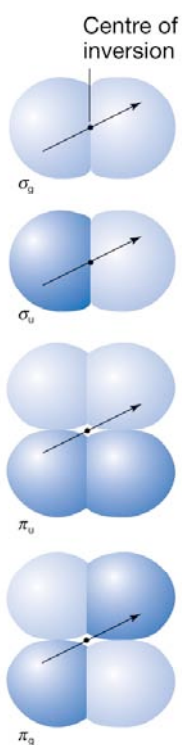


Spectroscopy 2: electronic transitions

The energies needed to change the electron distributions of molecules are in the order of several electronvolts ($1 \text{ eV} = 8065.5 \text{ cm}^{-1} \approx 100 \text{ kJ mol}^{-1}$) – the photons emitted or absorbed when such changes occur lie in the visible and ultraviolet regions of the spectrum. In some cases the relocation of electrons may be so extensive that it results in ionization or dissociation of the molecule.



The nuclei in a molecule are subjected to different forces after an electronic transition and the molecule may respond by starting to vibrate. The resulting vibrational structure can be resolved for gaseous samples, but in a liquid or solid the lines usually merge together and results in a broad, almost featureless band. Superimposed on the vibrational transitions that accompany the electronic transition of a molecule in the gas phase is an additional branch structure from rotational transitions. The electronic spectra of gaseous samples are therefore very complicated, but informative.

The electronic spectra of diatomic molecules

Parity. The molecular orbitals of homonuclear diatomic molecules are labeled with a subscript g or u that specifies their **parity**, their behavior under inversion with respect to the central point. If, after the inversion, the orbital has the same sign, it is denoted g (from *gerade*, the German word for even). If the orbital has opposite sign, it denoted u (*ungerade*). The parity designation applies only to homonuclear diatomic molecules (and, in general, to the symmetry groups, which contain a center of inversion).

The bonding σ orbital - σ_g ; antibonding - σ_u . However, the bonding π orbital is π_u and antibonding - π_g .

Term symbols

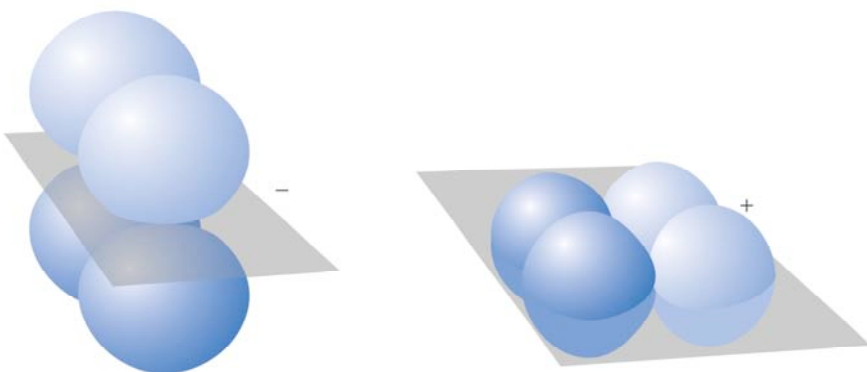
The term symbols of linear molecules (analogs of, for example, ^2P for atoms) are constructed in a similar way to those for atoms, but now we must pay attention to the component of total angular momentum about the internuclear axis, $\Lambda\hbar$. The value of $|\Lambda|$ is denoted by the symbols $\Sigma, \Pi, \Delta, \dots$ for $|\Lambda| = 0, 1, 2, \dots$, respectively – analogs of S, P, D for atoms. The value of Λ is the sum of values of λ for the individual electrons. A single electron in a σ orbital has $\lambda = 0$: the orbital is cylindrically symmetrical and has no angular nodes when viewed along the internuclear axis. If the only electron is present, $\Lambda = 0$. The term symbol for H_2^+ is Σ .

We use a superscript with the value of $2S + 1$ to denote the multiplicity of the term. The component of total spin angular momentum about the internuclear axis is denoted Σ ; $\Sigma = S, S - 1, S - 2, \dots, -S$. For H_2^+ , because there is only one electron, $S = s = 1/2$ ($\Sigma = \pm 1/2$) and the term symbol is $^2\Sigma$, a double term. The overall parity is added as a right subscript. For H_2^+ , the parity of the only occupied orbital is g, so the term is also g, and in full dress is $^2\Sigma_g$. If there are several electrons, the overall parity is calculated by using

$$g \times g = g \quad u \times u = g \quad u \times g = u$$

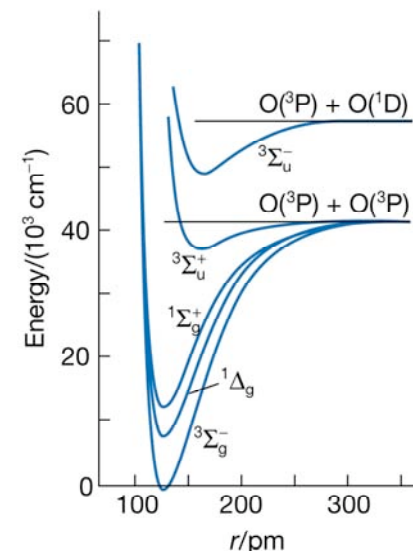
The term symbol for the ground state of any closed-shell homonuclear diatomic molecule is $^1\Sigma_g$ because the spin is zero (a singlet term in which all electrons are paired), there is no orbital angular momentum from a closed shell, and the overall parity is g.

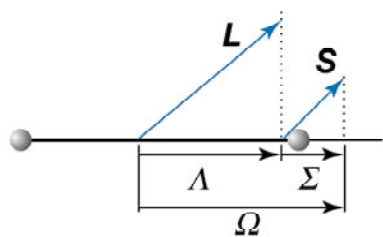
A π electron in a diatomic molecule has one unit of orbital angular momentum about the internuclear axis ($\lambda = \pm 1$) and, if it is the only electron outside a closed shell, gives a rise to a Π term. If there are two π electrons (the ground state of O_2 : $\pi_u^2 \pi_g^2 \pi_g^1 \pi_g^1$) then the term symbol may be either Σ (if the electrons are traveling in opposite directions when they occupy different π orbitals, one with $\lambda = +1$ and the other with $\lambda = -1$) or Δ (if they are traveling in the same direction when they occupy the same π orbital, both $\lambda = +1$). For O_2 , the two π electrons occupy different orbitals with parallel spins (a triplet term), so the ground term is ${}^3\Sigma$. The overall parity of the molecule is (closed shell) $\times g \times g = g$ the term symbol is ${}^3\Sigma_g^-$.



For Σ terms, a superscript + or - denotes the behavior of the molecular wavefunction under reflection in a plane containing the nuclei. O_2 has one electron in π_x , which changes sign under reflection in the yz -plane, and the other electron in π_y , which does not change sign under reflection in the same plane, so the overall symmetry is (closed shell) $\times (+) \times (-) = (-)$

and the full term symbol of the ground electronic state of O_2 is ${}^3\Sigma_g^-$.





The term symbols of excited states are constructed in a similar way. The term symbol for the excited state of O_2 formed by placing two electrons in a π_x (or in a π_y) orbital is ${}^1\Delta_g$ because $|\Lambda| = 2$ (two electrons in the same π orbital), the spin is zero (all electrons are paired), and the overall parity is (closed shell) $\times g \times g = g$.

Selection rules

The selection rules related to angular momentum:

$$\Delta\Lambda = 0, \pm 1 \quad \Delta S = 0 \quad \Delta\Sigma = 0 \quad \Delta\Omega = 0, \pm 1$$

$\Omega = \Lambda + \Sigma$ the quantum number for the total angular momentum along the internuclear axis. The origin – conservation of angular momentum.

