

# Chapter 4

## Interaction of photons with matter

### 4.1 Very short wavelengths ( $< 10^{-12}$ m, $\gamma$ -rays)

The method that uses  $\gamma$ -rays to characterize materials is called *Mössbauer spectroscopy*. Key to the success of the technique is the discovery of *recoilless  $\gamma$ -ray emission and absorption*, now referred to as the *Mössbauer effect*, after its discoverer Rudolph Mössbauer, who first observed the effect in 1957 and received the Nobel Prize in Physics in 1961 for his work.

#### 4.1.1 Mössbauer effect

Nuclei in atoms undergo a variety of energy level transitions, often associated with the emission or absorption of a gamma ray. These *energy levels are influenced by their surrounding environment, both electronic and magnetic*, which can change or split these energy levels. These changes in the energy levels can provide information about the atom's local environment within a system and ought to be observed using resonance-fluorescence. There are, however, two major obstacles in obtaining this information:

- the *'hyperfine' interactions between the nucleus and its environment are extremely smaller*,
- the *recoil of the nucleus* (as the gamma-ray is emitted or absorbed) *prevents the resonance*.

Just as a gun recoils when a bullet is fired, conservation of momentum requires a free nucleus (such as in a gas) to recoil during emission or absorption of a gamma ray

- If a nucleus at rest emits a gamma ray, the energy of the gamma ray is slightly less than the natural energy of the transition (difference is equal to the recoil energy  $E_R$ )
- but in order for a nucleus at rest to absorb a gamma ray, the gamma ray's energy must be slightly greater than the natural energy.

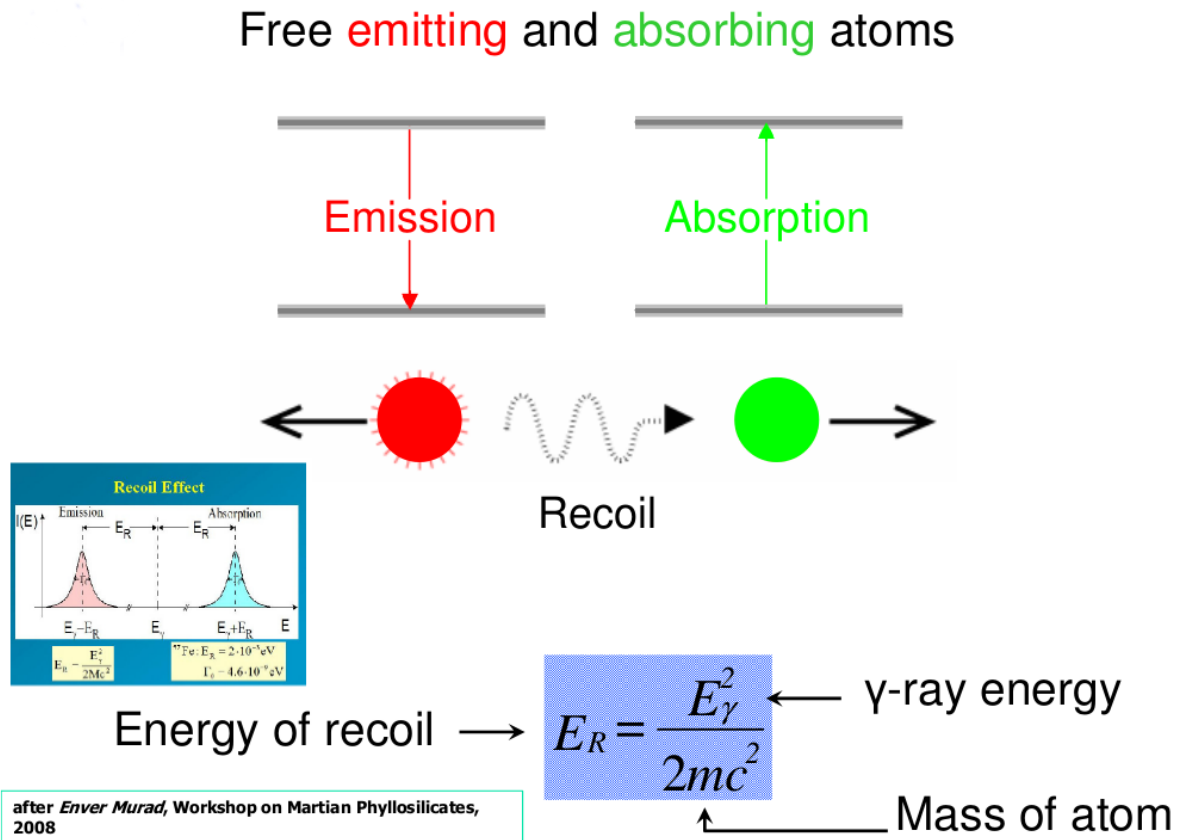


Figure 4.1: Recoil of free nuclei in emission or absorption of a gamma-rays

$\Rightarrow$  This means that nuclear resonance (emission and absorption of the same gamma ray by identical nuclei) is unobservable with free nuclei, because the shift in energy is too great and the emission and absorption spectra have no significant overlap. In order to achieve resonance in emission and absorption the loss of the recoil energy must be overcome in some way.

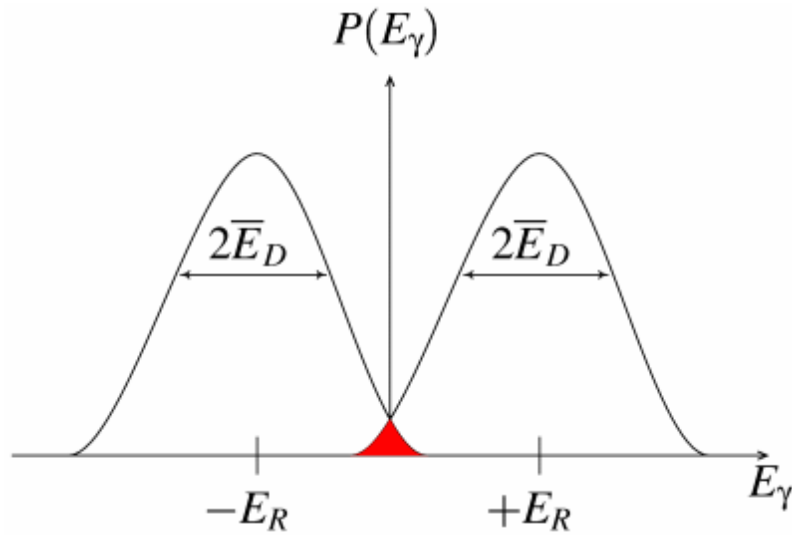
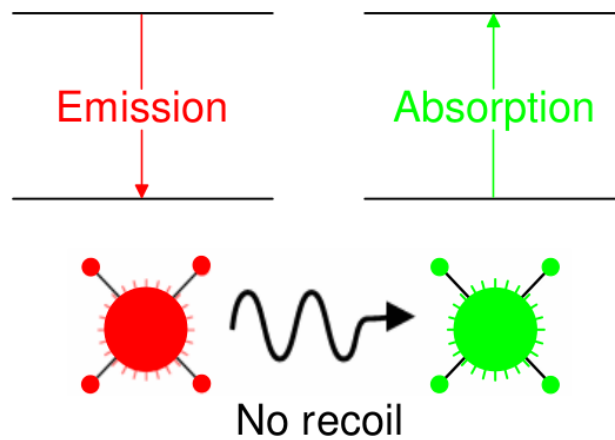


Figure 4.2: Resonant overlap in free atoms. The overlap shown shaded is greatly exaggerated.

