

Part 6. Electronic Spectroscopy

Electrons are the “glue” that hold molecules together, so the importance of electronic transitions cannot be overestimated.

Relatively simple (and quite accurate) expressions can be developed for the quantum mechanical translational, rotational, and vibrational energies of molecules. Unfortunately, simple expressions for molecular electronic energy levels are not available in most cases. We will have to make do with the qualitative features of electronic transitions.

The energies required to change the electron distributions in molecules are typically several electron volts (1 eV is about 8000 cm^{-1} or 100 kJ mol^{-1}). This places the photons emitted or absorbed in electronic transitions in the visible or ultraviolet region of the electromagnetic spectrum.

Important electronic transitions include spontaneous radiative decay processes (fluorescence and phosphorescence), stimulated radiative decay (the basis for the operations of lasers), ionization, bond dissociation and formation (*this is chemistry!*), and molecular dynamics.

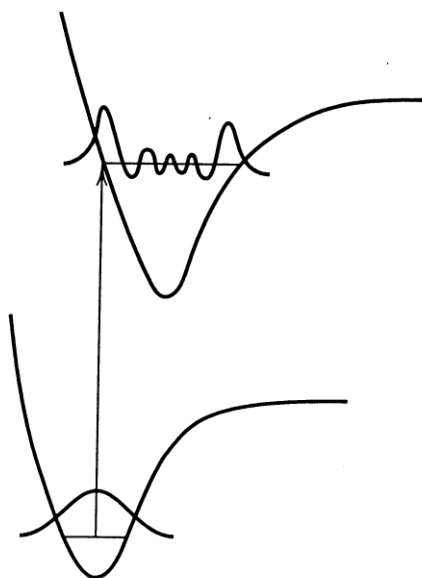
Frank-Condon Principle

Electrons in molecules move very rapidly. Typical electron speeds are a few per cent of the speed of light. Nuclei, which are thousands of times more massive, move thousands of times more slowly. Electronic transitions can therefore be considered instantaneous because they occur within a nuclear framework that can be considered stationary. This feature is called the **Frank-Condon Principle**.

When an electronic transition occurs, electron density builds up rapidly in one part of a molecule and decreases rapidly in another part of the molecule, causing a sudden change in the forces acting on the nuclei. The nuclei respond by starting to vibrate to and fro, starting from their initial separation which was maintained during the rapid electronic transition.

The consequences of the Franck-Condon principle are important and can be developed in considerable detail. In the simplest case, a molecule initially in its ground vibrational state and ground electronic state absorbs a photon and is “instantaneously” converted to an excited electronic state. Changes in rotational energies are ignored because they are relatively small.

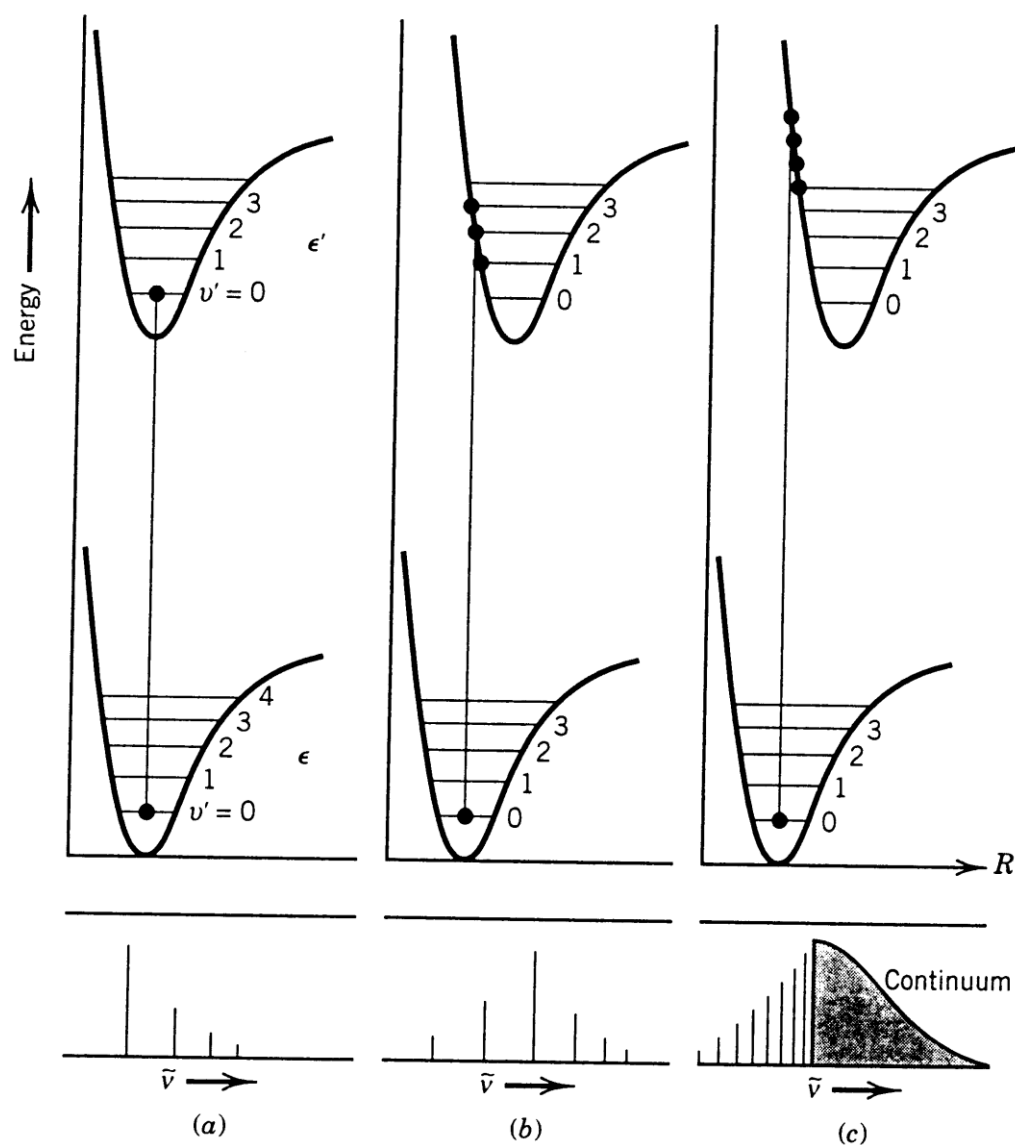
The most probable location of the nuclei is at their equilibrium separation. According to the Franck-Condon principle, the nuclear positions remain fixed during an electronic excitation. The transition can be interpreted as occurring “vertically” (*i.e.*, fixed R) in the energy diagram connecting the initial ground state and the excited state.



The overlap of the ground vibrational wavefunction in the lower electronic state and the vibrational wavefunctions for the various excited states is greatest for the vibrational level whose classical turning point is at the equilibrium separation in the lower state.

Using MO theory, the initial and final states can be predicted. Three cases are generally observed:

- a) In rare cases, the minimum in the potential energy of the ground state coincides with the minimum in the potential energy of the excited state.
- b) More usually, bonding in the excited molecule is weaker, so the minimum in the potential energy shifts to a larger bond length. In this case, the electronically excited molecule is raised to an excited vibrational level.
- c) Absorption of a photon with sufficient energy can raise the molecule to an unbound excited state with a dissociated bond. A continuous spectrum is observed when the energy of the incident photon equals or exceeds the dissociation energy, providing a spectroscopic technique for the measurement of bond strengths.



