c speed of light (3×10^{10} cm s^{-1})
h Planck's constant
ν frequency (Hz or s^{-1})
λ wavelength (cm)
$\tilde{\nu}$ wavenumber (cm^{-1})

The normal region of an IR spectrum lies between 4000 and 400 cm^{-1}.

Many functional groups in organic molecules show characteristic vibrations, which correspond to absorption bands in defined regions of the IR spectrum. These molecular vibrations are essentially localised within the functional groups and do not extend over the rest of the molecule. Thus such functional groups can be identified by their absorption bands. This fact, together with the simple measurement technique, makes IR spectroscopy the easiest, quickest, and often most reliable method of assigning a substance to a particular class of compounds. Usually it is possible to decide immediately if an alcohol, amine, or ketone, or an aliphatic or aromatic compound is present. From closer inspection of the position and intensity of the bands it is possible to draw even more detailed conclusions, for example as to the type of substitution of aromatics, or the presence of carboxylic acid, ester, or amide functions. Furthermore there are now large collections of reference spectra available in catalogues or data bases for comparison. Thus it is often possible to unambiguously identify an unknown compound from its IR spectrum alone. The number of IR spectra catalogued or published in the literature currently amounts to ca. 100,000. This immense range of reference material is increasingly becoming available to computerised search methods.

2. Basic Principles and Selection Rules

To comprehend the processes which lead to an IR spectrum it is useful to consider a simple model derived from classical mechanics. If atoms are considered as point masses, the vibrations in a diatomic molecule (e.g. HCl) can be described as in Fig. 2.1. The molecule consists of the masses m_1 and m_2, which are joined by an elastic spring (**a**). If the equilibrium distance r_0 between the masses is increased by the amount $x_1 + x_2$ (**b**) a restoring force K ensues. On release the system vibrates about the equilibrium distance.

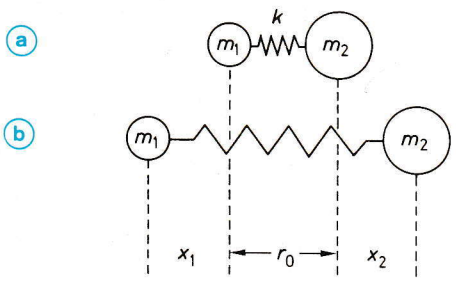


Fig. 2.1 Mechanical model of a vibrating diatomic molecule. (Extension $\Delta r = x_1 + x_2$)

According to Hooke's Law the restoring force is to a first approximation proportional to the extension Δr

$$K = -k \cdot \Delta r.$$

The negative sign arises since the force is opposed to the extension. In the mechanical model the proportionality constant k is the elasticity constant of the spring. In the molecule k (the force constant) is a measure of the bond strength between the atoms.

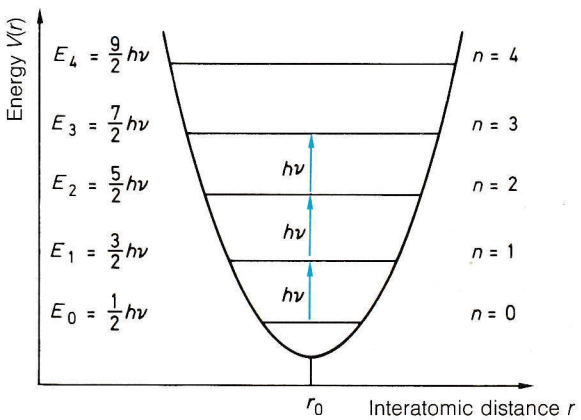


Fig. 2.2 Potential energy curve of a harmonic oscillator with discrete vibrational levels E_i

The energy of the vibration can be derived from the model of a harmonic oscillator (Fig. 2.2). Its potential energy is a function of the internuclear distance r*

$$V(r) = \tfrac{1}{2} k \cdot x^2 = 2\pi^2 \mu \nu_{osc}^2 \cdot x^2$$

V potential energy
k force constant
x extension

$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2} = \text{reduced mass}$$

ν_{osc} vibration frequency of the oscillator

* see standard physics textbooks

From the above equation the vibration frequency of a diatomic molecule can be calculated from the mechanical model as

$$\nu_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}.$$

The vibrational frequency ν is thus higher, the higher the force constant k is, i.e. the stronger the bond is. And furthermore, the smaller the masses of the vibrating atoms, the higher the frequency.

This relationship is useful for spectral interpretation, since it allows qualitative predictions of absorption frequencies in the IR spectrum. For example from the bond strengths of carbon-carbon bonds it follows that (see also p. 39).

$$k_{c\equiv c} > k_{c=c} > k_{c-c}$$

The application of the mechanical model to diatomic molecules fails to explain certain phenomena, for example the dissociation of the molecule on irradiation with sufficient energy. A better description is the non-harmonic oscillator model (Fig. 2.3). Its potential energy curve is asymmetric, and the vibrational levels are no longer equally separated.

Finally quantum theory must be considered, since at the molecular level energy and the absorption of radiation are quantised. This leads to further rules for the non-harmonic oscillator.

There are only discrete energy levels and therefore vibrational levels. The vibrational state with the quantum number $\nu=0$ is called the ground state, and has non-zero energy (so-called zero point energy). The amount of energy absorbed for a vibrational transition ΔE_{VIB} is the difference between two adjacent energy eigenvalues E_{n+1} and E_n.

From the Schrödinger equation it follows that:

$$E_{VIB} = h\nu_{osc}\left(n+\frac{1}{2}\right) = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}\left(n+\frac{1}{2}\right)$$

$$n \quad = 0, 1, 2, \ldots$$

$$\Delta E_{VIB} = E_{n+1} - E_n = h\nu_{osc}$$

n	Vibrational quantum number
h	Planck's constant
E_{VIB}	Vibrational energy

The excitation of a vibration corresponds to the absorption of a quantum of light by the molecule, thus raising it from a vibrational level with quantum number n to a higher level, typically with $n+1$. The energy difference between the two levels must be equal to the energy of the light quantum (resonance condition). The separation between adjacent levels becomes smaller as n becomes larger, until finally the dissociation limit is reached (Fig. 2.3).

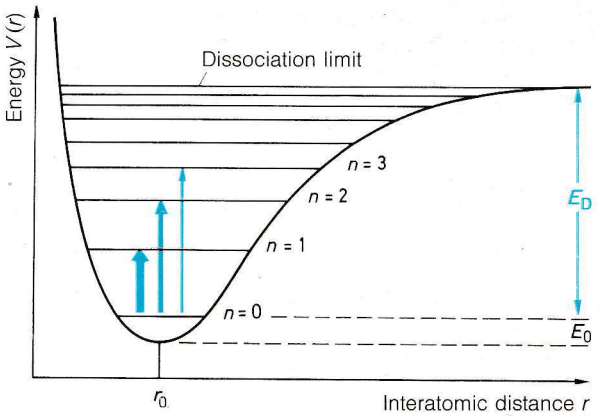


Fig. 2.3 Potential energy plot of an anharmonic oscillator (E_0 zeropoint energy; E_D dissociation energy; the different widths of the arrows indicates the different transition probabilities)

The transition from $n=0$ to $n=1$ is the base transition, from $n=0$ to $n=2$ is the first overtone, which has approximately double the frequency. The probability of these transitions and therefore the intensity of the absorption bands reduces very sharply as the size of the change in n increases.