*Nuclei in a solid crystal are not free to recoil* because they are bound in place in the crystal lattice. When a nucleus in a solid emits or absorbs a gamma ray, some energy can still be lost as recoil energy, but in this case it always occurs in discrete packets called *phonons* (quantized vibrations of the crystal lattice). Any whole number of phonons can be emitted, including zero, which is known as a "*recoil-free*" event. In this case the conservation of momentum is satisfied by the momentum of the crystal as a whole, so practically no energy is lost.

Mössbauer realised that for the resonance effect to occur both emitting and absorbing atoms must be bound in a lattice where the lowest vibrational excitation energy is greater than the nuclear recoil energy  $\Rightarrow$  the atom is unable to recoil and  $\gamma$ -ray may be emitted and absorbed without loss of energy.

### Emitting and absorbing atoms fixed in a lattice



Mössbauer spectroscopy is the recoil-free emission and absorption of  $\gamma$ -rays

$$E_R = \frac{E_\gamma^2}{2Mc^2}$$

(VERY LARGE)

Mass of particle

after Enver Murad, Workshop on Martian  
Phyllosilicates, 2008

Figure 4.3: Atoms fixed in lattice.

### 4.1.2 Mössbauer absorption spectroscopy

Mössbauer spectroscopy involves the emission and absorption of *gamma*-rays to determine the chemical state of atoms in lattice. It is primarily used to study iron containing materials but not exclusively because the effect can be observed for over 40 elements.

Mössbauer spectroscopy is only possible ("recoil-free" event) when atoms are fixed in a solid crystal lattice at a temperature below certain critical value, the Debye characteristic temperature. Then gamma rays emitted by one nucleus can be resonantly absorbed by a sample containing nuclei of the same isotope, and this absorption can be measured.

In its most common form, Mössbauer absorption spectroscopy,

- a solid sample is exposed to a beam of gamma radiation,
- and a detector measures the intensity of the beam transmitted through the sample.

The atoms in the source emitting the gamma rays must be of the same isotope as the atoms in the sample absorbing them.

If the emitting and absorbing nuclei were in identical chemical environments, the nuclear transition energies would be exactly equal and resonant absorption would be observed with both materials at rest. *The difference in chemical environments, however, causes the nuclear energy levels to shift in a few different ways.*

Although these energy shifts are tiny (often less than a micro-electronvolt), the extremely narrow spectral linewidths of gamma rays for some radionuclides make the small energy shifts correspond to large changes in absorbance. To bring the two nuclei back into resonance it is necessary *to change the energy of the gamma ray slightly*, and in practice this is always done using the *Doppler effect*.  $\Rightarrow$  the source is accelerated through a range of velocities using a linear motor to produce a Doppler effect and scan the gamma ray energy through a given range. A typical range of velocities for  $^{57}\text{Fe}$ , for example, may be  $\pm 11$  mm/s ( $1$  mm/s = 48.075 neV).

In the resulting spectra, gamma ray intensity is plotted as a function of the source velocity. At velocities corresponding to the resonant energy levels of the sample, a fraction of the gamma rays are absorbed, resulting in a drop in the measured intensity and a corresponding dip in the spectrum. The number, positions, and intensities of the dips (also called peaks; dips in transmitted intensity are peaks in absorbance) provide information about the chemical environment of the absorbing nuclei and can be used to characterize the sample.

*Mössbauer spectroscopy is limited by the need for a suitable gamma-ray source.* Usually, this consists of a radioactive parent that decays to the desired isotope. For example,

- the source for  $^{57}\text{Fe}$  consists of  $^{57}\text{Co}$ , which decays by electron capture to an excited state of  $^{57}\text{Fe}$ ,
- then subsequently decays to a ground state emitting the desired gamma-ray.
- The radioactive cobalt is prepared on a foil, often of rhodium.

Ideally the parent isotope will have a sufficiently long half-life to remain useful, but will also have a sufficient decay rate to supply the required intensity of radiation.

Mössbauer spectroscopy has an extremely fine energy resolution and can detect even subtle changes in the nuclear environment of the relevant atoms. Typically, there are three types of nuclear interactions that are observed

- isomer shift (or chemical shift) - is a relative measure describing a shift in the resonance energy of a nucleus due to the transition of electrons within its s orbital. The whole spectrum is shifted in either a positive or negative direction depending upon the s electron charge density. This change arises due to alterations in the electrostatic response between the non-zero probability s orbital electrons and the non-zero volume nucleus they orbit.
- quadrupole splitting - reflects the interaction between the nuclear energy levels and surrounding electric field gradient (EFG). Nuclei in states with non-spherical charge distributions, i.e. all those with angular quantum number ( $I$ ) greater than  $1/2$ , produce an asymmetrical electric field which splits the nuclear energy levels. This produces a nuclear quadrupole moment.

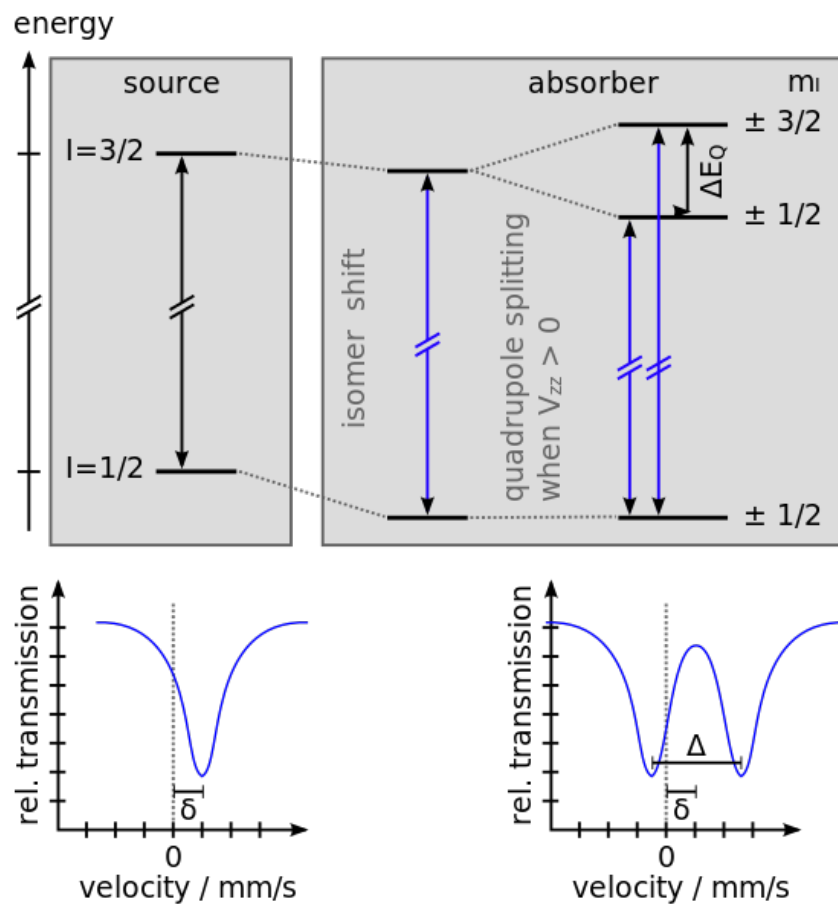


Figure 4.4: Chemical shift and quadrupole splitting of the nuclear energy levels and corresponding Mössbauer spectra