Selection Rules for Electronic Transitions

The selection rules for electronic transitions in molecules are quite complicated. For diatomic molecules consisting of “light” ($Z < 40$) atoms, the following selection rules apply:

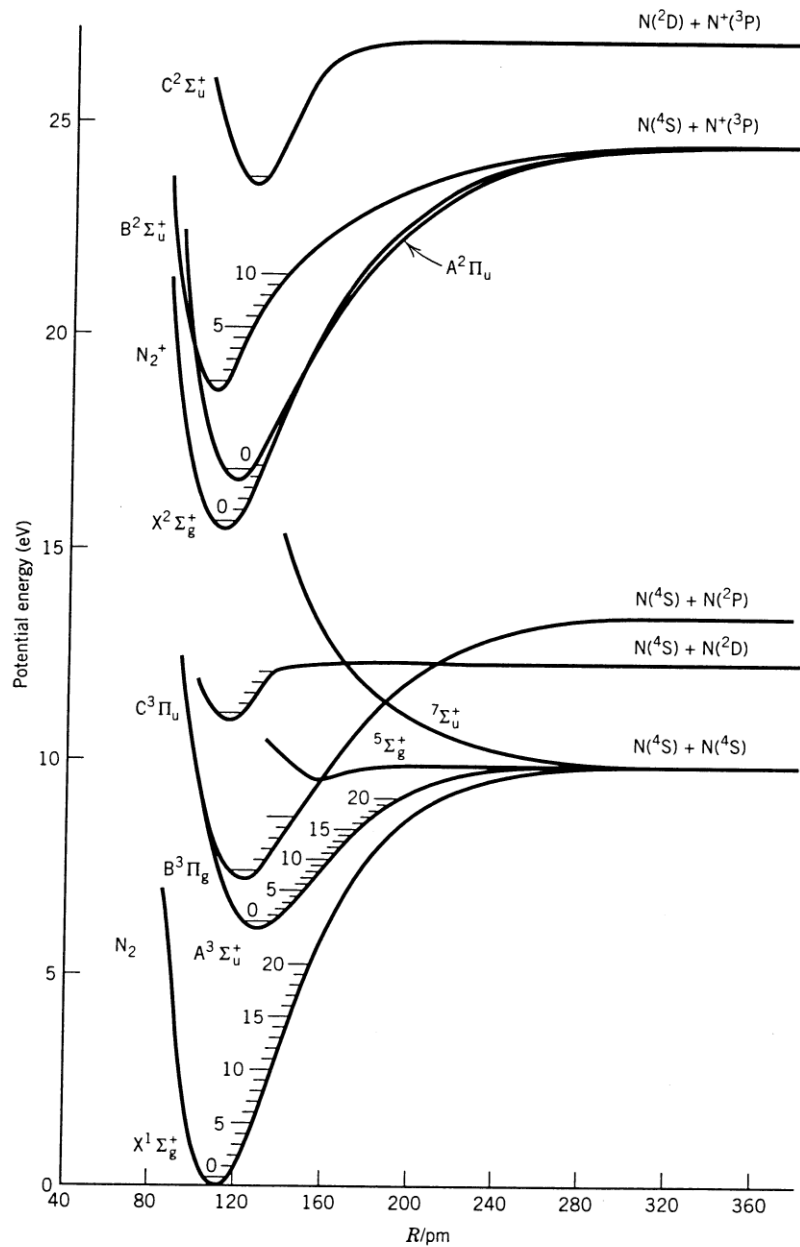
- 1. $\Delta M_L = 0, \pm 1$** for the quantum number for the orbital angular momentum along the z axis. Electronic states for $L = 0, 1, 2, 3, \dots$ are designated by $\Sigma, \Pi, \Delta, \Phi, \dots$. Transitions such as $\Sigma \leftrightarrow \Sigma, \Pi \leftrightarrow \Sigma, \Delta \leftrightarrow \Pi$ are allowed. Transitions such as $\Delta \leftrightarrow \Sigma, \Pi \leftrightarrow \Phi, \Sigma \leftrightarrow \Phi$ are forbidden.
- 2. $\Delta S = 0$** for the spin quantum number. Singlet \leftrightarrow singlet and triplet \leftrightarrow triplet transitions are allowed, but not singlet \leftrightarrow triplet transitions.
- 3. $\Delta M_S = 0$** for the spin quantum number along the z axis.
- 4. $\Delta \Omega = 0, \pm 1$** for the quantum number for the total (spin + orbital) angular momentum along the bond axis (z axis).

Forbidden transitions occur, but they are usually several orders of magnitude weaker than allowed transitions.

Spectra for low-pressure gas-phase samples can often be analyzed completely. At high pressures, collisions broaden the lines. For samples in liquid solutions, collisions with solvent molecules produce smooth, continuous spectra and obscuring the large number of lines that may be present.

In addition to the term symbols, the electronic states of molecules are given letter symbols. The ground electronic state is labeled “X”. Excited states of the same multiplicity are designated by A, B, C, ... Excited states of different multiplicity are labeled a, b, c, ...

Potential Energy Diagram for N_2 and N_2^+



Specific Kinds of Electronic Transitions

The absorption of photons involved in electronic transitions can often be traced to the excitation of electrons around a few groups of atoms or to electrons in a particular bond. Carbonyl (-C=O) groups, for example, have an electronic transition that absorbs photons with wavelengths of about 290 nm photons (uv blockers!). Groups of atoms with characteristic optical absorptions are called **chromophores** (Greek for “**color bringers**”).

d-d Transitions All five d orbitals are degenerate (have equal energy) for free atoms. In a d-metal complex such as $\text{Ti(OH}_2\text{)}^{3+}$, the environment of the central atom is no longer spherical, which removes the degeneracy. This is called **ligand field splitting**. Electronic transitions between the split d-levels produces many optical absorbances that are responsible for the intense colors of many d-metal complexes.

Charge Transfer Transitions The absorption of radiation by a complex can provide enough energy to excite electrons from the ligands into the d orbitals of the central metal atom. In these charge-transfer transitions, the excited electron can move large distances, producing relatively large dipole transition moments and intense absorptions. The intense purple color of aqueous permanganate ions (MnO_4^-), for example, is a consequence of charge transfer transitions in the 400 to 700 nm range. In this case, the electron migrates from orbitals centered on an oxygen atom to an orbital that is largely confined on the Mn atom. This is an example of a ligand-to-metal charge transfer reaction. The reverse migration, metal-to-ligand charge transfer reactions are also well known.

π to π^* and n to π^* Transitions Absorption of photons by a C=C double bond can excite a π electron into an antibonding π^* orbital. The energy change for an unconjugated double bond is about 7 eV, which corresponds to an absorption at 180 nm. For double bonds that are part of conjugated chains, the energies of the molecular orbitals are closer together (*why?*) and the π to π^* transitions shift to lower energy which can lie in the visible spectrum for sufficiently long conjugated chains.

An important example of ***π to π^* transitions*** is provided by the photochemical mechanism of vision. The retina of eyes contains “visual purple”, a protein bound to the conjugated 11-*cis*-retinal molecule. The conjugated bonds allow the *cis*-retinal

chromophore to absorb over most of the visual spectrum. In its electronically excited state, the conjugated chain has enough energy to isomerize to form the 11-*trans*-retinal chain, triggering a nerve impulse to the brain.

The transition responsible for the absorption by carbonyl groups ($-\text{C}=\text{O}$) can be traced to electrons in the lone pairs of the oxygen atom that are not involved in bonding to the carbon atom. One of these electrons is excited into an empty non-bonding π^* orbital (called a **n to π^* transition**) by radiation with a wavelength of about 290 nm (4 eV).

