

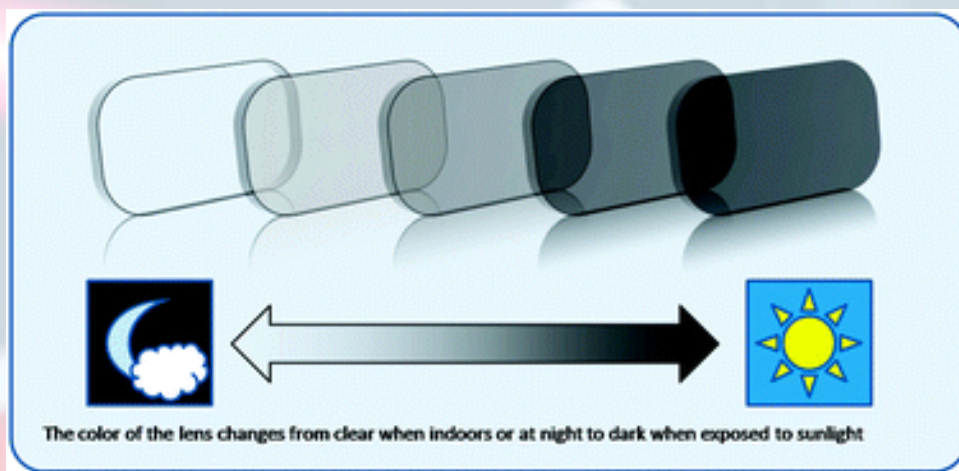
Importance of photochemistry:

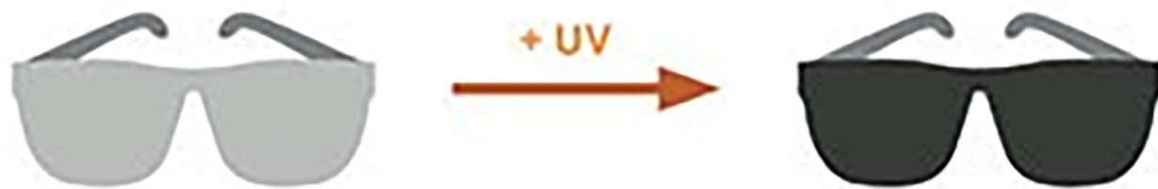
- ✓ Prebiotic formation of organic compounds such as proteins and nucleic acid by radiation with methane, ammonia, water and carbon dioxide as raw materials
- ✓ Photochromic materials
- ✓ Optical whiteners
- ✓ Fluorescence and phosphorescence

Photochromic materials:

Photochromic materials are those that show a reversible change in optical properties (color) through the action of light, i.e., electromagnetic radiation.

They belong, therefore, to the chromogenic class of materials.





INORGANIC



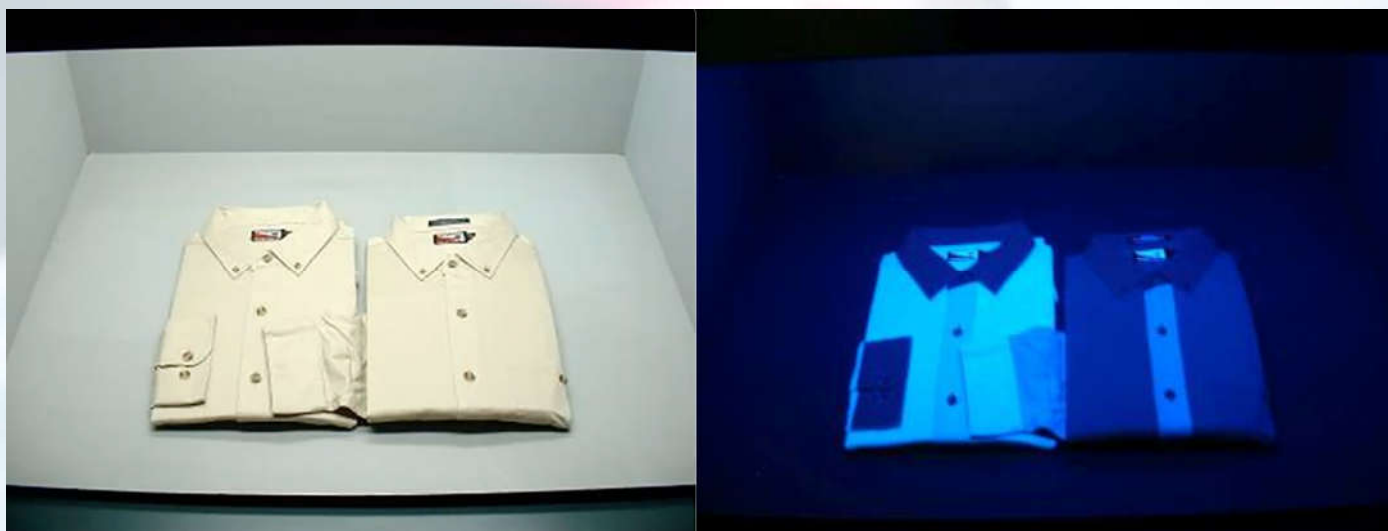
*The silver atoms form clusters which absorb UV and visible light.
Cu⁺ ions in the glass reduce the Cl atoms, stopping them from escaping.*

Optical whiteners:

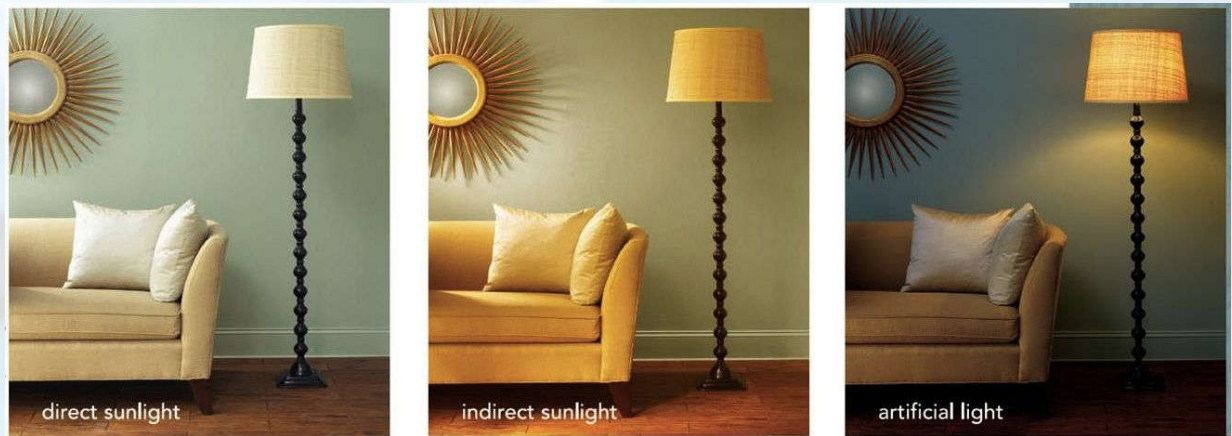
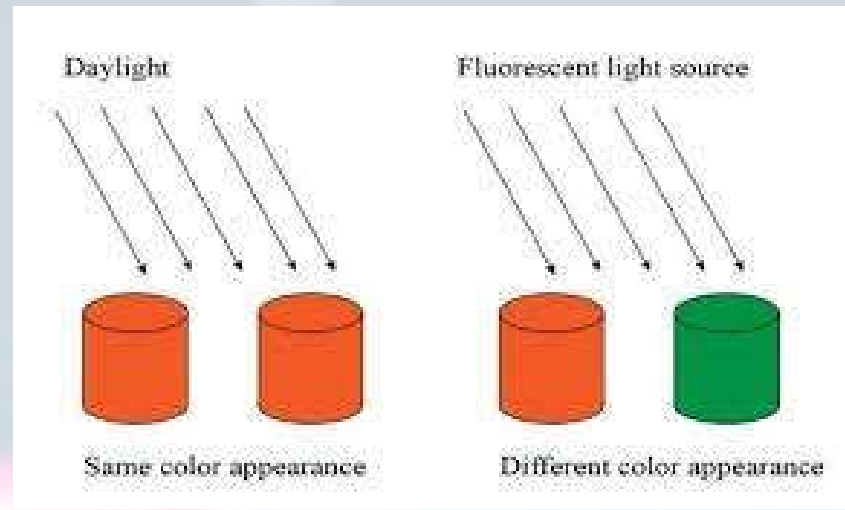
Or optical brighteners are a type of chemical used to enhance the white or bright appearance of fabrics. They're often used during the manufacturing process of new white or lightly colored fabrics, and are commonly added to laundry detergents to maintain the appearance of brightness after successive washes.



