between neighboring molecules. Statistically random in energy, and amplitude depends on polarity.

Treated using classical view point because energy levels are considered as a property of the "medium".

Molecular orbitals, energy levels, and transitional energy levels

Formaldehyde

H
 \
  C=O   or
 /
H

(2s atomic orbital)   (2p atomic orbital)

n Orbitals

C + O → σ Orbital

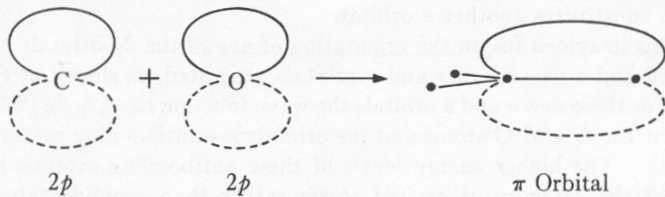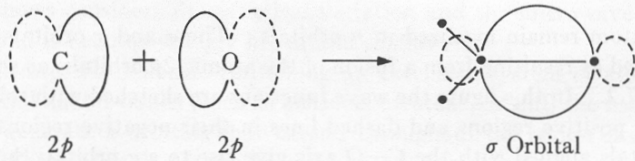2p   2p

C + O → π Orbital

2p   2p

FIGURE 7.2. *Molecular electron orbitals in formaldehyde. The profiles of the wave functions (Ψ) are sketched crudely around the atoms involved in the orbitals. Positive and negative regions are indicated by solid and dashed curves; the sign is arbitrary. In the sketch of a π orbital the molecular plane is perpendicular to the paper.*
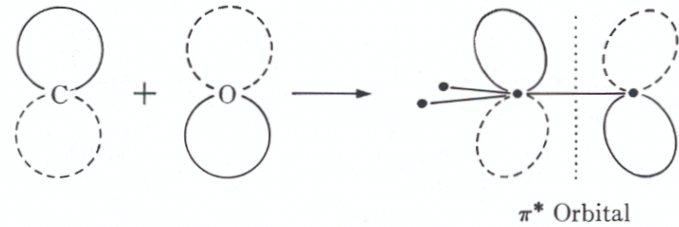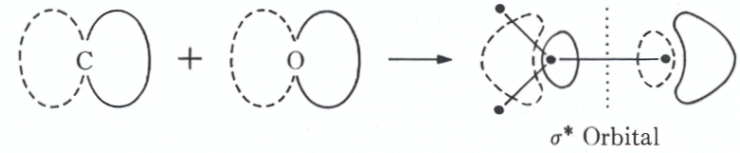

C + O → σ* Orbital

C + O → π* Orbital

FIGURE 7.3. *Antibonding orbitals representing excited states in formaldehyde. Wave functions are sketched as in Figure 7.2. The dotted lines show the presence of nodes (Ψ = 0) between the C and O atoms.*
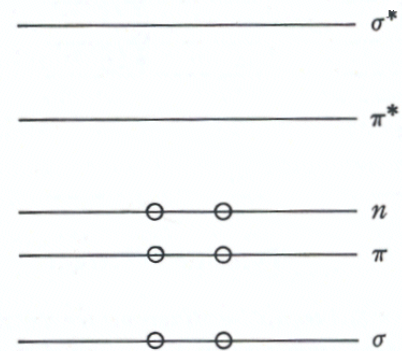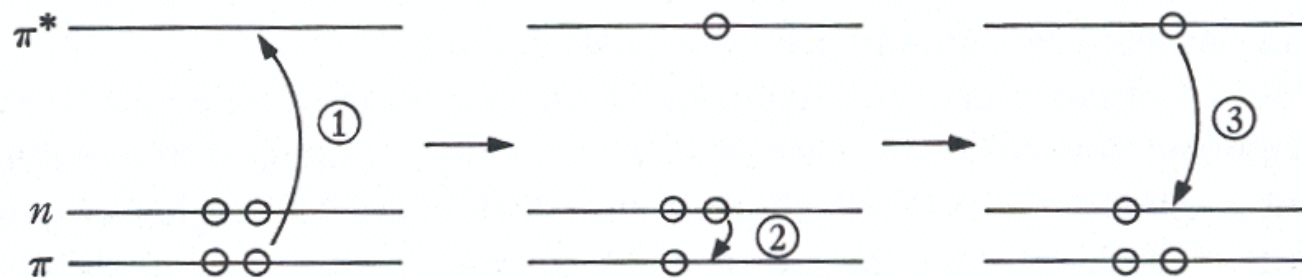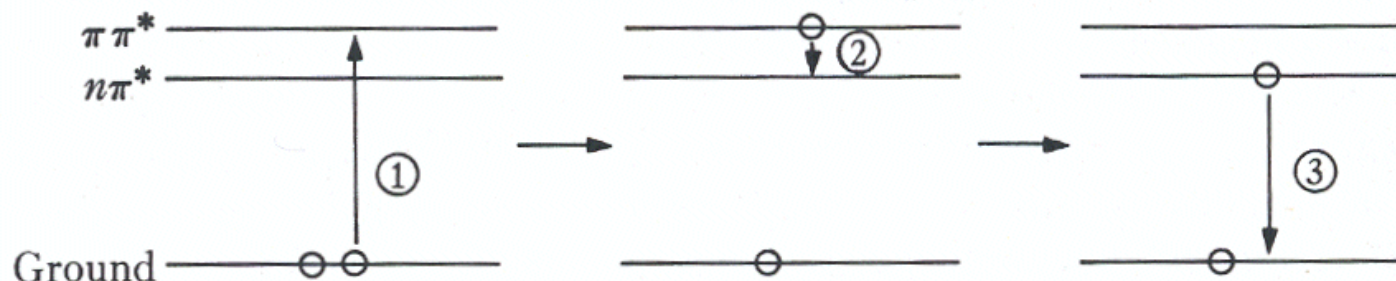

σ*

π*

n

π

σ

FIGURE 7.4. *Energy levels of the orbitals shown in Figures 7.2 and 7.3. The three lowest states are occupied, each orbital having two electrons with opposite spins.*

FIGURE 7.5. *Energy level and transition diagrams for a molecule such as formalde-hyde. Three events are represented: promotion of an electron from the π to the π* orbital, transfer of an electron from the n to the π orbital, and a transition of the π* electron to the n orbital. In terms of molecular states these events are ππ* excitation, ππ* → nπ* interconversion, and de-excitation from nπ* to ground.*

