SEMINAR II
Infrared Spectroscopy

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Abstract

Infrared spectroscopy is a powerful tool in the study of molecular structure or composition and it is therefore widely used technique. Here only some aspects of it are covered. This includes introductionary theory of vibrational and rotational spectra, basic infrared instrumental components, some experimental techniques and a few examples of deriving informations from the spectra.
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1 Introduction

Infrared spectroscopy deals with processes of the interaction of the electromagnetic radiation with matter which produce a variation in the vibrational and/or rotational motions of the molecules. The study of these motions is of paramount importance for understanding of several physical properties of molecular compounds and represents a powerful tool for the investigation of molecular structure. By far the most popular use of the information derived from the vibrational and rotational spectra is the analysis of the chemical constitution of the molecules - the masses of the atoms and also molecular structure and binding forces between the atoms. Information concerning the intermolecular forces is also carried by the molecular vibrational frequencies, since they are very sensitive to the molecular environment. In the case of hydrogen-bonded systems, shifts of several hundred wavenumbers are observed for some bands involving the motion of the hydrogen-bonded groups.

The energy of a molecule consists of translational, rotational, vibrational and electronic energy. (For a first approximation these energy contributions can be considered separately). Molecular vibrations give rise to absorption or emission throughout most of the infrared region of the spectrum - the regions where other energy transitions take place are listed in Table 1. In this seminar we shall mainly be concerned with the interaction of electromagnetic radiation with molecular vibrations and rotations. [1],[2]

In principle the infrared spectrum of a chemical compound can be observed either in absorption or in emission. In practice the absorption spectrum is much more convenient for laboratory measurements, except in special cases (astrophysical problems, emissions of flames, etc.).

<table>
<thead>
<tr>
<th>Transitions</th>
<th>Region</th>
<th>$\lambda$</th>
<th>$\tilde{\nu}$ [cm$^{-1}$]</th>
<th>$E$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic</td>
<td>UV</td>
<td>100 - 400 nm</td>
<td>10$^6$ - 25000</td>
<td>120 - 3</td>
</tr>
<tr>
<td></td>
<td>Visible</td>
<td>400 - 700 nm</td>
<td>25000 - 12800</td>
<td>3 - 1.5</td>
</tr>
<tr>
<td></td>
<td>Near IR</td>
<td>0.7 - 2.5 $\mu$m</td>
<td>12800 - 4000</td>
<td>1.5 - 0.5</td>
</tr>
<tr>
<td>Vibrational</td>
<td>Infrared</td>
<td>0.7 $\mu$m - 1 mm</td>
<td>12800 - 10</td>
<td>1.5 - 10$^{-3}$</td>
</tr>
<tr>
<td>Rotational</td>
<td>Far IR</td>
<td>0.05 - 1 mm</td>
<td>200 - 10</td>
<td>0.02 - 10$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>Microwaves</td>
<td>1 mm - 1 m</td>
<td>10 - 0.01</td>
<td>&lt; 10$^{-4}$</td>
</tr>
</tbody>
</table>

Table 1: Values for $\lambda$, $\tilde{\nu}$ and $E$ for different regions of the electromagnetic spectrum

In the infrared region of the electromagnetic spectrum the practical unit for wavelength is 1 $\mu$m. It is also customary for chemists to use units of cm$^{-1}$ for the frequencies of vibration $\tilde{\nu}$, defined as $1/\lambda$. The frequency in cycles per second is then equal to $\tilde{\nu}c$, where $c$ is the velocity of light. Infrared spectra have been presented so that the horizontal coordinate is either linear with wavelength or with wavenumber, the vertical coordinate is usually transmittance $T$ or absorbance $A$, which are correlated with expression

$$A = -\log_{10} T.$$  \hspace{1cm} (1)
According to the quantum theory the energy of a photon is given by $E_p = h\nu$. This photon energy may be absorbed or emitted by a molecule in which case the rotational, vibrational, or electronic energy of the molecule will be changed by an amount $\Delta E_m$. According to the principle of conservation of energy we can write:

$$\Delta E_m = E_p = h\nu \quad (2)$$

2 Theory of Vibrational and Rotational Transitions in Molecule

In the study of molecular vibrations and rotations we can start with a classical model of the molecule where the nuclei are represented by mathematical points with mass and the internuclear forces holding the molecule together are assumed to be similar to those exerted by massless springs which tend to restore bond lengths or bond angles to certain equilibrium values. We assume also that we can separate the electronic motions from the vibrational and rotational movements of nuclei. The calculations are done in the harmonic approximation.