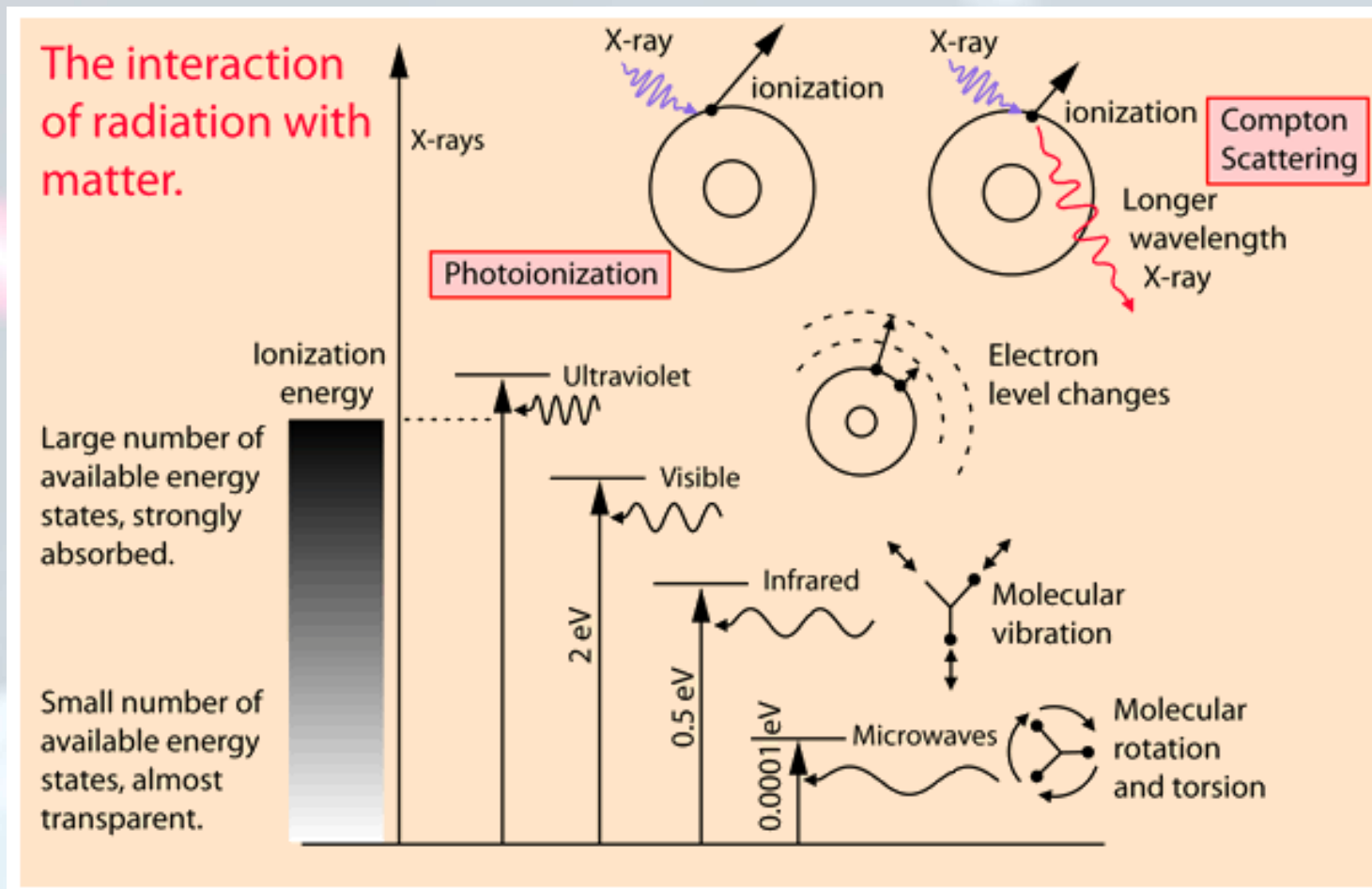
'Optical brighteners' is a general term for a group of chemicals, also known by other names such as 'Fluorescent Whitening Agents (FWAs)'. They're used in several industries, including fabrics, laundry detergents, paper, plastics and some cosmetics, and are derived from non-renewable sources such as pyrene (from coal tar). Optical brighteners can be considered as a type of dye, and they work by absorbing UV (ultraviolet) light and reflecting blue light. This makes materials look less yellow to the human eye, and thus appear whiter, brighter and 'cleaner'.



*A manufacturer sewed them using fabric from different suppliers. Although they appear to be the same color white in daylight, as soon as the ultraviolet light is flipped on you can see they are quite different. This is a phenomenon called “**metamerism**” – when two things appear to match under one light source, but no longer match when you change the lighting.*



Interaction of electromagnetic radiation with matter:



Microwave Interactions:

The quantum energy of microwave photons is in the range 0.00001 to 0.001 eV which is in the range of energies separating the quantum states of molecular rotation and torsion. The interaction of microwaves with matter other than metallic conductors will be to rotate molecules and produce heat as result of that molecular motion.

Small number of available energy states, almost transparent.

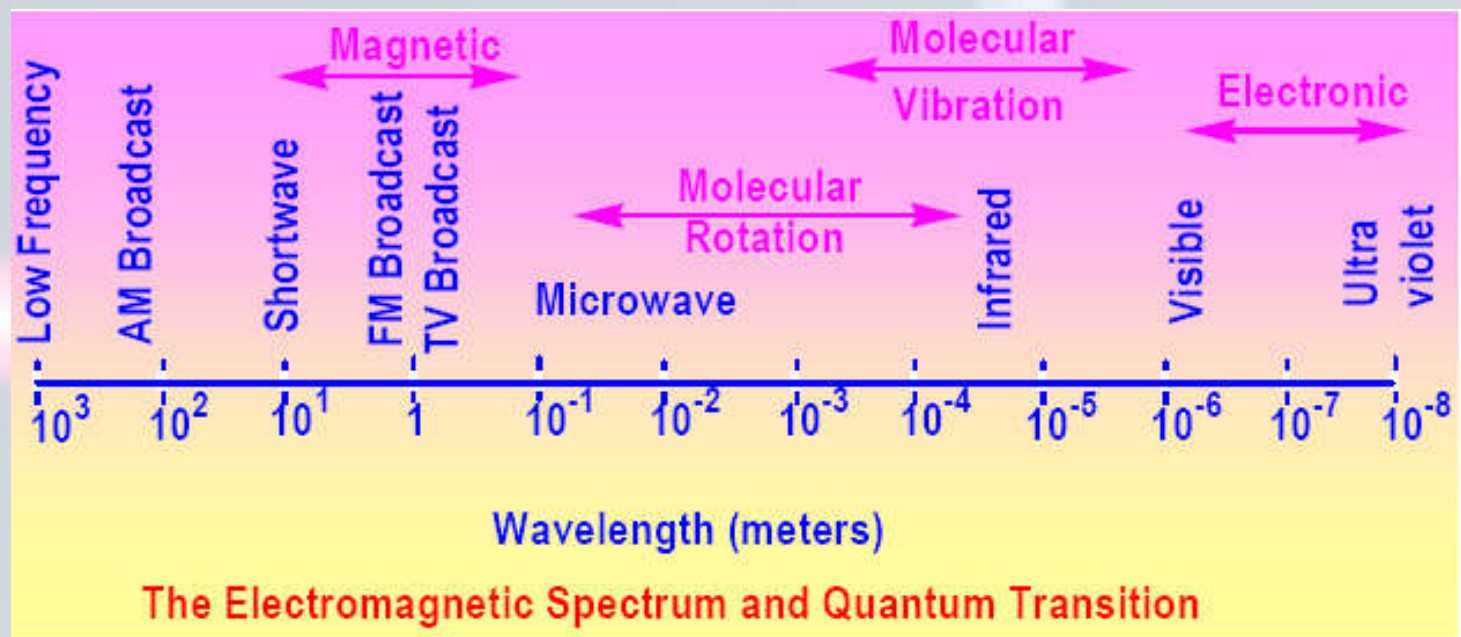


Microwaves rotate molecules

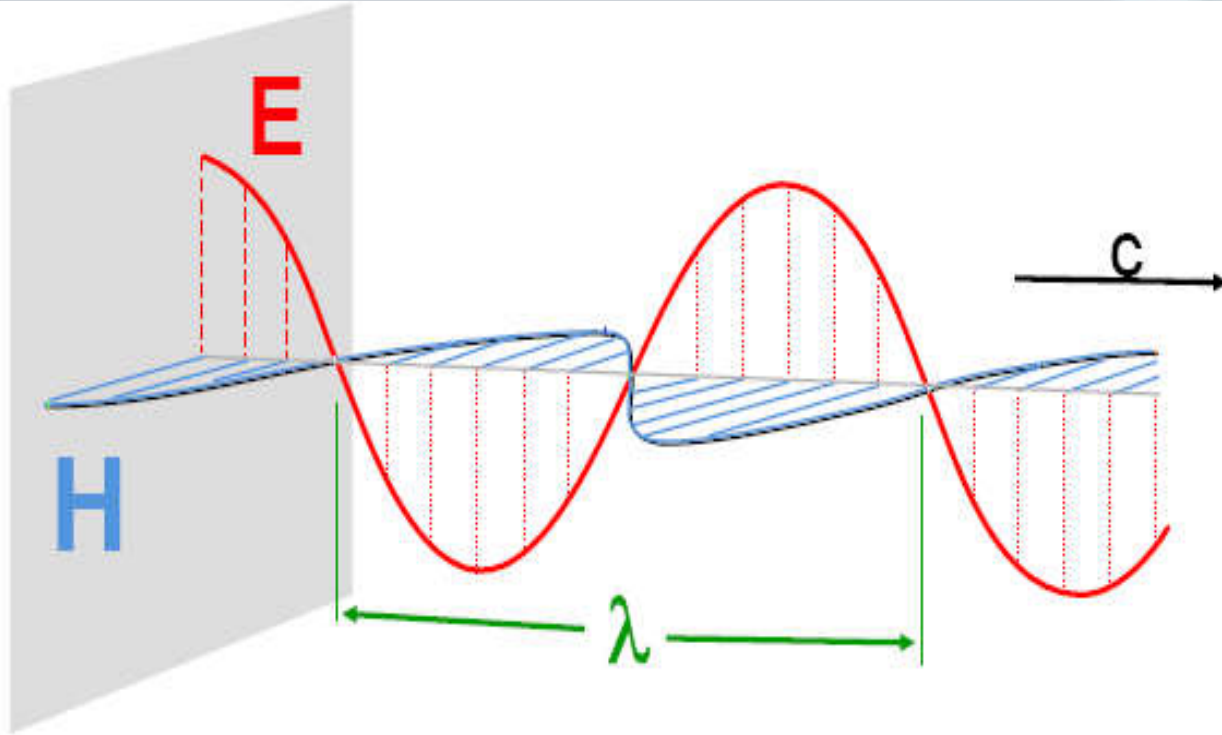


MW heating reduces the processing time and energy cost and has been known in the food industry for over half a century; its use in chemistry, however, started only since 1986.