Apart from the quantum conditions the appearance and intensity of absorption bands depend on the dipole moment of the molecule. Infrared light is only absorbed when the dipole moment interacts with the electrical vector of the light. A simple rule makes it easy to determine whether this interaction can occur: the dipole moment of the molecule at one extremity of the vibration must be different from that at the other extremity. In contrast the Raman effect depends on an interaction between the irradiating light and the polarisability of the molecule. This leads to different selection rules (see p. 67).

The most important consequence of these selection rules is that in a molecule with a centre of symmetry all vibrations which are symmetric with respect to the centre of symmetry are IR inactive (i.e. forbidden), since they produce no change in the dipole moment. These vibrations are however Raman active, since they produce a change in the polarisability. Conversely, those vibrations which are not symmetric about the centre of symmetry are Raman inactive and active in the IR. Raman and IR spectra are thus complementary. The IR spectrum, which is easier to obtain, provides the chemist with more information, however, since the majority of functional groups do not have a centre of symmetry. Therefore IR spectroscopy has a much greater importance for structural determination than Raman spectroscopy.

The symmetry properties of a molecule in a crystal lattice can be different from those in the vapour or in solution. Accordingly the solid state spectrum is then different from the gas-phase or solution spectrum.

3. IR Spectrometers

Two basically different types of IR spectrometer are currently in use, the traditional grating or prism (*scanning*) instruments having been largely replaced by the more powerful Fourier Transform (FT)-IR spectrometers.

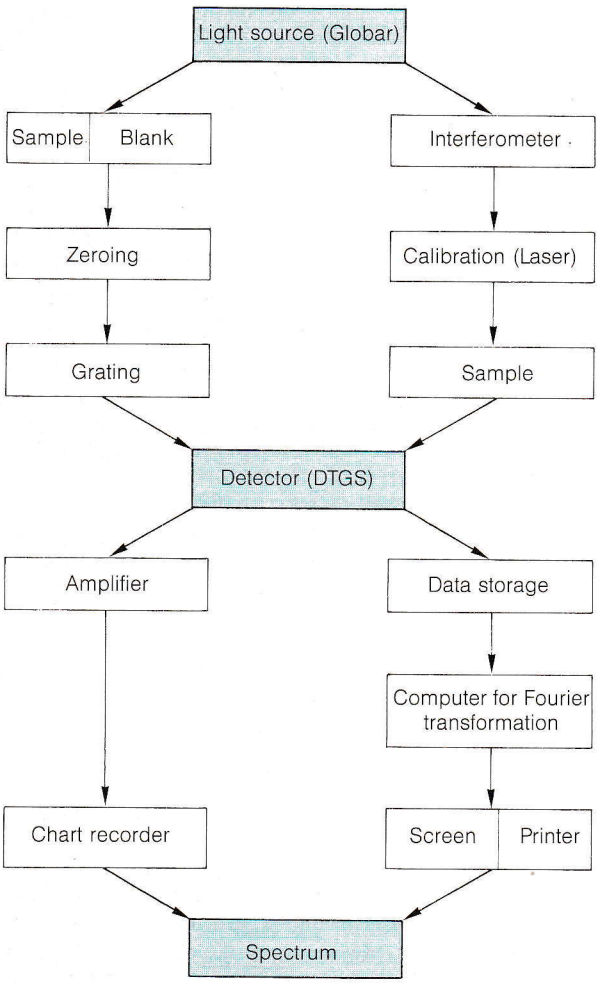


Fig. 2.4 Schematic design of grating (left) and Fourier transform (right) IR spectrometers

Both types work on the same basic principle. An IR source emits radiation, which is reduced in strength as it passes through the sample. This reduction is frequency dependent, corresponding to the excited molecular vibrations. The residual radiation is measured with a detector and electronically converted into a spectrum (Fig. 2.4).

The decisive requirement for the radiation source is that it must constantly emit light covering the total frequency range of interest. Commonly used light sources which fulfil this requirement are a white hot Nernst filament (zirconium dioxide with rare earth additives) or the so-called Globar made from silicon carbide (operating temperature: 1500 K).

The purpose of the detector is to collect the incoming radiation and convert the optical signals into electrical signals. The most common type is the DTGS detector (**d**euteriated **t**rigly**c**ine **s**ulfate).

Whereas the radiation source and the detector are identical for both types of spectrometer, the measurement of the frequency dependence of the absorption and the signal processing are fundamentally different.

3.1 Classical (Scanning) IR Spectrometers

These instruments usually operate on the double beam principle: a beam splitter (*chopper*) divides the continuous radiation from the source into two beams of equal intensity. One of the beams is passed through the sample, the other serves as a control beam and usually passes through air, in the case of solution measurements through a cell with pure solvent. After optical comparison in the photometer the light beams are recombined. The monochromator (a prism or diffraction grating) spectrally analyses the resultant radiation. Thus the spectrum can be recorded as a function of wavelength (*scanning*) – at any point in time a single frequency is recorded. After amplification the signals are plotted on a chart recorder as a spectrum (abscissa: wavelength increasing from right to left, ordinate: % transmittance). The recording of a spectrum typically takes about 10 minutes.

3.2 Fourier-Transform IR Spectrometers

The Fourier-transform technique is a development of IR spectroscopy using the possibilities of modern computer technology for the storage and processing of large amounts of data. It has established itself as the standard method and largely superseded conventional spectrometers in the market.

The basic principle is the simultaneous collection of data at all frequencies in the IR spectrum, thus eliminating the time required for scanning through the different frequencies. This is achieved by using an interferometer to convert the intense, multifrequency IR radiation, which is constant with time, into an interferogram, which is not a function of the frequency, but of time (i.e. conversion from a **frequency** domain into a **time** domain). After this "prepared" radiation is passed through the sample the interferogram is converted back to the spectrum (i.e. into the frequency domain) by a mathematical operation, the Fourier transform (see Fig. 2.5).