If there are $N$ atomic nuclei in the molecule, there will be a total of $3N$ degrees of freedom of motion for all the nuclear masses. After substracting the translational and rotational degrees of freedom, we are left with $3N - 6$ internal degrees of freedom for a nonlinear molecule and $3N - 5$ degrees of freedom for a linear molecule. Rotation of a linear molecule about the molecular axis is not considered as degree of freedom since no displacements of nuclei are involved.

Given the masses, the molecular geometry and the force constants, complete mathematical procedures exist for calculating the form and frequencies of vibration and rotation of relatively simple molecules. As the molecules become more complex the difficulty of the mathematical treatment increases enourmously. Here the diatomic vibrational and rotational calculations serve as the model. [1],[2]

2.1 Classical Treatment

2.1.1 Vibrational Frequency Formula for a Diatomic Molecule

Let the diatomic molecule be represented by two masses $m_1$ and $m_2$ connected by a massless spring with the force constant $k$ and the displacements of each mass from equilibrium along the axis be $X_1$ and $X_2$. We obtain two equations:

$$k(X_2 - X_1) = m_1 \frac{d^2X_1}{dt^2} \quad \text{and} \quad -k(X_2 - X_1) = m_2 \frac{d^2X_2}{dt^2} \quad (3)$$

Since these equations of motions are function of $X$ and its second derivative, one possible solution is that both $X_1$ and $X_2$ vary periodically as a sine or cosine function, so we can write trial solutions for $X_1$ and $X_2$

$$X_1 = A_1 \exp (i\omega t) \quad \text{and} \quad X_2 = A_2 \exp (i\omega t) \quad (4)$$
We note that while each mass oscillates along the spring axis with a different maximum amplitude $A_i$, each mass oscillates with the same frequency and phase constant, which means that both masses go through their equilibrium positions simultaneously. Substituting the values for $X_i$ and their second derivatives into the original equations of motion (Eq. 3) we get

$$k(A_2 - A_1) = m_1A_1\omega^2 \quad \text{and} \quad k(A_2 - A_1) = m_2A_2\omega^2$$

Eliminating $A_1/A_2$ and solving for $\omega$ we obtain

$$\omega^4 = \omega^2\frac{k(m_1 + m_2)}{m_1m_2}$$

In one solution we obtain $\omega = 0$ and $A_1 = A_2$ or for any time $X_1$ is equal to $X_2$. This zero frequency vibration is actually a translation along the spring axis or $X$ direction.

For the other solution we obtain

$$\omega = \sqrt{\frac{k}{m_1m_2}}$$

where $\mu$ is the reduced mass. We note that the vibrational frequency is independent of amplitude.

When this value of $\omega$ is substituted into amplitude equation we obtain

$$\frac{A_1}{A_2} = -\frac{m_2}{m_1} \quad \text{or} \quad \frac{X_1}{X_2} = -\frac{m_2}{m_1}$$

which indicates that the center of gravity does not move.

These two solutions for $\omega$ correspond to the two degrees of freedom the two masses have in the spring axis direction: (1) translation without vibration and (2) vibration without translation.

Given the frequency and the reduced mass, the force constant can be calculated by $F = \omega^2\mu$.