There are two selection rules concerned with changes in symmetry:

- 1) For Σ terms, only $\Sigma^+ \leftrightarrow \Sigma^+$ and $\Sigma^- \leftrightarrow \Sigma^-$ transitions are allowed.
- 2) The **Laporte selection rule: The only allowed transitions are transitions that are accompanied by a change in parity.** $u \rightarrow g$ and $g \rightarrow u$ transitions are allowed but $g \rightarrow g$ and $u \rightarrow u$ transitions are forbidden.

A forbidden $g \rightarrow g$ transition can become allowed if the center of symmetry is eliminated by an asymmetrical vibration. A transition that derives its intensity from an asymmetrical vibration of a molecule is called a **vibronically allowed transition**.

Vibrational structure

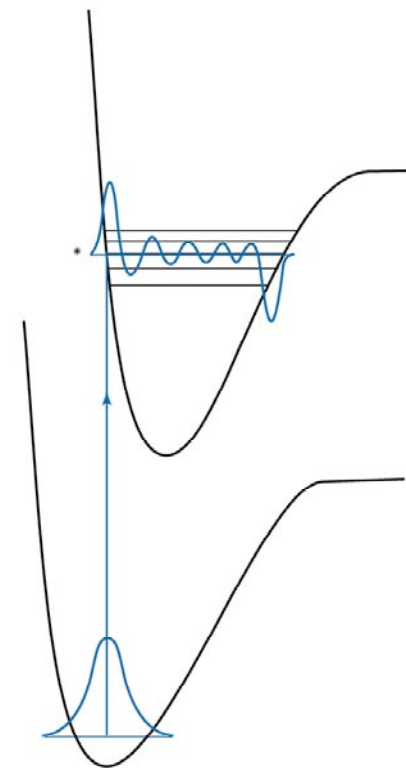
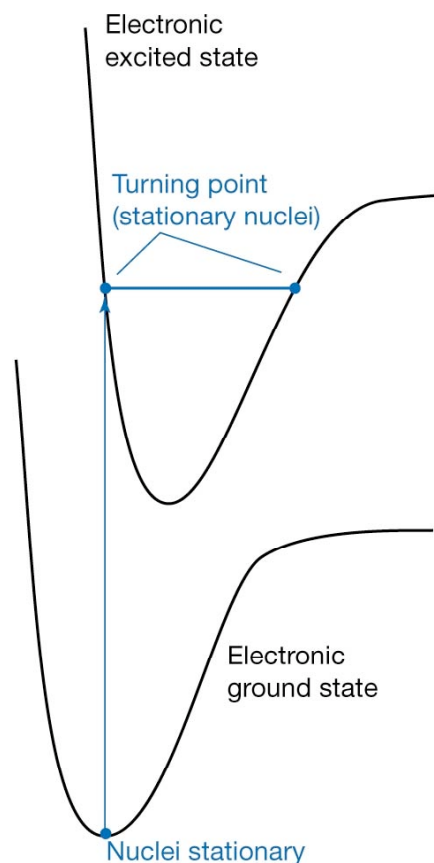
Franck-Condon principle:

Because the nuclei are so much massive than the electrons, and electronic transition takes place much faster than the nuclei can respond.

As a result of the transition, electron density is rapidly build up in new regions of the molecule and removed from the others, and the initially stationary nuclei suddenly experience a new force field. They respond to the new force by beginning to vibrate. In quantum mechanical terms: before the absorption, the molecule is in the lowest vibrational state of its lowest electronic state; the most probable location of the nuclei is at R_e . The electronic transition is most likely to take place when the nuclei have this

separation. When the transition occurs, the molecule is excited to the state represented by the upper curve. According to the Franck-Condon principle, the nuclear framework remains constant during this excitation, so we may

imagine the transition as being up the vertical line (**vertical transition**, an electronic transition that occurs without change of nuclear geometry). The vertical transition cuts through several vibrational levels of the upper electronic state. The level marked by * is the one in which the nuclei are most probably at the same initial separation R_e (because the vibrational wavefunction has maximum amplitude there).



So, this vibrational state is the most probable state for the termination of the transition. However, it is not the only accessible vibrational state because several nearby states have an appreciable probability of the nuclei being at the separation R_e . Therefore, transitions occur to all the vibrational states in this region, but most intensely to the state with a vibrational wavefunction that peaks most strongly near R_e .

The vibrational structure of the spectrum depends on the relative horizontal positions of the two potential energy curves, and a long **vibrational progression**, can be generated if the upper potential energy curve is appreciably displaced to greater equilibrium bond lengths. The upper curve is usually displaced to greater equilibrium bond lengths because electronically excited states usually have more antibonding character than electronic ground states.

The separation of the vibrational lines of an electronic absorption spectrum depends on the vibrational energies of the *upper* electronic state. Hence, electronic absorption spectra may be used to assess the force fields and dissociation energies of electronically excited molecules (by using a Birge-Sponer plot).

Rotational structure

Just as in vibrational spectroscopy, where a vibrational transition is accompanied by rotational excitation, so rotational transitions accompany the excitation of the vibrational excitation that accompanies electronic excitation. Therefore P, Q, and R branches can be seen for each vibrational transition. Electronic excitation can result in much larger changes in bond length than vibrational excitation, and the rotational branches have a more complex structure than in vibration-rotation spectra.

Suppose that the rotational constants of the electronic ground and excited states are B and B' , respectively. The rotational energy levels of the initial and final states are

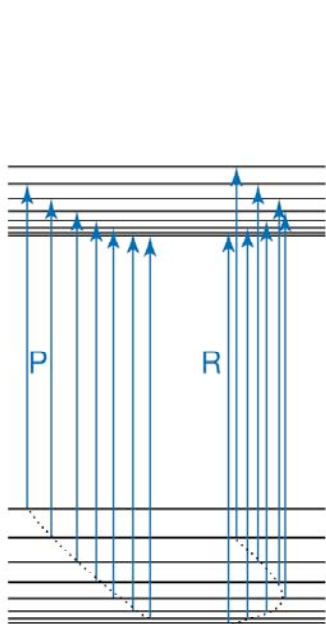
$$E(J) = hcBJ(J + 1) \qquad E(J') = hcB'J'(J' + 1)$$

and the rotational transitions occur at the following positions relative to the vibrational transition of wavenumber $\tilde{\nu}$:

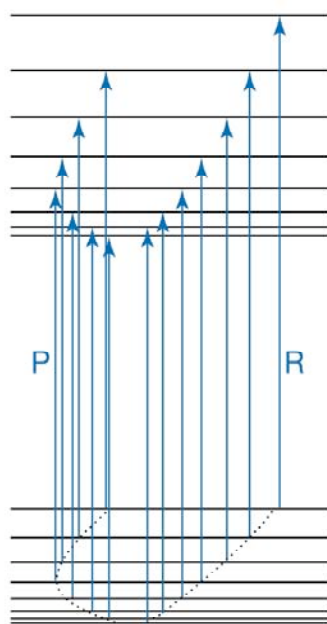
P branch ($\Delta J = -1$): $\tilde{\nu}_P(J) = \tilde{\nu} - (B' + B)J + (B' - B)J^2$

Q branch ($\Delta J = 0$): $\tilde{\nu}_Q(J) = \tilde{\nu} + (B' - B)(J + 1)$

R branch ($\Delta J = +1$): $\tilde{\nu}_R(J) = \tilde{\nu} + (B' + B)(J + 1) + (B' - B)(J + 1)^2$



(a) $B' < B$



(b) $B' > B$

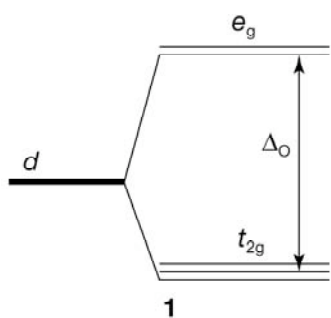
If the bond length in the electronically excited state is greater than that in the ground state, $B' < B$ and $B' - B$ is negative. In this case the lines of the R branch converge with increasing J and, when J is such that $|B' - B|(J + 1) > B' + B$, the lines start to appear at decreasing wavenumber – the R branch has a **band head**. When the bond is shorter in the excited state than in the ground state, $B' > B$ and $B' - B$ is positive. Then, the lines of the P branch begin to converge and go through a head when J is such that $(B' - B)J > B' + B$.