Fates of Excited Electronic States

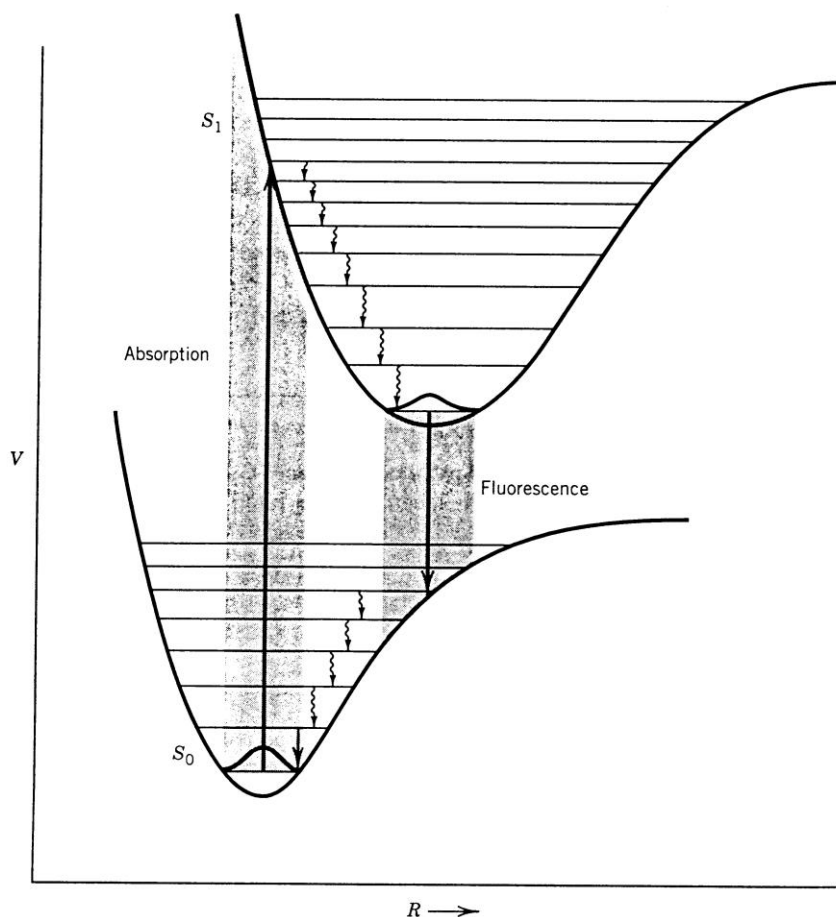
A **radiative decay process** occurs when an atom or molecule gets rid of excitation energy by emitting a photon. For molecules, a more common fate is nonradiative decay in which excess energy is transferred into vibration, translation, and rotation degrees of freedom by collisions with other molecules. **Nonradiative processes** convert excitation energy into “heat”, the thermal motions of surrounding molecules. An excited molecule can also shed energy by taking part in a chemical reaction.

Fluorescence In fluorescence, radiation is emitted during a transition between states of the same spin multiplicity.

The first step is the absorption of a photon by a ground-state molecule. In most cases, this means exciting a ground-state singlet state to an excited electronic singlet state. The molecule is also in an excited vibrational state. Collisions with other molecules remove vibrational energy nonradiatively (called “vibrational relaxation”), lowering the electronically excited molecule to its lowest vibrational state. When the excited molecule radiates (fluoresces), the frequency of the emitted photon is lower than that of the photon that initially excited the molecule.

The lifetimes of the excited states are typically microseconds to nanoseconds, so the emitted radiation stops almost immediately when the excited radiation is turned off.

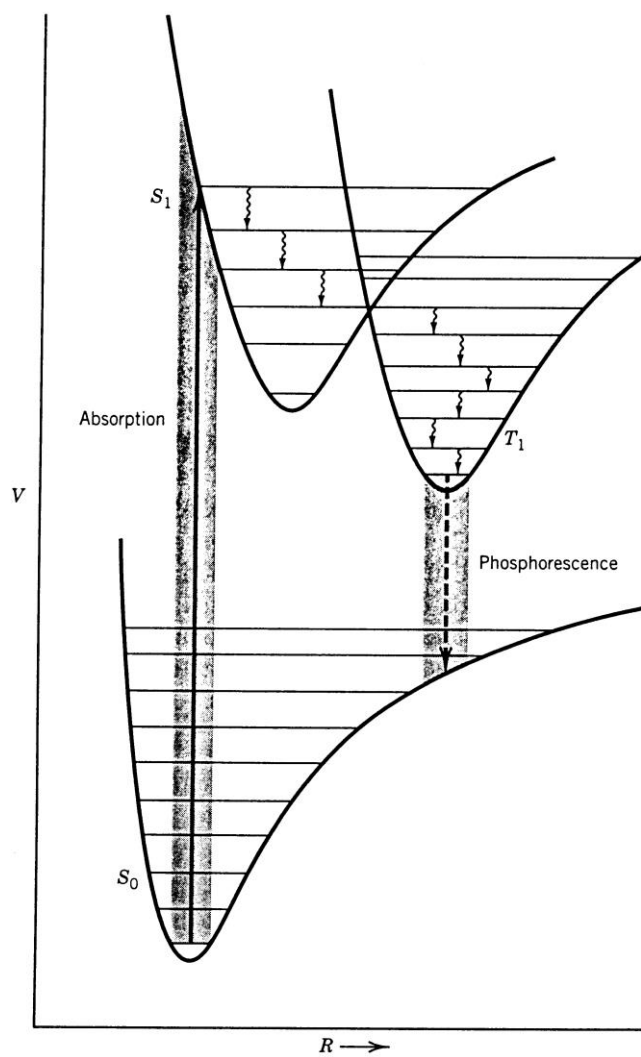
Fluorescence



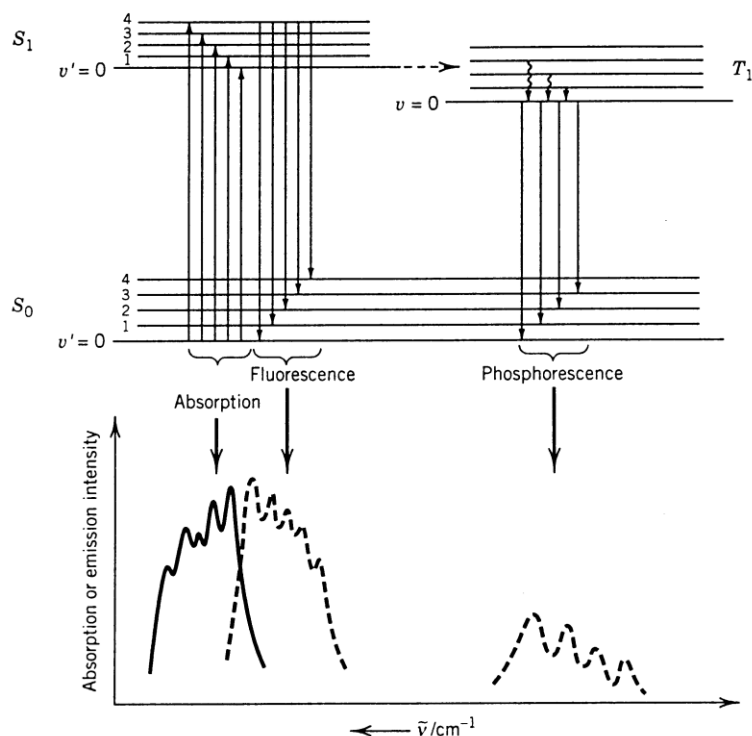
Phosphorescence Before a molecule can fluoresce, other processes can occur. For example, the molecule can react chemically, it can lose energy in collisions with other molecules, or undergo a transition to another excited state. Nonradiative transitions to states with the same multiplicity are called **internal conversion**.

Nonradiative transitions between states of different multiplicity are called **intersystem crossing**. An electron spin flip is required, usually provided by spin-orbit coupling. Intersystem crossing can convert excited singlet states to excited triplet states. An excited triplet state can emit a photon and drop to the ground singlet state, but transition is forbidden and therefore occurs very slowly. For this reason, excited triplet states are often called “metastable” states. Triplet states are important in chemical reactions because of their high energy and long lifetime (even hours).

Phosphorescence



Fluorescence and Phosphorescence Spectra



Lasers

A light beam passing through an absorbing medium generally loses intensity. But if molecules are present in a suitable excited state, **stimulated emission** can occur to make the light beam more intense. Lasers operate by this mechanism. The word laser is an acronym for **l**ight **a**mplification and **s**timulated **e**mission.