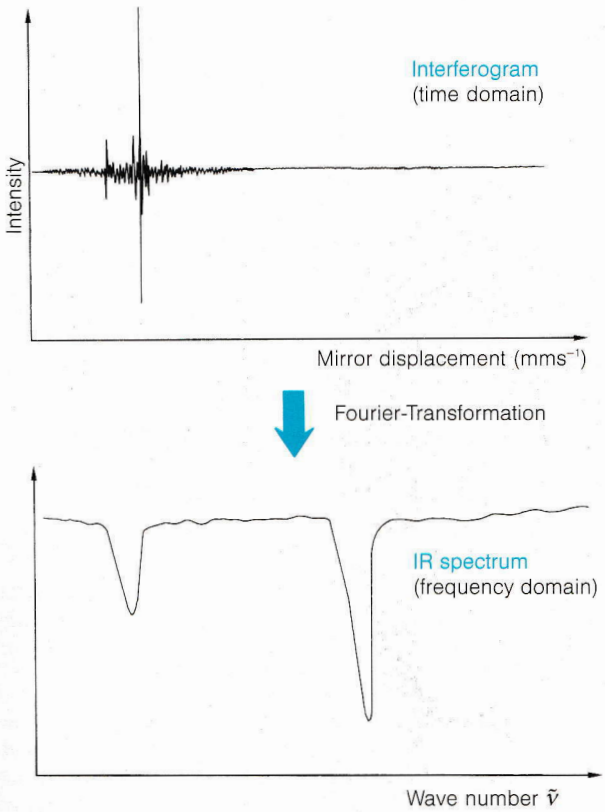


Fig. 2.5 From interferogram to IR spectrum *via* Fourier transformation

This technique requires a totally different design of the spectrometer, as shown in Fig. 2.6. The heart of the instrument is a Michelson interferometer; the IR radiation is led into it through a semi-transparent plate (KBr or CsI coated with germanium) which acts as a beam splitter. One half of the light falls onto a fixed mirror, the other onto a movable mirror, the distance of which from the interferometer can be varied. Both mirrors reflect the light onto the plate, where interference (constructive or destructive) takes place. The signal produced is comparable to the information modulated onto a carrier frequency in a radio transmitter. Since the IR radiation is polychromatic, the interferogram obtained is a superimposition or summation of the interferograms of all the individual frequencies. The modulated radiation is now passed through the sample, where it is selectively absorbed, depending on the vibrations excited in the sample. The detector records the emerging radiation as an interferogram, converts the optical signals into electrical signals and passes them on to the data storage system. A computer extracts the frequency information contained in the interferogram by Fourier transformation and produces the usual, interpretable band spectrum.

Compared to the conventional techniques FTIR spectroscopy offers three advantages:

1) a considerable saving of time: since light of all frequencies is simultaneously recorded in the detector, the measurement time is reduced to a few seconds compared to ca. 10 minutes (multiplex or Fellgett advantage).

2) a better signal to noise ratio: in contrast to the scanning technique, where only one wavelength is recorded at a time (and the rest of the intensity is lost) the whole power of the light source is available at all times (Jacquinot advantage).

3) high wavenumber precision: monochromatic light from a laser source, the frequency of which is very precisely known, can be added to the signal to provide an internal reference (Connes advantage).

These advantages are obtained at the cost of the computationally intensive Fourier transformation. Since this however can be easily achieved with an ordinary personal computer (e.g. 486 PC) in a few seconds, it is no longer a limiting factor.

The FT technique also renders unnecessary the splitting of the light into measurement and comparison beams, a common source of technical problems; FTIR spectrometers are single beam instruments. Comparison and measurement samples are mounted in holders on a sliding mechanism, which measures the samples in the single beam one after another (if air is used as the blank the relevant holder is simply left empty). The spectra are acquired and stored separately and the comparison or background spectrum subtracted from the sample spectrum in the computer.

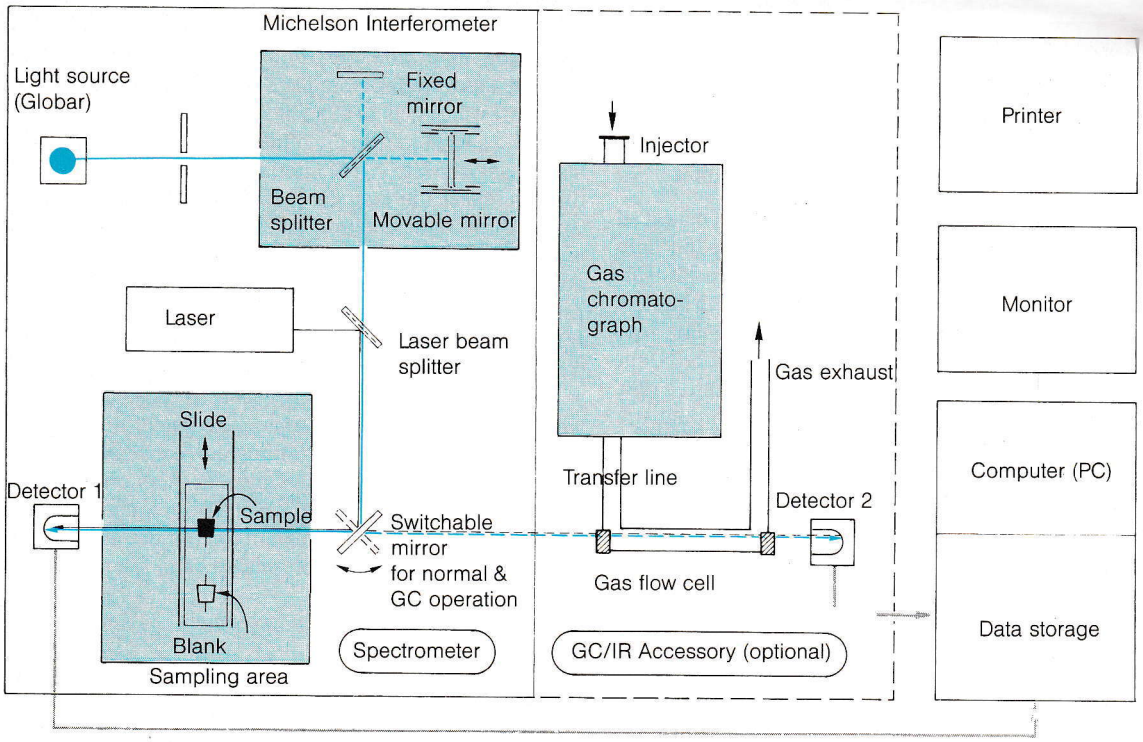


Fig. 2.6 Design of an FTIR spectrometer (with GC/IR accessory)

Because of the speed of FTIR measurements a very useful application for the organic chemist has become available: the coupling of gas chromatography and IR spectroscopy. Gas phase spectra of the fractions eluted from the GC column are measured directly (see also Sec. 4.1). Most FTIR instruments can be fitted with a special detector for these purposes (see also Fig. 2.6). GC/FTIR spectroscopy has become in many cases a genuine alternative or supplement to GC/MS.

4. Sample Preparation

IR spectra can be measured on substances in all three phases of matter (gaseous, liquid, solid) as well as in solution. The choice of the appropriate method depends on the nature and physical properties of the sample, such as melting point and solubility.