The electronic spectra of polyatomic molecules

The absorption of a photon can be traced to the excitation of specific types of electrons or to electrons that belong to a small group of atoms in a polyatomic molecule. For example, when a carbonyl group is present ($>C=O$), an absorption at ~ 290 nm is normally observed, but its precise location depends on the nature of the rest of the molecule. Groups with characteristic optical absorptions are called **chromophores** (Greek for ‘color bringer’).

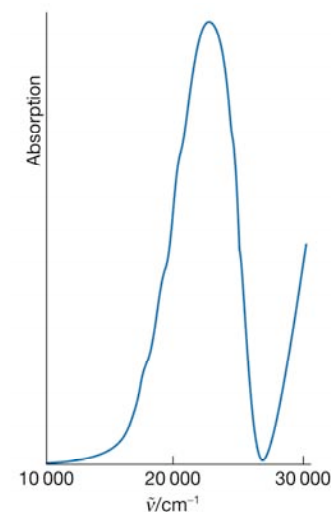
Group	$\tilde{\nu}_{\max}/\text{cm}^{-1}$	λ_{\max}/nm
C=C ($\pi^* \leftarrow \pi$)	61000	163
	57300	174
C=O ($\pi^* \leftarrow n$)	37-35000	270-290
H ₂ O ($\pi^* \leftarrow n$)	60000	167

d-d transitions



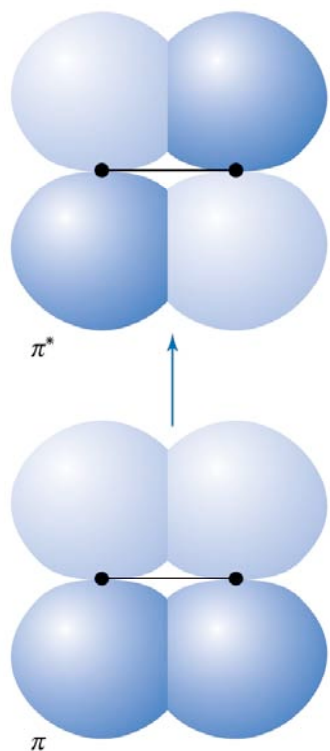
All five d orbitals of a given shell are degenerate in a free atom. In a d-metal complex, where the environment of the atom is no longer spherical, the d orbitals are not all degenerate and electrons can absorb energy by making transitions between them.

In an octahedral complex, such as $[\text{Ti}(\text{OH}_2)_6]^{3+}$, the five d orbitals of the central atom are split into two sets, a triply degenerate set t_{2g} and a doubly degenerate set e_g . The separation is not large and the transitions between the two sets of orbitals occur in the visible region of the spectrum. For $[\text{Ti}(\text{OH}_2)_6]^{3+}$, the wavenumber of the absorption maximum suggests that $\Delta_o \approx 20000 \text{ cm}^{-1}$ (about 2.4 eV). According to the Laporte rule, in octahedral complex these g-g transitions are forbidden but they are weakly allowed by asymmetrical vibrations.



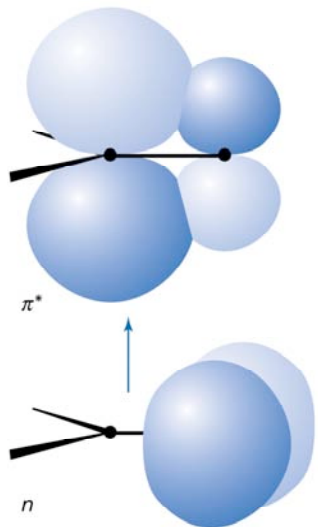
Charge-transfer transitions

A complex may absorb radiation as a result of the transfer of an electron from the ligands into the d orbitals of the central atom, or vice versa. In such **charge-transfer transitions** the electron moves through a considerable distance, which means that the transition dipole moment may be large and the absorption is correspondingly intense. This mode of chromophore activity is shown by the permanganate ion, MnO_4^- , and accounts for its intense violet color (strong absorption within 420-700 nm). In this oxoanion, the electron migrates from an orbital that is largely confined to the O atoms to an orbital that is largely confined to the Mn atom. This is an example of a **ligand-to-metal charge-transfer transition** (LMCT). The reverse migration, a **metal-to-ligand charge-transfer transition** (MLCT) can also occur.



$\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ transitions

Absorption by a C=C double bond excites a π electron into an antibonding π^* orbital. The chromophore activity is due to a $\pi^* \leftarrow \pi$ transition. Its energy is about 7 eV for an unconjugated double bond (at ~ 180 nm – in the ultraviolet). When the double bond is part of a conjugated chain, the energies of the molecular orbitals lie closer together and the $\pi^* \leftarrow \pi$ transition moves to longer wavelength; it may even lie in the visible region if the conjugated system is long enough. An important example of an $\pi^* \leftarrow \pi$ transition is related to the photochemistry of vision.



The transition responsible for absorption in carbonyl compounds can be traced to the lone pairs of electrons on the O atom (a pair of electrons in an orbital confined largely to one atom and not appreciably involved in bond formation). One of these electrons may be excited into an empty π^* orbital of the carbonyl group, which gives rise to a $\pi^* \leftarrow n$ transition. Typical absorption energies are ~ 4 eV (290 nm). Because $\pi^* \leftarrow n$ transitions in carbonyls are symmetry-forbidden, the absorptions are weak.

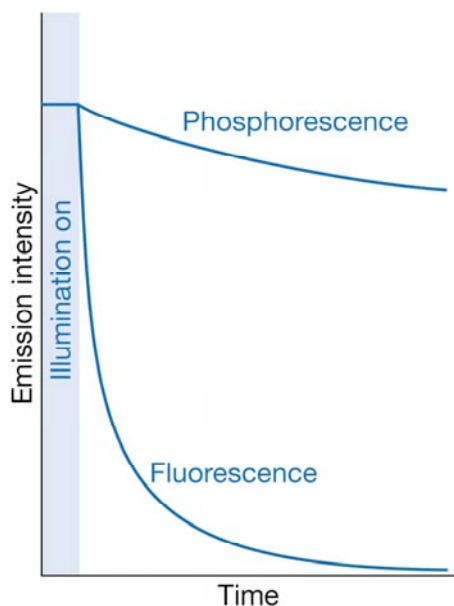
The fates of electronically excited states

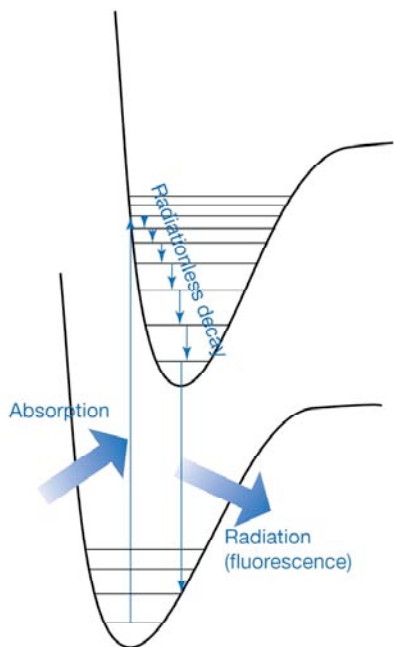
A **radiative decay process** – a molecule discards its excitation energy as a photon. A more common fate is **nonradiative decay**, in which the excess energy is transferred into the vibration, rotation and translation of the surrounding molecules. This converts the excitation energy completely into thermal motion of the environment (to heat). An excited molecule may also take part in a chemical reaction.