Table 17.2 *Typical vibrational wavenumbers*

Vibration type	$\tilde{v}/cm^{-1}$
C—H stretch	2850–2960
C—H bend	1340–1465
C—C stretch, bend	700–1250
C=C stretch	1620–1680
C≡C stretch	2100–2260
O—H stretch	3590–3650
C=O stretch	1640–1780
C≡N stretch	2215–2275
N—H stretch	3200–3500
Hydrogen bonds	3200–3570

$$E_{Vib.} = \text{const.} \times (v + \tfrac{1}{2})$$
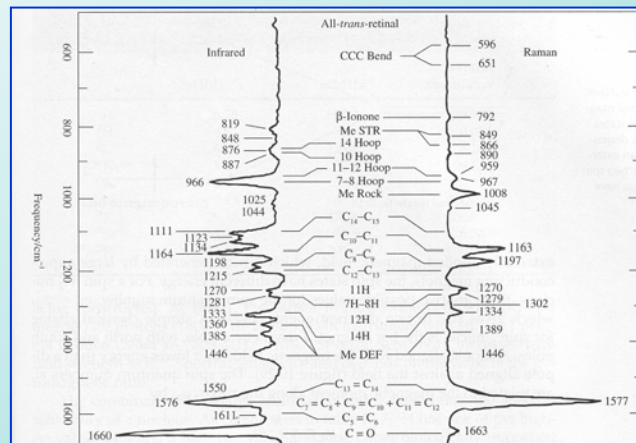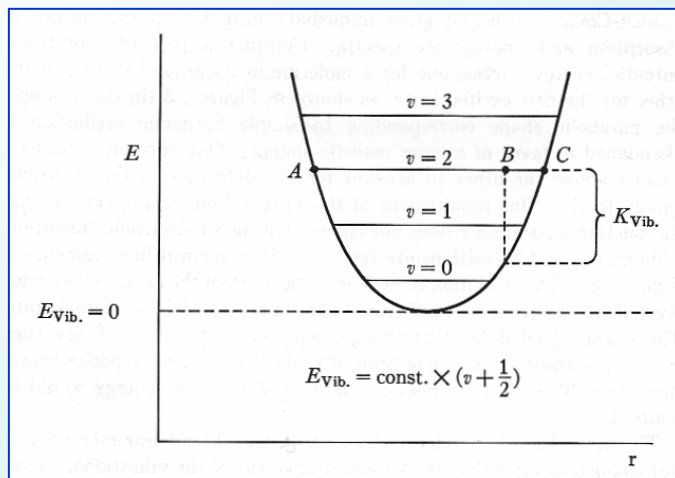
▲ FIGURE 10.28

Vibrational modes

Over the small range about the mean bond distance, the changes in energy with bond length can be represented by a parabola. However, the bonds vibrate and change energy levels. These changes are quantized, as shown by the horizontal lines, at energy values given by $E_{vib} = \text{const.} \times (v + \tfrac{1}{2})$, where the vibrational quantum number v can be 0, 1, 2 . . . etc. The energy values for these transitions are in the IR.

For a molecule in the any vibrational level (for example, $v = 2$), the vibrational energy is, in classical terms, all potential energy (the nuclei are at rest), for values of r corresponding to points A and C on the parabola. At point B, the energy is part kinetic, as shown by K_{vib}.

A single point in the diagram specifies three things, the energy of the molecule, the internuclear distance, r, and the momenta of the nuclei as implied by the kinetic energy of vibration.

Electronic transitions are much faster, $\sim 10^{15}$ s^{-1}, than nuclear vibrations (10^{13} s^{-1}). As a consequence, electronic transitions represent vertical displacement in diagrams like the last one, - the nuclear position (as indicated on the r scale) does not change appreciably while the electron moves. This is the Franck-Condon principle. In the diagram on the right, electronic transitions are shown between the ground and excited states of a simple diatomic molecule, but similar diagrams could be drawn to represent transitions in more complicated molecules like chlorophylls.

The other consequence of the Franck-Condon principle is that the kinetic energy of the nuclei does not change during the electronic transition. This usually necessitates transitions between points where the vibrational energy levels meet the parabola (A, A'; B, B'; D, D'), when the nuclei are at rest. Transitions like C, C' can only occur if the nuclei have the same kinetic energy, indicated by the hatched lines.
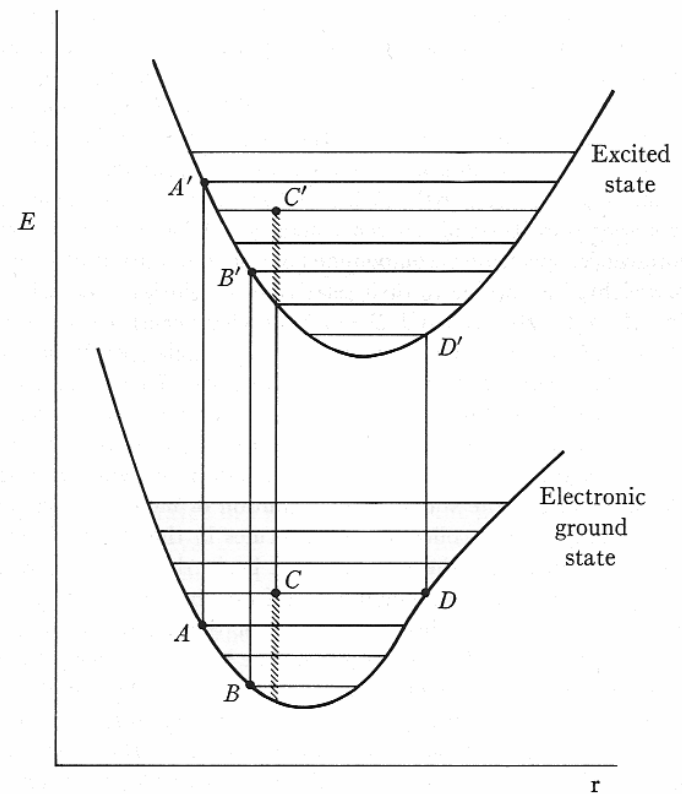
FIGURE 7.8. *Energy diagram for a diatomic molecule in its ground state and in an electronic excited state. Transitions compatible with the Franck-Condon principle (see text) are shown by the vertical lines.*

A consequence of the Franck-Condon principle is that all transitions are quantized.

If an excitation populates a higher vibrational level, the molecule can relax within the excited state to lower vibrational levels by emission of IR quanta.