- hyperfine splitting (or Zeeman splitting) - is a result of the interaction between the nucleus any surrounding magnetic field. A nucleus with spin,  $I$ , splits into  $2I + 1$  sub-energy levels in the presence of magnetic field. For example, a nucleus with spin state  $I= 3/2$  will split into 4 non-degenerate sub-states with  $m_I$  values of  $+3/2, +1/2, -1/2$  and  $-3/2$ . Each split is hyperfine, being in the order of  $10^{-7}$ eV. The restriction rule of magnetic dipoles means that transitions between the excited state and ground state can only occur where  $m_I$  changes by 0 or 1. This gives six possible transitions for a  $3/2$  to  $1/2$  transition.

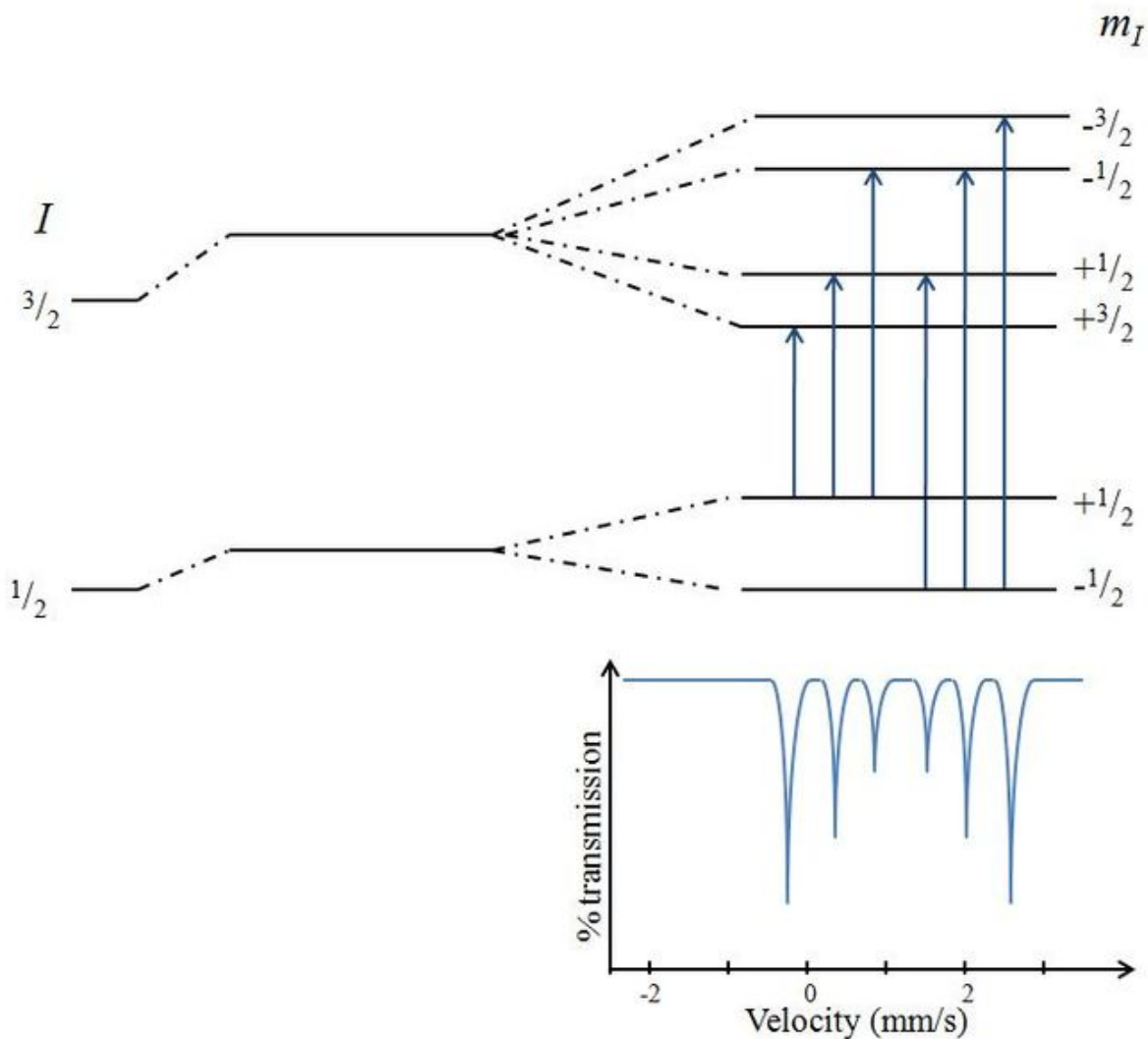


Figure 4.5: Magnetic splitting of the nuclear energy levels and the corresponding Mössbauer spectrum

## 4.2 Short wavelengths ( $10^{-12}$ to $10^{-9}$ m, including X-rays and ultraviolet)

If photon has enough energy to excite electron to high energy levels, two effects can occur:

- **internal photoeffect** (e.g. photoconductivity)
- **external photoeffect** or the photoemission.

The kinetic energy is:

$$\frac{1}{2}mv^2 = E_F \pm \delta E - E_{af} + h\nu - \Delta E. \quad (4.1)$$

At 0 K the kinetic energy is maximum

$$\left(\frac{1}{2}mv^2\right)_{\max} = h\nu - (E_{af} - E_F) = h\nu - \chi = h(\nu - \nu_0), \quad (4.2)$$

where  $\nu_0$  is the frequency of photoelectric effect.

In the case of photoemission induced absorption (**X-ray**), the photon has enough energy to excite an electron from some inner layers of solid.

$$\frac{1}{2}mv^2 = h\nu - \chi - E_B, \quad (4.3)$$

where  $E_B$  is the binding energy of the inner layers. The binding energy is characteristic for each substance, so the kinetic electrons emitted bear information related to the electronic structure and thus, the type of material.