4.1 Measurements in the Gas Phase

Gases are measured in gas cells which are fitted with stopcocks and have IR transparent NaCl plates at the ends. Because of the low density of gases the optical path length through the cell is chosen to be as long as possible (normally 10 cm). Since most organic compounds have relatively low vapour pressures, this method is rarely used.

Cells for coupled GC/IR measurements are designed in basically the same way. The sample is introduced into the cell, which is fitted with entry and exit ports, by a stream of carrier gas (hydrogen or helium). Because of the short dwell time of the sample in the cell and the small amount of substance, GC/IR coupled measurements are only possible with the FT technique (see also Fig. 2.6).

Gas phase spectra show two special features:

1) for certain small molecules (e.g. HCl) rotational fine structure is observable, which arises from excitation of the rotational states of the molecule simultaneously with the vibrational excitation; in larger molecules and in condensed phases these transitions are not resolved; and

2) some bands which are strong in the condensed phase, and get their intensity from intermolecular interactions (e.g. hydrogen bonded OH and NH) are weak, since the molecules in the gas phase are isolated and these interactions do not occur.

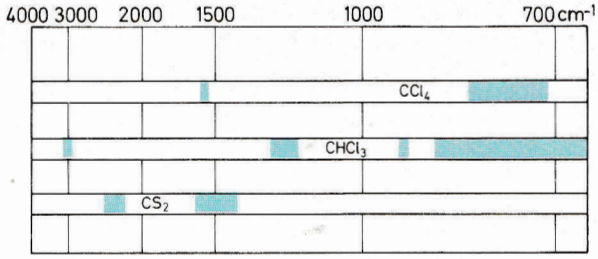


Fig. 2.7 The marked wavenumber regions are where the solvents themselves absorb (cf. Fig. 2.15, spectrum of $CHCl_3$)

4.2 Measurements on Liquids

A drop of the liquid is pressed between two flat sodium chloride plates (transparent in the range 4000 to 667 cm^{-1}). This is the simplest of all methods.

If the liquid absorbs weakly, spacers can be positioned between the plates to increase the thickness of the liquid layer.

Samples with a water content of more than 2% are unsuitable, since the surface of the plates will be damaged; cloudiness of the liquid is also undesirable, since it causes reflections and diffraction of the IR beam which lead to a strong background absorption.

4.3 Measurements in Solution

The compound is dissolved in carbon tetrachloride or for better solubility in alcohol free chloroform (about 1 to 5% solution). This solution is placed in a special sodium chloride cell with a path length of 0.1 to 1 mm. A second cell of the same dimensions, which only contains the solvent, is placed in the path of the other beam of the spectrometer, in order to compensate for the absorption of the solvent. It is generally advisable to record such spectra in non-polar solvents, since intermolecular interactions - which are particularly strong in the crystalline phase - are at a minimum. However many compounds are insoluble in non-polar solvents, and all solvents absorb in the infrared; if the solvent absorbs more than 65% of the incident light a spectrum cannot be measured. In such cases the amount of light transmitted is insufficient for the detector to function properly. Fortunately carbon tetrachloride and chloroform only absorb strongly in **those** ranges (see Fig. 2.7 and 2.15) which are of lesser interest for analytical purposes. Other solvents can of course be used. The region of interest should first be checked carefully with due consideration of the path length of the cell. In exceptional cases even aqueous solutions can be useful, but special cells made from calcium fluoride must be used.

4.4 Measurements in the Solid State

a) As **suspension in oil**. About 1 mg of the solid substance is ground to a fine paste with a drop of paraffin oil (e.g. Nujol) in a small agate mortar. The paste obtained is then pressed between two sodium chloride plates so that a film is formed free from bubbles. If (C–H) vibrations are to be measured, the paraffin oil is replaced by hexachloro- or hexafluorobutadiene.

   This method is simple and has the advantage that no interference is likely from the very non-polar paraffin oil, unlike the strongly polar potassium bromide. Especially air and moisture sensitive materials can be easily measured in this way.

b) As **KBr disc**. The solid substance is intimately mixed with the 10 to 100 fold amount of potassium bromide in a small agate mortar and subsequently compressed under vacuum in a hydraulic press. The substance then sinters **under cold flow** conditions to a transparent tablet which appears like a single crystal. If the powder is too fine or too coarse the sintering is incomplete leading to dispersion losses, detectable as a baseline rising to the right of the spectrum.

   This technique is the most commonly used for solids. It has the advantage that potassium bromide has no IR bands of its own, and also better spectra can be obtained than with method a). Potassium bromide is however hygroscopic, so that traces of water can rarely be totally excluded during the grinding and pressing. Therefore a weak OH band is usually observed at 3450 cm^{-1}.

Because of intermolecular interactions the positions of the bands in solid state spectra are often different from those observed for the same substance in solution. This is especially true for functional groups which form hydrogen bonds. Also the number of resolved bands in solid state spectra is often higher. If for example a synthetic product is to be compared with a natural product, the measurement is best carried out in the solid state, assuming that both samples exist in the same crystal modification. However a synthetic racemate should be compared with a natural product **in solution**.

5. The IR Spectrum

In Fig. 2.8 the simple spectrum of Nujol, a paraffin, is given as an example. Nujol is used for the preparation of samples which are to be measured as a suspension (see above); its absorption bands are therefore overlaid on the spectrum of the sample. Fig. 2.8 shows how IR spectra are displayed. The transmittance as a percentage % is the ordinate (y axis). That represents the proportion, by comparison with the reference beam, of the radiation which is transmitted by the sample. More rarely the percentage absorption (% A) is given instead, where

$$\% T = 100 - \% A$$

The abscissa (x axis) is calibrated both in µm (wavelength λ) and in cm^{-1} (wavenumber $\tilde{\nu}$). The scale is linear in wavenumbers. This has the advantage that the peaks are symmetrical. Energy differences can be easily recognised.

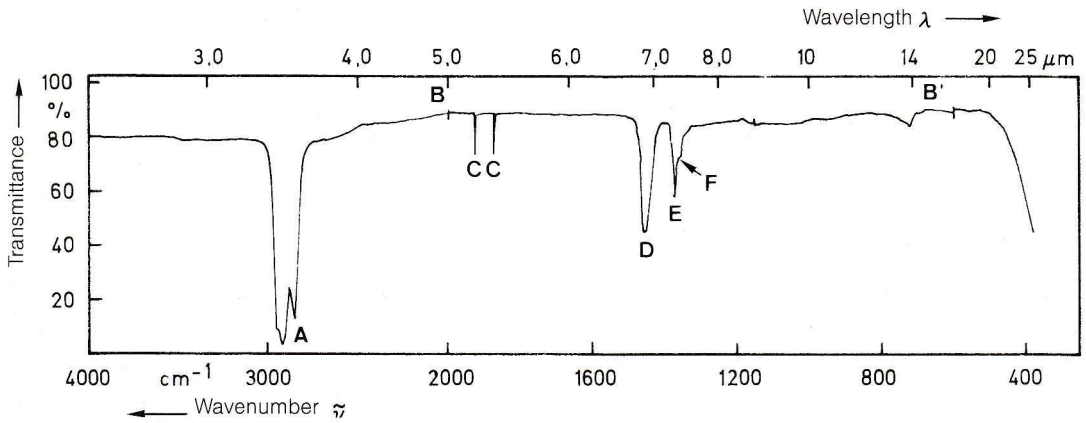


Fig. 2.8 IR spectrum of a paraffin (Nujol measured as a liquid film)

A Absorption band, i.e. at this wavelength the molecule absorbs the maximum amount of radiation energy. In this case the vibrations responsible are the (C–H) stretching vibrations of the CH_3 and CH_2 groups.