Fluorescence
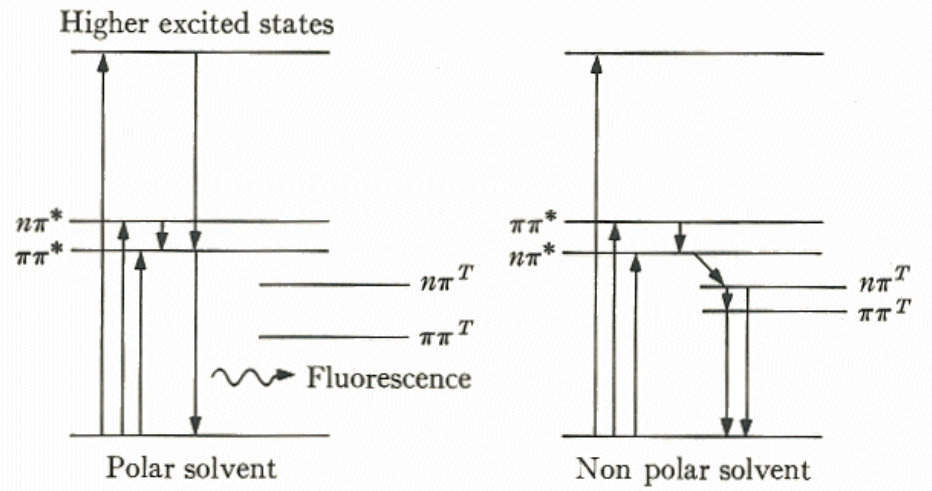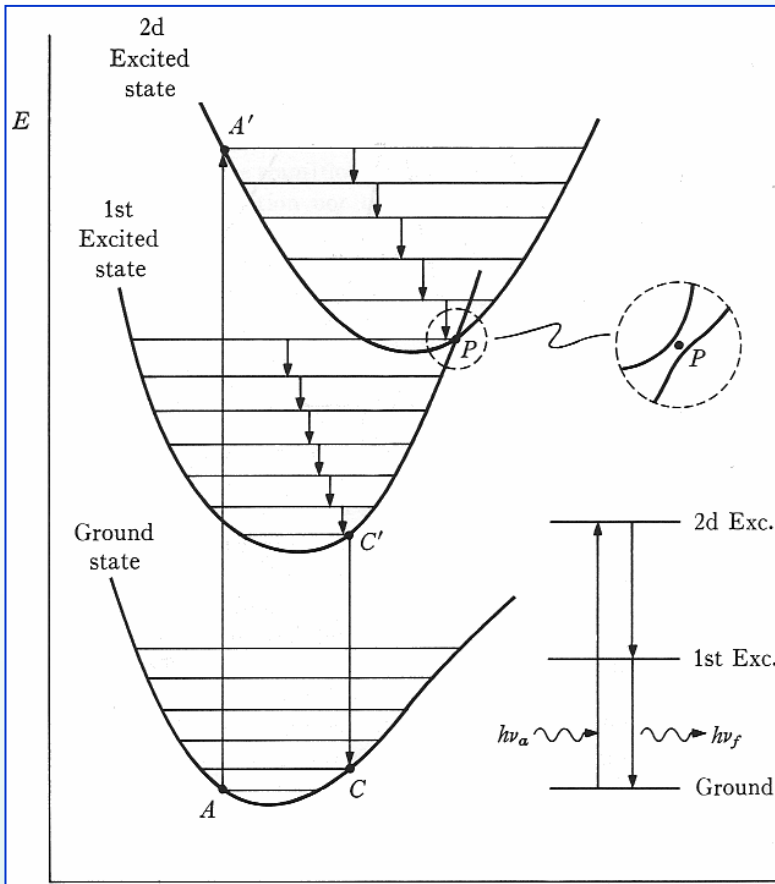
FIGURE 8.2. *Hypothetical levels of excited states, and transitions corresponding to these states, for Chl dissolved in polar and nonpolar solvents. Less probable transitions are omitted.*

Where energy gaps are large, the downward transition is less probable, or "forbidden". The life-time of the excited state is prolonged, and the energy is released in a single quantum of fluorescence. Because some energy can be lost rapidly through vibrational relaxation in the excited state, fluorescence is always shifted to the red.

FIGURE 7.9. *Absorption and fluorescence spectra for a molecular electronic transition, as dictated by the Franck-Condon principle.*

Stimulated emission

Photons are promiscuous, - they will take advantage of any transition that matches their energy. A "down" transition has the same energy gap as an "up" transition, so a photon can be adsorbed, and promote a transition, in either direction.
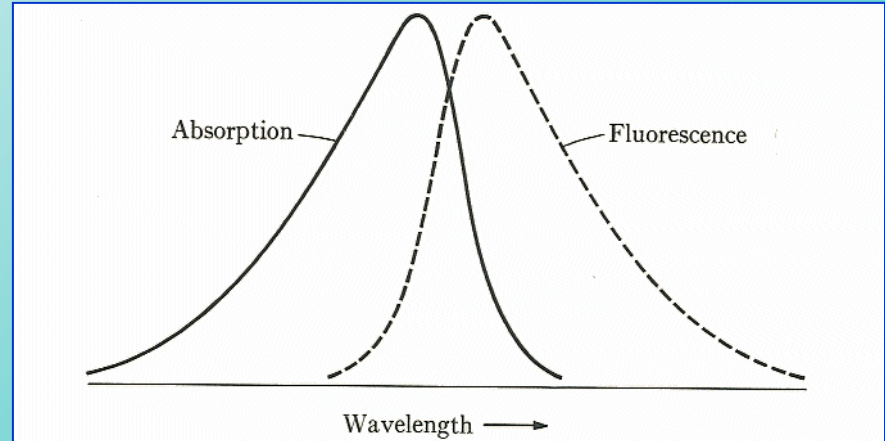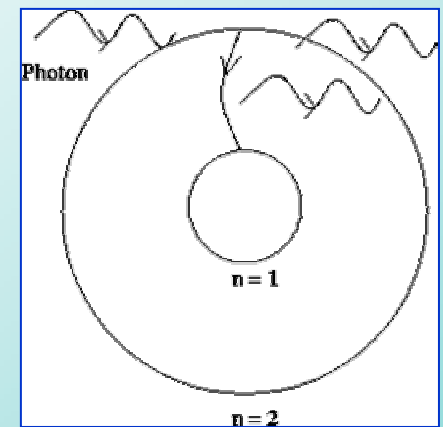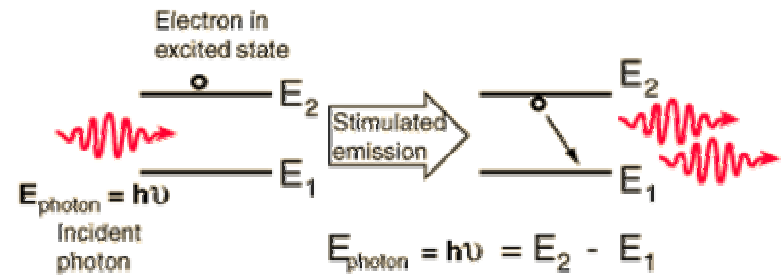

The laws of energy conservation require that the energy absorbed must be given up, together with the energy of the transition. As a consequence, two photons are emitted, of equal energy to the one absorbed, to give one emitted net.

Stimulated emission is of importance only when the excited state is well populated. For transitions with $\Delta E \gg kT$, this only occurs on excitation at high intensity; - as in the laser.

For transitions with $\Delta E \ll kT$, as in EPR and NMR applications (see later), the populations of states are nearly equal. These transitions involve flipping magnetic spins. If our two spins are in almost equal populations, all the ↑ spins will absorb one photon, and all the ↓ spins will emit one photon. We therefore do not see these changes in population. Absorption is by the very small fraction representing the *difference* in these populations. We will consider *saturation effects* later.

Electrons and nuclei have magnetic properties **only** because they carry charges and move. The magnetic force generated by a moving charge is proportional to the current. In the case of a spinning entity, this translates into how fast it spins. For an electron, with a charge of -1, this is easy to see. What about the nucleus?

Why do different isotopes have different nuclear magnetic properties?
Since the nuclear charge is dependent on atomic number (the number of protons), and different isotopes have the same atomic number (otherwise they are different elements), they must all carry the same charge. Since there's no change in charge on adding neutrons, why is there a change in magnetic properties?

If a nucleus has an even number of protons and an even number of neutrons, all the spins compensate, and the nucleus has no net spin. The nuclear magnetism **arises from the spin** introduced by an extra neutron, which gives a net angular momentum.

The rate of spinning is dependent on angular momentum and therefore on mass. For any particular mass, a given increment in spin on adding a neutron will start the whole nucleus spinning at a rate dependent on the combined mass.

The magnetic difference between isotopes therefore depends in a complicated way on the mass of the nucleus (the atomic weight), the number of charges it carries (the atomic number), and how many unpaired nucleons are present.