### 4.2.1 Fowler's theory for metal/vacuum interfaces

Fowler proposed a theory in 1931 which showed that the photoelectric current variation with the light frequency could be accounted for by the effect of temperature in the number of electrons available for emission, in accordance with the distribution law of Sommerfeld's theory for metals. Sommerfeld's theory had resolved some of the problems surrounding the original models for electron in metals. In classical Drude theory, a metal had been envisaged as a three-dimensional potential well (box) containing a gas of freely mobile electrons. This adequately explained their high electrical and thermal conductivities. However, because experimentally it was found that metallic electrons do not show a gas-like heat capacity, the Boltzman distribution law is inappropriate. A Fermi-Dirac distribution function is required, consistent with the need that the electrons obey the Pauli exclusion principle and this distribution function has the form

$$P(E) = \frac{1}{1 + \exp[(E - E_F)/kT]} \quad (4.4)$$

At ordinary temperatures, the Fermi energy  $E_F \gg kT$ . Fowler's law, referred to above as the "square law", is readily tested in practice since it predicts at  $T=0$  K

$$i \propto (\nu - \nu_0)^2 \quad (4.5)$$



#### 4.2. SHORT WAVELENGTHS ( $10^{-12}$ TO $10^{-9}$ M, INCLUDING X-RAYS AND ULTRAVIOLET) 9

where  $\nu_0$  is the photoelectric threshold frequency and  $\nu$  refers to a range of energies from threshold to a few  $kT$  above threshold. To a good approximation, the photoelectric yield per unit light intensity near  $\nu_0$  is proportional simply to the number of electrons incident per unit time. The energy condition can be written

$$(1/2m)p^2 + h\nu > \phi \quad (4.6)$$

where  $p$  is the initial momentum of the electron normal to the surface. The escaping electrons have been termed the "available electrons".

Fowler's derivation for the single photon does not explicitly involve the quantum mechanical form of current; instead, a semi-classical flux of electrons arriving at the metal surface is used. The electron gas in the metal will obey Fermi-Dirac statistics, and the number of electrons per unit volume having velocity components in the ranges  $u, u + du, \nu, \nu + d\nu$  and  $w + dw$  is given by the formula

$$n(u, \nu, w)dud\nu dw = 2\left(\frac{m}{h}\right)^2 \frac{dud\nu dw}{1 + \exp[\frac{1}{2}m(u^2 + \nu^2 + w^2) - E_F]/kT} \quad (4.7)$$

where  $u$  is the velocity normal to the surface and  $m$  is the electron mass. The number of electrons per volume,  $n(u)du$ , with their velocity component normal to the surface in the range  $u, u + du$  is given by:

$$n(u)du = \frac{4\pi kT}{m} \left(\frac{m}{h}\right)^3 \log[1 + \exp(E_F - \frac{1}{2}mu^2)/kT]du \quad (4.8)$$

The solution for the photoelectric current resulted in the form

$$i \propto \frac{(h\nu - \phi)^{3/2}}{(\phi_0 - h\nu)^{1/2}} \quad (4.9)$$

A method for determining the threshold frequency of the illuminated surface  $\nu_0$  is that which makes use of the complete photoelectric emission. When a metal surface is exposed to the total thermal radiation from a black body with a temperature  $T$ , the total photoelectric current is given by:

$$i = A' T^2 e^{-\frac{h\nu_0}{kT}} \quad (4.10)$$

where  $A'$  is a constant.

#### 4.2.2 Measurement of the photoelectric work function

- Fowler isotherm: measurement of the photocurrent depending on the frequency of incident radiation at constant temperature, the  $\ln i_f/T^2$  is expressed as  $h\nu/kT$  and compared with the theoretical curve

$$\ln \frac{i_f}{T^2} = \ln(\alpha A_0) + \ln f(x) = B + \Phi\left[\frac{h}{kT}(\nu - \nu_0)\right]. \quad (4.11)$$

From the Fowler equation, giving the relation between temperature and photoelectric emission,  $\nu_0$  can be determinate by plotting the  $\ln f(\Delta)$  as a function of  $\Delta$ . A universal curve is obtained. Then  $\ln \frac{i_f}{T^2}$  is plotted against  $\frac{h\nu}{kT}$ . A curve us obtained of the same shape as the universal curve, which can be made to coincide with it by a parallel shift. The vertical shift is measure of  $B$ , the horizontal is equal to  $\frac{h\nu_0}{kT}$ .

- duBridge isochromatic method: measurements at one frequency  $\nu$  but different temperatures. For this purpose  $\ln f(\Delta)$  is plotted against  $\ln |\Delta|$ , and again a universal curve is obtained. From the experimental data  $\ln i_f/T^2$  is plotted against  $\ln 1/T$ . For different frequencies the temperature dependence of the photoemission differs
- for  $\nu = \nu_0$  is  $i_f = \alpha A_0 = \pi^2/12T^2$
- for  $x \gg 1$ ;  $\nu > \nu_0$ , is  $f(x) = \pi^2/6 + x^2/2$  and

$$i_f = \frac{\alpha A_0}{2} \left[ \frac{h^2(\nu - \nu_0)^2}{k^2} + \frac{\pi^2}{3} \right], \quad (4.12)$$

where the parabolic dependence is applied only when the first term in the brackets is sufficiently small.

- for  $x \ll 1$ ,  $\nu < \nu_0$ , is  $f(x) = e^x$  and

$$i_f = \alpha A_0 T^2 \exp\left(-\frac{h(\nu_0 - \nu)}{kT}\right). \quad (4.13)$$

### 4.2.3 Interaction of excited electrons with matter

The **hot-electron** problem represents the study of the deviations from the linear response regime due to heating of charge carriers above the thermal equilibrium. Studies have been carried out in 1930s, mainly by Russian physicist Landau and Davidov. This means that electron temperature  $T_e$  which, in the presence of an external high electric field, is higher than the lattice temperature  $T$ .

Nonlinear transport deals with problems that arise when a sufficiently strong electric field is applied to a semiconductor sample, so that the current deviates from the linear response. This effect is typical of semiconductors and cannot be seen on metals since, owing to their large conductivities, Joule heating would destroy the material before deviations from the linearity could be observed.

Considering

$$v^{(i)}(t) = v_0^{(i)} + a\Delta t^{(i)} \quad (4.14)$$

where  $v^{(i)}(t)$  is the instantaneous velocity of the  $i$ -th electron at time  $t$ ,  $\Delta t^{(i)}$  is the same time elapsed after its last scattering event, and  $a = eE/m$  is the electron acceleration, due to a constant and uniform applied electric field  $E$ . The region of field strengths where transport starts to deviate from linearity is called **warm-electron region**.

### 4.2.4 Photoemission from semiconductors

There are some differences when we speak about the photoemission from metals and semiconductors. All high quantum yield photocathodes are semiconductor ones. The absorption of light is affected by:

- internal absorption due to their band gap

- external absorption from the external layer

The Fermi level is influenced by the surface layers and the type of semiconductor used. Electron coming from different depths have different space charge and work function  $\Rightarrow$  as they would have different work function for different photoelectrons excited at different wavelengths.

The density of states around Fermi level increases strongly and we cannot assume that photon absorption is independent from electron's energy state. The quantum yield increases with the temperature faster than in metals.

### 4.2.5 Photocathode

- IR region: Ag-O-Cs, also called S-1. This was the first compound photocathode material, developed in 1929. Sensitivity from 300 nm to 1200 nm. Since Ag-O-Cs has a higher dark current than more modern materials photomultiplier tubes with this photocathode material are nowadays used only in the infrared region with cooling.
- visible region: Sb-Cs has a spectral response from UV to visible and is mainly used in reflection-mode photocathodes. and also bi-alkali (antimony-rubidium-caesium Sb-Rb-Cs, antimony-potassium-caesium Sb-K-Cs). Spectral response range similar to the Sb-Cs photocathode, but with higher sensitivity and lower dark current than Sb-Cs. They have sensitivity well matched to the most common scintillator materials and so are frequently used for ionizing radiation measurement in scintillation counters.
- UV region: metals and Cs-Te (Cs-I). These materials are sensitive to vacuum UV and UV rays but not to visible light and are therefore referred to as solar blind. Cs-Te is insensitive to wavelengths longer than 320 nm, and Cs-I to those longer than 200 nm.