Stimulated emission is a quantum mechanical effect. It occurs when an excited atom or molecule is stimulated by a photon to emit a photon of the same frequency. This is a positive feedback mechanism: the more photons present, the higher the probability of emission. In addition to amplifying the intensity, the generated light is **coherent**, which means the waves are in phase and therefore constructively interfere.

Applications: Lasers represent one of the most important practical applications of electronic transitions. They are used in high-speed high-capacity communications using optical fibers, surveying, weapons (range finding and target designation), bar-code scanners, metal cutting, sources amplifiers, surgery, CD readers and writers for data storage, laser pointers, ... Lasers have revolutionized spectroscopy by providing high intensity, nearly monochromatic radiation, some of which can provide ultra-short pulses (down to femtoseconds) for studies of atomic and molecular dynamics.

Two-Level Systems Won't Work! When a two-state system consisting of molecules in ground state 1 with excited state 2 is irradiated, the rate of change of the number of molecules in the excited state, ignoring small contributions from spontaneous emission, is

$$\frac{dN_2}{dt} = B\rho(\nu)(N_1 - N_2)$$

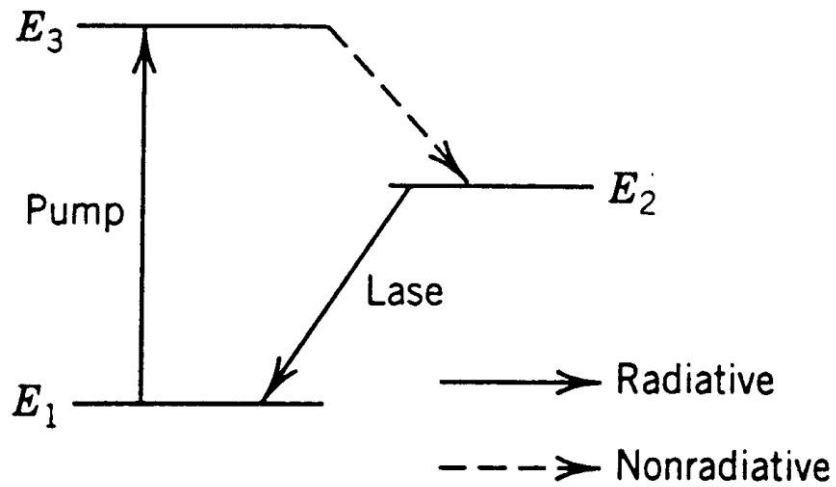
B is the Einstein coefficient and $\rho(\nu)$ is the energy density of radiation at frequency ν . As long as there are more molecules in the ground state than in the excited state ($N_1 > N_2$), absorption occurs. As irradiation continues, N_2 eventually equals N_1 , and the net absorption at frequency ν drops to zero. The transition is said to be saturated.

If it could be somehow arranged to have more molecules in the excited state, which is known as a **population inversion** ($N_2 > N_1$), then dN_2/dt would be negative and stimulated emission would increase the number of emitted photons. In other words, the incident radiation would be amplified and the additional radiation would be generated coherently.

Laser radiation requires a population inversion. Unfortunately, population inversions cannot be generated by irradiating two-level systems.

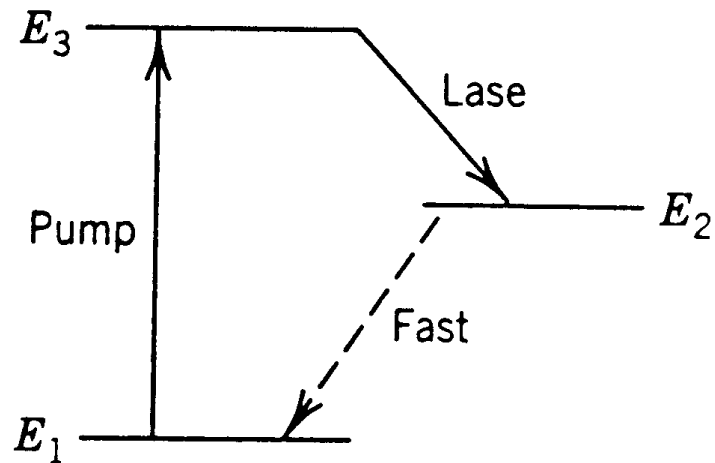
Three-Level Laser Systems Population inversions can be generated in multi-level systems. Three level systems are the simplest cases. In the scheme sketched below, molecules are raised from ground state E_1 to excited state E_3 , usually by absorption of a flash of "pump" radiation. Molecules in state E_3 then undergo a nonradiative transition to state E_2 . If the system can be pumped hard enough to maintain $N_2 > N_1$, then lasing action occurs for the transition $E_2 \rightarrow E_1$.

3-Level Laser (Case A)



The following is a more efficient three-level laser design.

3-Level Laser (Case B)

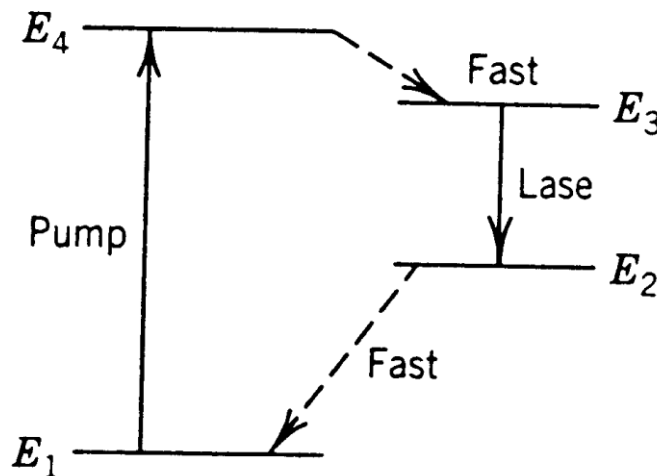


As before, pump radiation raised molecules from ground state E_1 to excited state E_3 , but now laser action occurs in the transition from E_3 to excited state E_2 , which requires

$N_3 > N_2$. This population inversion is readily achieved because N_2 , the number of molecules in excited state 2, is initially zero. (The previous three-level laser system, in contrast, requires $N_2 > N_1$, and significant numbers of molecules are always in the ground state, $N_1 > 0$.)

Four-Level Laser Systems A number of lasers employ four level systems. In one particularly efficient design, the lasing action occurs between two levels that are not involved in the pumping process.

4-Level Laser



Resonance Cavities The intensity of laser radiation is increased substantially by placing partially-reflecting mirrors on the ends of the laser cavity. Light reflected back and forth along the axis of the cavity will interfere constructively and build in intensity if the length of the cavity, L , is an integer multiple of one half of the wavelength of the light.

$$L = i\lambda/2 \quad i = 1, 2, 3, \dots$$

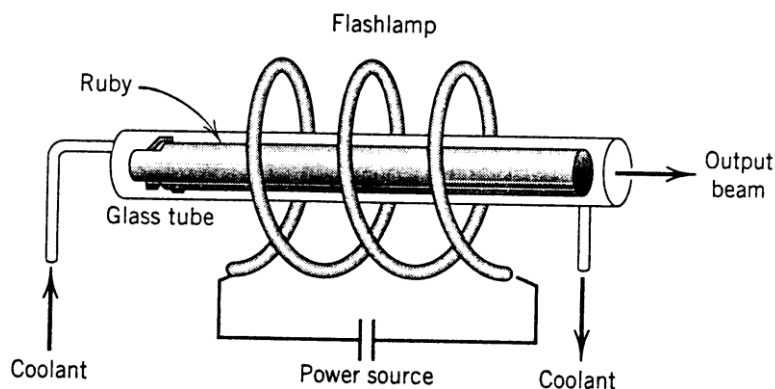
in which case a **resonant cavity** is produced. This arrangement is analogous to a “particle in a box” system, with photons acting as the particles.