In Table 2.1.1 are presented some calculated force constants for some diatomic molecules. These are arranged in order of decreasing force constants including triple (N≡N), double (O=O), single (H-Cl) and ionic bonds (Na$^+$Cl$^-$). [1]

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\bar{\nu}$ [cm$^{-1}$]</th>
<th>$\mu$ [10$^{-26}$ kg]</th>
<th>$F$ [10$^2$ N/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>2331</td>
<td>1.1625</td>
<td>22.4</td>
</tr>
<tr>
<td>CO</td>
<td>2143</td>
<td>1.1384</td>
<td>18.6</td>
</tr>
<tr>
<td>O$_2$</td>
<td>1556</td>
<td>1.3279</td>
<td>11.4</td>
</tr>
<tr>
<td>H$_2$</td>
<td>4159</td>
<td>0.0837</td>
<td>5.1</td>
</tr>
<tr>
<td>HCl</td>
<td>2886</td>
<td>0.1627</td>
<td>4.8</td>
</tr>
<tr>
<td>NaCl</td>
<td>378</td>
<td>2.3162</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table 2: Observed vibrational frequencies and calculated force constants for selected diatomic molecules

2.1.2 The Dipole Moment

While the absorption frequency depends on the molecular vibrational frequency, the absorption intensity depends on how effectively the infrared photon energy can be transferred to the molecule,
which depends on the **change in the dipole moment** that occurs as a result of molecular vibration. Since the wavelength of infrared radiation is far greater than the size of most molecules, the electric field of the photon can be considered uniform over the whole molecule. The oscillating electric field exerts forces on the molecular charges, tending to change spacing between positive and negative centers of charge, tending to induce the dipole moment of the molecule to oscillate at the frequency of the photon, respectively. In order to absorb infrared radiation, a molecular vibration must cause a change in the dipole moment of the molecule. [1],[2]

Consider, for instance, the spectrum of the **CO\(_2\) molecule**. It has 4 \((3 \times 3 - 5)\) normal modes of vibration. In the first type of vibration the two oxygen atoms move in phase away from the carbon atom (calculated frequency for this motion is 1537 cm\(^{-1}\)). The dipole moment that was zero by symmetry for equilibrium configuration, remains constantly zero during the vibration and there is no absorption band in the spectrum at this frequency. In the second type of vibration, the oxygen atoms move together toward the right while the carbon atom moves toward the left in a half-cycle (\(\bar{\nu} = 2349\) cm\(^{-1}\)). During the vibration the molecular symmetry is lost and a periodic variation of the dipole moment is thus produced. In the third and fourth type of vibration the angle between bonds is changing (bending vibration). These vibrations are actually the same, only that one is rotated for 90\(^\circ\) to other and vibrate therefore with the same frequency (667 cm\(^{-1}\)). [2],[5]

![Figure 1: The spectrum of the CO\(_2\) molecule [8]](image)
2.2 Quantum Treatment

2.2.1 Vibrational Transitions and Infrared Absorption

We assume that we can separate the electronic motions from the vibrational and rotational movements of nuclei:

\[ \mathcal{H} = \mathcal{H}_e + \mathcal{H}_n = \mathcal{H}_e + \mathcal{H}_v + \mathcal{H}_r \]

(9)

The quantum mechanical vibrational Hamiltonian operator for a molecule has the form of

\[ \mathcal{H}_v = -\frac{\hbar^2}{2} \sum_{i=1}^{3N-6} \left( \frac{\partial^2}{\partial Q_i^2} - \frac{\lambda_i}{\hbar^2} Q_i^2 \right), \]

(10)

where \( Q_i \) are a set of \( 3N - 6 \) (\( 3N - 5 \) for the linear molecule) independent variables. The wavefunction \( \Psi_v \) of the equation \( \mathcal{H}_v \Psi_v = E_v \Psi_v \) can be written as the product of \( 3N - 6 \) independent functions \( \Psi_{vi}(Q_i) \) and the vibrational energy \( E_v \) as the sum of \( 3N - 6 \) terms \( E_{vi} \). By application of the Hamiltonian operator to the wavefunction we obtain \( 3N - 6 \) independent equations in one variable which are the well known Schrödinger equations for a one-dimensional harmonic oscillator. Using the dimensionless normal coordinate \( q_i \) \( (q_i^2 = \sqrt{\lambda_i / \hbar^2 Q_i^2}) \), equations can be solved exactly. The eigenvalues are given by

\[ E_{vi} = h\nu_i(n_i + \frac{1}{2}) \]