## 4.3 Intermediate wavelengths (including visible and ultraviolet light)

Spectrophotometry (measurements of reflectance  $R$  or transmittance  $T$ ) and ellipsometry for determination of thin film thickness and its optical properties.

### 4.3.1 Principles of R/T method

By reflectance (R) and/or transmittance (T) method the ratio of reflected to incident and/or transmitted to incident light energies are measured. If the studied system is surrounded on both sides by the same medium the reflectance and/or transmittance are given simply by the ratio of the electric field amplitudes:

$$R_q = \left| \frac{\hat{E}_r}{\hat{E}_i} \right|_q^2 \quad \text{and/or} \quad T_q = \left| \frac{\hat{E}_t}{\hat{E}_i} \right|_q^2 \quad (4.15)$$

where  $q = p, s$  and  $\hat{E}_{iq}$ ,  $\hat{E}_{rq}$  and/or  $\hat{E}_{tq}$  denote complex amplitudes of the electrical fields of the p-polarised and s-polarised incident, reflected and/or transmitted electrical waves.

The reflectance  $R_{p,s}$  and the transmittance  $T_{p,s}$  are obtained from their definition as

$$R_{p,s} = |\hat{r}_{p,s}|^2 \quad \text{and} \quad T_{p,s} = |\hat{t}_{p,s}|^2, \quad (4.16)$$

where  $\hat{r}_p$  and/or  $\hat{r}_s$  and  $\hat{t}_p$  and/or  $\hat{t}_s$  denote the reflection Fresnel coefficient of the system for the p-polarised and/or s-polarised wave and the transmission Fresnel coefficient of the system for the same waves, respectively.

Usually the measurements is performed in a natural light that is represented by randomly polarised one. The detected total reflectance and/or transmittance that does not distinguish p- and s-polarisation state can be than expressed as

$$R = \frac{|\hat{r}_p|^2 + |\hat{r}_s|^2}{2} \quad \text{and/or} \quad T = \frac{|\hat{t}_p|^2 + |\hat{t}_s|^2}{2}. \quad (4.17)$$

In the basic configuration for reflectance measurements the light intensity reflected by the sample  $I_{sm}$  is compared with the light intensity reflected by a reference sample  $I_r$ . Usually the angle of incidence is less than  $15^\circ$  and very often it is considered to be equal to  $0^\circ$  because of equation simplifying. However, this assumption is not necessary in numerical methods of optical constant determining. Then the reflectance of sample  $R_{sm}$  is given by

$$R_{sm} = R_n \frac{I_{sm}}{I_r} \quad (4.18)$$

where  $R_n$  is the reflectance of the normal. A disadvantage of this method consists in the necessary knowledge of the reference sample reflectance. The main sources of systematic errors are listed below:

1. bad stability of the light source,
2. change of the position of incidence light on the detector area,
3. bad stability of the optical parameters of the reference sample.

The polished silicon wafer was used as the reference sample for the measurements on films deposited on silicon. When the measurements of films on glass substrates were carried out the quartz plate was taken as the reference.

For the transmittance measurements it is not necessary to use any reference sample because there is no technical problem to measure transmitted and incident light intensity in the same experimental arrangement. Therefore the third systematic error from previous paragraph is excluded. However, when the transmittance spectra of the substrate are very complicated it can be useful to divide the sample transmittance by the substrate transmittance to exclude the substrate transmittance features from the measurements. Besides the possible systematic errors mentioned in the previous section there is another one caused by different properties of the bare substrate and the substrate with the film.

### 4.3.2 Principles of ellipsometry

Ellipsometry is a technique enabling us to measure the polarisation state of the polarised light wave emerging from the system studied owing to the polarisation state of the polarised light wave incident on this system. In practice the ellipsometric measurements are mostly employed for specularly reflected or directly transmitted light waves by the system.

If the system is optically isotropic the measured quantities are related to

$$\rho = \frac{\hat{r}_p}{\hat{r}_s} \quad \text{or} \quad \rho = \frac{\hat{t}_p}{\hat{t}_s}. \quad (4.19)$$

The symbols  $\hat{r}_p$  and/or  $\hat{r}_s$  and  $\hat{t}_p$  and/or  $\hat{t}_s$  denote the reflection Fresnel coefficient of the system for the p-polarised and/or s-polarised wave and the transmission Fresnel coefficient of the system for the same waves, respectively.

Further, one can write

$$\rho = \tan \Psi e^{i\Delta}, \quad (4.20)$$

where  $\Psi$  and  $\Delta$  represent the ellipsometric parameters of the system for the reflected or transmitted light waves ( $\Psi$  and/or  $\Delta$  is called the azimuth and/or the phase change).

### 4.3.3 Optical quantities of the thin film system

In this section an interaction of the light waves with the thin film systems corresponding to the ideal model defined in section ?? will be described by means of the optical quantities. In case that the system is formed by the isotropic materials it is sufficient to determine the values of the complex Fresnel coefficients  $\hat{r}_p$ ,  $\hat{r}_s$ ,  $\hat{t}_p$  and  $\hat{t}_s$ . Using these coefficients one can determine the ellipsometric quantities, i. e.  $\Psi$  and  $\Delta$  (see section 4.3.2) or the reflectance  $R$  and the transmittance  $T$  (see section 4.3.1).

#### Thin films on semi-infinite substrates

By solving the Maxwell equations for boundary surface of two materials (see Figure ??) under assumption that in all the material currents caused by external electrical fields and free electric charges will not take place we get the following expressions for the Fresnel reflection and transmission coefficients at the  $j$ -th boundary ( $r_{jp}$ ,  $r_{js}$  and  $t_{jp}$ ,  $t_{js}$ , respectively)

$$\hat{r}_{jp} = \frac{\hat{n}_j \cos \hat{\theta}_{j-1} - \hat{n}_{j-1} \cos \hat{\theta}_j}{\hat{n}_j \cos \hat{\theta}_{j-1} + \hat{n}_{j-1} \cos \hat{\theta}_j}, \quad (4.21)$$

$$\hat{t}_{jp} = \frac{2 \hat{n}_{j-1} \cos \hat{\theta}_{j-1}}{\hat{n}_j \cos \hat{\theta}_{j-1} + \hat{n}_{j-1} \cos \hat{\theta}_j}, \quad (4.22)$$

$$\hat{r}_{js} = \frac{\hat{n}_{j-1} \cos \hat{\theta}_{j-1} - \hat{n}_j \cos \hat{\theta}_j}{\hat{n}_{j-1} \cos \hat{\theta}_{j-1} + \hat{n}_j \cos \hat{\theta}_j}, \quad (4.23)$$

$$\hat{t}_{js} = \frac{2 \hat{n}_{j-1} \cos \hat{\theta}_{j-1}}{\hat{n}_{j-1} \cos \hat{\theta}_{j-1} + \hat{n}_j \cos \hat{\theta}_j}, \quad (4.24)$$

where the symbols  $\hat{n}_{j-1}$ ,  $\hat{n}_j$ ,  $\hat{\theta}_{j-1}$  and  $\hat{\theta}_j$  denote the complex refractive indices of both the  $(j - 1)$ -th and  $j$ -th materials and the complex angles of incidence and refraction by the boundary, respectively. The complex angles  $\hat{\theta}_{j-1}$  and  $\hat{\theta}_j$  fulfil the Snell's law, i. e.