Practical Lasers

Solid-State Lasers

The first successful laser, a **ruby laser** built in 1960, is an example of a solid-state laser. Ruby is aluminum oxide containing small amounts of dissolved Cr^{3+} ions (a solid solution!) that provide the intense red color. The ruby laser operates as a three-level system (type A). An intense flash of light from lamp pumps ground-state Cr^{3+} ions into an excited state, followed by a radiationless transition to a lower-energy excited state. The transition from the lower-energy excited state to the ground state provides laser radiation at 694 nm.

Solid-State Ruby Laser Pumped by a Flash Lamp



Because this system is relatively inefficient, continuous lasing is difficult in practice. Typical ruby lasers generate 10 ns pulses containing about 2 J of radiation (corresponding to a power of 200 megawatts).

A **neodymium laser** is an example of a four-level laser. One design employs Nd^{3+} ions dissolved in yttrium aluminum garnet (YAG). Neodymium lasers operate at several frequencies in the infrared. The transition at 1064 nm is most efficient.

Gas Lasers

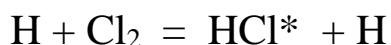
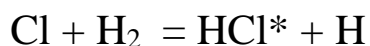
Gas lasers can be efficiently cooled by circulating the gas through the laser cavity and a heat exchanger. This feature allows very high laser powers to be generated.

In the **helium-neon laser**, the gas is a mixture of helium and neon in a mole ratio of about 5:1. An electrical discharge through the gas excites He atoms from the $1s^2$ ground state to the $1s^1 2s^1$ excited electronic state. During collisions between Ne and excited He atoms, energy is transferred to Ne atoms, producing highly excited Ne atoms with unpopulated intermediate states (good for laser action!). Most of the laser radiation is produced at 633 nm. About 100 other wavelengths are also generated.

The **argon-ion laser** is one example of the class of “ion lasers”. An electrical discharge is used to generate excited-state Ar^+ and Ar^{2+} ions, which undergo laser transitions to lower-energy states, followed by a transition in the ultraviolet to reach the ground state. The strongest emissions from an argon-ion laser are at 488 nm (blue) and 514 nm (green). The operation of the krypton-ion laser is similar. It is less efficient, but generates a wider range of wavelengths. The most intense line is at 647 nm (red). Argon-ion and krypton-ion lasers are widely used in research and in laser light shows.

Chemical Lasers

Chemical reactions can be used to generate population inversions. For example, the photolysis of Cl_2 molecules leads to the formation of excited Cl atoms which attack H_2 molecules, producing H atoms and vibrationally excited (“hot”) HCl^* molecules. The H atoms then attack Cl_2 molecules to produce additional excited HCl molecules with population inversions suitable for lasing.



Laser action results from the radiation emitted by the excited HCl molecules. Other **chemical lasers** employ excited XeCl and KrF molecules. Chemical lasers are interesting because chemical energy is converted to laser radiation.

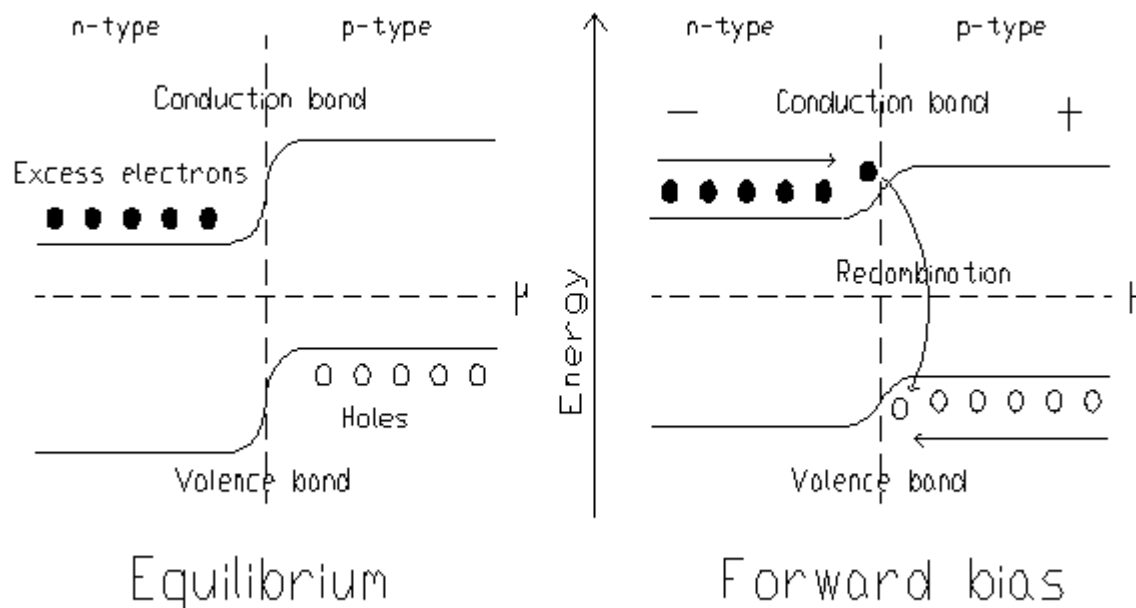
Tunable Dye Lasers

Solid-state, gas, and chemical lasers operate at discrete frequencies. **Dye lasers** are useful in practice because radiation is generated over a range of wavelengths. This is accomplished by excited states of a dye dissolved in a liquid (*e.g.*, Rhodamine 6G in methanol). A flash lamp is used to excite the dye. In this case, the transitions of the dye are broadened by the solvent, turning discrete line spectra into continuous bands which can be tuned over a range of wavelengths by rotating a diffraction grating.

Semiconductor Lasers

A semiconductor is classified as “n-type” if its conduction band is partially populated with electrons, and as “p-type” if its valence band has a small number of “holes” (missing electrons). For laser operation, an electric potential difference is applied across a junction between p-type and n-type semiconductors to inject electrons from the conduction band in the n-type semiconductor into the p-type semiconductor, where they fall into the holes in the valence band, releasing laser radiation. Gallium arsenide semiconductor lasers are very widely used as rugged and relatively inexpensive sources of red light (830 nm).

Semiconductor Laser Mechanism



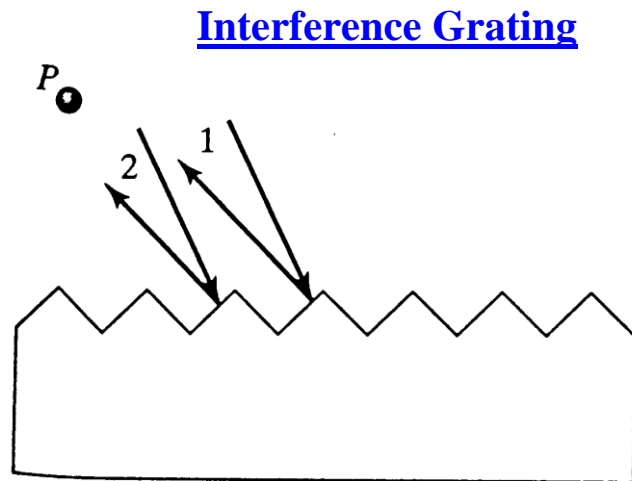
Light emitting diodes emit light by the same mechanism. Light-emitting diodes, however, lack resonant cavities and stimulated emission and therefore not lasers.

Fourier Transform Spectroscopy

Most spectrometers contain four essential elements:

- a radiation source (tungsten filament, mercury arc, tunable laser, *etc.*)
- a sample cell
- a dispersing element (usually a prism or a diffraction grating)
- a detector

In a typical absorption measurement, radiation from the sample cell is dispersed into its component wavelengths by a prism or **diffraction grating**.



Grooves cut in the grating material reflect the incident radiation. The path lengths traveled by waves 1 and 2 to reach point P are not the same. In this case, wave 1 must travel a longer distance, so interference patterns develop. Constructive interference at certain angles and wavelengths allows radiation at a selected wavelength to be directed into the detector.