Microwave irradiation plays an important role in fast and simple synthesis of nanocrystals. It has been observed that significantly different results can be obtained by conventional heating and microwave heating.



MW reactors operate at 2.45 GHz.



E= electric field

H= magnetic field

l= wavelength (12.2 cm for 2450 MHz)

c= speed of light (300,000 km/s)

1946: Original patent (P. L. Spencer)

1947: First commercial oven

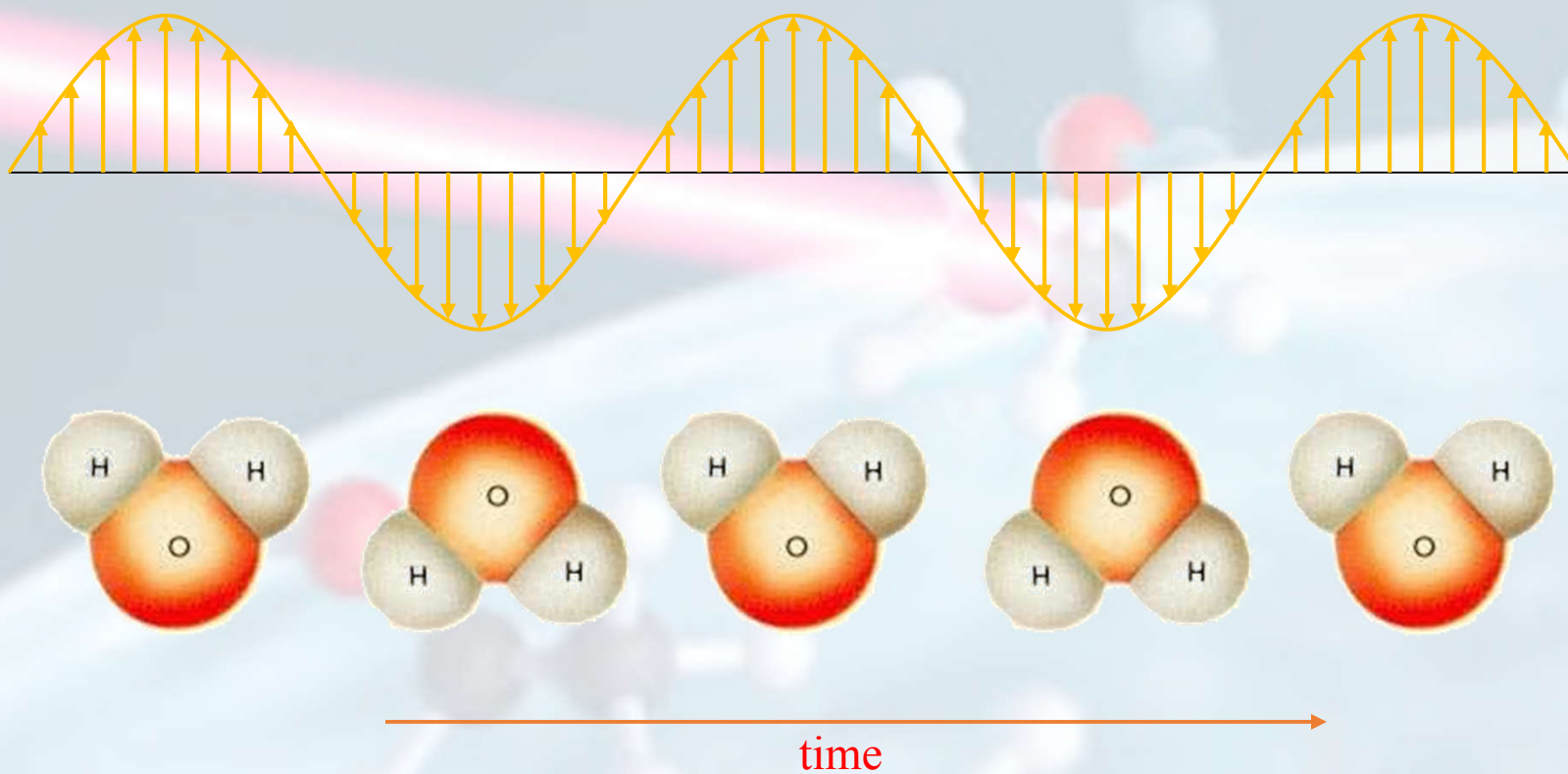
1955: Home models

1967: Desktop model

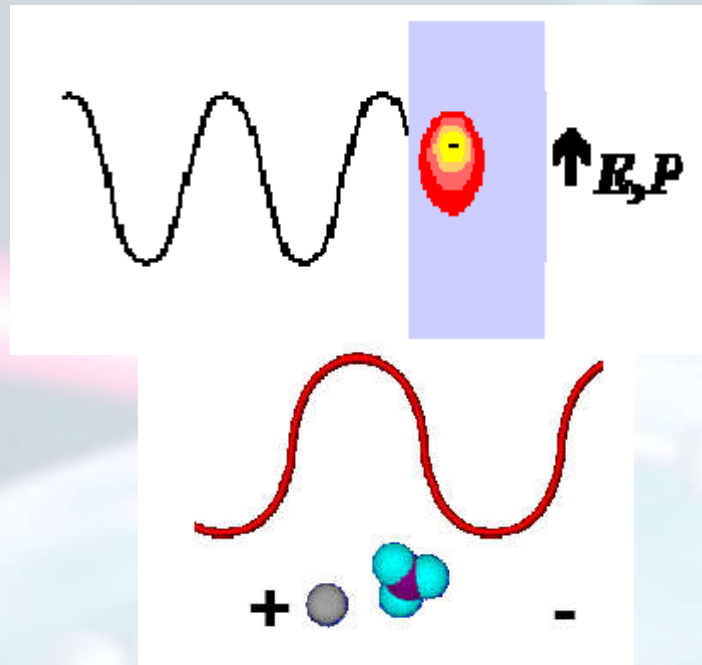
1975: U.S. sales exceed gas ranges

1976: 60% of U.S. households have
microwave ovens

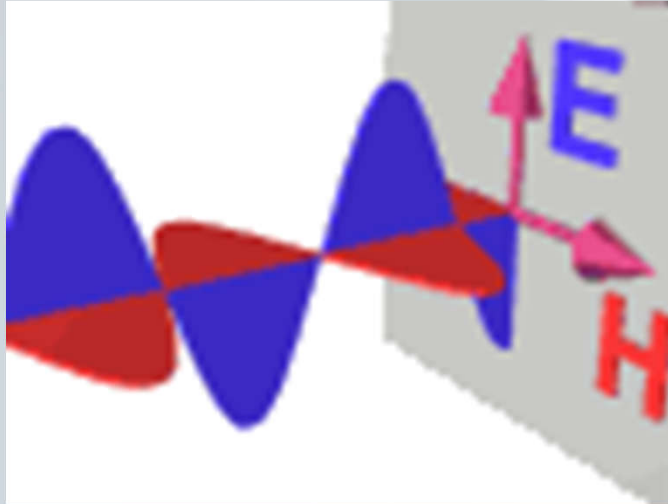
Dipolar Polarization Mechanism



Conduction Mechanism



Ions in solution will move by the applied electric field



The ability of a solvent molecule to absorb microwave energy and pass it on in the form of heat to other molecules partly depends on the dissipation factor ($\tan\delta$) defined as the ratio of the dielectric loss (ϵ'') to the dielectric constant (ϵ') of the solvent. Thus a study of the effect of solvents with different dielectric constants on microwave method is of great importance.