$$\hat{n}_{j-1} \sin \hat{\theta}_{j-1} = \hat{n}_j \sin \hat{\theta}_j. \quad (4.25)$$

Let us consider the system consisting of the ambient with real refractive index  $n_0$  (the subscript 0) and a single thin film (the subscript 1) on the semi-infinite substrate (the subscript 2). The complex symbols  $\hat{r}_{p,s}$  and  $\hat{t}_{p,s}$  denoting the Fresnel coefficients for reflected and transmitted waves by the system, respectively are given as follows [?]

$$\hat{r}_{p,s} = \frac{\hat{r}_{1p,s} + \hat{r}_{2p,s} e^{-i\hat{x}_1}}{1 + \hat{r}_{1p,s} \hat{r}_{2p,s} e^{-i\hat{x}_1}} \quad (4.26)$$

$$\hat{t}_{p,s} = \frac{\hat{t}_{1p,s} \hat{r}_{2p,s} e^{-i\hat{x}_1/2}}{1 + \hat{r}_{1p,s} \hat{r}_{2p,s} e^{-i\hat{x}_1}}. \quad (4.27)$$

where  $\hat{x}_1$  is a phase difference gained in the thin film,  $\hat{r}_{1p,s}$  and  $\hat{t}_{1p,s}$  and/or  $\hat{r}_{2p,s}$  and  $\hat{t}_{2p,s}$  are the Fresnel coefficients for the first and/or the second boundaries.

If the thin film is homogeneous the Fresnel coefficients for the ambient-film boundary ( $\hat{r}_{1p,s}$ ) and the film-substrate boundary ( $\hat{r}_{2p,s}$ ) are given by [?]

$$\hat{r}_{1p} = \frac{\hat{n}_1 \cos \phi_0 - \cos \hat{\phi}_1}{\hat{n}_1 \cos \phi_0 + \cos \hat{\phi}_1} \quad (4.28)$$

$$\hat{r}_{1s} = \frac{\cos \phi_0 - \hat{n}_1 \cos \hat{\phi}_1}{\cos \phi_0 + \hat{n}_1 \cos \hat{\phi}_1} \quad (4.29)$$

$$\hat{r}_{2p} = \frac{\hat{n}_1 \cos \hat{\phi}_1 - \hat{n}_2 \cos \hat{\phi}_2}{\hat{n}_1 \cos \hat{\phi}_1 + \hat{n}_2 \cos \hat{\phi}_2} \quad (4.30)$$

$$\hat{r}_{2s} = \frac{\hat{n}_2 \cos \hat{\phi}_2 - \hat{n}_1 \cos \hat{\phi}_1}{\hat{n}_2 \cos \hat{\phi}_2 + \hat{n}_1 \cos \hat{\phi}_1} \quad (4.31)$$

and the phase difference  $\hat{x}_1$  is expressed as

$$\hat{x}_1 = \frac{4\pi}{\lambda} \hat{n}_1 d_1 \cos \hat{\phi}_1 \quad (4.32)$$

where  $\hat{n}_1 = n_f - ik_f$  and  $\hat{n}_2 = n_s - ik_s$  denote the complex refractive indices of the film and the substrate, respectively,  $\phi_0$  is the angle of incidence on the film,  $\hat{\phi}_1$  and  $\hat{\phi}_2$  are the complex angles of refraction in the film and in the substrate, respectively,  $d_1$  is the film thickness and  $\lambda$  wavelength.

### Thin films on absorbing substrates

If the analyzed thin film system is prepared on the absorbing substrate the only ellipsometry in the reflected light or the measurements of reflectance can be performed. The light reflected from the back side of the substrate is not needed to be considered. Then the reflection Fresnel coefficients  $\hat{r}_p$ ,  $\hat{r}_s$  expressed by Eq. (4.26) can be used directly for the calculation of the ellipsometric parameters according to Eqs. (4.19) and (4.20) or the reflectance given by Eq. (4.16).

A typical example of such application is represented by thin film systems on silicon substrates characterized in the UV-VIS spectral region.

### Thin films on transparent substrate

If the substrate is transparent or slightly absorbing it is necessary to take into account the light incoherently reflected from its back side. On the other hand we can get additional information from the transmitted light and the light reflected from the side of substrate.

If the angles of incidence differ significantly from the perpendicular direction, i. e. in the ellipsometry measurements, and substrate is sufficiently thick the light spot reflected from the thin film system can be distinguished from the reflection on the back side of the substrate. Then the relations (4.26) and (4.27) for Fresnel coefficients  $\hat{r}_p$ ,  $\hat{r}_s$ ,  $\hat{t}_p$ ,  $\hat{t}_s$  can be used and we can easily calculate the ellipsometric parameters from Eqs. (4.19) and (4.20). If the substrate is not so thick the theory of the ellipsometric measurements becomes seemingly complicated due to the present depolarisation.

In the R/T method carried out at the near normal incidence we can further assume that the angle of incidence is  $0^\circ$ . Then the terms p- and s- polarisation lose their meaning. The reflectance measured from the side of the thin film system on thick transparent substrate  $\mathcal{R}$ , the reflectance from the side of the substrate  $\mathcal{R}'$  as well as the transmittance of the same system  $\mathcal{T}$  can be expressed by the addition of reflected and/or transmitted intensities. In this way we get the relation between the theoretical values of the reflectances and the transmittance of a thin film system on the semi-infinite substrate,  $R$ ,  $R'$  and  $T$ , respectively and the measured values  $\mathcal{R}$ ,  $\mathcal{R}'$  and  $\mathcal{T}$  as follows [?]

$$\mathcal{R} = R + \frac{T^2 R_{s0} e^{-2\alpha D}}{1 - R' R_{s0} e^{-2\alpha D}} \quad (4.33)$$

$$\mathcal{R}' = R_{s0} + \frac{(1 - R_{s0})^2 e^{-2\alpha D}}{1 - R' R_{s0} e^{-2\alpha D}} \quad (4.34)$$

$$\mathcal{T} = \frac{T T_{s0} e^{-\alpha D}}{1 - R' R_{s0} e^{-2\alpha D}} \quad (4.35)$$

where

$$\alpha = \frac{4\pi k_s}{\lambda}, \quad (4.36)$$

$R_{s0}$  and/or  $T_{s0}$  are the reflectance and/or transmittance at the boundary between the substrate and surrounding medium ( $n_0 = 1$ )

$$R_{s0} = \left| \frac{\hat{n}_s - 1}{\hat{n}_s + 1} \right|^2 \quad (4.37)$$

$$T_{s0} = \left| \frac{4\hat{n}_s}{(\hat{n}_s + 1)^2} \right|, \quad (4.38)$$

and  $\hat{n}_s$  and  $D$  are the complex refractive index ( $\hat{n}_s = n_s - ik_s$ ) and the thickness of the substrate, respectively.