(11)

where \( \nu_i \) is the classical frequency of vibration and \( n_i \) is a quantum number which can take any integral positive value including zero. The eigenfunctions are given by

\[ \Psi_{vi} = \left( \frac{2\sqrt{\lambda_i}}{\hbar} \right)^{1/4} \sqrt{\frac{1}{2^{n_i!}} \left( \frac{\hbar}{2} \right)^{n_i}} H_{n_i}(q_i) e^{-\frac{q_i^2}{2}} \]

(12)

where \( H_{n_i}(q_i) \) are the Hermite polynomials of degree \( n_i \).

In the quantum mechanical harmonic oscillator the vibrational quantum number may change only by \( \pm 1 \). All other transitions are forbidden if the vibration is harmonic. \[1\],\[2\]

\[ \Delta E_m = [(n + 1) + \frac{1}{2}]h\nu_m - (n + \frac{1}{2})h\nu_m = h\nu_m \rightarrow \nu_p = \nu_m, \Delta n = \pm 1 \]

(13)

2.2.2 Rotation

In order to absorb infrared (or microwave) radiation the rotating molecule must possess a permanent dipole moment.

The quantum mechanical rotational energy for molecules is not continuously variable (in contrary with classical rotational energy). For the rigid diatomic molecule the rotational energy levels are given by

\[ E_{rot} = \frac{\hbar^2 J(J + 1)}{8\pi^2 I} \]

(14)

where \( J \) is the rotational quantum number which can assume only integer values \( 0,1,2,3,... \). In a nonrigid rotating diatomic molecule centrifugal distortion will elongate the bond as the rotational frequency increases. To accurately fit the energy levels, a correction term must be added \( E_{rot} = BJ(J + 1) - Dhc[J(J + 1)]^2 \).
If the absorbed photon increase rotational quantum number by one, the molecule gains rotational energy

$$\hbar \nu_p = \Delta E_{\text{rot}} = B[(J+1)(J+2) - J(J+1)] = B(J+1) \tag{15}$$

The classical rotational frequency $\nu_c$ for the linear molecule in the energy level $J$ is equal to $2B\sqrt{J(J+1)}$. The frequency of the photon $\nu_p$ having the right energy to cause transition from $J$ to $J+1$ is given by $2B(J+1)$ and after substracting these equations together, we obtain

$$\nu'_J : \nu_p : \nu'_{J+1} = \sqrt{J} : \sqrt{J+1} : \sqrt{J+2} \tag{16}$$

so that the frequency of the absorbed photon is intermediate between the initial and final classical rotational frequencies of molecule when the quantum number is changed by one. \[1\]

### 2.2.3 Vibrational Rotational Spectrum

Total energy for the linear molecule is given by equation

$$E_{v+r} = (n + \frac{1}{2})\hbar \nu_0 + B[J(J+1)] \tag{17}$$

A poliatomic molecule can have two types of vibrational-rotational bands, parallel ($\Delta J = \pm 1$) and perpendicular ($\Delta J = 0$), depending from orientation of the dipole moment.

Let $J_0$ represent the rotational quantum number in the ground vibrational state $n = 0$ and $J_1$ represent the rotational quantum number in the first excited vibrational state $n = 1$. The average internuclear distance and hence the moment of inertia increases as the vibrational quantum number increases, that is why the rotational constant $B$ has the smaller value in the excited state ($B_1$) than in the ground state ($B_0$). We can now write:

$$\Delta E_{v+r} = h\nu_0 + B_1[J_1(J_1+1)] - B_0[J_0(J_0+1)] \tag{18}$$

For so called Q branch $\Delta J$ is equal to 0 and so $J_1 = J_0$. For the R branch $\Delta J = +1$ and for the P branch $\Delta J = -1$.