$$\tan \delta = \frac{\epsilon''}{\epsilon'}$$

Solvent (bp °C)	Dielectric Constant (ϵ')	Solvent	Tan δ	Solvent	Dielectric Loss (ϵ'')
Water (100)	80.4	Ethylene Glycol	1.350	Ethylene Glycol	49.950
Formic Acid (100)	58.5	Ethanol	.941	Formic Acid	42.237
DMSO (189)	45.0	DMSO	.825	DMSO	37.125
DMF (153)	37.7	2-Propanol	.799	Ethanol	22.866
Acetonitrile (82)	37.5	1-Propanol	.757	Methanol	21.483
Ethylene Glycol (197)	37.0	Formic Acid	.722	Nitrobenzene	20.497
Nitromethane (101)	36.0	Methanol	.659	1-Propanol	15.216
Nitrobenzene (202)	34.8	Nitrobenzene	.589	2-Propanol	14.622
Methanol (65)	32.6	1-Butanol	.571	Water	9.889
NMP (215)	32.2	Isobutanol	.522	1-Butanol	9.764
Ethanol (78)	24.3	2-Butanol	.447	NMP	8.855
Acetone (56)	20.7	2-Methoxyethanol	.410	Isobutanol	8.248
1-Propanol (97)	20.1	<i>o</i> -Dichlorobenzene	.280	2-Butanol	7.063
MEK (80)	18.5	NMP	.275	2-Methoxyethanol	6.929
2-Propanol (82)	18.3	Acetic Acid	.174	DMF	6.070
1-Butanol (118)	17.1	DMF	.161	<i>o</i> -Dichlorobenzene	2.772
2-Methoxyethanol (124)	16.9	1,2-Dichloroethane	.127	Acetonitrile	2.325
2-Butanol (100)	15.8	Water	.123	Nitromethane	2.304
Isobutanol (108)	15.8	Chlorobenzene	.101	MEK	1.462
1,2-Dichloroethane (83)	10.4	Chloroform	.091	1,2-Dichloroethane	1.321
<i>o</i> -Dichlorobenzene (180)	9.9	MEK	.079	Acetone	1.118
Dichloromethane (40)	9.1	Nitromethane	.064	Acetic Acid	1.079
THF (66)	7.4	Acetonitrile	.062	Chloroform	0.437
Acetic Acid (113)	6.2	Ethyl Acetate	.059	Dichloromethane	0.382
Ethyl Acetate (77)	6.0	Acetone	.054	Ethyl Acetate	0.354
Chloroform (61)	4.8	THF	.047	THF	0.348
Chlorobenzene (132)	2.6	Dichloromethane	.042	Chlorobenzene	0.263
<i>o</i> -Xylene (144)	2.6	Toluene	.040	Toluene	0.096
Toluene (111)	2.4	Hexane	.020	<i>o</i> -Xylene	0.047
Hexane (69)	1.9	<i>o</i> -Xylene	.018	Hexane	0.038

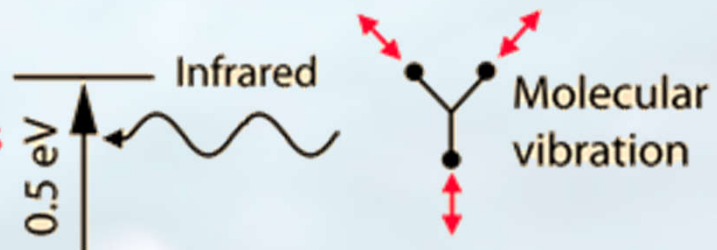
Infrared Interactions:

The quantum energy of infrared photons is in the range 0.001 to 1.7 eV which is in the range of energies separating the quantum states of molecular vibrations. Infrared is absorbed more strongly than microwaves, but less strongly than visible light. The result of infrared absorption is heating of the tissue since it increases molecular vibrational activity. Infrared radiation does penetrate the skin further than visible light and can thus be used for photographic imaging of subcutaneous blood vessels.

Higher density of energy levels than in the microwave range, more strongly absorbed.

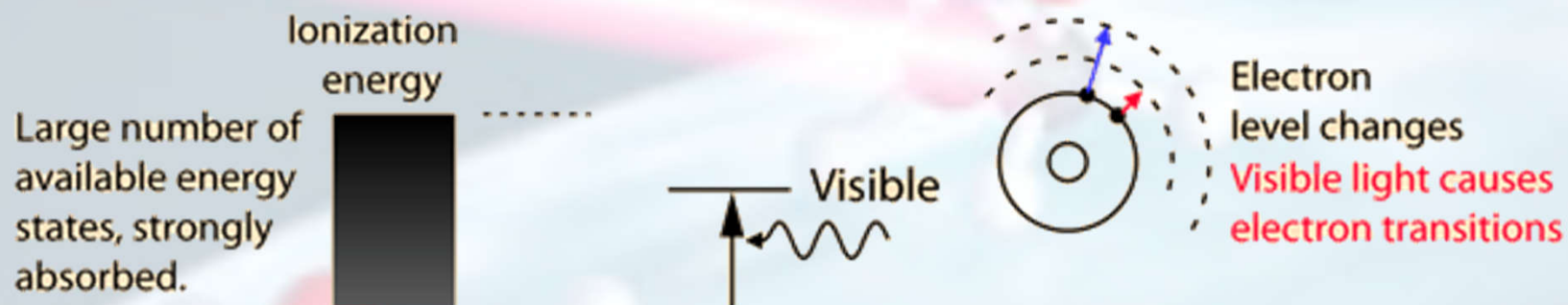


Infrared radiation vibrates molecules



Visible Light Interactions:

The primary mechanism for the absorption of visible light photons is the elevation of electrons to higher energy levels. There are many available states, so visible light is absorbed strongly.



Ultraviolet Interactions:

UV photons above the ionization energy can disrupt atoms and molecules.

high UV or X-ray photon
ionization



Photoionization

Large number of available energy states, strongly absorbed.

Ionization energy



Ultraviolet



Electron level changes

UV photons below the ionization energy are strongly absorbed in producing electron transitions.

Interaction of electromagnetic radiation UV-visible with matter/organic compounds:

- Transition from ground state to excited state
- Changes electronic distribution, geometry and uncoupling of electronic spin
- Electron moves from ground state energy level of a molecular to a higher level i.e. an unoccupied orbital of higher energy
- Energy level of a molecule are quantized

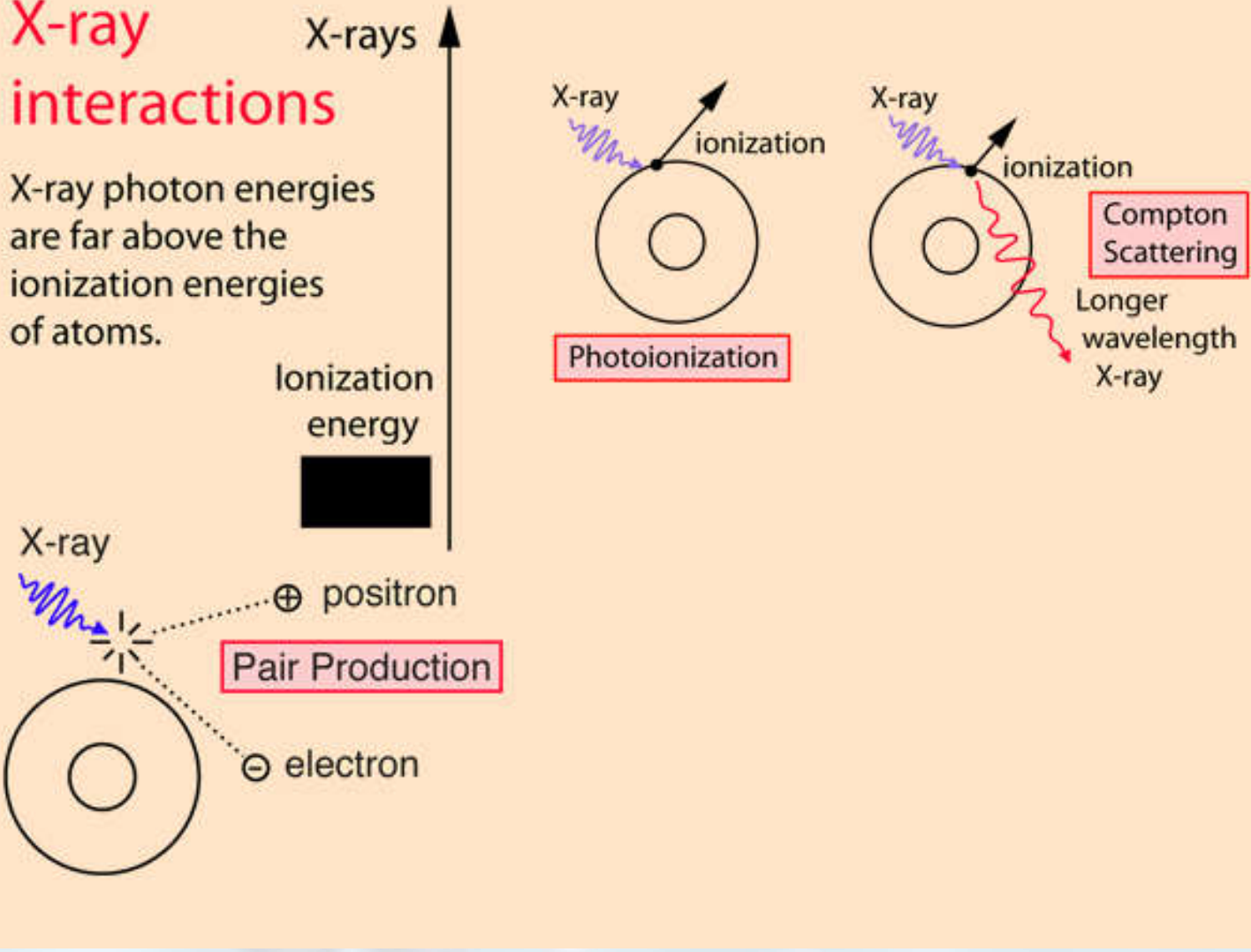
The amount of energy required to raise an electron in a given molecule from one level to a higher energy one is a fixed quantity i.e. $\Delta E = h\nu$ for one molecule and for n number of molecules it is $\Delta E = nh\nu$

X-Ray Interactions:

Since the quantum energies of x-ray photons are much too high to be absorbed in electron transitions between states for most atoms, they can interact with an electron only by knocking it completely out of the atom. That is, all x-rays are classified as ionizing radiation. This can occur by giving all of the energy to an electron (photoionization) or by giving part of the energy to the electron and the remainder to a lower energy photon (Compton scattering). At sufficiently high energies, the x-ray photon can create an electron positron pair.