In some cases, e. g. for the characterisation of films on one side polished silicon substrates in the infrared region, it is necessary to measure transmittance of thin films on transparent substrates with a rough back side. As it is difficult to describe the problem theoretically it is better to treat

further the ratio  $\mathcal{T}_{\text{rel}}$  of the transmittance of the film-substrate system  $\mathcal{T}$  and the transmittance of the bare substrate  $\mathcal{T}_{\text{subs}}$ . The relative transmittance  $\mathcal{T}_{\text{rel}}$  can be expressed as

$$\mathcal{T}_{\text{rel}} = \frac{\mathcal{T}}{\mathcal{T}_{\text{subs}}} = \frac{T(1 - R_{\text{s}0}^2)e^{-2\alpha D}}{T_{\text{s}0}(1 - R'R_{\text{s}0})e^{-2\alpha D}} \quad (4.39)$$

where  $R_{\text{s}0}$ ,  $T_{\text{s}0}$ ,  $R$ ,  $R'$ ,  $T$ ,  $\alpha$  and  $D$  have the same meaning as before.

## 4.4 Long wavelengths (infrared)

Infračervená spektroskopie (IR - infrared) patří mezi základní analytické metody. IR oblastí rozumíme oblast vlnočtů od  $12500 \text{ cm}^{-1}$  do  $250 \text{ cm}^{-1}$ . Oblast od  $5000 \text{ cm}^{-1}$  do  $250 \text{ cm}^{-1}$  bývá označována jako střední IR oblast, od  $12500 \text{ cm}^{-1}$  do  $5000 \text{ cm}^{-1}$  jako blízká IR oblast a oblast od  $250 \text{ cm}^{-1}$  jako vzdálená IR oblast. Elektromagnetické IR záření je využíváno v infračervené spektroskopii k určení chemické struktury, jelikož každá látka má své unikátní IR absorpční spektrum a většina molekul je v IR oblasti spektra aktivní. Tato metoda bývá často doplněna Ramanovskou spektroskopií, pomocí které lze detekovat molekuly neaktivní v IR oblasti a naopak.

V molekulách se valenční elektrony na vnějších slupkách účastní tvorby vazby mezi atomy a jsou delokalizovány na molekulových orbitalech. Naproti tomu elektrony na vnitřních slupkách atomů zůstávají v blízkosti svých jader a jejich energie není vznikem molekuly podstatně ovlivněna. Každému molekulovému orbitalu odpovídá určitá hodnota energie. Tyto energie tvoří soubor nespojitých elektronových energetických hladin. Energie molekuly je také ovlivňována pohybem jednotlivých atomů, které neustále vibrují kolem svých rovnovážných poloh. Energie vibračního pohybu je kvantována a jednotlivým vibračním stavům (vibračním s různou amplitudou) přísluší jednotlivé vibrační energetické hladiny. Molekuly nacházející se v jednom určitém energetickém elektronovém stavu mohou mít různou vibrační energii, takže každá elektronová hladina je rozštěpena na určitý počet vibračních podhladin. Molekula jako celek vykonává také rotační pohyby, jejich energie je také kvantována. To vede k rozštěpení každé vibrační hladiny na rotační podhladiny. Pro rozdíly energií mezi jednotlivými rotačními, vibračními a elektronovými stavy platí:

$$\Delta E_{\text{rot}} \ll \Delta E_{\text{vibr}} \ll \Delta E_{\text{el}} \quad (4.40)$$

Molekula, která je ozářena spojitým spektrem IR záření může z hlediska kvantové mechaniky takové kvantum světla absorbovat a přejít do excitovaného vibračního stavu. Spektrum zbývajícího záření prokazuje absorpci na určité frekvenci, která odpovídá určitému vibračnímu a rotačnímu stavům molekuly. Molekula přejde ze stavu s nižší energií  $E_1$  do excitovaného stavu s energií vyšší  $E_2$ . Dojde k pohlcení určité energie  $\Delta E$ , které odpovídá elektromagnetické vlnění o dané frekvenci  $\nu$ , pro rozdíl energií platí:

$$\Delta E = E_2 - E_1 = h\nu \quad (4.41)$$

kde  $h$  je Planckova konstanta. Valenční a vnitřní elektrony atomů ani vazebné či nevazebné elektrony molekulových orbitalů látek nejsou v IR záření excitovány. Energie IR fotonů je ale dostatečná ke změně vibračního či rotačního stavu molekuly.



Existuje mnoho způsobů vnitřních vibrací celé molekuly, rozlišujeme různé vibrační módy odpovídající různým vazebným silám a úhlům atomů v molekule. Molekula tvořená  $N$  atomy má  $3N$  stupňů volnosti. Zajímáme-li se čistě o vibrační módy, musí se odečíst tři stupně volnosti pro translační pohyb a tři stupně volnosti pro rotaci okolo tří os pro nelineární molekuly. Zůstává tedy  $3N - 6$  stupňů volnosti z nichž každý odpovídá jedné fundamentální vibraci. Pro lineární molekulu se pro rotaci odečítají jen dva stupně volnosti, a proto má  $3N - 5$  fundamentálních vibrací. Vibrační frekvence, které odpovídají absorbovanému rozdílu energií  $\Delta E$  lze určit ze znalosti hmotností kmitajících atomů a pevnosti vazby, která je spojuje. Pro dvouatomovou molekulu s jedním vibračním stupněm volnosti platí Hookův zákon z klasické mechaniky:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (4.42)$$

kde  $k$  je silová konstanta daná typem vazby a  $\mu$  je redukovaná hmotnost dána vztahem  $\mu = \frac{m_1 m_2}{m_1 + m_2}$ .

U lineární molekuly lze rozlišit vibrace, při kterých dochází ke změně mezijaderné vzdálenosti tzv. valenční vibrace (stretching), mohou být symetrické i nesymetrické. Vibrace, při kterých se mění velikost valenčních úhlů jsou tzv. deformační vibrace (bending). Vibrace lineární molekuly jsou znázorněny na obrázku 4.6. U nelineární molekuly rozeznáváme rovněž symetrickou a nesymetrickou valenční vibraci, deformačních vibrací rozlišujeme více. Některé z těchto vibrací jsou znázorněny na obrázcích 4.7 a 4.8.

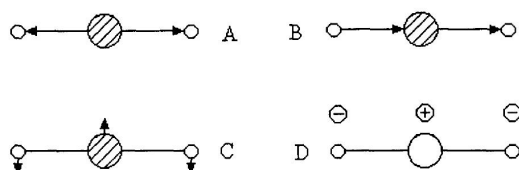


Figure 4.6: Vibrační pohyby molekuly oxidu uhličitého  $\text{CO}_2$ : A - symetrická valenční vibrace, B - asymetrická valenční vibrace, C,D - deformační vibrace (znaménka značí vibraci nad a pod rovinou nákresny).