The rotational lines appear as a fine structure of the vibrational bands because the separation between rotational levels ($\sim 0.01$ eV) is much smaller than the separation between vibrational levels ($\sim 1$ eV). If the spectrum is measured under sufficient resolution, the vibrational bands may show a fine structure consisting of several sharp lines. The separation between rotational lines is large enough to be observed only if the moments of inertia of the molecule are relatively small (this is valid for small molecules only). \[1\]

### 2.2.4 Boltzmann Distribution Function

A rotatational transition ($J \rightarrow J+1$) give rise to an individual line in the pure rotational spectrum whose intensity is proportional to the $J$ rotational energy level population $n_j$ as given by the Boltzmann distribution function

$$\frac{n_j}{n_0} = \frac{g_j}{g_0} \exp^{-(E_j-E_0)/kT} \tag{19}$$
Here the factor $g_j$ is the number of energy states with the same energy $E_j$. In the rotational case the lowest level ($J = 0$) is a single state ($g_0 = 1$) but the higher levels have a $(2J + 1)$ multiplicity of states in each level. At 300 K higher rotational levels are more occupied than the ground level, because the rotational energy levels distinguish for about 0.01 eV, what gives a factor around $\exp(-0.4) \sim 0.7$. In contrary almost all molecules are in ground vibrational state, because here the factor is around $\exp(-40) \sim 10^{-18}$. The so-called hot transitions between the higher levels arise at higher temperatures only. [1],[5]

2.3 Anharmonicity

The vibrational spectra of molecular systems show definite deviations from the predictions of the harmonic model. The selection rules for harmonic oscillator predict that overtones (transitions from $n = 0$ to $n = 2, 3, 4...$ etc.) and combination bands (they appear near the frequency of the sum of two fundamental frequencies) should be forbidden, but in actual spectra these are very often observed, sometimes with significant amplitude. The harmonic model also predicts that overtones should occur at exactly $n$-times the frequency of the fundamental mode (transition from $n = 0$ to $n = 1$) and that hot bands (transitions from $n = 1$ to $n = 2$ etc.) should occur at the same frequency as the fundamental. In practice this is never observed, because frequency is no longer completely independent of amplitude when anharmonicity is present (terms higher than second are retained in the potential function). It depends from the nature of the bond, how much the anharmonic terms are present. For instance, stretching vibrations are quite harmonic, on the other hand, the potential function for the hydrogen bond is strongly anharmonic, because the proton does not have exact position. [1],[2]

2.3.1 The Morse Function

An often used empirical equation called the Morse function (illustrated in Figure 2) is a usefull approximation for the diatomic molecule potential energy

$$V(r) = D_e (1 - \exp^{-\beta(r-r_e)})^2,$$

where $r$ is the internuclear distance, $r_e$ is the equilibrium internuclear distance, $D_e$ is the energy of dissociation and $\beta$ is a constant, equal to $\beta = \omega_e \sqrt{u/2D_e}$. Near equilibrium the Morse function resembles the harmonic oscillator function.

3 Infrared Experimental Considerations

3.1 Spectrometers

3.1.1 Source of Infrared Radiation

A source of infrared radiation is usually some solid material heated to incandescence by an electric current. We can approximate its energy distribution with the theoretical black body radiation. It is important to note that energy output falls off very rapidly at long wavelengths. Most IR
Figure 2: The potential energy of a diatomic molecule plotted as a function of internuclear distance - the red line. The blue line is the harmonic oscillator potential function. [1]

sources are operating at a temperature where the energy maximum is near the short wavelength limit of the spectrum. We (PE 2000) use voltage-stabilized air-cooled wire coil that operates at about 1350 K for mid infrared region. [1]

3.1.2 Infrared Detectors

The infrared detector is a device which measures the infrared energy of the source which has passed through the spectrometer. These devices change radiation energy into electrical energy which can

Figure 3: A simple spectrometer layout [9]
be processed to generate a spectrum. There are two basic types, thermal detectors (thermocouples, bolometers, pyroelectric detectors) which measure the heating effects of radiation and respond equally well to all wavelengths, and selective detectors (photoconductive cell) whose response is markedly dependent on the wavelength, but they have a very rapid response and a high sensitivity.