Some nuclear magnets of importance in biological studies

Gyromagnetic Ratios, NMR Frequencies (in a 4.7-T Field), and Natural Abundances of Isotopes

Isotope	I	$\gamma/10^7$ T$^{-1}\cdot$s^{-1}	ν/MHz	Natural Abundance (%)
^{1}H	$\frac{1}{2}$	26.75	200	99.985
^{2}H	1	4.11	30.7	0.015
^{13}C	$\frac{1}{2}$	6.73	50.3	1.108
^{14}N	1	1.93	14.5	99.63
^{15}N	$\frac{1}{2}$	2.71	20.3	0.37
^{17}O	$\frac{5}{2}$	3.63	27.2	0.037
^{19}F	$\frac{1}{2}$	25.17	188.3	100
^{31}P	$\frac{1}{2}$	10.83	81.1	100
^{33}S	$\frac{3}{2}$	2.05	15.3	0.76

As we shall see later, the gyromagnetic ratio (γ) determines the energy at which electromagnetic radiation will flip the spin of a nuclear magnet. A flip occurs when the energy matches (or is in **resonance** with) the energy of the transition. The energy needed (expressed in terms of frequency) depends on the applied magnetic field (the strength of the magnet), - 4.7 Tesla in this case.

What is the difference between the electron and the nucleus as magnets?

1. The spin quantum numbers for the electron, proton and neutron, all have the same value of ½. This is an *intrinsic* angular momentum, - every electron, proton and neutron has this property.

2. Because of the relation between angular momentum and mass, a spin ½ body has a frequency of rotation determined by the mass. Because nuclear particles (nucleons) have masses 1,836 × that of the electron, the nucleus spins much more slowly.

3. Because the magnetic field depends on the rate of rotation, electrons have magnetic fields ~2,000 × that of protons, which have higher fields than more massive nuclei. Hence magnetic resonance occurs at much higher energies for EPR than NMR.
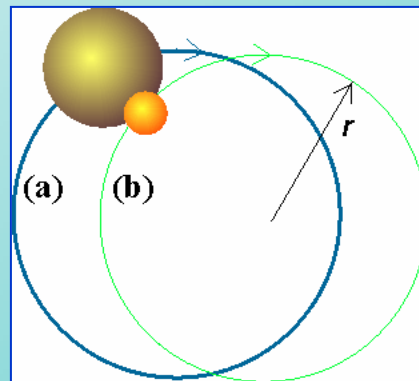
Spin coupling

In addition to the angular momentum and magnetic properties arising from its spin, an electron in a molecular orbital has an orbital angular momentum, which also generates a magnetic field. The interaction between these two magnetic fields is called spin-orbit coupling. The antiparallel arrangement (bottom, right) has the lower energy, and is therefore favored. The electron magnetic field depends on the total angular momentum, J. In general, both electrons and nucleons spin-couple with other magnets in their environment. This coupling to neighboring spins can be measured in pulsed EPR and NMR applications which look at the kinetics of decay of spin states populated by a pulse of excitation. Analysis of the results provides structural information, - distance and types of atoms close enough to couple.
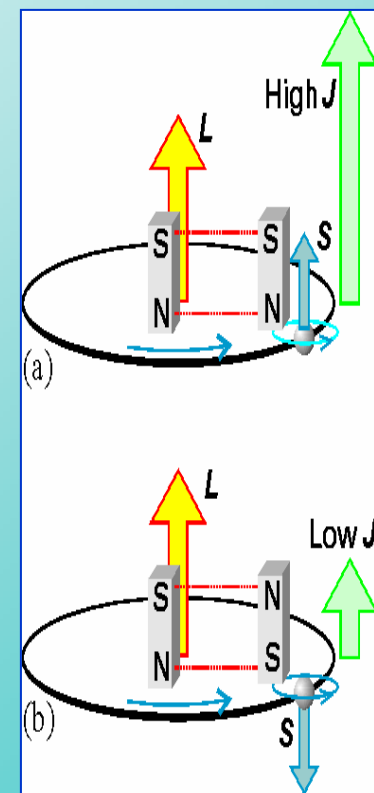
Electric Transitions | Molecular Vibrations | Molecular Rotations ESR, NMR

	UV	VIS	near IR	mid IR	far IR	Microwave	Radio
λ(m)			10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}
λ(cm)			10^{-4}	10^{-3}	10^{-2}	10^{-1}	1	10
$\bar{\nu}$(cm^{-1})			10,000	1,000	100	10	1	0.1
ν(Hz)			3×10^{14}	3×10^{13}	3×10^{12}	3×10^{11}	3×10^{10}	3×10^{9}
ΔE (kcal/mol)			~30	3	0.3	0.03	0.003	0.0003

NMR ~10-200 MHz @ 4.7 T

EPR ~9.5GHz @ 0.34 T

RT=0.002 kcal/mol at 10°K

Energy of transition

$$\nu = E/h$$

$$(E = h\nu)$$

RT=0.593 kcal/mol at 298°K

ν - frequency Hz

$\tilde{\nu}$ - wavenumber cm^{-1}

λ- wavelength nm

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$$

Energy (ν)

$m_I = -\tfrac{1}{2}$

$m_I = \pm\tfrac{1}{2}$

$$\Delta E = h\nu = \frac{\gamma B_0 h}{2\pi}$$

$m_I = +\tfrac{1}{2}$

0

magnetic field strength (B_0)

Energy (ν)

$m_s = -\tfrac{1}{2}$

$m_s = \pm\tfrac{1}{2}$

$$\Delta E = h\nu = g\beta B_0$$

$m_s = +\tfrac{1}{2}$

0

magnetic field strength (B_0)
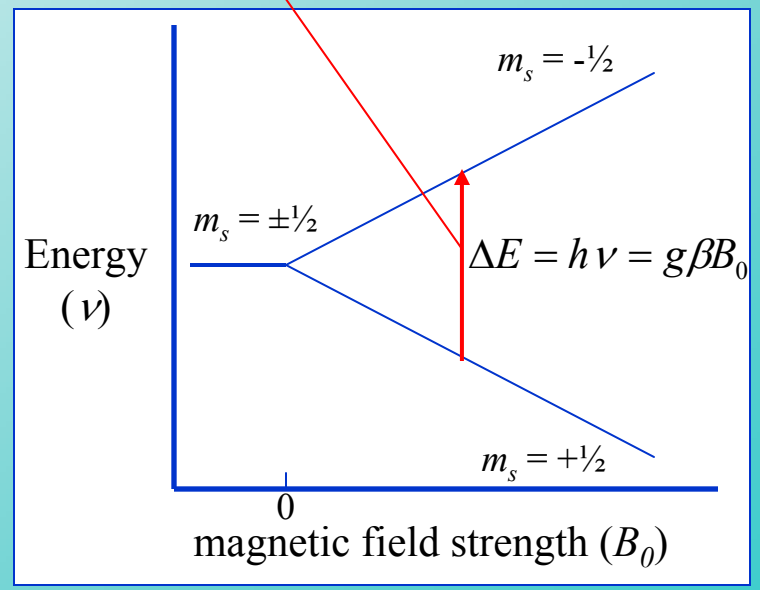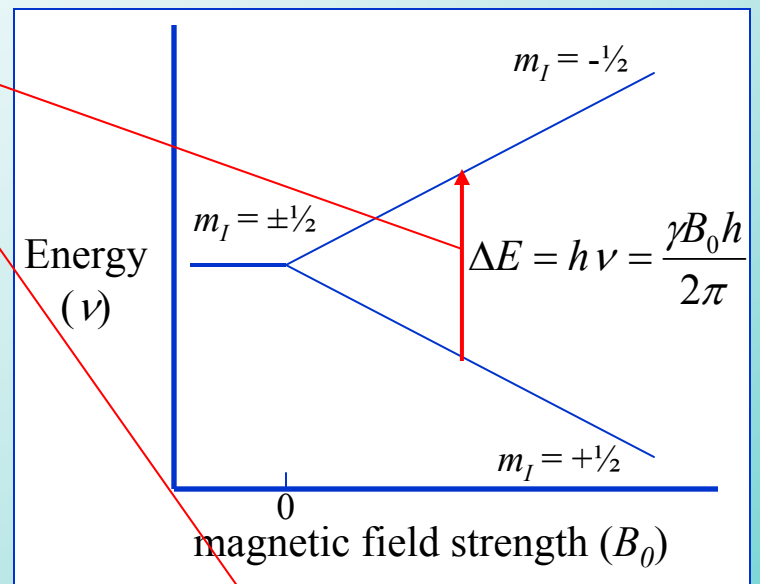
Magnetic Resonance Spectroscopy