B,B' Switching points; at certain frequencies (here 2000 and 600 cm^{-1}) larger instruments change gratings, filters, or the plotting scale; the paper stops moving while the switching takes place. The switching points can act as a check as to whether the paper is inserted properly. They do not occur in FTIR instruments.

C so called spikes; these are pen deflections caused by uncontrolled voltage irregularities, recognisable by their narrow width. Do not appear with FTIR instruments.

D (C–H) bending vibrations of CH_3 and CH_2 groups. For CH_3 groups this is the asymmetric (C–H) bending vibration (abbreviated: $\delta_{as}(CH_3)$), for CH_2 groups the symmetric (abbrev. δ_s (CH_3)). These terms are explained below.

E symmetric (C–H) bending vibration of CH_3 groups ($\delta_s(CH_3)$).

F Shoulder; arises from the overlap of two or more bands.

In the short wavelength region (left) the scale of the abscissa (from 2000 cm^{-1}) is generally smaller. This form of spectral display has become more and more usual with modern spectrometers. A linear wavelength (λ, μm) scale is most commonly found with older prism instruments. Such spectra may look clearer, but the bands are asymmetrical, energy differences cannot be immediately read off, and the resolution in the short wavelength region is poorer.

The spectrum of this hydrocarbon also shows that the (C-C)-chain does not give noticeable absorptions. They only appear with thicker layers of sample, between 1350 and 750 cm^{-1}. For cyclic hydrocarbons stronger bands often appear, arising from vibrations of the ring.

A complex molecule possesses many possible vibrations. Their number can be determined from a simple rule: a molecule with N atoms has, because of three independent spatial co-ordinates of each atom, a total of $3 \cdot N$ degrees of freedom. Three of these are taken up by the translational movement of the molecule along the three axes, and a further three by rotations about the same three axes. Linear molecules lose one degree of freedom, since the moment of inertia about the linear axis is 0. The actual number n of degrees of freedom thus reduces to:

Degrees of freedom of linear molecules $n = 3N - 5$
Degrees of freedom of non-linear molecules $n = 3N - 6$
(N = number of atoms)

The vibrations calculated from these formulae are called **normal** or **basis** vibrations.

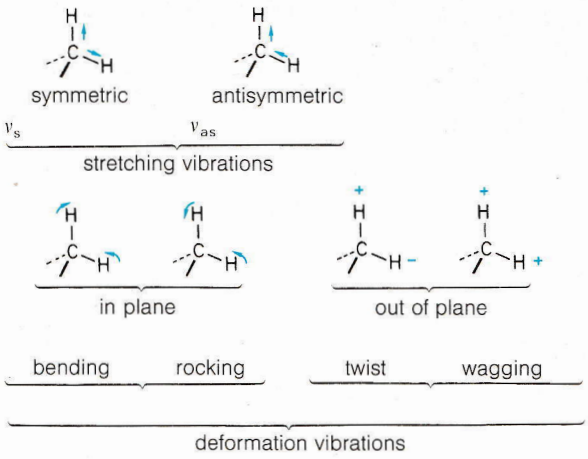
Depending on the **type of vibration** they can be divided into:

- **Stretching** vibrations: these alter the bond lengths and
- **Bending** vibrations (planar or non-planar): these alter the bond angles, while the bond lengths remain essentially unchanged.

A further division is possible on **symmetry grounds**, giving

- symmetric vibrations (Index s): retain the full molecular symmetry;
- antisymmetric vibrations (Index as): disturb one or more symmetry elements;
- degenerate vibrations (Index e): distinct vibrations, which because they have the same energy content absorb at the same frequency and therefore only lead to **one** absorption band.

The most useful vibrations for spectral interpretation are those which to a first approximation only involve one bond in the molecule, i.e. localised vibrations. The methylene group, for example, consisting of three atoms, has the following localised vibrations:



+ = vibration to the front of the plane of the page
− = vibration to the rear of the plane of the page

For the specification of localised vibrations the following symbols are used:

ν = stretching vibration (also called bonding vibration)
δ = deformation vibration (also called bending vibration)
γ = **out of plane** deformation vibration
τ = torsional vibration (alteration of the torsion angle)
etc.; for example
$\nu_s(CH_2)$ and $\nu_{as}(CH_2)$
= symmetric and antisymmetric (C-H)-stretching vibrations of a CH_2 group
$\delta_s(CH_3)$ and $\delta_{as}(CH_3)$
= symmetric and antisymmetric (C-H)-deformation vibrations of a CH_3 group
Many localised vibrations help to identify functional groups.

The skeletal vibrations of a molecule result in absorption bands at relatively low energy (below 1500 cm^{-1}), the positions of which are characteristic for the molecule as a whole. These bands make the assignment of localised vibrations below 1500 cm^{-1} difficult, since much overlap of bands occurs. Often bands are observed below 1500 cm^{-1} which cannot be assigned to normal vibrations, but which arise from **overtone** or **combination vibrations**. Overtones occur at double, treble, etc., of the frequency value of the corresponding normal vibration. Combination vibrations occur at frequencies which correspond to the combination of two or more normal vibrations. The bands from overtones or combination vibrations are generally much weaker than those from normal vibrations. Occasionally these bands are of diagnostic value, but in general they are of little use. A special case is the so-called **Fermi**

resonance: if an overtone or combination vibration coincidentally has the same frequency as a normal vibration, the two frequencies move apart. Two bands of similar intensity are observed. The bands can then no longer be assigned to individual vibrations.

An IR spectrum therefore exists of two main regions: above 1500 cm^{-1} lie absorption bands which can be assigned to the individual functional groups, whereas the region below 1500 cm^{-1} contains many bands and characterises the molecule as a whole. This region is therefore known as the **fingerprint region**. The use of this fingerprint region to identify a substance by comparison with an authentic sample is in most cases more reliable than using mixed melting points or thin-layer chromatography. The bands within the fingerprint region which arise from functional groups can be used for identification, but such assignments should be considered as only an aid to identification and not as conclusive proof.

The regions in which specific functional groups absorb can be shown by the example of acetone (Fig. 2.9): the stretching vibrations of single bonds to hydrogen (such as C–H, O–H, N–H) absorb at the highest frequencies, as a consequence of the small mass of the hydrogen atom (extreme left-hand region in Fig. 2.9). As the atomic masses increase the absorption bands are shifted to lower wavenumbers, as the following series demonstrates.