Fluorescence and phosphorescence

Fluorescence – spontaneous emission of radiation which occurs within a few nanoseconds after the exciting radiation is extinguished.

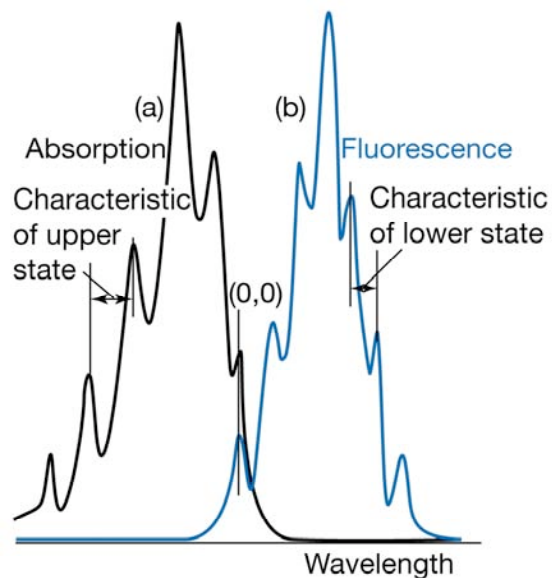
Phosphorescence – the spontaneous emission may persist for long periods (even hours, but typically seconds or fractions of seconds). The difference suggests that fluorescence is a fast conversion of absorbed radiation into re-emitted energy, but phosphorescence involves the storage of energy in reservoir from which it slowly leaks.



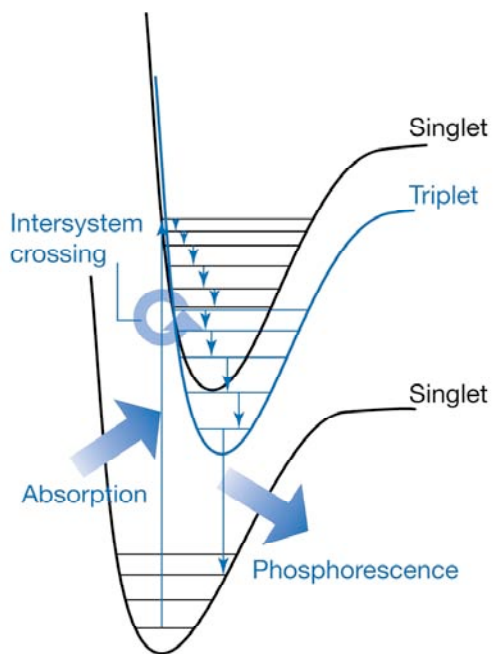


The sequence of steps involved in fluorescence: The initial absorption takes the molecule to an excited electronic state. The excited molecule is subjected to collisions with the surrounding molecules, and as it gives up energy nonradiatively it steps down the ladder of vibrational levels to the lowest vibrational level of the electronically excited molecular state. The surrounding molecules, however, might now be unable to accept the larger energy difference needed to lower the molecule to the ground electronic state.

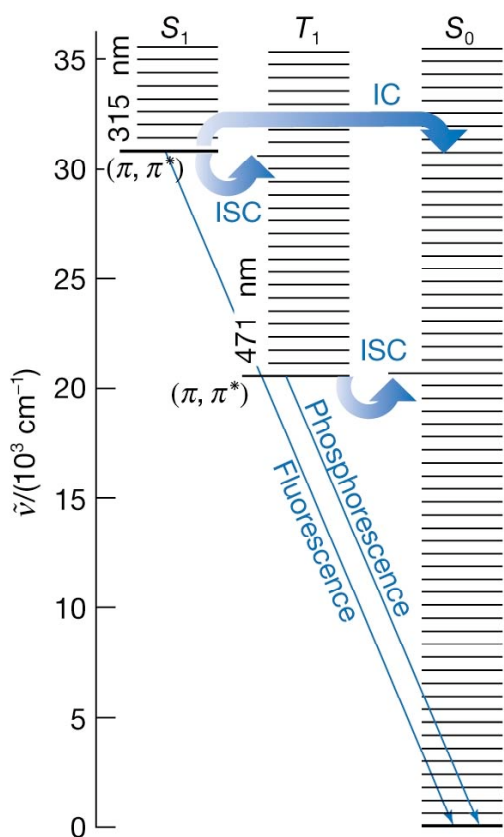
Therefore, it might survive long enough to undergo spontaneous emission and emit the remaining excess energy as radiation. The downward electronic transition is vertical (according to the Franck-Condon principle) and the fluorescence spectrum has a vibrational structure characteristic for the lower electronic state.



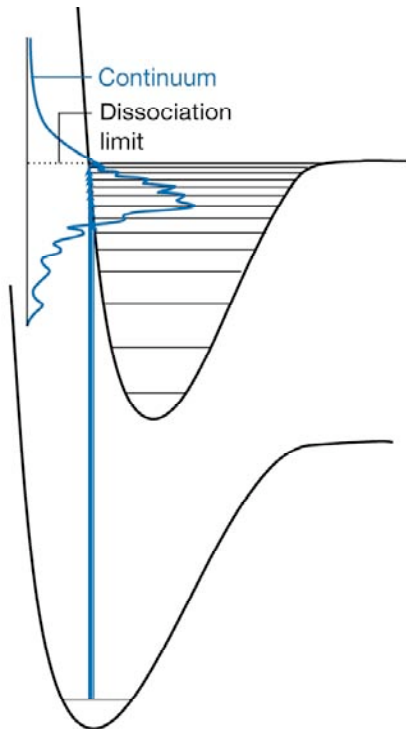
Fluorescence occurs at a lower frequency than the incident radiation because the emissive transition occurs after some vibrational energy has been discarded into the surroundings. The vivid oranges and greens of fluorescent dyes manifest this effect: they absorb in the ultraviolet and blue, and fluoresce in the visible.



Phosphorescence: the first steps are the same as in fluorescence but the presence of a triplet excited state plays a crucial role. The singlet and triplet excited states share a common geometry where their potential energy curves intersect. If there is a mechanism for unpairing two electron spins, the molecule can undergo **intersystem crossing**, a nonradiative transition between states of different multiplicity, and become a triplet state. Remember that in atoms singlet-triplet transitions may occur in the presence of spin-orbit coupling, and the same is true for molecules. We can expect intersystem crossing to be important when a molecule contains a moderately heavy atom, because then the spin-orbit coupling is large.