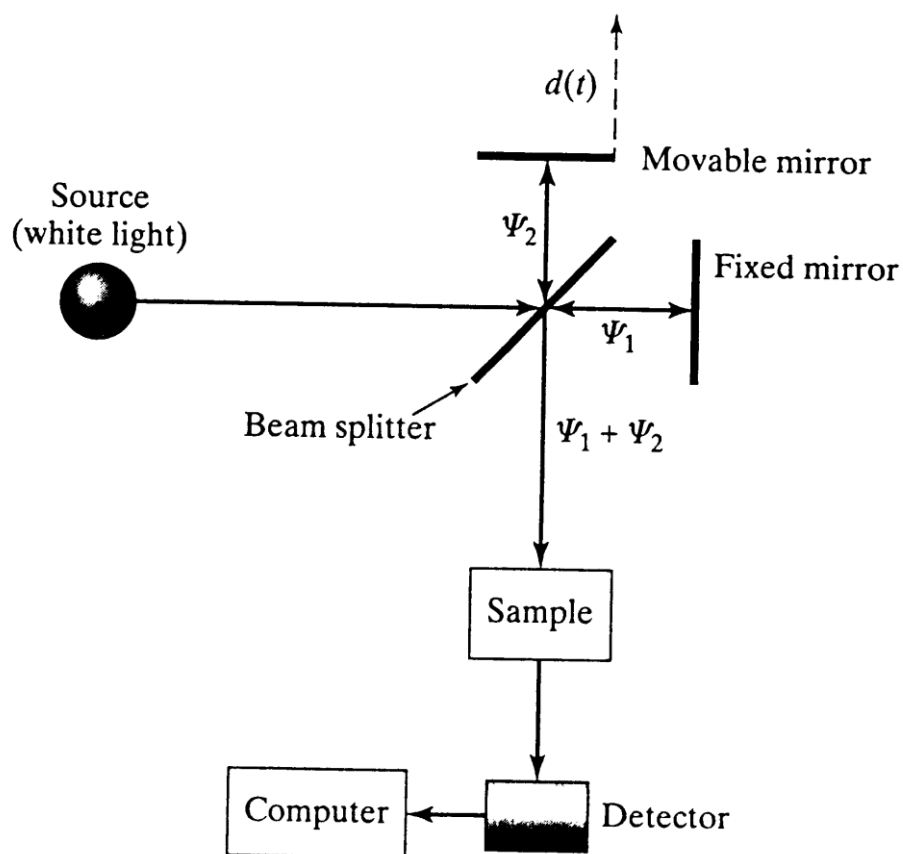
Mechanically rotating the prism or grating permits the measurement of absorption over a wide range of scanned wavelengths.

Many modern spectrometers, especially nmr and infrared spectrometers, use ingenious Fourier transform techniques instead of dispersing elements. Omitting the dispersion step has two key advantages: it makes Fourier spectrometers **a) faster** (there is no need to scan the range of wavelengths) and **b) more sensitive** (all of the radiation from the sample is used, instead of a narrow band of wavelengths selected by a grating).

How does Fourier transform spectroscopy work?

FTIR spectrometers use an **interferometer** like the one sketched below.

FTIR Spectrometer



A mercury arc in a quartz jacket or a heated ceramic filament provides a beam of blackbody radiation with a continuous distribution of frequencies. The radiation strikes a **beam splitter**, which is analogous to a partially silvered mirror. It transmits about half of the incident radiation (beam Ψ_1) and reflects the other half (beam Ψ_2). The transmitted portion is reflected by a fixed mirror back to the beam splitter, where it is partially reflected into the sample cell. The portion of radiation that was reflected by the beam splitter (Ψ_2) strikes a mirror that is moving at a fixed velocity v_0 . Beam Ψ_2 is reflected from the **moving mirror** and directed back to the beam splitter, where it is partially transmitted and recombines with beam Ψ_1 .

The recombined beams Ψ_1 and Ψ_2 continue into the sample cell. Because the two beams have traveled different distances from the source, they interfere with each other. In the sample cell, radiation at certain wavelengths causes rotational-vibrational transitions and is absorbed. The radiation leaving the sample cell travels to a detector. It monitors the radiation intensity as a function of time.

What does the detector see? The key point to remember is that beam Ψ_2 reflected from the moving mirror travels a longer distance, proportional to $v_0 t$, where v_0 is the velocity of the moving mirror. Consider the simplest case where the radiation source provides a monochromatic beam of wavelength λ . The beam Ψ_1 transmitted by the splitter can be represented, without loss of generality, by the sine function

$$\Psi_1(t) = A \sin\left(\frac{2\pi x}{\lambda}\right)$$

x is the distance the radiation has traveled from the source.

Beam Ψ_2 , reflected by the splitter to the moving mirror, travels a longer distance $d(t)$, which is proportional to $v_0 t$.

$$\Psi_2(t) = A \sin\left(\frac{2\pi[x + d(t)]}{\lambda}\right)$$

The additional distance traveled by beam Ψ_2 produces an **interference pattern** with beam Ψ_1 in the signal $S(t)$ reaching the detector.

$$S(t) = \Psi_1(t) + \Psi_2(t) = A \sin\left(\frac{2\pi x}{\lambda}\right) + A \sin\left(\frac{2\pi[x + d(t)]}{\lambda}\right)$$

If the mirror has moved an integral multiple of the wavelength at time t

$$d(t) = n\lambda$$

we have constructive interference

$$S(t) = A \sin\left(\frac{2\pi x}{\lambda}\right) + A \sin\left(\frac{2\pi[x + n\lambda]}{\lambda}\right) = 2A \sin\left(\frac{2\pi x}{\lambda}\right)$$

producing a signal with twice the amplitude and therefore four times the intensity.

On the other hand, if

$$d(t) = (n + 1/2)\lambda$$

we have destructive interference

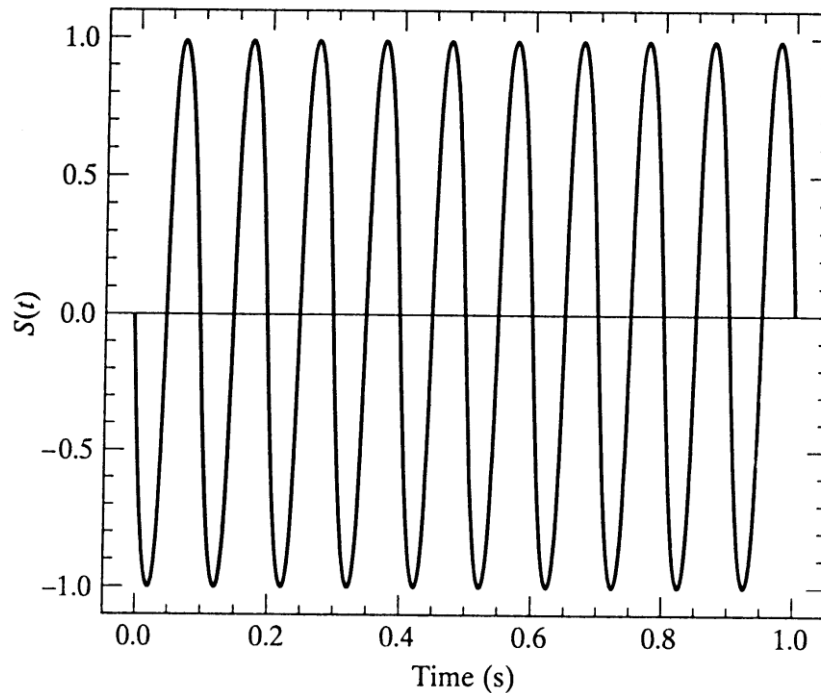
$$S(t) = A \sin\left(\frac{2\pi x}{\lambda}\right) + A \sin\left(\frac{2\pi[x + n\lambda]}{\lambda}\right) = 0$$

and the detector signal is zero. When $d(t)$ is between these two extreme values, the detector signal will be an intermediate value.