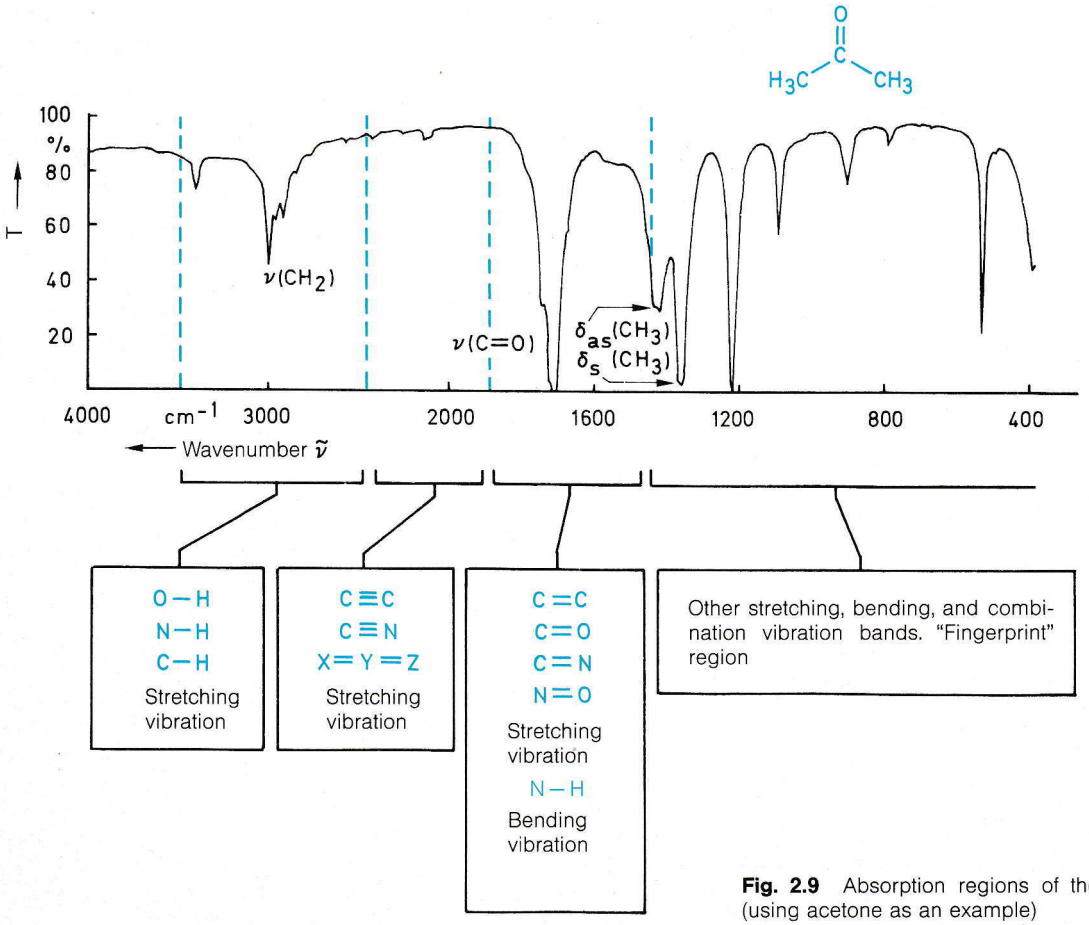


Fig. 2.9 Absorption regions of the IR spectrum (using acetone as an example)

Bond	$\tilde{\nu}$ (C–X)(cm^{-1})	Atomic mass of X
C—H	≈3000	1
C—D	≈2100	2
C—C	≈1000	12
C—Cl	≈ 700	35

(cf. Sec. 2; wavenumber $\tilde{\nu}$ and frequency are proportional to one another)

Otherwise the frequencies of stretching vibrations follow the rule: the stronger the bond between two atoms, the higher the vibrational frequency. Triple bonds therefore absorb at higher wavenumbers than double and single bonds:

$\tilde{\nu}$(C≡C) ≈ 2200 cm^{-1}
$\tilde{\nu}$(C=C) ≈ 1640 cm^{-1}
$\tilde{\nu}$(C—C) ≈ 1000 cm^{-1}

Bending vibrations only alter bond angles, not bond lengths. These vibrations occur at lower wavenumbers, generally in the fingerprint region below 1500 cm^{-1}. An exception is the (NH)-bending vibration, which appears in the region around 1600 cm^{-1} (Fig. 2.9).

Tabular summary

Group	Table	Page
Single bonds		
C—H	2.1 to 2.3	44–45
O—H	2.4	45
N—H	2.5, 2.6	46
S—H	2.7	46
P—H	2.7	46
Triple bonds		
C≡C	2.8	47
X≡Y	2.8	47
Cumulated double bonds		
C=C=C	2.9	47–48
N=C=O	2.9	47
X=Y=Z	2.9	47

Group	Table	Page
Double bonds		
C=O	2.10	48–51
C=N	2.11	52
N=N	2.12	52
C=C	2.13	52
N=O	2.14	52
Aromatics		
	2.15	53
	2.16	53
Fingerprint region		
S-derivatives	2.17	54
P-derivatives	2.18	54
C–O single bonds	2.19	54
Halogen compounds	2.20	54
Inorganic ions	2.21	54

6. Overview of Characteristic Absorptions

In Fig. 2.9 the IR spectrum is divided into 4 regions, which are more fully described in the assignment summaries (Fig. 2.10 - 2.14). In the region 1800 - 1500 cm^{-1} carbonyl bands (Fig. 2.13) are listed separately from other absorptions (Fig. 2.12).

For each individual functional group wavenumber regions are given where an absorption might appear; typical intensities (which can be an aid to assignments) are also given. Intensities in IR spectra are not as easy to measure as in UV; they are generally described by the subjective terms strong (**s**), medium strong (**m**), weak (**w**), and variable (**v**).

In Tabs 2.1 to 2.21 typical bands of functional groups are listed in detail. The summary on page 39 serves as an index.

For the **interpretation** of the IR spectrum of an unknown compound the following procedure is recommended:

Firstly the three regions above 1500 cm^{-1} are checked using Figs. 2.10 - 2.13 to see if there are indications of particular structural elements or if structures can be excluded.