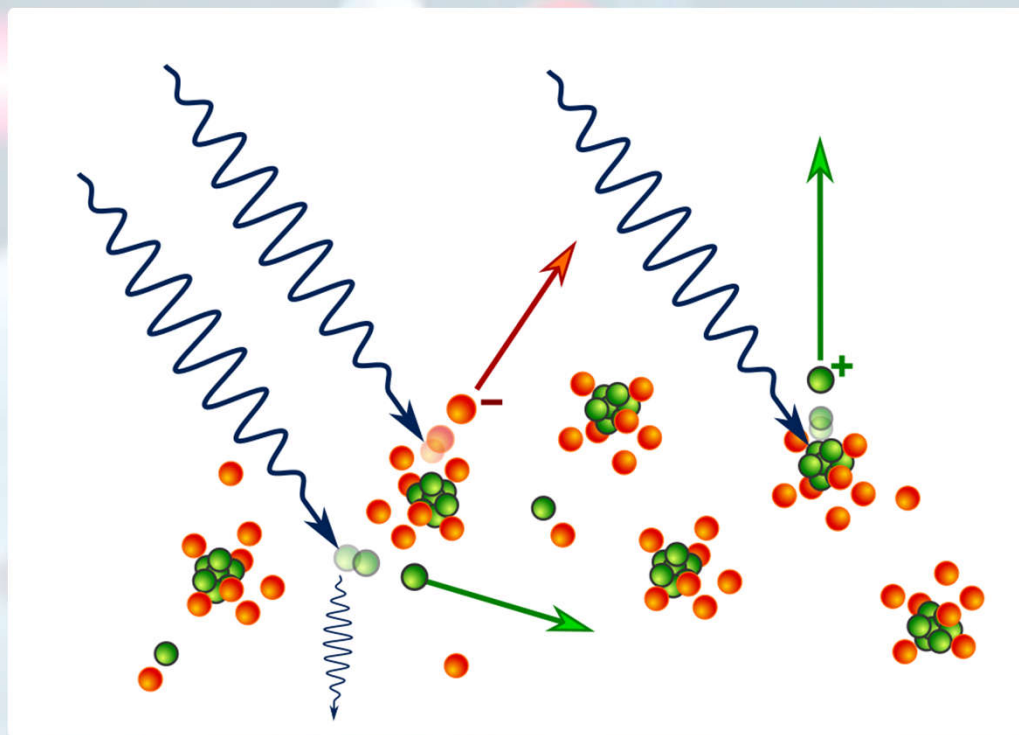
X-ray interactions

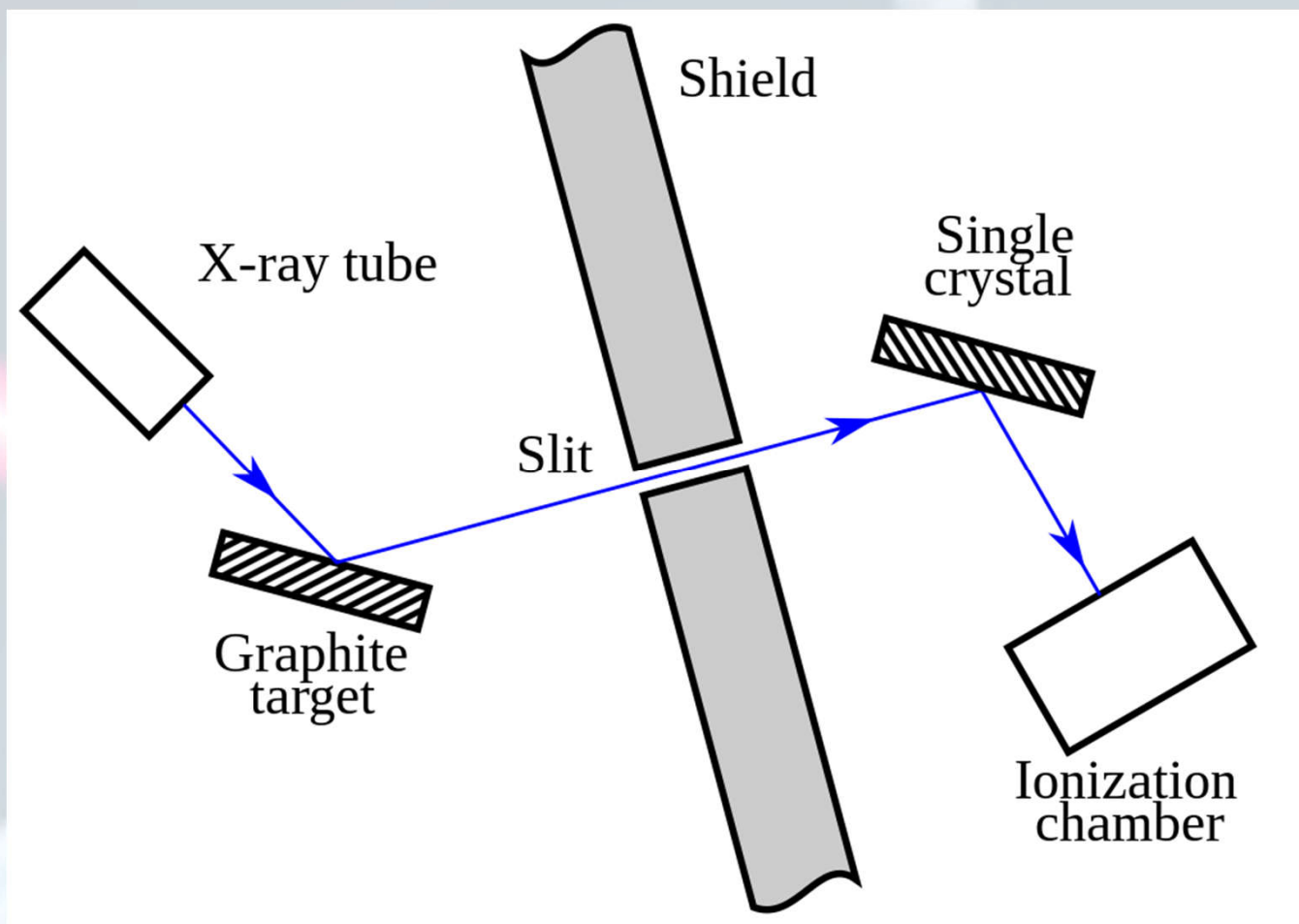
X-ray photon energies are far above the ionization energies of atoms.



Compton scattering:

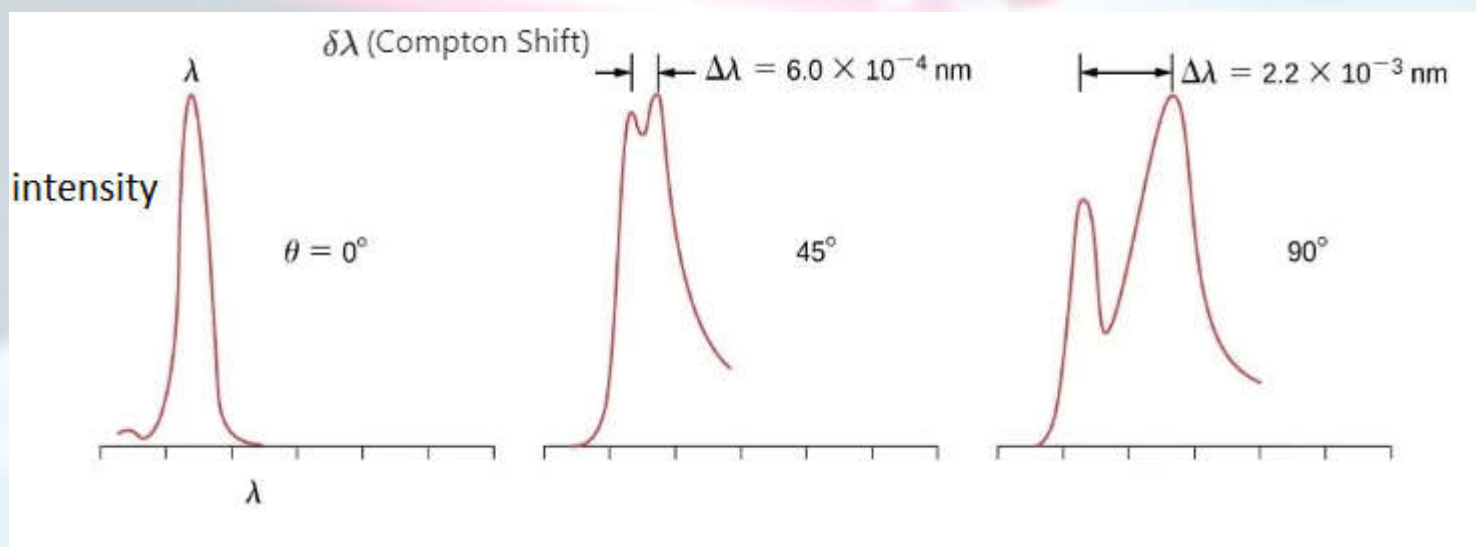
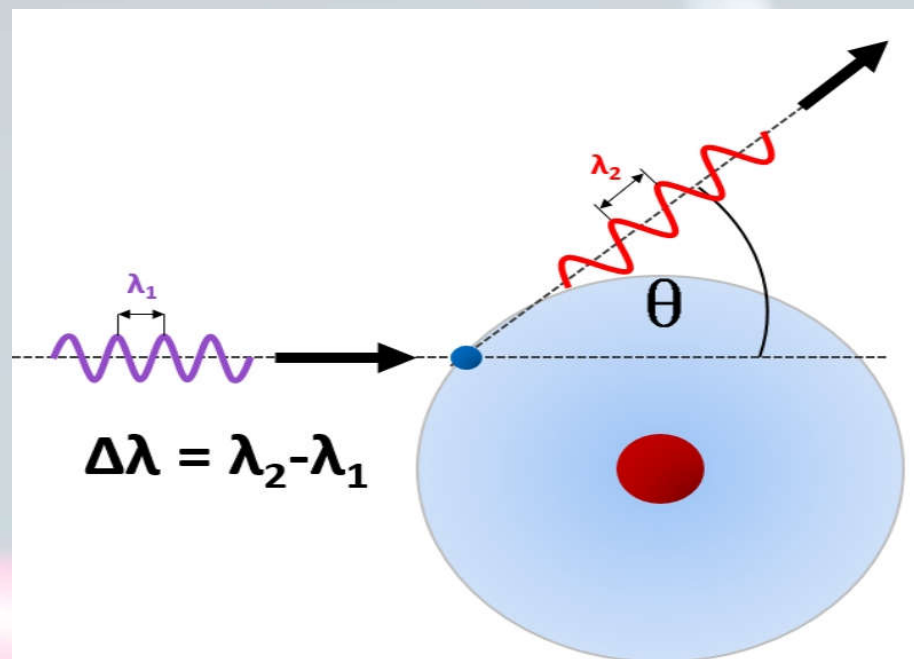
Compton scattering (or the Compton effect) is the quantum theory of high frequency photons scattering following an interaction with a charged particle, usually an electron. Specifically, when the photon hits electrons, it releases loosely bound electrons from the outer valence shells of atoms or molecules.





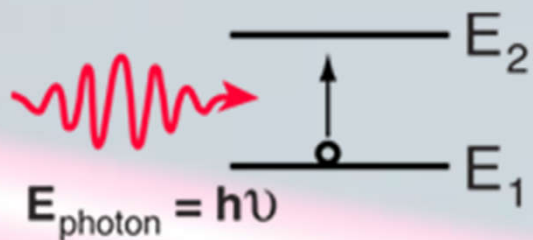
In Compton's original experiment, the energy of the X ray photon (≈ 17 keV) was significantly larger than the binding energy of the atomic electron, so the electrons could be treated as being free after scattering. The amount by which the light's wavelength changes is called the Compton shift. Although nucleus Compton scattering exists, Compton scattering usually refers to the interaction involving only the electrons of an atom. Compton scattering is commonly described as inelastic scattering, because the energy in the scattered photon is less than the energy of the incident photon.

The effect is significant because it demonstrates that light cannot be explained purely as a wave phenomenon.



Quantum Properties of Light:

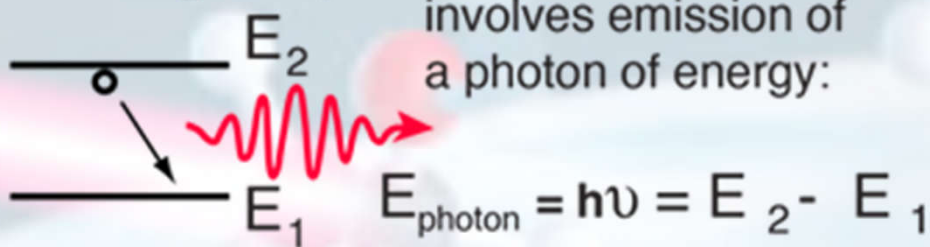
Radiation is quantized such that for a given frequency of radiation, there can be only one value of quantum energy for the photons of that radiation. The energy levels of atoms and molecules can have only certain quantized values. Transitions between these quantized states occur by the photon processes absorption, emission, and stimulated emission. All of these processes require that the photon energy given by the Planck relationship is equal to the energy separation of the participating pair of quantum energy states.



Absorption can occur only when

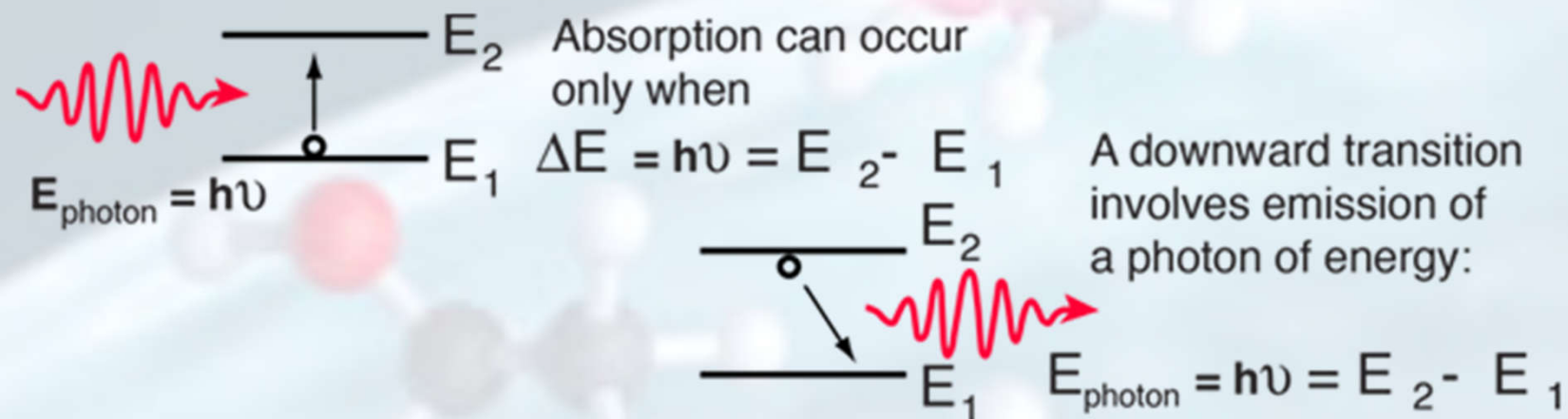
$$\Delta E = h\nu = E_2 - E_1$$

A downward transition involves emission of a photon of energy:



Absorption and Emission:

Taking the electron transitions associated with visible and ultraviolet interactions with matter as an example, absorption of a photon will occur only when the quantum energy of the photon precisely matches the energy gap between the initial and final states. In the interaction of radiation with matter, if there is no pair of energy states such that the photon energy can elevate the system from the lower to the upper state, then the matter will be transparent to that radiation.



THE BEER–LAMBERT LAW:

The extent of absorption of light varies a great deal from one substance to another, with the probability of absorption being indicated by the molar absorption coefficient (ϵ). As light is absorbed, the intensity of light entering the substance, I_{in} , is greater than the intensity of the emerging light, I_{out} , and there is an exponential relationship between the relative absorption (I_{out}/I_{in}) and the concentration (c) and path length (l) of the absorbing substance:

$$I_{\text{out}}/I_{\text{in}} = 10^{-\epsilon cl}$$

Taking logarithms to the base 10 gives us:

$$\log(I_{\text{out}}/I_{\text{in}}) = -\epsilon cl$$

Thus:

$$\log(I_{\text{in}}/I_{\text{out}}) = \epsilon cl$$

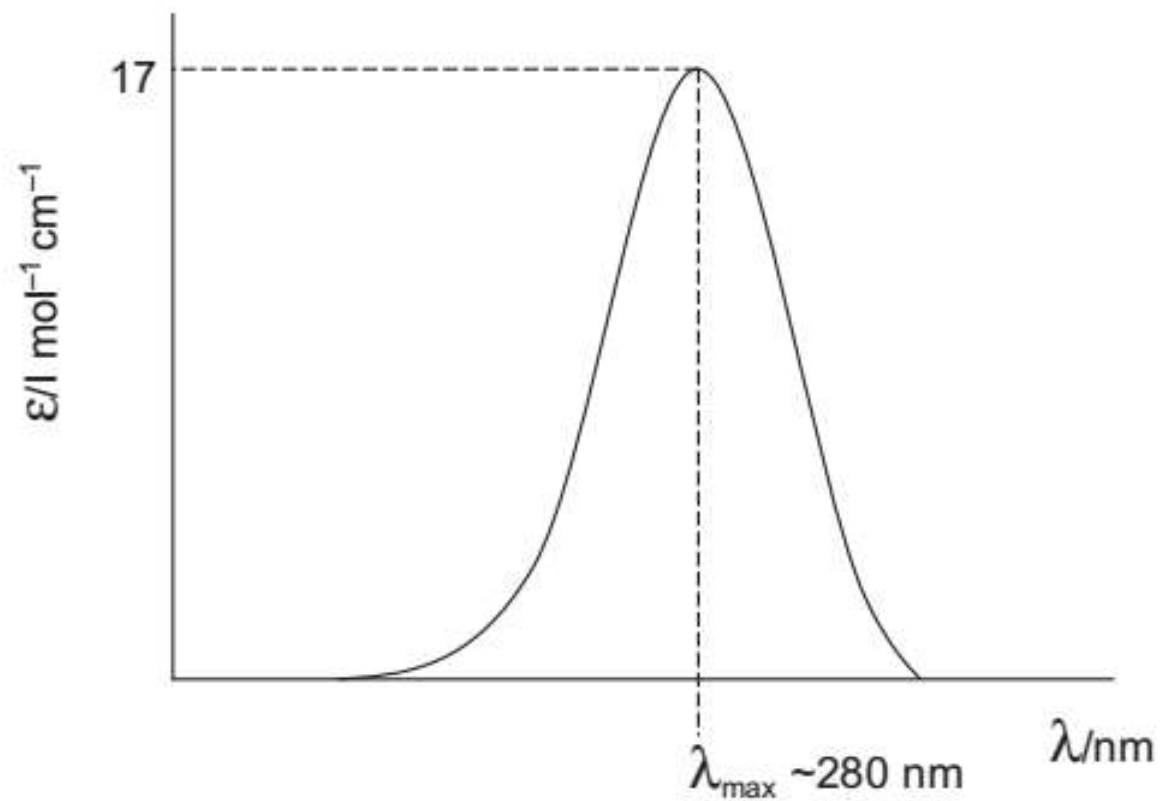
The left-hand-side quantity is the absorbance, A , and the linear relationship between absorbance, concentration and path length is known as the Beer–Lambert law:

$$A = \epsilon cl$$

- ❖ Concentration, c , traditionally has units of moles per litre, mol l^{-1} .
- ❖ Path length, l , traditionally has units of centimetres, cm .
- ❖ A has no units since it is a logarithmic quantity.

So the units of ϵ usually given are: $\text{cm}^{-1} \times (\text{mol l}^{-1})^{-1} = \text{l mol}^{-1} \text{cm}^{-1}$

For a given substance, the molar absorption coefficient varies with the wavelength of the light used. A plot of ϵ (or $\log\epsilon$) against wavelength (or wavenumber) is called the absorption spectrum of the substance. The principal use of absorption spectra from the photochemist's point of view is that they provide information as to what wavelength (λ_{\max}) a compound has at its maximum value of the molar absorption coefficient (ϵ_{\max}). Thus, irradiation of the compound at λ_{\max} allows optimum photoexcitation of the compound to be carried out.



Absorption spectrum of propanone (acetone)

THE PHYSICAL BASIS OF LIGHT ABSORPTION BY MOLECULES:

Light-absorbing molecules contain antennae groups known as chromophores or chromophoric groups which are responsible for the absorption of light. When the oscillating electromagnetic radiation encounters an appropriate chromophore, an electron in the chromophore can be promoted to a higher-energy excited state provided there is an energy correspondence between the photon and the pair of quantized electronic energy levels involved in the electronic transition.

Now, the total energy of molecules is made up of electronic energy and energy due to nuclear motion (vibrational and rotational):

$$E_t = E_e + E_v + E_r$$

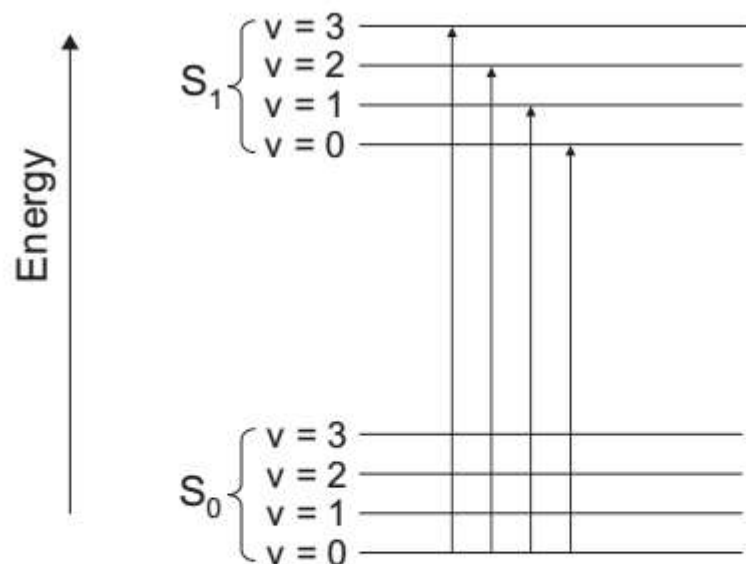
where the subscripts refer to the total energy, electronic energy, vibrational energy and rotational energy, respectively. Because of the large differences between electronic, vibrational and rotational energies, it is assumed that these can be treated separately. This assumption is known as the Born –Oppenheimer approximation.

At thermal equilibrium the population of any series of energy levels is described by the Boltzmann distribution law. If N_0 molecules are in the ground state then the number N_1 in any higher energy level is given by the equation:

$$N_1/N_0 = \exp(-\Delta E/RT)$$

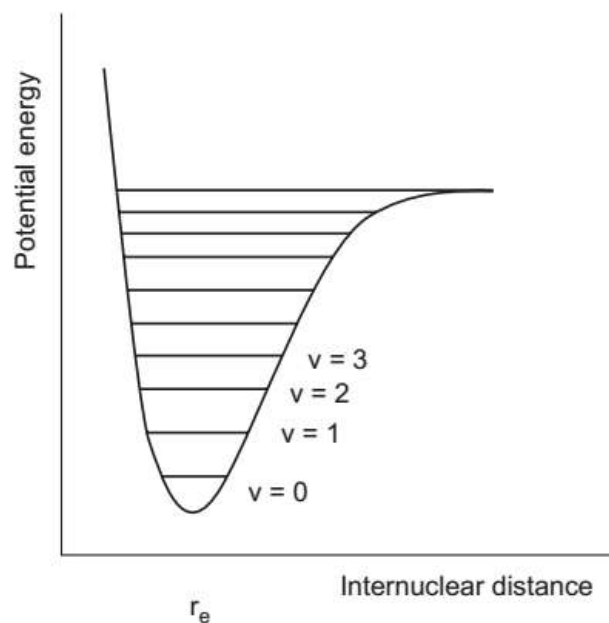
where exp refers to the exponential function (e^x on calculators), ΔE is the energy difference between the two energy levels, R is the gas constant (which has a value of $8.314\text{J K}^{-1} \text{mol}^{-1}$) and T is the absolute temperature.

Calculations based on the Boltzmann distribution law show that, at room temperature, most molecules will be in the $v = 0$ vibrational state of the electronic ground state and so absorption almost always occurs from $S_0 (v = 0)$.



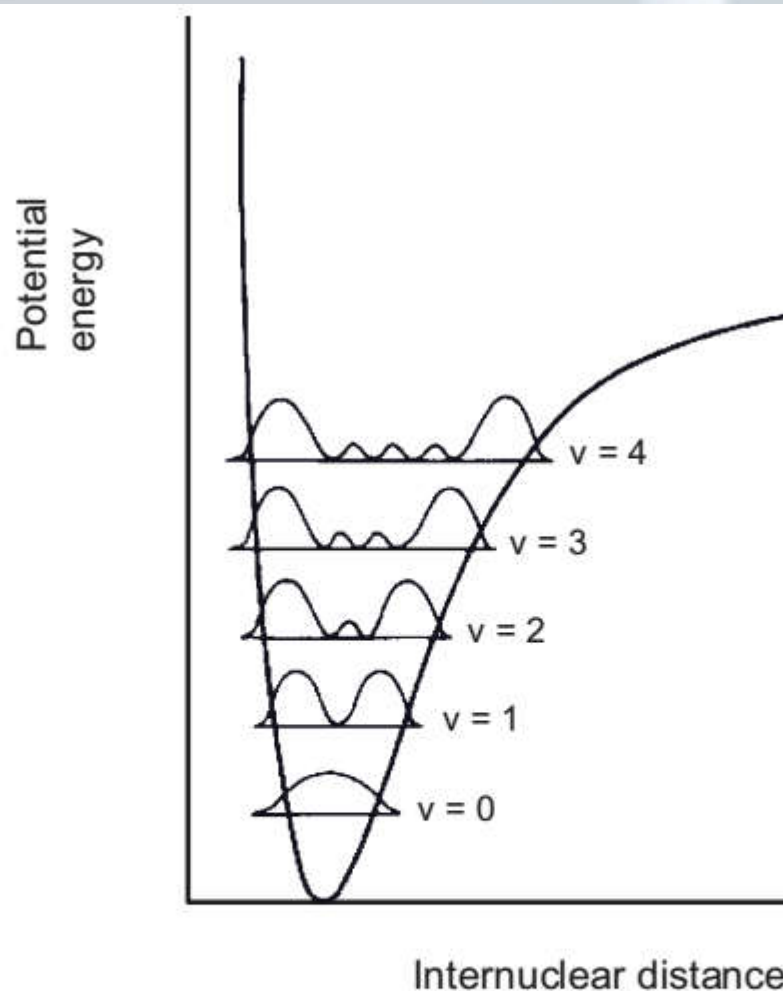
Schematic diagram of the electronic ground state and the first excited electronic state, with their associated quantised vibrational energy levels, for an organic molecule. The vertical arrows show vibronic transitions due to the absorption of photons

Figure shows the potential energy curve for a diatomic molecule, often referred to as a Morse curve, which models the way in which the potential energy of the molecule changes with its bond length. At the points where the horizontal lines meet the Morse curve, the energy is wholly potential. In between, the energy is partly kinetic and partly potential.