If an excited molecule crosses into a triplet state, it continues to deposit energy into the surroundings. It is stepping down the triplet's vibrational ladder. The solvent cannot absorb the final, large quantum of electronic excitation energy and the molecule cannot radiate its energy because the return to the ground state is spin-forbidden. However, the radiative transition is not totally forbidden because the spin-orbit coupling breaks the selection rule. The molecules are therefore able to emit weakly, and the emission may continue long after the original excited state was formed.



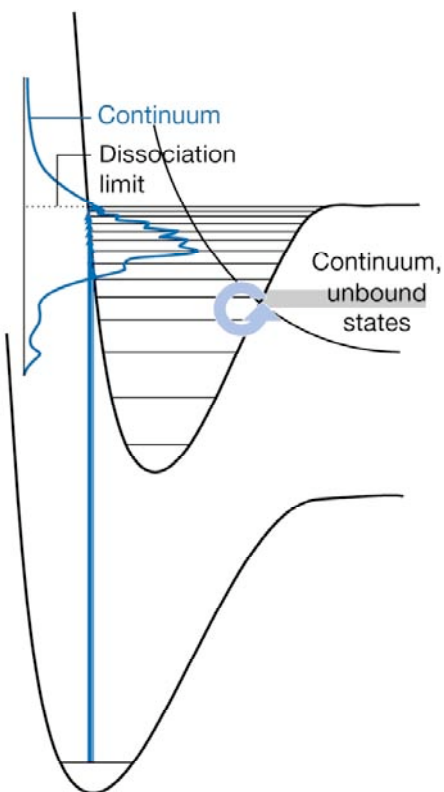
Phosphorescence should most intense from solid samples: energy transfer is then less efficient and intersystem crossing has time to occur as the singlet state steps slowly past the intersection point. The phosphorescence efficiency depends on the presence of a moderately heavy atom (with strong spin-orbit coupling).

The various types of nonradiative and radiative transitions are represented on a **Jablonski diagram**. Here nonradiative transitions include internal conversion (IC) and intersystem crossing (ISC).

Dissociation and predissociation

Another fate for an electronically excited molecule – **dissociation**. The onset of dissociation can be detected in an absorption spectrum by seeing that the vibrational structure of a band terminates at a certain energy. Absorption occurs in a continuous band above this **dissociation limit** because the final state is an unquantized translational motion of the fragments. Locating the dissociation limit – a valuable way to determine the bond dissociation energy.

Sometimes the vibrational structure disappears but then resumes at higher photon energies. This corresponds to **predissociation**. When a molecule is excited to a vibrational level, its electrons may undergo a reorganization resulting in **internal conversion**, a radiationless transition to another state of the same multiplicity.



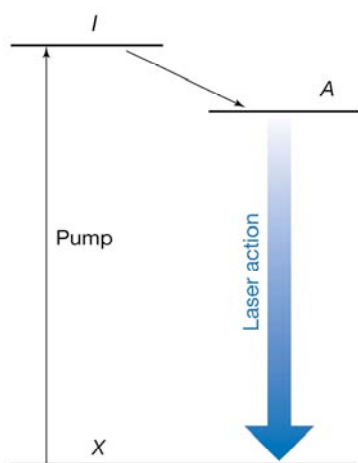
An internal conversion occurs most readily at the point of intersection of two molecular potential energy curves, because there the nuclear geometries (and energies) of the two states are the same. The state into which the molecule converts may be dissociative, so the states near the intersection have a finite lifetime, and hence their energies are imprecisely defined. As a result, the absorption spectrum is blurred in the vicinity of the intersection. When the incoming photon brings more energy and excites the molecule to a vibrational energy well above the intersection, the internal conversion does not occur and the well-defined vibrational structure resumes.

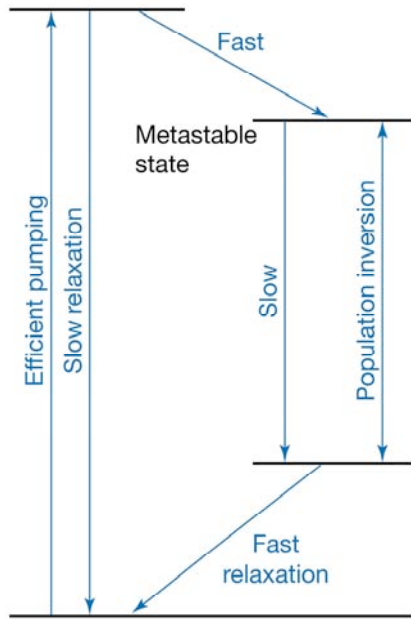
Lasers

Laser – **light amplification by stimulated emission of radiation**. In stimulated emission, an excited state is stimulated to emit a photon by radiation of the same frequency

Population inversion

One requirement of laser action – the existence of a **metastable excited state**, an excited state with a long enough lifetime for it to participate in stimulated emission. Another requirement – the existence of a greater population in the metastable state than in the lower state where the transition terminates. Because at thermal equilibrium the opposite is true, it is necessary to achieve a **population inversion** in which there are more molecules in the upper state than in the lower. For example, the molecule can be excited to an intermediate state I , which then gives up some of its energy nonradiatively and changes into a lower state A ; the laser transition is the return of A to the ground state X – a **three-level laser**. The $I \leftarrow X$ transition is stimulated with an intense flash of light (**pumping**).

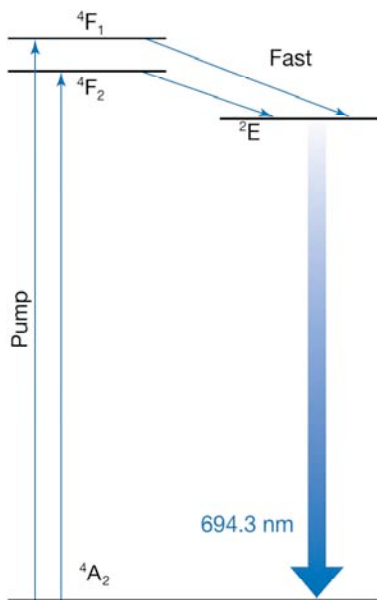


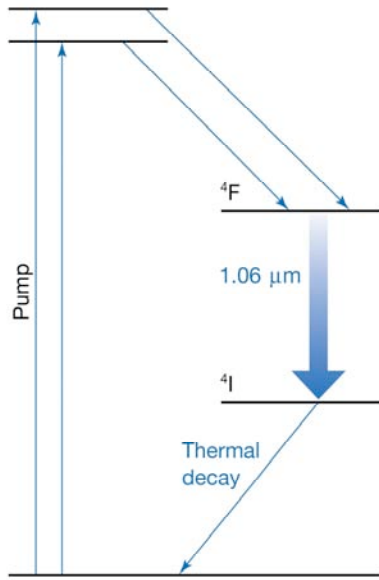


The pumping is often achieved with an electric discharge through xenon or with the light of another laser. The conversion from I to A should be rapid and the laser transition from A to X should be relatively slow. The disadvantage of the three-level arrangement – it is difficult to achieve population inversion. The arrangement in a **four-level laser** simplifies this task by having the laser transition terminate in a state A' other than the ground state. A' is unpopulated initially and so any population of A corresponds to a population inversion. This population inversion can be maintained if the $A' \rightarrow X$ transition are rapid.