For purposes of illustration, suppose the mirror is moving at a speed of 0.010 cm s^{-1} , the amplitude is $A = 1$ in arbitrary units, and the fixed distance from the source to the detector for beam Ψ_1 is $x = 10^4 \lambda$. The detector signal is then

$$S(t) = \sin(20000\pi) + \sin\left(20000\pi + \frac{0.02\pi t}{\lambda}\right) = \sin\left(\frac{0.02\pi t}{\lambda}\right)$$

Detector Signal $S(t) = \sin(0.02\pi t/\lambda)$



Notice that $S(t)$ goes through 10 complete oscillations in 1 second. Therefore, the frequency of the detected signal is $\nu_s = 10 \text{ s}^{-1}$. As usual, the wavelength is the speed divided by the frequency

$$\lambda = \frac{v_0}{v_s} = \frac{0.01 \text{ cm s}^{-1}}{10 \text{ s}^{-1}} = 0.001 \text{ cm}$$

The corresponding frequency of the radiation is

$$\nu = \frac{c}{\lambda} = \frac{c v_s}{v_0} = \frac{2.998 \times 10^{10} \text{ cm s}^{-1}}{0.001 \text{ cm}} = 2.998 \times 10^{13} \text{ s}^{-1}$$

The radiation frequency is directly proportional to the frequency of the detector signal and inversely proportional to the speed of the moving mirror.

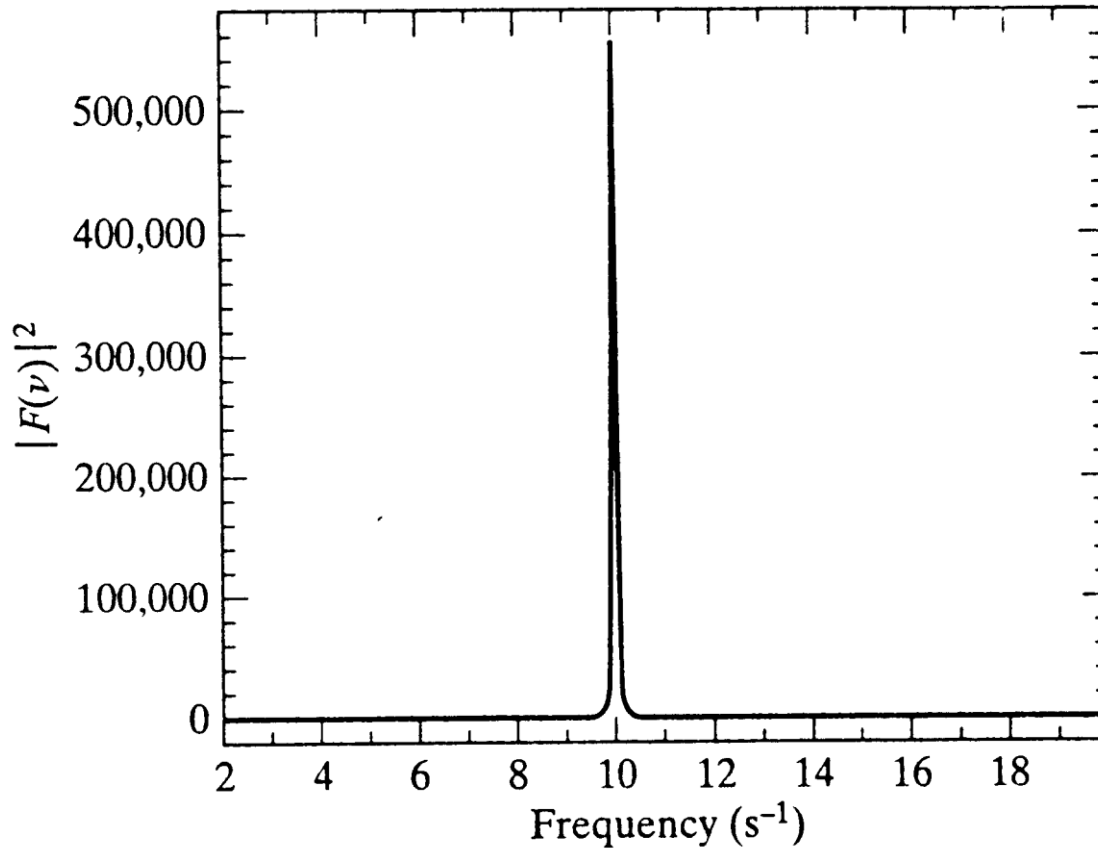
In the preceding example, it was easy to calculate the oscillation frequency of the detector signal. There was only one oscillation frequency! What happens for a real sample when $S(t)$ is composed of signals with many different frequencies? In this case, we resort to a powerful mathematical technique called the **Fourier transform** of $S(t)$ defined as

$$F(\nu) = \frac{1}{2\pi} \int_0^{\infty} S(t) e^{-i2\pi\nu t} dt$$

The component frequencies of the detector signal are obtained by plotting $|F(\nu)|^2$ against the frequency ν . This kind of graph is called a **power spectrum**. The power spectrum is a distribution function: $|F(\nu)|^2 d\nu$ is proportional to the intensity of the signal at frequencies in the range from ν and $\nu + d\nu$.

For the example we have been considering with detector signal $S(t) = \sin(0.02\pi t/\lambda)$ and the single frequency 10 s^{-1} , the power spectrum obtained by numerical integration of the Fourier integral over the time interval from 0 to 15 seconds is

Power Spectrum for the Detector Signal $S(t) = \sin(0.02\pi t/\lambda)$



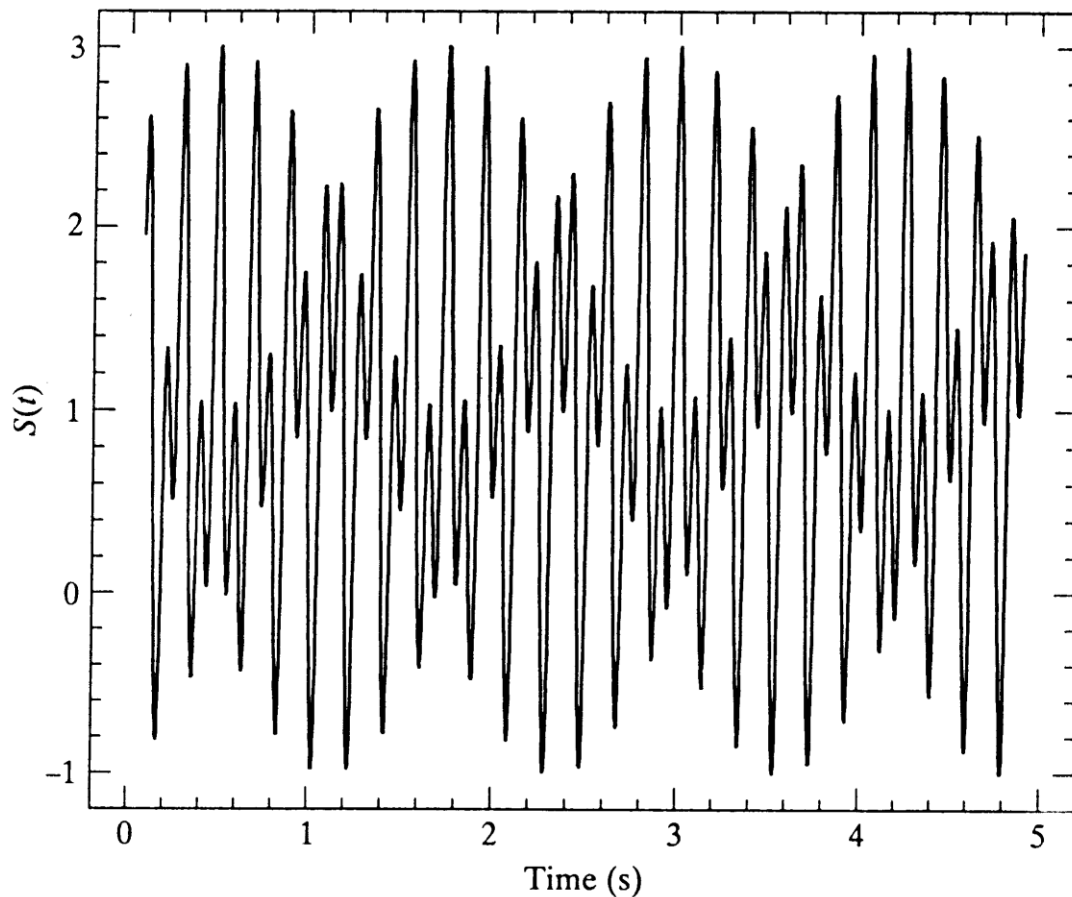
Notice the very sharp maximum in the power spectrum near 10 s^{-1} . For longer integration times, the maximum becomes even sharper.