A thermal detector, which is commonly used, is a pyroelectric crystal such as deuterated triglycine sulfate (DTGS). Its residual polarization is sensitive to changes in temperature. An example for selective detectors is the mercury cadmium telluride detector (MCT), which has to be cooled with liquid nitrogen. The photoconductive cells show an increase in electrical conductivity when illuminated by infrared light. It is used for samples with low transmittance or for ATR (attenuated total reflection) spectroscopy. [1]

3.1.3 Interferometers

Between the source and detector, there must be some kind of device to analyze the radiation so that an intensity can be evaluated for each wavelength resolution element. There are two basic types: monochromators, used in dispersive instruments, and interferometers used in Fourier transform instruments.

In a monochromator, a prism or grating separates the components of polychromatic radiation by bending it by an amount that varies with wavelength. The whole spectrum is measured one wavelength at time, which has some deficiencies compared to interferometers.

The biggest advantage that Fourier transform spectrometers have over dispersive spectrometers is the large signal-to-noise ratio: the intensities of all the resolution elements are measured simultaneously that means the whole time the total radiation is reaching the detector. In addition a complete spectrum can be obtained very rapidly.

The basic principle of the Michelson Interferometer is to split a beam into two and then recombining the two beams after introducing a path difference using fixed and moveable mirror, so an interference pattern is obtained. The interferogram is measured by recording the detector signal as a function of the path difference between two beams. For signal averaging, successive interferograms have to be measured at exactly the same points; this is achieved by using a helium-neon laser as a reference. The customary spectrum, showing energy as a function of frequency, can be obtained by the mathematical process of Fourier Transformation, which analyzes the interferogram as the sum of a series of sine and cosine waves with discrete frequencies.

\[
S(k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(x) \exp(ikx)dx, \quad k = \frac{2\pi}{\lambda},
\]

where \(S(k)\) is the spectral distribution of light that passed through the sample and \(f(x)\) is the difference between energy reaching the detector through the empty machine (the background spectrum) and through the sample. Usually a number of scans are taken and signal-averaged by the computer, which reduces the noise by the square root of the number of scans. The resolution is constant over the whole spectrum and is increased by increasing the length of travel of moveable
3.1.4 Infrared Transmitting Materials

Cells for holding samples, or windows within the spectrometer must be made of infrared transmitting material. Some of the most useful window materials for mid IR are NaCl (approximate transmission limit around 600 cm$^{-1}$; it depends on the thickness of material being used), KBr (350 cm$^{-1}$) and ZnSe (450 cm$^{-1}$). Because some of them (NaCl, KBr) are quite soluble in water which can occur badly scratches, they have to be polished with alcohol occasionally. For the far IR below 600 cm$^{-1}$ polyethylene is used. [1]

3.2 Sample Preparation

The IR spectra of the substance in the gas phase at low pressure can be considered as characteristic of the isolated molecules without intermolecular interactions. Under sufficient resolution the spectrum may show a fine rotational structure of broad vibrational bands. Absorption spectra of gases can be measured in gas cells ranging from a few centimeters to many meters in path lengths. Gas cells are basically gas tight cylinders with IR transmitting windows on the ends.

In the IR spectra of liquids the intermolecular forces and high rate of molecular collisions produce frequency shifts of several hundreds cm$^{-1}$, additional bands and absence of fine rotational structure. Variations of the environment around each molecule are responsible for line broadening. In most instances spectra of liquids are measured in liquid cells. The cell windows are separated by some spacer material (insoluble plastic or metal foil). A drop of liquid sample, along with the spacer, is simply sandwiched between the cell windows and clamped gently together in the cell holder. The cell thickness is not reproducible even if reassembled with the same spacer.