Electron Paramagnetic Resonance (EPR) spectroscopy

1. Electrons have "spin", - rotation of the charge about its axis generates a magnetic field at each electron.

2. Electrons in orbitals with two electrons are spin-paired, - one with m_s +½ (↑, α), one with m_s -½ (↓, β), - so that the spins and magnetic fields cancel (↑↓).

3. Most molecular bonds are formed by coalescence of atomic orbitals so as to satisfy the lower energy state arising from spin-pairing. Most molecules therefore have all orbitals occupied by magnetically "silent" electron pairs.

4. If an electron is added to or subtracted from such a molecule (by reduction or oxidation) an unpaired electron is introduced which is not spin coupled, and therefore acts as a magnet. Such molecules are said to be **paramagnetic.**

5. Some bonds have unpaired electrons, giving them an inherent **paramagnetic** property.

6. In EPR spectroscopy, we take advantage of this paramagnetic property to measure properties of the the paramagnetic center, and its interaction with other local magnets. These interactions provide information about local structure, including local environment, distances, angles, polarity, etc.
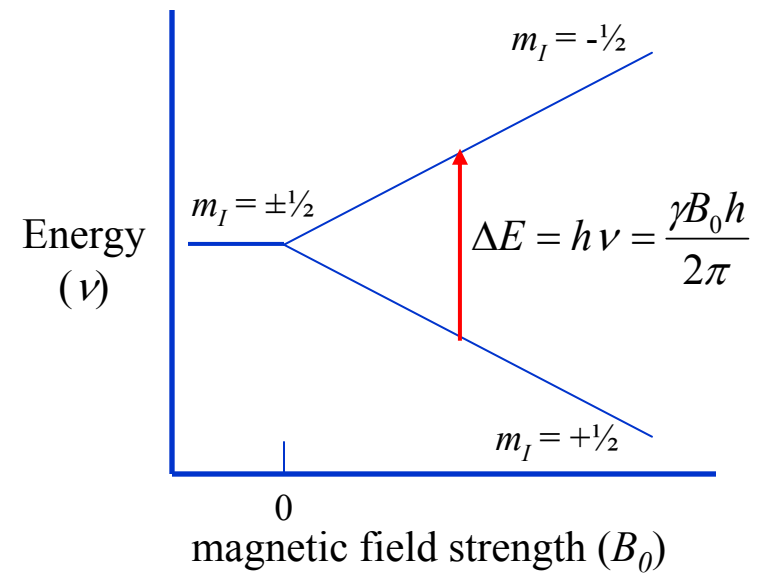
Nuclear Magnetic Resonance (NMR) spectroscopy

1. The atomic nucleus is made up of protons (+-ve charge) and neutrons (neutral).

2. Like electrons, protons and neutrons (or nucleons) are quantum mechanical entities, and their energetic properties can be described by operators, wave functions, and quantum numbers.

3. Both protons and neutrons have a spin ½, with spin quantum number, m_I, which can have values of ↑ (up, +½, or α), or ↓ (down, -½, or β).

4. Total nuclear energy levels are lower if the constituent protons and neutrons are spin-paired, so that for most nuclei, the spins (and magnetic fields) cancel. Protons are spin-paired with protons, neutrons with neutrons.

5. Isotopes that have an odd number of either protons or neutrons have a net spin, according to the Table below:

Number of protons	Number of neutrons	Nuclear spin, (I)
Even	Even	0
Even	Odd	$1/2$ or $3/2$ or $5/2$ …
Odd	Even	$1/2$ or $3/2$ or $5/2$ …
Odd	Odd	1 or 2 or 3 …

Nuclear Magnetic Resonance

In the absence of an external magnetic field, the spins of the nuclei are arranged more or less at random. When a magnetic field is applied, the spins align with the field, just like bar magnets. However, because the energy involved is so small, they can flip direction relatively easily.

Energy (ν)

$m_I = -\frac{1}{2}$

$m_I = \pm\frac{1}{2}$

$\Delta E = h\nu = \dfrac{\gamma B_0 h}{2\pi}$

$m_I = +\frac{1}{2}$

0

magnetic field strength (B_0)

The consequence is that the energy level of the nucleus splits in a magnetic field, as shown on the right. The population of spins in the m_I +½ (α) state is (very slightly) higher than in the mI -½ (β) state, because the energy is lower.

B_o
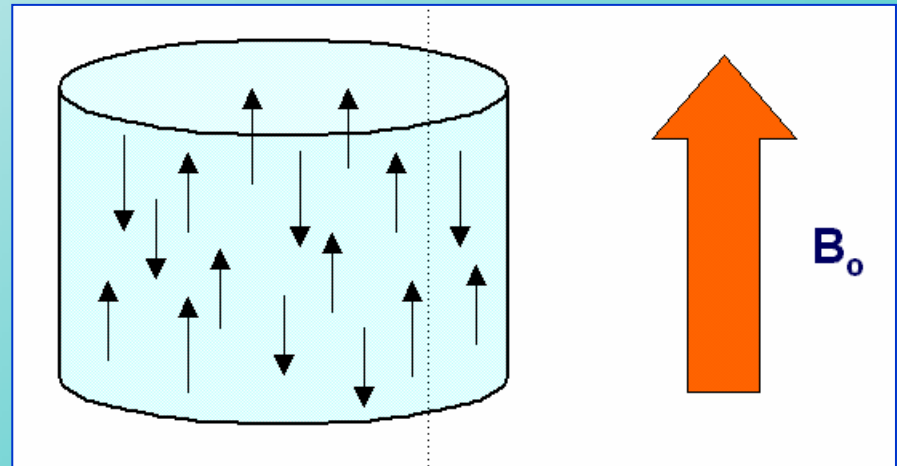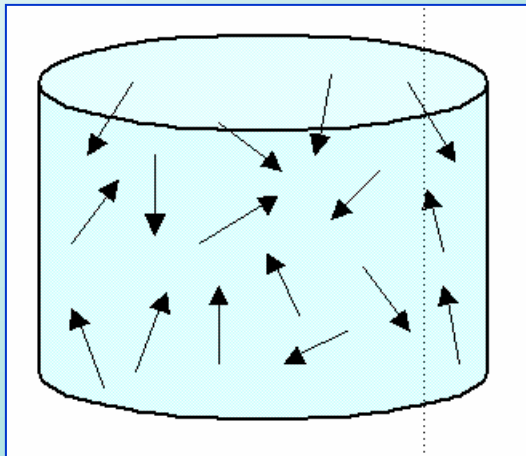
When photons of the "right" energy are absorbed, the spin of the nucleus flips between the two states. If we look at the diagram, we can see that the energy gap between the two states is dependent on the strength of the applied magnetic field. As a consequence, photons are absorbed which have a particular energy at a particular field. This is what is meant by **resonance**.

$$\Delta E = h\nu = \frac{\gamma B_0 h}{2\pi}$$

Here, γ is the gyromagnetic ratio for the nucleus, B_0 is the magnetic field strength, and h is Planck's constant.