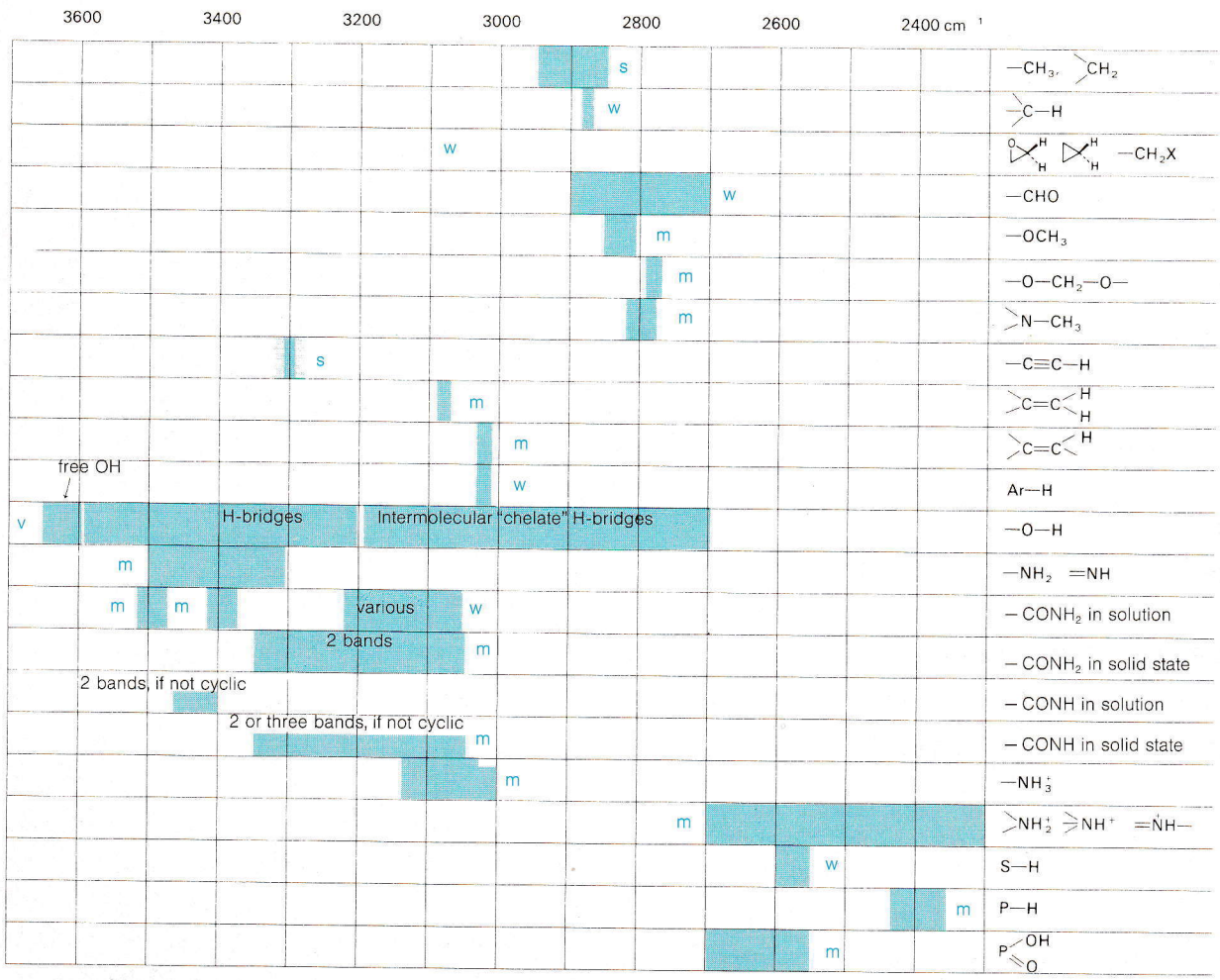


Fig. 2.10 Positions of the stretching vibrations of hydrogen (in the shaded areas the borders are less well defined); band intensity **s** strong, **m** medium, **w** weak, **v** variable.

A comparison of the *fingerprint* region with Fig. 2.14 will then show if typical bands are present, the presence or absence of which can support or disprove the structural hypothesis. Where there are uncertainties the Tables for individual functional groups (Tab. 2.1 to 2.21) can be consulted. If a firm structural hypothesis is indicated, it should always be checked by comparing the spectrum with one of an authentic sample (e.g. from a spectral catalogue); care must be taken to check whether the same measurement conditions (e.g. KBr/liquid film/Nujol) were used, since these can influence the spectrum (cf. Sec. 4.4, p. 35). If no comparison spectrum is available, the structure should be confirmed using other spectroscopic methods (e.g. NMR, MS).

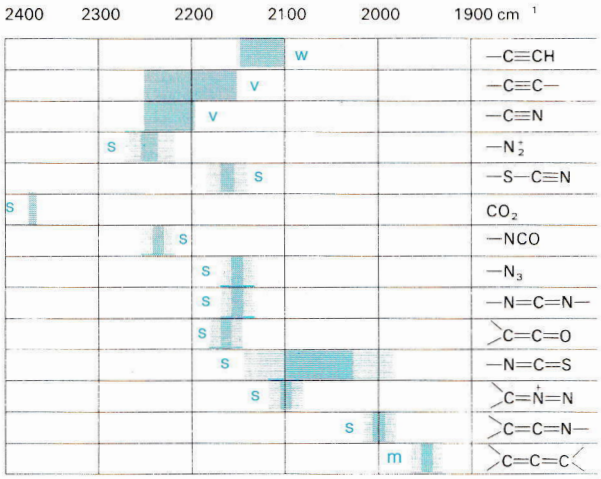


Fig. 2.11 Positions of the stretching vibrations of triple bonds and cumulated double bonds (**s** strong, **m** medium, **w** weak, **v** variable)

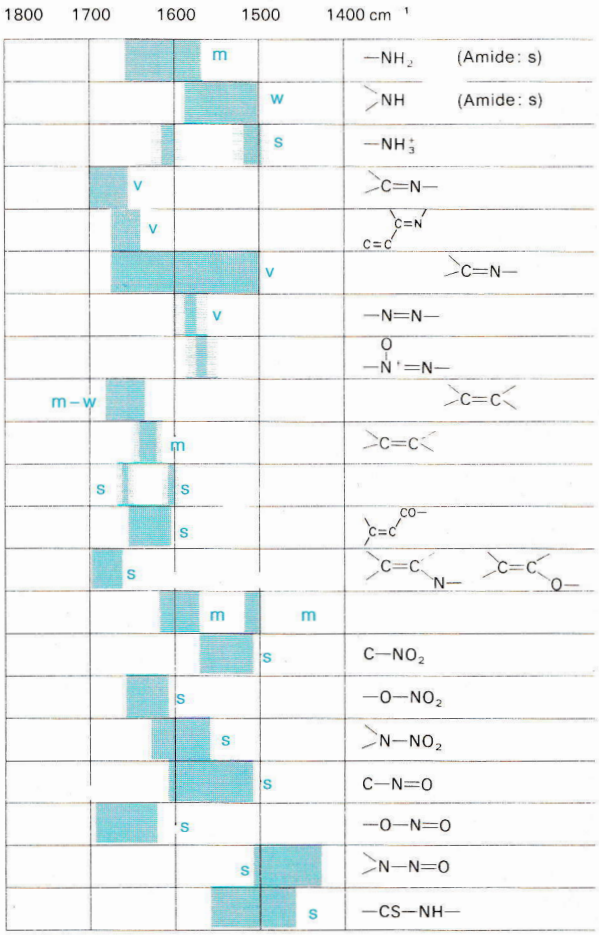


Fig. 2.12 Positions of the double bond stretching vibrations and (N–H) bending vibration (for carbonyl groups see Fig. 2.13); **s** strong, **m** medium, **w** weak, **v** variable

12. Examples of IR Spectra

The following spectra show the position, appearance and relative intensity of the absorption bands for typical representatives of some classes of compounds. The variety in the **fingerprint** region demonstrates the utility of this region of the IR spectrum for the identification of compounds.