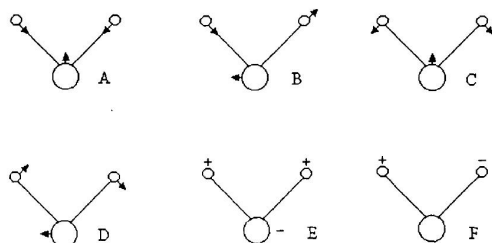


Figure 4.7: Vibrační pohyby molekuly skupiny  $\text{CH}_2$ : A - symetrická valenční, B - asymetrická valenční, C - nůžková, D - kolébavá (rocking), E - kývavá (wagging), F - krouživá (twisting).

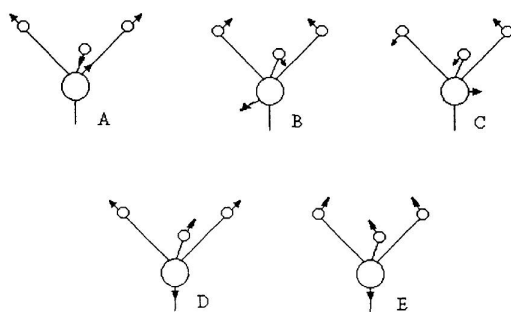


Figure 4.8: Vibrační pohyby molekuly skupiny  $\text{CH}_3$ : A - degenerovaná valenční, B - degenerovaná deformační, C - kolébavá, D - symetrická valenční, E - symetrická deformační.

Srovnáním s vazbami a funkčními skupinami můžeme dokonce identifikovat různé sloučeniny. Frekvence absorpčního pásu ve spektru se zvětšuje se silovou konstantou vazby a zmenšuje se s rostoucí hmotností atomů.

Podle mezinárodní konvence se pozice absorpčních píků vyjadřují pomocí vlnočtu ( $\text{cm}^{-1}$ ). Toto vyjádření je výhodné, protože je přímo úměrné absorbované energii, díky tomu je možné výsledné absorpční spektrum lehce interpretovat.

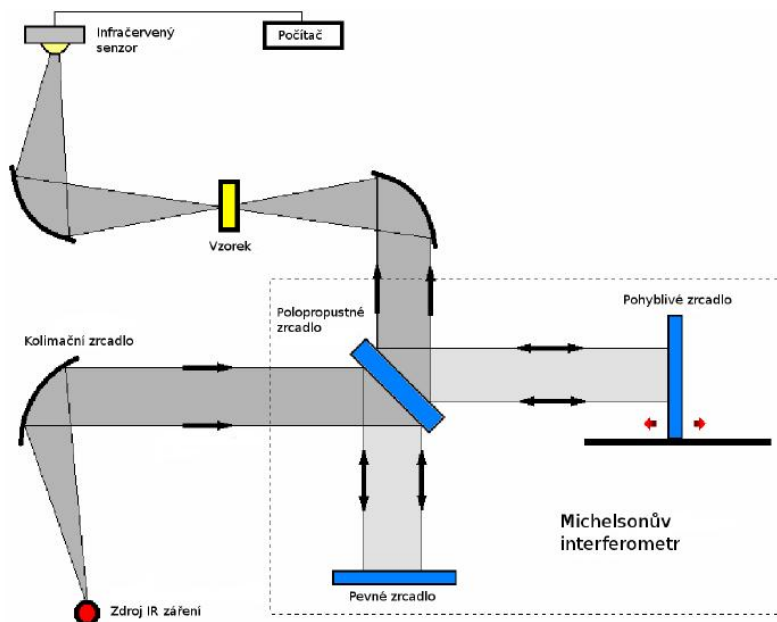


Figure 4.9: Základní schéma FTIR spektrometru - Michelsonův interferometr s pohyblivým zrcadlem

Propustnost  $T$  (transmittance) je dána poměrem intenzity světla  $I$  prošlého látkou po absorpci k intenzitě záření dopadajícího na měřený vzorek  $I_0$ :

$$T = \frac{I}{I_0} \quad (4.43)$$

V infračervené spektroskopii rozlišujeme skupinové frekvence a tzv. frekvence fingerprint (otisku prstu). Skupinové frekvence jsou charakteristické jen pro určité malé skupiny atomů, zatímco frekvence fingerprint vznikají díky vibraci molekuly jako celku. Skupinová frekvence je vždy nalezena ve spektru molekuly obsahující tuto skupinu a vždy se objevuje ve stejném rozmezí frekvencí. Důležitým lomítkem ve spektru je vlnočet  $1500\text{ cm}^{-1}$ , protože pro větší vlnočty se u píků s velkou intenzitou jedná o skupinovou frekvenci. Pro vlnočty menší než  $1500\text{ cm}^{-1}$  se může jednat o skupinovou frekvenci i o frekvenci fingerprint. Se snižující se frekvencí roste pravděpodobnost, že se jedná o frekvenci fingerprint. Skupinová frekvence pod  $1500\text{ cm}^{-1}$  bývá charakterizována velkou intenzitou, šířkou, nezvyklou ostrostití či zdvojením.

Speciálním případem infračervené spektroskopie je **Fourierovská infračervená spektroskopie**. Je to měřicí technika založená na časové modulaci signálu, ze kterého se následně Fourierovou transformací získá spektrální závislost. Časová modulace signálu je prováděna pomocí Michelsonova interferometru s pohyblivým zrcadlem viz. obrázek 4.9. Během jednoho měření se zrcadlo posouvá konstantní rychlostí, čímž vytváří časové zpoždování paprsku. Detektor zachycuje interferogram, ve kterém je vzdálenost interferenčních proužků  $d$  funkcí frekvence záření  $\nu$  a rychlosti pohyblivého zrcadla  $u$ . Provedením zpětné Fourierovy transformace intenzity  $I(d)$  se získá spektrální rozložení intenzity  $I(\nu)$ .

## 4.5 Interaction of matter with very long wavelengths photons ( $\geq 1\text{mm}$ ) - including radio and microwaves

All nucleons, that is neutrons and protons, composing any atomic nucleus, have the intrinsic quantum property of spin. The overall spin of the nucleus is determined by the spin quantum number  $I$ . Some nuclei have integral spins (e.g.  $I = 1, 2, 3 \dots$ ), some have fractional spins (e.g.  $I = 1/2, 3/2, 5/2 \dots$ ), and a few have no spin,  $I = 0$  (e.g.  $^{12}\text{C}$ ,  $^{16}\text{O}$ ,  $^{32}\text{S}$ , ...). Isotopes of particular interest and use to organic chemists are  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}$ , all of which have  $I = 1/2$ .

A non-zero spin is always associated with a non-zero magnetic moment  $\mu$

$$\mu = \gamma S \quad (4.44)$$

where  $\gamma$  is the gyromagnetic ratio.

It is this magnetic moment that allows the observation of nuclear magnetic resonance (NMR) absorption spectra caused by transitions between nuclear spin levels in the presence of external magnetic field (spin states splitting).

<http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/nmr/nmr1.htm>

*Electron spin resonance (ESR)* or *electron paramagnetic resonance (EPR)* is a related technique in which transitions between electronic spin levels are detected rather than nuclear ones. The basic principles are similar but the instrumentation, data analysis, and detailed theory are significantly different. Moreover, there is a much smaller number of molecules and materials with unpaired electron spins that exhibit ESR absorption than those that have NMR absorption spectra. ESR has much higher sensitivity than NMR does.