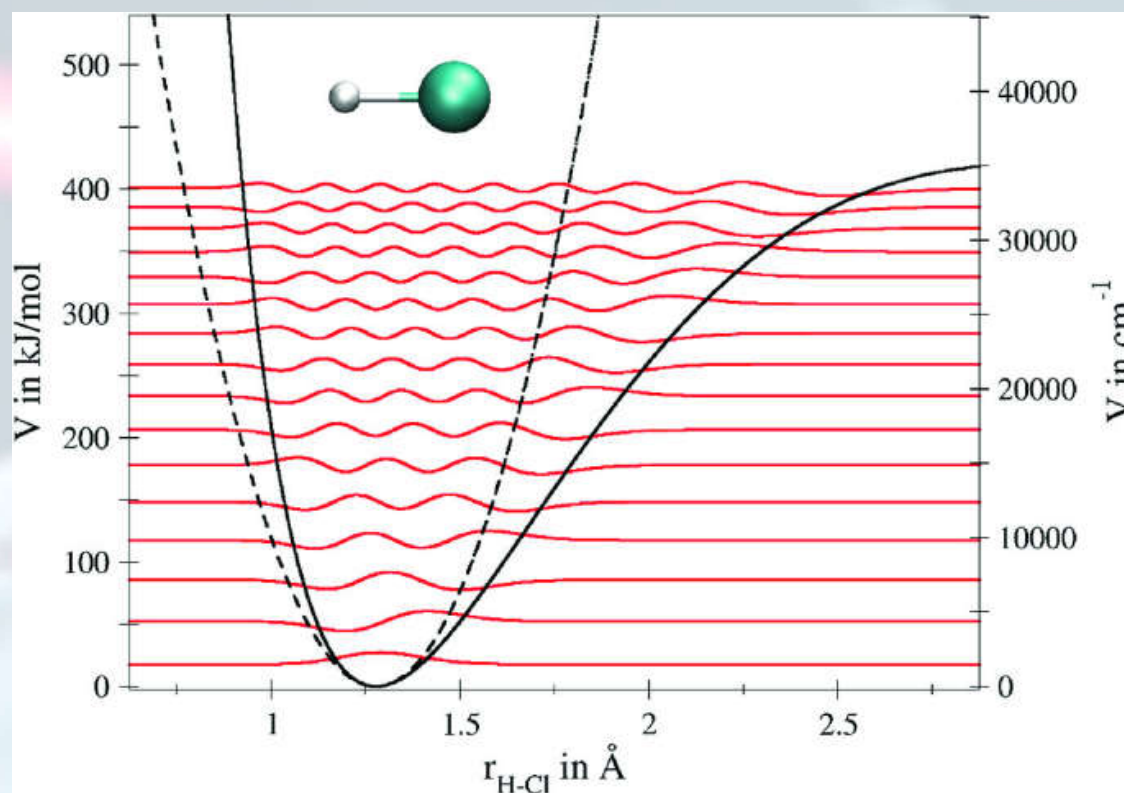
A Morse curve for a diatomic molecule, showing the quantised vibrational energy levels. The minimum on the curve represents the equilibrium bond distance, r_e

Each vibrational energy level has an associated wavefunction, the square of which relates to the most probable internuclear distance for a given vibrational quantum number, v . Figure shows the vibrational probability function for a series of vibrational quantum numbers. For the $v = 0$ level, the square of the wavefunction shows that the molecule spends most of its time in the region of the equilibrium configuration.

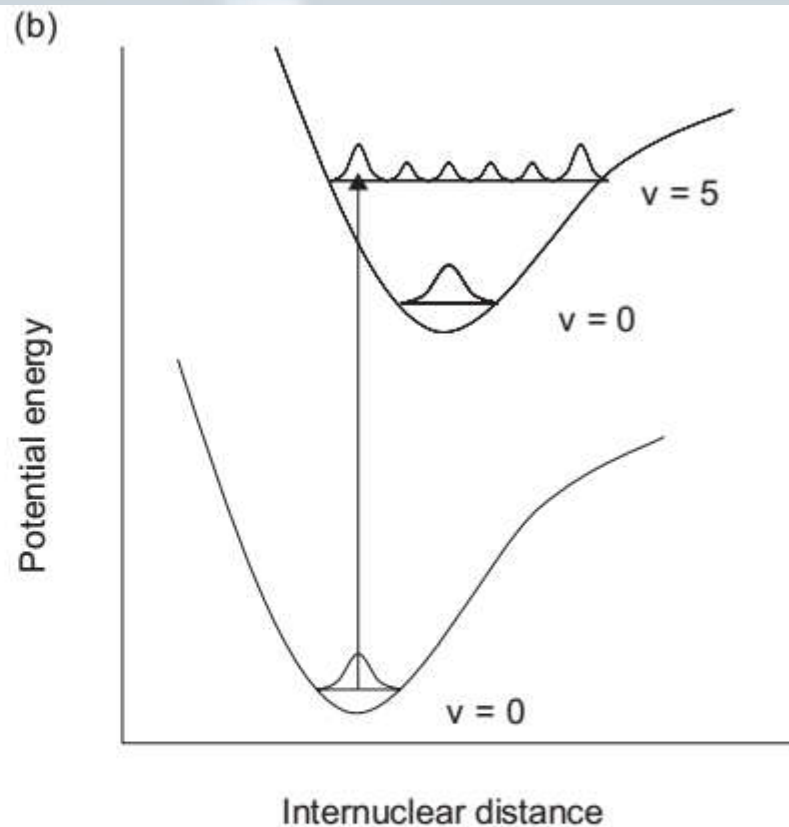
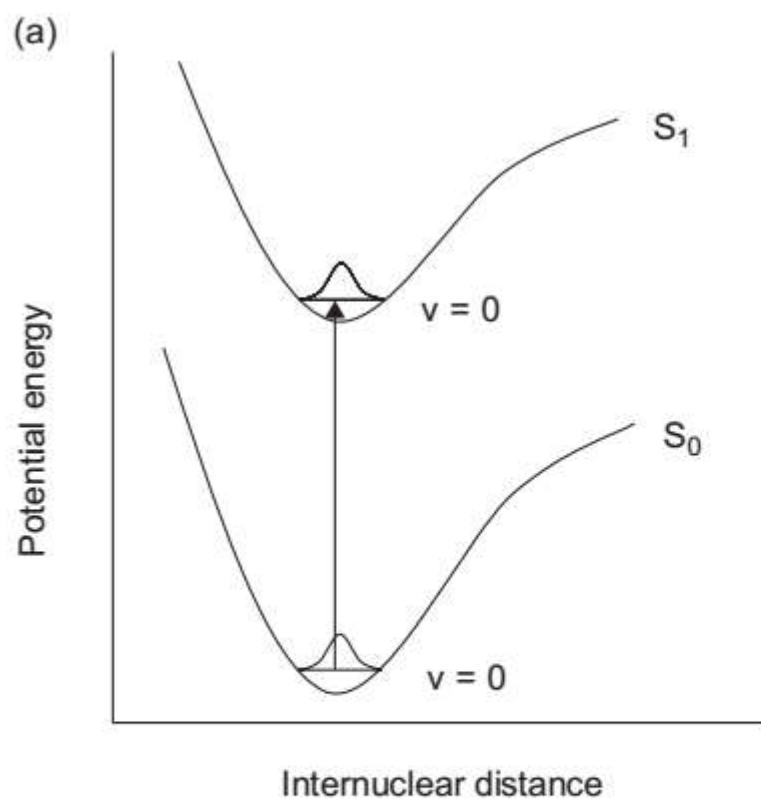


Vibrational probability functions for a series of vibrational quantum numbers. Note that for the higher v there is a greater probability of the molecule having a bond length at the two limits shown by the Morse curve. Notice also that for each value of v , there are $v + 1$ maxima

However, for an excited vibrational energy level, the magnitude of the ψ^2 function is greatest close to the turning points of the vibrational motion, which shows that the bond spends most of its time in the fully compressed or fully-extended configuration.



Nuclei move much more slowly than the much-lighter electrons, so when a transition occurs from one electronic state to another, it takes place so rapidly that the nuclei of the vibrating molecule can be assumed to be fixed during the transition. This is called the Franck – Condon principle, and a consequence of it is that an electronic transition is represented by a vertical arrow such as that shown in Figure; that is, an electronic transition occurs within a ‘ stationary ’ nuclear framework. Thus the electronic transition accompanying the absorption of a photon is often referred to as a vertical transition or Franck – Condon transition.



Electronic transitions with the greatest probability of absorption from $S_0(v = 0)$: (a) where both electronic states have similar geometries, shown by the minima of the curves being coincident ; (b) where the excited state has a larger internuclear distance than the ground state