When we come to discuss pulsed NMR, we will need to refer to circular motion. Here the preferred frame of reference is that of the circular motion of precession. We define the *precession* or *Larmor* frequency:

$$\omega = 2\pi\upsilon$$

or by substitution in the above,

$$\omega_0 = \gamma B_0$$

Some consequences of the energy scale.

The transitions leading to NMR absorption have energies in the radio frequency range, depending on nucleus (γ) and the strength of the magnetic field generated by the magnet.

NMR machines are rated by the frequency at which the proton is in NMR resonance for the magnet they are built around, so we have 200 MHz, 500 MHz, 750 MHz and even 1 GHz NMR spectrometers. To achieve the higher fields, high electrical currents are needed, which can be achieved using superconducting coils, - these are generally called superconducting magnets (costing $M).

Since $\omega = 2\pi\nu = \gamma B_0$, for a 200 MHz machine we need a magnet generating 4.7 Tesla; for a 500 MHz machine we need 11.74 Tesla, etc.

As we increase the energy gap (increase frequency), the small differences of energy for transitions of nuclear magnets in different environments are also increased, and our NMR spectrum will be better resolved. In addition, we also increase the population difference for the two spin states as we increase the energy ($\Delta E/RT$ is increased), as discussed in the next slide.

These factors make a big difference in the amount of time needed to generate a data set, - for example in solution of the structure of a protein.

As we have seen, the energy of electromagnetic waves is generally expressed in frequency, but energy scales are all related through Planck's constant and the speed of light, so we can express these energies in J/mol, eV, or any other energy units.

For a particular temperature, any transition can be described in terms of an equilibrium between two states. For example, when we flip the energy level of a proton in a magnetic field, we have two states, $\uparrow$ or α, and $\downarrow$ or β, separated by ΔE, calculated as above. Let us use N_α and N_β to represent the relative populations in the two states. We can represent the equilibration between these two states by $N_\alpha \leftrightarrows N_\beta$. Then the ratio of these populations is given by the Boltzman distribution:

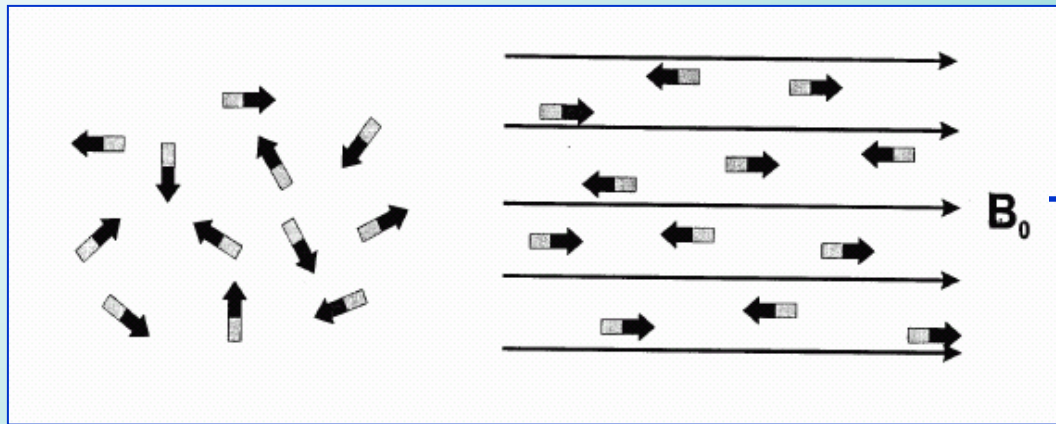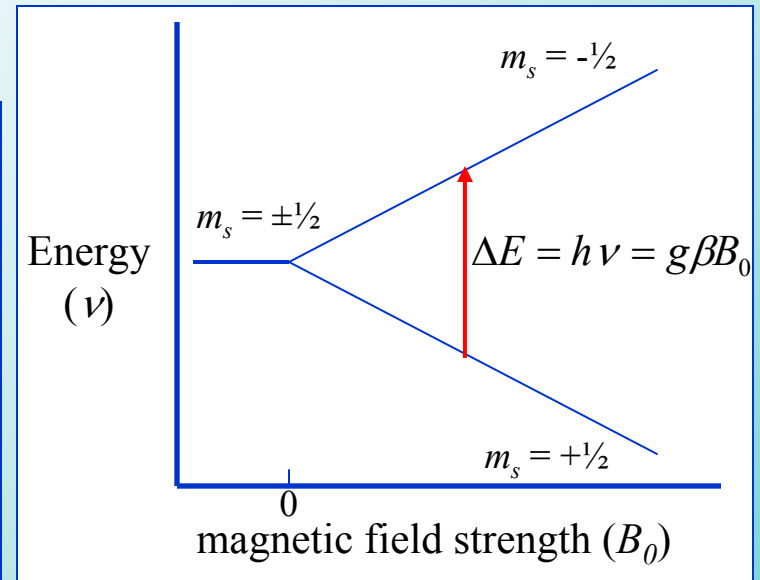$$N_\alpha / N_\beta = e^{\Delta E / RT}$$

Remembering that the energies of the transitions associated with NMR (and those of EPR) are both very much less than RT, we can see that only a **very small** excess of states will be in the lower energy level. For the proton at 500 MHz, at ~25°C, since $E = h\nu$, and Planck and Avagadro constants are $6.626.10^{-34}$ J.s and $6.02.10^{23}$ mol^{-1} respectively, energies in the RF range (~500 MHz) are 0.2 J/mol.

$$N_\alpha / N_\beta = 1.00008$$

It is these one in ten thousand spins that are available to absorb a photon to provide an NMR signal.

Electron Paramagnetic Resonance

The same general considerations apply to EPR. The photon energy for resonance depends on the applied field. The field aligns the spins, to give a splitting of the electron energy levels, with a population in the $m_s +\frac{1}{2}$ state that is greater than that in the $m_s -\frac{1}{2}$ state. Absorption of a photon at the resonance energy flips the spins. The net absorbance is due to transitions from $m_s +\frac{1}{2}$ to $m_s -\frac{1}{2}$ levels.

$m_s = -\frac{1}{2}$

$m_s = \pm\frac{1}{2}$

Energy (ν)

$\Delta E = h\nu = g\beta B_0$

$m_s = +\frac{1}{2}$

0

magnetic field strength (B_0)

B_0

No field

External field applied

Absorption of microwaves changes the energy level so that the small fraction of spins in the lower energy state are flipped into the opposite orientation. **Saturation** occurs when flips in both directions occur with equal probability. The power needed to saturate depends on the relaxation time of the spin transition.