The IR spectra of solids show very sharp vibrational bands because of the absence of collisions and the rotational structure. The bands are split into several components depending upon the unit cell form and symmetry. Since the symmetry is lower than the symmetry of the isolated molecule, additional bands, inactive in the gas phase, may appear. We observe the states above the continuum of the crystal lattice.

Techniques for obtaining the infrared spectra of solids are more diversified than for either gases or liquids, here only a few of them will be mentioned.

If a suitable solvent is available, the solid may be dissolved and measured in the manner described for liquids. Suitable solvents are limited in number and none are totally transparent. Most used are carbon tetrachloride (CCl$_4$), chloroform (CHCl$_3$), dimethyl sulfoxide and dioxane. Here (Fig. 4) are some spectra of solid samples in different commonly used solvents (amino acids in CDCl$_3$, dioxane and DMSO).

An extremely valuable technique for solid samples is the mineral oil (Nujol) mull method. A small amount of solid sample is mulled in a mortar with the small amount of Nujol to yield a paste which is then mulled directly between the salt plates. This technique has the advantage of
nonreactivity with samples, reproducibility of results and rapidity of preparation. Another valuable method involves the potassium bromide disc technique. In this method a very small amount of finely ground solid sample is intimately mixed with powdered potassium bromide and then pressed in a die under high pressure. The resulting discs are transparent and yield excellent spectra. However, KBr discs usually have a little water absorbed in the KBr, seen as a weak band about 3440 cm$^{-1}$ and at 1640 cm$^{-1}$. One never knows for sure whether this is water impurity in the sample or in the KBr. [1]

3.3 Attenuated Total Reflection (ATR)

Attenuated total reflection (ATR) or internal reflection spectroscopy is an important method for obtaining the infrared spectra of solids, thin films or water solutions in a reproducible way.

In the case of total reflection an evanescent (vanishing) wave persist beyond the interface into the rare medium with the same frequency as the totally reflected radiation and with logarithmically diminishing amplitude. Such an evanescent wave is capable of interacting with an absorbing medium just beyond the interface leading to a reduction (attenuation) of the totally reflected radiation.

In this technique the sample is pressed into contact with a high index refraction prism (made from diamond or germanium). The IR band intensities are the equivalent of a penetration of a few
microns into the substance and are independent of the sample thickness. Because of this, sample preparation is simplified.

ATR spectra are not exact duplicates of transmission spectra. The effective penetration of the evanescent wave into the sample is a direct function of the wavelength of the radiation, so when the wavelength increases, bands get deeper relative to those in a transmission spectrum. Secondly, the effective penetration of the evanescent wave is also function of the refraction index of the sample which fluctuates sharply in the region of an absorption band. [1],[5]

3.4 Sample Measurement

In order to generate a percent transmission (or absorption) spectrum, first the reference single beam spectrum (the background spectrum) is generated, then stored in the computer and ratioed with a sample spectrum later. Overall shape of the background (see Fig. 5) single beam spectrum is determined by the characteristics of the beamsplitter and the source. [1],[3]

![Figure 5: The background spectrum from ATR measurement. The bands around 2000 cm$^{-1}$ are of diamond prism.](image)

Any change in water vapour or carbon dioxide concentration results in extraneous bands, that is why the spectrometer has to be purged, with nitrogen for instance. It has to be insured that the degree of purge is the same for sample and background measurements. Because this is not always exactly true, we sometimes have to measure so called "empty sample" - after background measurement we simple repeat the scanning without sample (Fig. 6). By handling of the spectra we can differ this "empty sample" from our measurements and obtain the spectra without water or CO$_2$ impurities. After we obtained the proper spectra, we can manipulate it: correct the baseline, make the difference or comparison to the other spectra, calculate the optical properties of the sample, etc. and use it for further processing of data, which we are interested in.

It is found empirically that certain submolecular groups of atoms consistantly produce bands in a characteristic frequency region of the vibrational spectrum. These bands are the characteristic group frequencies. Some of them are listed in Table 3. On the other hand, the vibrational
Figure 6: "The empty spectrum" consisting generally of noise and some bands with very low intensities.