Practical lasers

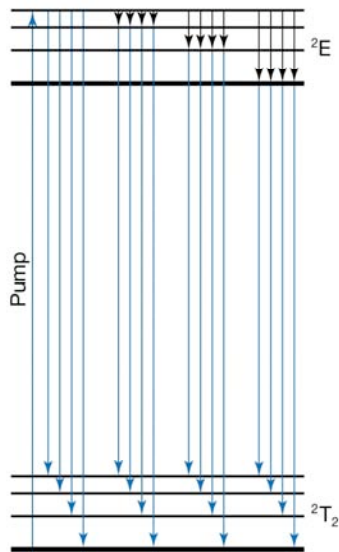
A **solid-state laser** – the active medium is in the form of a single crystal or a glass. The first successive laser is the ruby laser built by Theodore Maiman in 1960. Ruby is Al_2O_3 containing a small portion of Cr^{3+} ions. Ruby is a three-level system. The ground state is 4A_2 with three unpaired electrons on each Cr^{3+} ion. The population inversion results from pumping the majority of the Cr^{3+} ions into an excited state by using an intense flash from another source followed by a radiationless transition to another excited state 2E . The pumping flash need not be monochromatic because the upper level consists of several states spanning a band of frequencies. The $^2E \rightarrow ^4A_2$ is the laser transition – red 694 nm radiation. The population inversion is very difficult to sustain continuously, and in practice the ruby laser is pulsed.





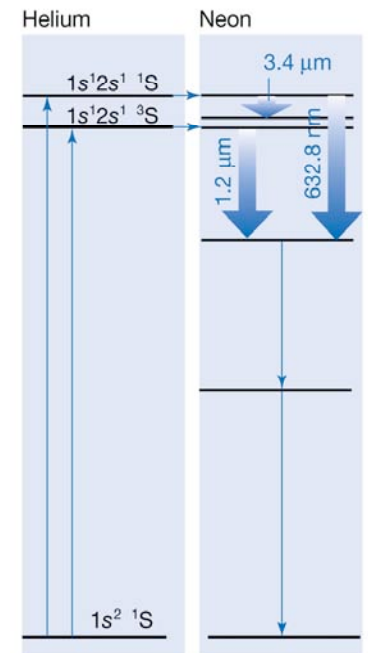
The **neodymium laser** – a four-level laser. In one form it consists of Nd^{3+} ions at low concentration in yttrium aluminum garnet (YAG, $\text{Y}_3\text{Al}_5\text{O}_{12}$) – Nd-YAG laser. A neodymium laser operates at a number wavelengths in the infrared, 1064 nm is the most common band. The transition at 1064 nm is very efficient and the laser is capable of substantial power output.

The **titanium sapphire laser** consists of Ti^{3+} ions at low concentration in a crystal sapphire (Al_2O_3). The electronic absorption spectrum of Ti^{3+} shows a broad absorption band centered at ~ 500 nm that arises from vibronically allowed d-d transitions of the Ti^{3+} ion in an octahedral environment provided by oxygen atoms of the host lattice. As a result, the emission spectrum of Ti^{3+} in sapphire is also broad and laser action occurs over a wide range of wavelengths. The titanium sapphire laser is usually pumped by another laser (Nd-YAG or an argon-ion laser), and can be operated in both continuous and pulsed modes.



Gas lasers

The pumping in gas lasers is normally achieved using a gas that is different from the gas responsible for the laser emission itself. In the **helium-neon laser** the active medium is a mixture of He and Ne (5:1). The initial step is excitation of a He atom to the metastable $1s^1 2s^1$ configuration by using an electric discharge.



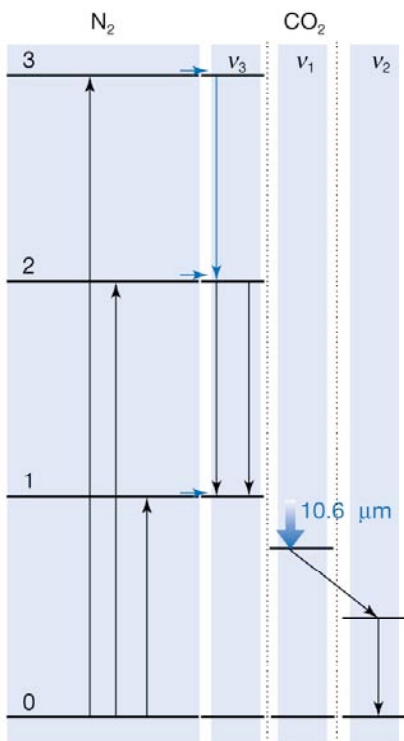
The excitation energy of this transition happens to match an excitation energy of Ne and during He-Ne collision efficient transfer of energy occurs, leading to the production of highly excited, metastable neon atoms with unpopulated intermediate states. Laser action generating 633 nm radiation (among ~100 other lines) then occurs.

The **argon-ion laser** consists of Ar at ~1 Torr, through which an electric discharge is passed. This results in formation of Ar^+ and Ar^{2+} ions in excited states, which undergo a laser transition into a lower state. The ions then revert to their ground states by emitting hard UV radiation (at 72 nm) and are then neutralized by a series of electrodes. There are many lines in the laser transition because the excited ions may make transitions to many lower states.

Two strong emissions from Ar^+ are at 488 nm (blue) and 514 nm (green); other transitions occur elsewhere in the visible region, in the infrared, and in the ultraviolet.

The **crypton laser** works similarly. It is less efficient, but gives rise to a wider range of wavelengths including 647 nm (red) and also can generate yellow, green, and violet lines. Both lasers are widely used in laser light shows and as laboratory sources of high-power radiation.

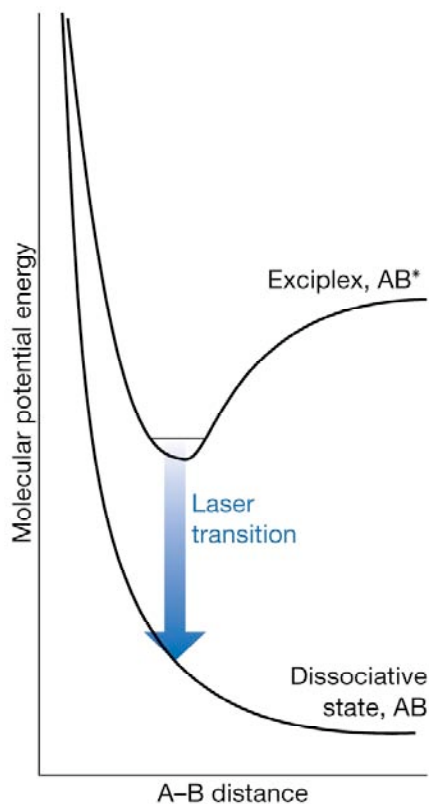
In the **carbon dioxide laser** radiation (between 9.2 and 10.8 μm , with strongest emission at 10.6 μm , in the infrared) arises from vibrational transitions. Most of the working gas is nitrogen, which becomes vibrationally excited by electronic and ionic collision in an electric discharge. The vibrational levels happen to coincide with the ladder of antisymmetric stretch (ν_3) energy levels of CO_2 , which pick up the energy during a collision.



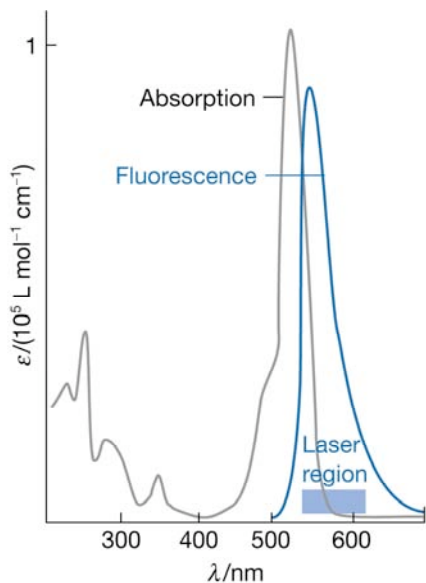
Laser action then occurs from the lowest excited level of ν_3 to the lowest excited level of the symmetric stretch (ν_1), which has remained unpopulated during the collisions. This transition is forbidden by selection rules of harmonic oscillators but is allowed by anharmonicities. Some helium is included in the gas to help to remove energy from this state and maintain the population inversion.