The general principles of EPR and NMR are essentially the same, but with the differences in energies already discussed.

However, the nomenclature is different, mainly for historical reasons. The resonance condition for EPR is described by the equations:

$$E = g\beta B_0 m_s$$

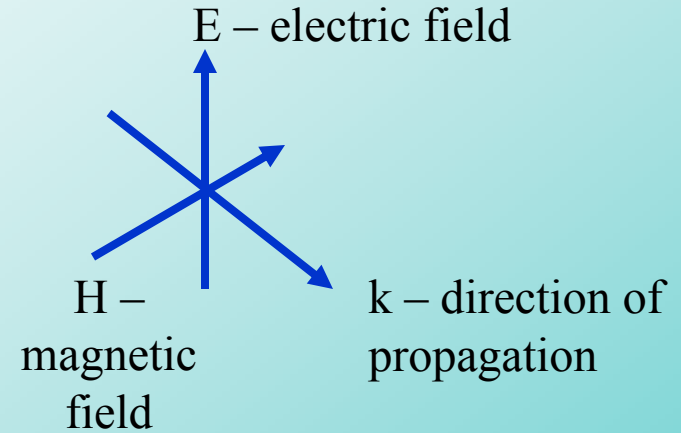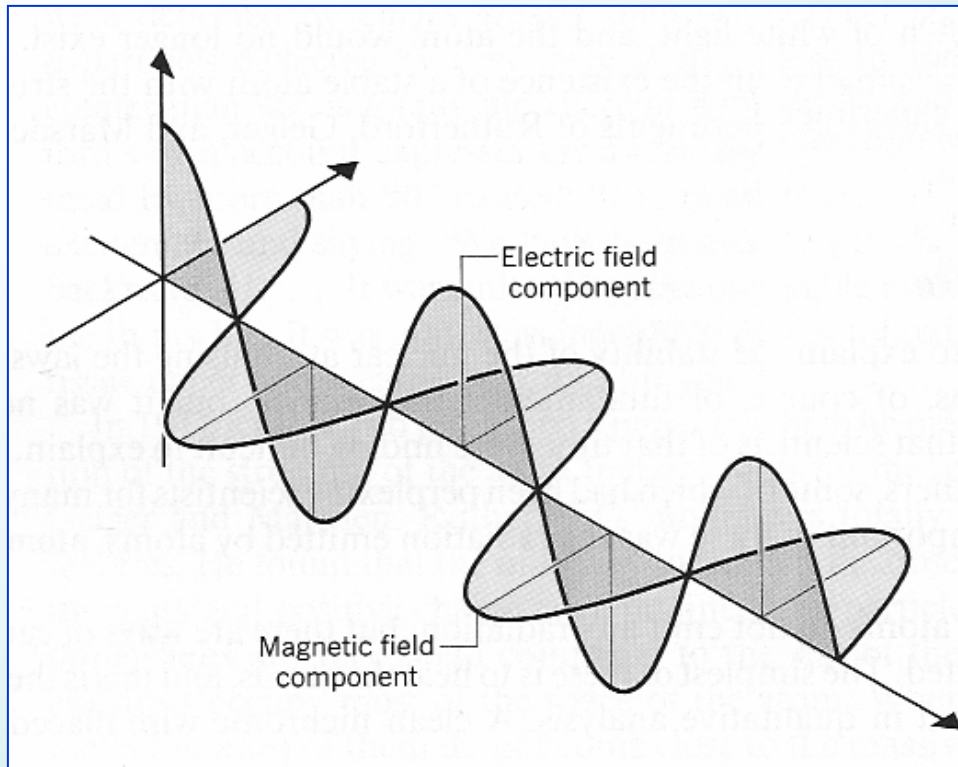$$\Delta E = h\nu = E_{+\frac{1}{2}} - E_{-\frac{1}{2}} = g\beta B_0$$

Here, g, the dimensionless Landé **g-value**, describes the resonance energy. Values around 2.003 are found for simple free-radical systems. The term β is the Bohr magneton:

$$\beta = eh/(4\pi m_e) = 927.4 \times 10^{-26} \text{ JT}^{-1} \text{ in SI units, or}$$

$$\beta_\nu = \beta/h = e/(4\pi m_e) = 13.996 \times 10^9 \text{ Hz T}^{-1} \text{ in frequency units, or}$$

$$\beta_{eV} = \beta/(e/C) = 5.7884 \times 10^{-5} \text{ eV T}^{-1} \text{ in electron volt units, where } (e/C)$$
$$\text{is the electron charge, } 1.602 \times 10^{-19} \text{ C.}$$

Refraction, optical rotation, interference, diffraction

Electric field component

Magnetic field component

E – electric field

H – magnetic field

k – direction of propagation

In classical theory, the refractive index depends on the strength of interaction of the electrical component of the electromagnetic field with the medium, and hence on polarizability of its molecules or atoms.

$$n_r = \varepsilon_r^{\frac{1}{2}}$$

where ε_r is relative permittivity, or dielectric constant.

What does this mean from a quantum mechanical perspective?

Refractive index, n_r of a medium is the ratio of the speed of light in a vacuum, c, to that in the medium, v.

$$n_r = c/v$$

Since the speed in a vacuum is constant and maximal, all values are > 1.0

We have seen that electromagnetic waves are neither electrical nor magnetic, and that their absorbance depends on the availability of a transient dipolar state of matching energy, orientation and phase. How does the medium provide transitions of appropriate character?
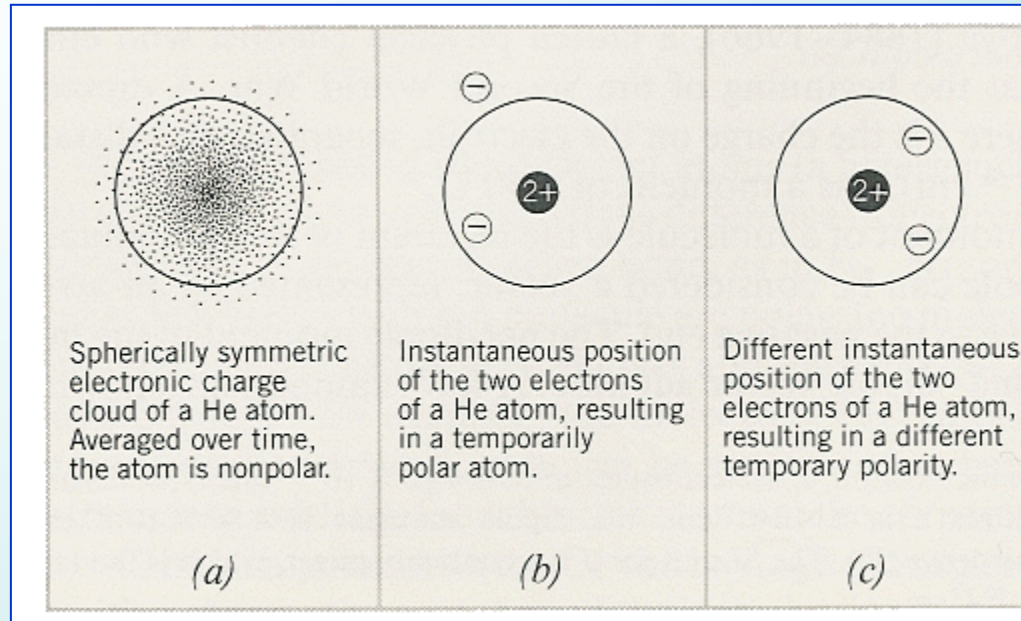
Spherically symmetric electronic charge cloud of a He atom. Averaged over time, the atom is nonpolar.