What happens for radiation with two different wavelengths? Let us assume again that $\nu_0 = 0.010 \text{ cm s}^{-1}$, $A = 1$, and $x = 10^4 \lambda_1$. As before, we will use $\lambda_1 = 0.001 \text{ cm}$ for the first wavelength and, for purposes of illustration, set the second wavelength equal to $\lambda_1 = 0.00217 \text{ cm}$.

The signal reaching the detector is

$$\begin{aligned}
S(t) &= \Psi_1(t) + \Psi_2(t) \\
&= \sin\left(\frac{2\pi x}{\lambda_1}\right) + \sin\left(\frac{2\pi x}{\lambda_2}\right) + \sin\left(\frac{2\pi[x + d(t)]}{\lambda_1}\right) + \sin\left(\frac{2\pi[x + d(t)]}{\lambda_2}\right) \\
&= \sin\left(\frac{20000\pi\lambda_1}{\lambda_2}\right) + \sin\left(\frac{0.02\pi t}{\lambda_1}\right) + \sin\left(\frac{200002\pi\lambda_1}{\lambda_2} + \frac{0.02\pi t}{\lambda_2}\right)
\end{aligned}$$

Detector Signal with Wavelength Components λ_1 and λ_2



Now it is not so easy to determine the frequencies by inspection!

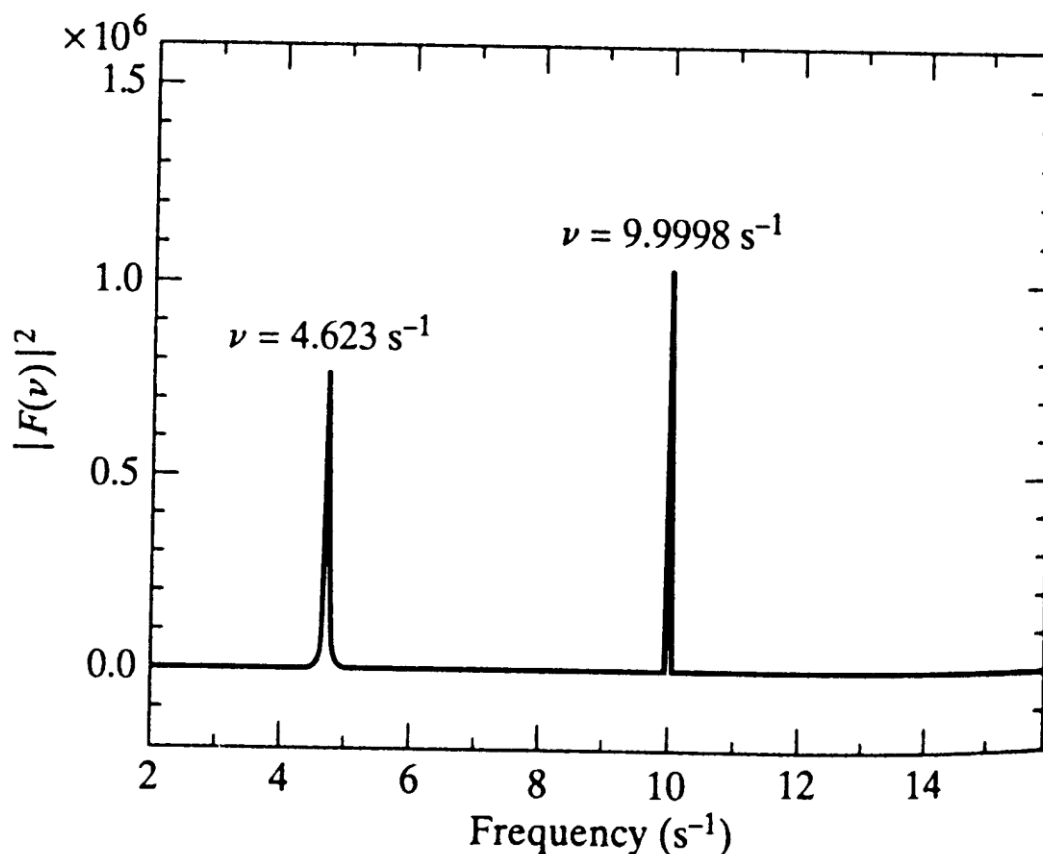
Taking the Fourier transform of the detector signal, however, provides a power spectrum with two well-defined signal frequencies:

$$4.62 \text{ s}^{-1} \qquad 10.00 \text{ s}^{-1}$$

corresponding to radiation wavelengths

$$0.00217 \text{ cm} \qquad 0.00100 \text{ cm}$$

Power Spectrum for a Signal with Wavelength Components λ_1 and λ_2



When the sample cell of the FTIR spectrometer is filled with molecules that absorb radiation at many different frequencies, the power spectrum will show corresponding dips at those frequencies.

How does the Fourier transform

$$F(\nu) = \frac{1}{2\pi} \int_0^{\infty} S(t) e^{-i2\pi\nu t} dt$$

disperse a complicated signal $S(t)$ into its component frequencies?

Knowledge of quantum mechanics helps!

For purposes of illustration, suppose the detector signal is the sum of cosine waves with frequencies $\nu_1, \nu_2, \nu_3, \nu_4, \dots$ and amplitudes $A_1, A_2, A_3, A_4, \dots$

$$S(t) = \sum_{n=1}^{\infty} A_n \cos(2\pi\nu_n t)$$

Taking the Fourier transform and recalling that $e^{-i2\pi\nu t} = \cos(2\pi\nu t) + i\sin(2\pi\nu t)$ gives

$$\begin{aligned} F(\nu) &= \frac{1}{2\pi} \int_0^{\infty} S(t) e^{-i2\pi\nu t} dt \\ &= \frac{1}{2\pi} \int_0^{\infty} \left[\sum_{n=1}^{\infty} A_n \cos(2\pi\nu_n t) \right] [\cos(2\pi\nu t) + i\sin(2\pi\nu t)] dt \end{aligned}$$

Sine and cosine functions are orthogonal, so the expression for the Fourier transform simplifies to

$$F(\nu) = \frac{1}{2\pi} \sum_{n=1}^{\infty} A_n \int_0^{\infty} \cos(2\pi\nu_n t) \cos(2\pi\nu t) dt$$

But cosine functions are orthogonal too! Consequently, the integrals

$$\int_0^{\infty} \cos(2\pi\nu_n t) \cos(2\pi\nu t) dt = 0 \quad \nu_n \neq \nu$$

will be zero when the frequency ν used in the integration does not match the frequency ν_n in the signal.

But when the integration frequency matches a frequency in the signal, we get

$$\int_0^{\infty} \cos(2\pi\nu_n t) \cos(2\pi\nu_n t) dt = \int_0^{\infty} \cos^2(2\pi\nu_n t) dt = \infty \quad \nu_n = \nu$$

When the frequency in the Fourier transform matches the frequency in the signal, the integral goes to infinity. In this way, the Fourier transform “picks out” the frequencies in the signal.

In practice, the Fourier transforms evaluated numerically never of course reach infinity because the integrations are performed numerically and the sampling times are finite (usually less than 100 s). Nevertheless, when an integration frequency matches a frequency in the signal, the relatively large value of the integral of $\cos^2(2\pi\nu_n t)$ (all positive!) makes a corresponding contribution to $F(\nu)$.