Chemical reactions may also be used to generate molecules with inverted populations. The photolysis of Cl_2 leads to the formation of Cl atoms that attack H_2 molecules and produce $\text{HCl} + \text{H}$. The latter then attacks Cl_2 to produce vibrationally 'hot' HCl molecules. The latter have non-equilibrium vibrational populations and laser action can result as they return to lower states.

The population inversion needed for laser action can be achieved in **exciplex lasers**, where the lower state does not effectively exist. This odd situation is achieved by forming an **exciplex**, a combination of two atoms or molecules that survives only in excited state and which dissociates as soon the excitation energy has been discarded. An example – a mixture of xenon, chlorine, and neon (the latter is a buffer gas). An electric discharge through the mixture produces excited Cl atoms, which attach to the Xe atoms to give the exciplex XeCl^* . The exciplex survives for about 10 ns, which is time for it to participate in laser action at 308 nm (in the ultra-



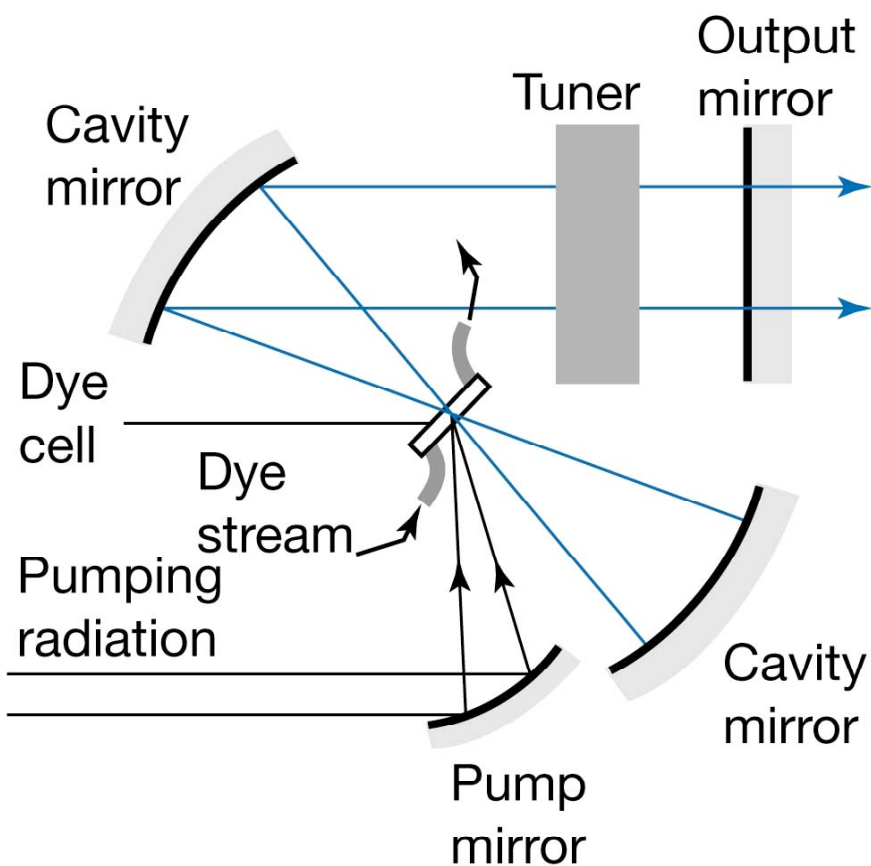
violet). As soon as XeCl^* has emitted a photon, the atoms separate because the molecular potential energy curve of the ground state is dissociative, and the ground state of the exciplex cannot become populated.



Dye lasers

Gas lasers and most solid state lasers operate at discrete frequencies and the laser cannot be tuned continuously. The tuning problem is overcome by using a titanium sapphire laser or a **dye laser**, which has broad spectral characteristics because solvent broadens the vibrational structure of the transitions into bands. Hence, it is possible to scan the wavelength continuously (by rotating the diffraction grating in the cavity) and achieve laser action at

any chosen wavelength. A commonly used dye is Rhodamine 6G in methanol. The excited states of the active medium, the dye, are sustained by another laser or a flash lamp, and the dye solution is flowed through the laser cavity to avoid thermal degradation.



Applications of lasers in chemistry have revolutionized spectroscopy and photochemistry giving rise to laser spectroscopy and laser photochemistry. They include, in particular, multiphoton spectroscopy, in which an advantage is taken of **multiphoton processes**. The large number of photons in an incident beam generated by a laser makes the photon density so high that more than one photon may be absorbed by a single molecule.

States inaccessible by conventional one-photon spectroscopy become observable because the overall transition occurs with no change of parity (or total angular momentum). For example, in one-photon spectroscopy, only $g \leftrightarrow u$ transitions are observable; in two-photon spectroscopy the $g \rightarrow g$ and $u \rightarrow u$ transitions are also allowed.

Raman spectroscopy was revitalized by the introduction of lasers. An intense excitation beam increases the intensity of scattered radiation, so the use of laser sources the sensitivity of Raman spectroscopy.

Other applications are numerous and include precision-specified transitions, state-to-state reactions dynamics, isotope separation through their selective photoionization, photodisso-ciation, or photoisomerization, time-resolved spectroscopy, etc.

Photoelectron spectroscopy

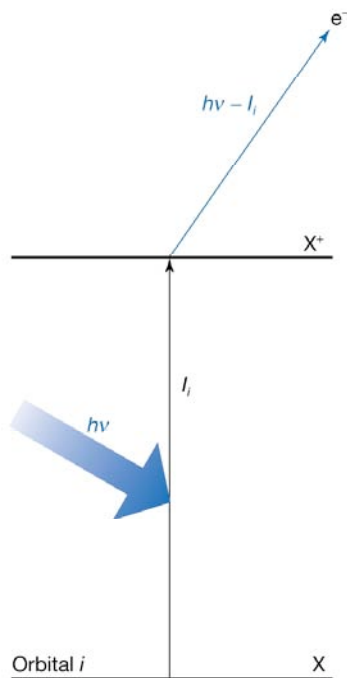
The technique of **photoelectron spectroscopy** (PES) measures the ionization energies of molecules when electrons are ejected from different orbitals, and uses information to infer the orbital energies.