Instantaneous position of the two electrons of a He atom, resulting in a temporarily polar atom.

Different instantaneous position of the two electrons of a He atom, resulting in a different temporary polarity.

(a)　　　　(b)　　　　(c)

Fig. 5.7.　The fluctuating dipole in a He atom, which averages to zero over time. The He atom is nonpolar; its dipole moment is zero.

$\delta+$ ──── $\delta-$ $\delta+$ ──── $\delta-$
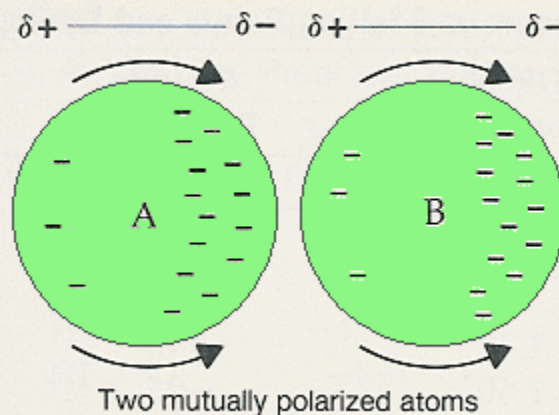
A　　B

Two mutually polarized atoms

Fig. 5.8.　The correlation of the electronic motion of two adjacent atoms, resulting in an attractive force between two atoms with temporary dipoles. A momentary distortion of the charge cloud of one atom induces a dipole moment in a nearby atom. Many such dipoles are formed and destroyed each second.

The interaction between induced dipoles underlies the London dispersion forces, or van der Waals forces that provide the weak interaction between molecules when they come into contact.

In addition to induced dipoles, molecules can have polar characteristics because of the asymmetry of charge in bonds.
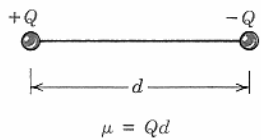
$\mu = Qd$

Fig. 5.4. Definition of the dipole moment, μ.

Resultant
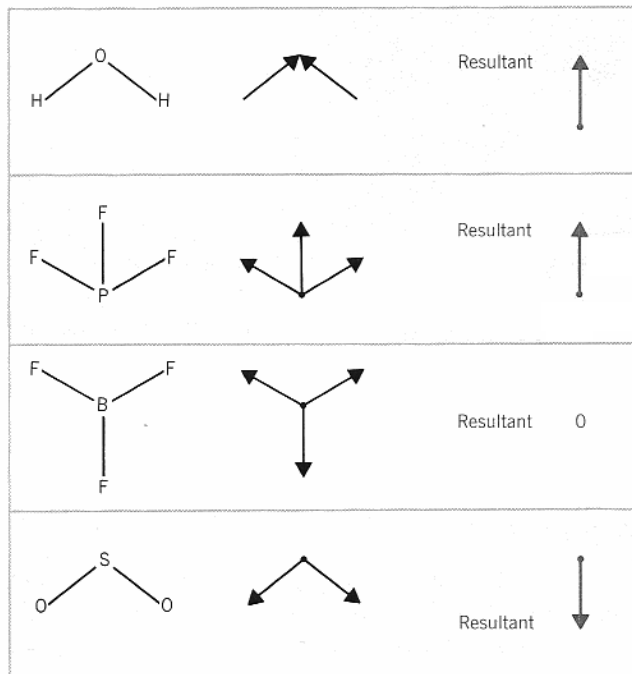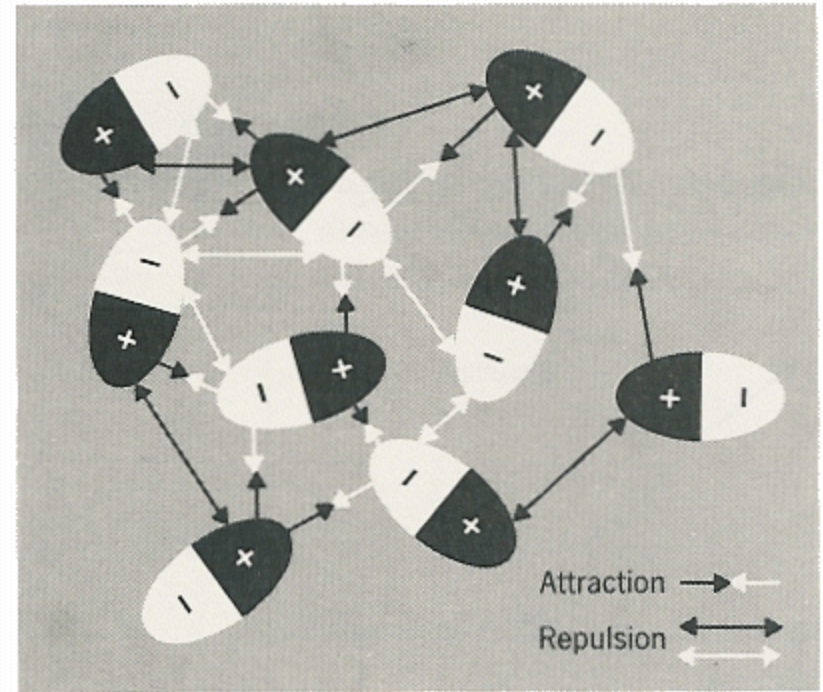
Resultant

Resultant   0

Resultant

Fig. 5.5. Bond–dipole vector addition. The arrow points from the positive to the negative end of a polar bond. The resultant vector is the net dipole of the molecule.

Attraction

Repulsion

All dipolar and dispersive interactions contribute to the polarizability of the medium, and introduce energy transitions of all energies and orientations.

As a consequence of the transient configurations and vibrational interactions, the numerous energy levels in the medium allow for absorption of photons over a wide energy range. However, these are not molecular transitions. There is no distinct spectrum such as that arising from absorption into specific transitions between molecular orbitals. The states excited are transient. As a consequence, the photon is re-emitted with the same energy, and with the same direction of propagation. The only thing that has changed is that it was temporarily tied to an atom or molecule, whose mass prevented movement of the energy through the medium (see Franck-Condon principle). The refractive index reflects the delay through these transient photonic interactions. The relation to dielectric constant reflects the difference in electrical polarizability, and hence the probability of encountering a suitable transition. The speed of light *between* interactions is the same as in vacuum.

Optical rotation of a medium or solution is simply the difference in refractive index for light of different polarization (orientation of the electrical field). It reflects the differential probability of interactions of the sort described above resulting from the asymmetry of the molecules in the medium.

Because these phenomena are related to the properties of the medium, and are statistical and random in nature, exact descriptions in terms of energy levels are inappropriate, and the classical treatment is usually used.

A nice descriptive treatment in terms of Quantum Electrodynamics is given by Richard Feynman in "QED – The Strange Theory of Light and Matter" (1985, Princeton University Press).