<table>
<thead>
<tr>
<th>Group</th>
<th>Frequency [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>≡C-H</td>
<td>3300</td>
</tr>
<tr>
<td>-O-H</td>
<td>(gas) 3680</td>
</tr>
<tr>
<td></td>
<td>(liquid) 3400</td>
</tr>
<tr>
<td>&gt;N-H</td>
<td>3350</td>
</tr>
<tr>
<td>-C≡N</td>
<td>2100</td>
</tr>
<tr>
<td>-C≡C</td>
<td>2050</td>
</tr>
<tr>
<td>&gt;C=O</td>
<td>1700</td>
</tr>
<tr>
<td>&gt;C=C&lt;</td>
<td>1650</td>
</tr>
<tr>
<td>≡C-Cl</td>
<td>650</td>
</tr>
</tbody>
</table>

Table 3: Some characteristic group frequencies - approximate values (bands can be shifted due to the molecular environment)

spectra of similar compounds have a number of bands not in common, which are the so-called fingerprint bands because they are characteristic of the individual chemical compound and are used to distinguish one compound from another. [1]

4 Examples

4.1 Histidine

An amino acid of major importance as a ligand in many metallo-enzymatic regions is histidine (Fig. 7). The pH is one of the driving forces in the orientation process, which plays a key role in the catalytic activity of enzymes. Aqueous solutions of L-histidine with addition of HCl or NaOH have been measured over the pH range 0 - 12 with increments of two pH units. The resulting set of bands in spectral region 1800 - 1000 cm$^{-1}$ can be interpreted as marker for the state of protonation (histidine can be present in five different pH-dependent ionic forms).
Figure 7: The structure formula of amino acid histidine

Figure 8: Infrared spectra of aqueous solutions of L-histidine at pH 0, 2, 4, 6, 8, 10 and 12.

4.2 Water and D₂O

The infrared spectrum of liquid water consist of three bands: first at 3400 cm⁻¹ is a combination of the symmetric and asymmetric stretch, second band at 1600 cm⁻¹ is the bending mode and at around 600 cm⁻¹ the librations (restricted rotations) are to be found. Because of the hydrogen bonding the bands become broader due to the variation in the molecular environment, frequencies of the stretching modes decrease and frequency of the bending mode increases. From Fig. 9 band
shifts due to the mass difference between H and D atom can be seen. This is called isotopic effect.

![Figure 9: The spectra of H\textsubscript{2}O and D\textsubscript{2}O and mixtures.](image)

5 Conclusion

Because of its many advantages infrared spectroscopy is a very widely used method of the chemical analysis in different scientific regions (chemistry, biochemistry, biophysics, medicine etc.) and has also industrial applications. It is a powerful tool for chemical analysis: we can match spectra to known database and so identify an unknown compound, monitor chemical reactions in-situ, determine what chemical groups are in specific compound and obtain the electronic information about compounds (measuring optical conductivity we can determine whether the sample is metal, insulator etc. and determine its optical properties).

The molecular vibrations and rotations can be studied also with Raman Spectroscopy, which gives us additional information, because some bands, inactive in IR spectra, are obtained. Another possibility for deriving similar type of information is Inelastic Scattering of Neutrons (neutrons do not posses electrical charge and can therefore penetrate deep in matter), but it is very expensive method, because there are only a few proper sources of neutrons available for doing such researches.
Infrared spectra can be run on gases, liquids or solids, it is easy to prepare and measure the samples, we can easily vary different physical properties of the samples, such as temperature, pressure and magnetic field.

It is impossible to mention all the facts connected with this region. Here only some aspects of it are covered. The theoretical calculations are presented on an introductionary level (diatomic molecules serve as the models). Some experimental techniques, basic instrumentation and a few examples were presented in this text.

6 The Bibliography


7. http://www.le.ac.uk/chemistry/schools/TeachersHO.pdf


11. http://lsbu.ac.uk/water/vibrat.html