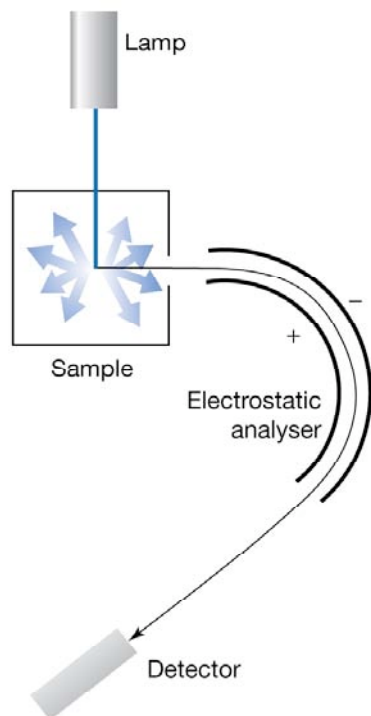
The energy is conserved when a photon ionizes a sample – the energy of the incident photon $h\nu$ must be equal to the sum of the ionization energy, I , of the sample and the kinetic energy of the **photoelectron**, the ejected electron:

$$h\nu = \frac{1}{2} m_e v^2 + I$$

Photoelectrons may originate from different orbitals with different ionization energies:

$$h\nu = \frac{1}{2} m_e v^2 + I_i$$





By measuring the kinetic energies of the photoelectrons and knowing ν , the ionization energies I_i (for the ejection of an electron from an orbital I) can be determined. Photoelectron spectra are interpreted in terms of an approximation called **Koopmans' theorem** – the ionization energy I_i is equal to the negative of the orbital energy of the ejected electron: $I_i = -\varepsilon_i$

The kinetic energy of the photoelectrons are measured using an electrostatic deflector that produces different deflections in the paths of photoelectrons as they pass between charged plates. As the field strength is increased, electrons at different speeds (and therefore kinetic energies) reach the detector. The electron flux can be recorded and plotted against kinetic energy to obtain the photoelectron spectrum.

The ejection of an electron may leave an ion in a vibrationally excited state. Then not all of the excess energy of the photon appears as kinetic energy of the photoelectron

$$h\nu = \frac{1}{2}m_e v^2 + I_i + E_{vib}^+$$

E_{vib}^+ - the energy used to excite the ion into vibration. Each vibrational quantum that is excited leads to a different kinetic energy of the photoelectron, and gives rise to the vibrational structure in the photoelectron spectrum.

The ionization energies of molecules are in the range of several eV even for valence electrons – it is necessary to work in at least the UV region of the spectrum at wavelength of less than ~ 200 nm. Much work has been done with radiation from a discharge through helium: the He(I) line ($1s^1 2p^1 \rightarrow 1s^2$) lies at 58.43 nm (a photon energy of 21.22 eV) – **ultraviolet photoelectron spectroscopy (UPS)**.

When core electrons are being studied, photons of even higher energies are needed to expel them: X-rays are used – the technique is denoted as XPS. A modern version of PES – uses synchrotron radiation, which may be continuously tuned between UV and X-ray energies.

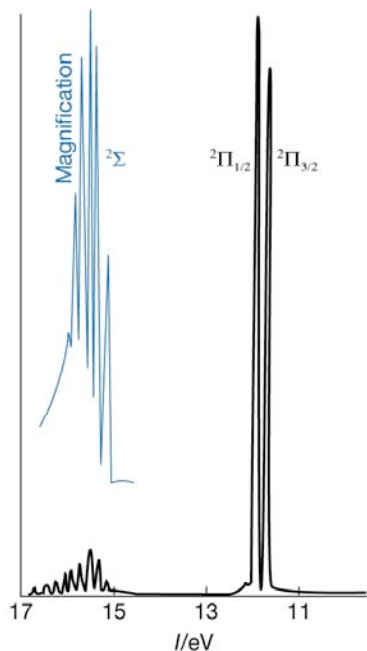
Example: photoelectrons ejected from N₂ with He(I) radiation had kinetic energies of 5.63 eV. Helium(I) radiation of wavelength 58.43 nm has wavenumber $1.711 \times 10^5 \text{ cm}^{-1}$ and therefore corresponds to an energy of 21.22 eV. Then, we have

$$21.22 \text{ eV} = 5.63 \text{ eV} + I_i \qquad I_i = 15.59 \text{ eV}$$

This ionization energy is the energy needed to remove an electron from the HOMO of the N₂ molecule, the $3\sigma_g$ bonding orbital.

Ultraviolet photoelectron spectroscopy

Consider a typical photoelectron spectrum of HBr. If we disregard the fine structure, the lines fall into two groups. The least tightly bound electrons (with the lowest ionization energies and hence highest kinetic energies when ejected) are those in the nonbonding lone pairs of Br ($I = 11.8 \text{ eV}$). The next ionization energy lies at 15.2 eV and corresponds to the removal of an electron from the H-Br σ bond. Ejection of a σ electron is accompanied by a long vibrational progression. The Franck-Condon principle would account for this progression if ejection were accompanied by an appreciable change of equilibrium bond length between HBr and HBr⁺ because the ion is formed in a bond-compressed state, which is consistent with the important bonding effect of the σ electrons. The lack of much vibrational structure in the two $^2\Pi$ bands is consistent with the nonbonding role of the Br $4p\pi$ lone pair of electrons – the equilibrium bond length is little changed when one is removed.



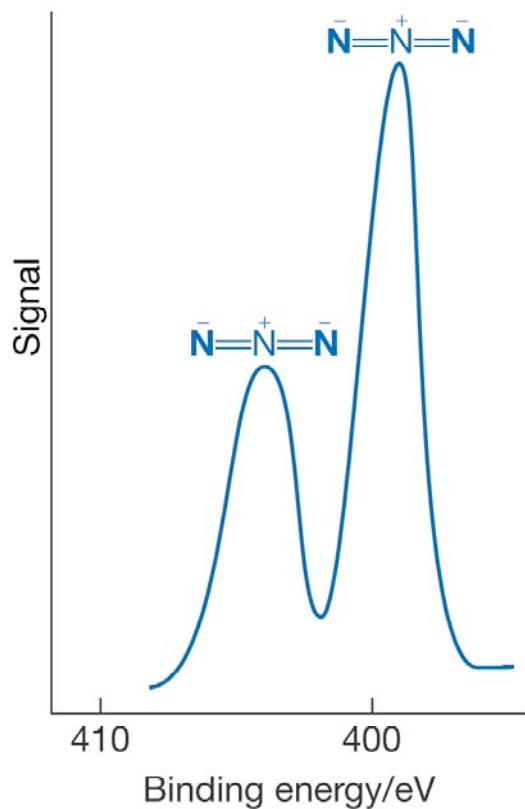
X-ray photoelectron spectroscopy

In XPS, the energy of the incident photon is so great that electrons are ejected from inner core of atoms. As a first approximation, core ionization energies are insensitive to the bonds between atoms because they are too tightly bound to be greatly affected by bond formation – core ionization energies are characteristic of the individual atom rather than the overall molecule. Consequently, XPS gives lines characteristic of the elements present in a compound or an alloy. *K*-shell ionization energies (in eV) of the second-row elements are

Li	Be	B	C	N	O	F
50	110	190	280	400	530	690

Detection of one of these values indicates the presence of the corresponding element – **electron spectroscopy for chemical analysis (ESCA)**.

The technique is mainly limited to the study of surfaces layers because, even though X-rays may penetrate into the bulk sample, the ejected electrons cannot escape except from within a few nm of the surface – the technique is very useful for studying the surface state of heterogeneous catalysts, the difference between surface and bulk structures.



Core ionization energies are slightly affected by bond formation – small but detectable shifts can be detected and interpreted in terms of the environments of the atoms. Consider, for example, the spectrum of the azide ion N_3^- . Although the spectrum lies in the region of 400 eV (typical of N1s electrons), it has a doublet structure with splitting 6 eV. This can be understood by noting that the structure of the ion is $\text{N}=\text{N}=\text{N}$, with more negative charge on the outer two N atoms than on the inner: the formal charges are (-1, +1, -1). The presence of the negative charges on the terminal atoms lowers the core ionization energies, whereas the positive charge on the central atom raises it. The inequivalence of the atoms results in two lines in the spectrum with intensities in the ratio 2:1. Observations like this can be used to obtain valuable information about the presence of chemically inequivalent atoms of the same element.