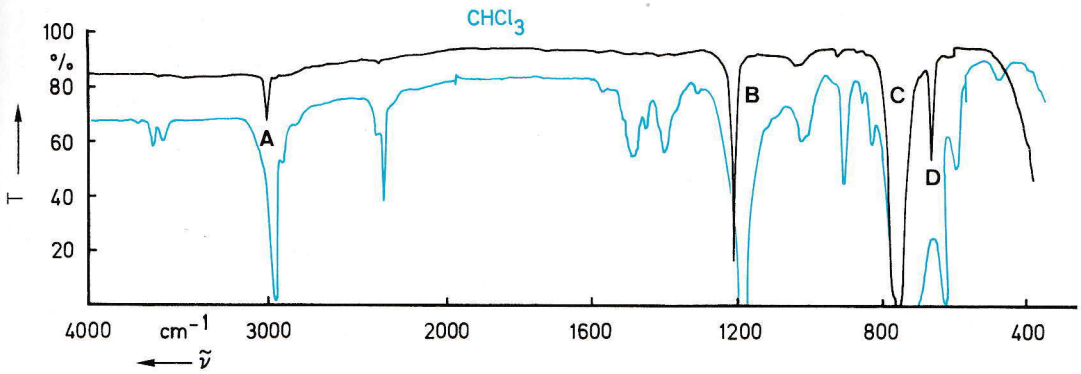


Fig. 2.15 Chloroform (as liquid film); black spectrum: 9 µm film thickness, blue spectrum: 100 µm. The figure shows the dependence of the strength of the bands on the thickness of the film for a commonly used solvent. In the regions of strong absorption the transparency using thick cells (>0.2 mm film thickness) is no longer sufficient for the detector to operate properly

A 3030 cm^{-1} (C–H) stretching vibration ν (CH)
B 1215 cm^{-1} (C–H) bending vibration δ (CH)
C 760 cm^{-1} asymmetric (C–Cl) stretching vibration
D 670 cm^{-1} symmetric (C–Cl) stretching vibration

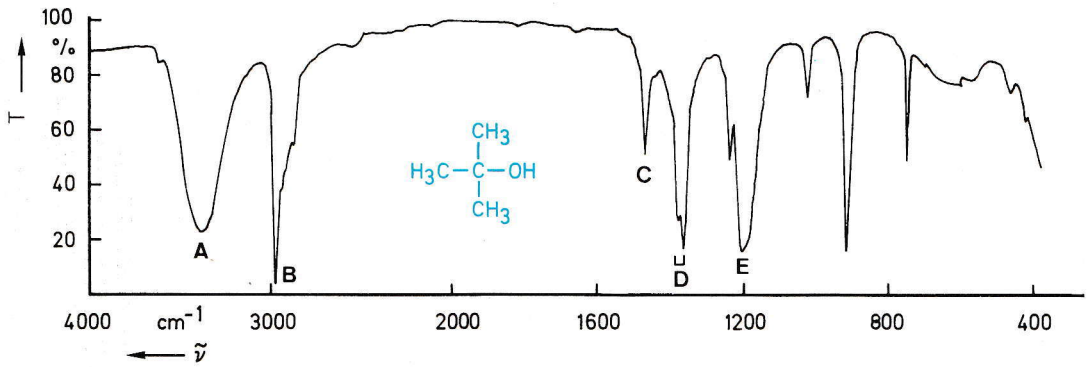


Fig. 2.16 *tert*-Butanol (as liquid film)
Alcohols are easily identified by the strong OH-band (A) and an intense and broad absorption between 1250–1000 cm^{-1} (E)

A ≈ 3400 cm^{-1} hydrogen bonded (O–H) stretching vibration; the preceding shoulder at 3605 cm^{-1} is presumably due to non-associated O–H
B 2975 cm^{-1} (C–H) stretching vibration $\nu_{as,s}(CH_3)$
C 1470 cm^{-1} asymmetric (C–H) bending vibration
D 1380 cm^{-1} characteristic double band for *t*-butyl groups
1365 cm^{-1} δ_s $(C(CH_3)_3$
E 1200 cm^{-1} (C–O) stretching vibration ν (C–O)

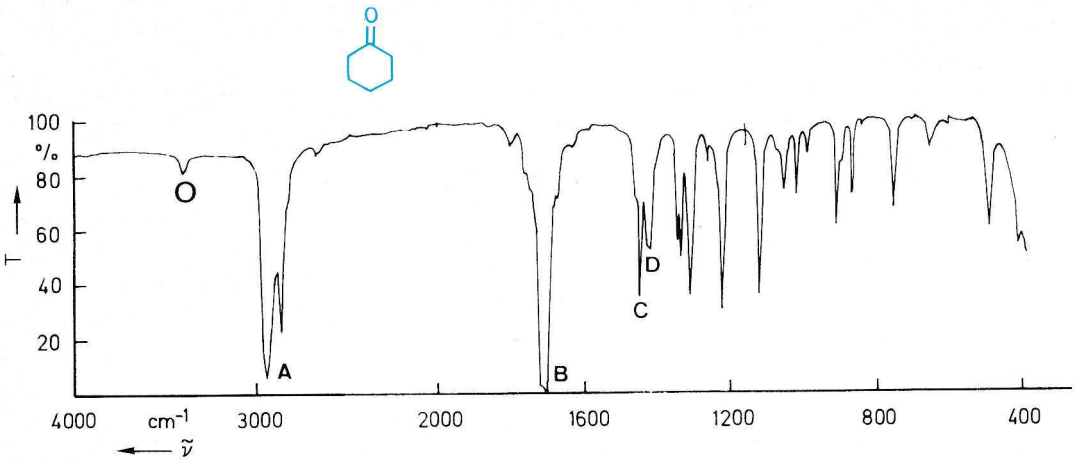


Fig. 2.17 Cyclohexanone (as liquid film)

O 3400 cm^{-1} overtone vibration of the carbonyl group (see also Fig. 2.20 and 2.9, p. 57 and 38)
A (C–H) stretching vibration $\nu_{as,s}(CH_3)$
B 1710 cm^{-1} (C=O) stretching vibration ν (C=O)
C 1450 cm^{-1} (C–H) bending vibration δ (CH_2)
D 1420 cm^{-1} (C–H) bending vibration next to C=O

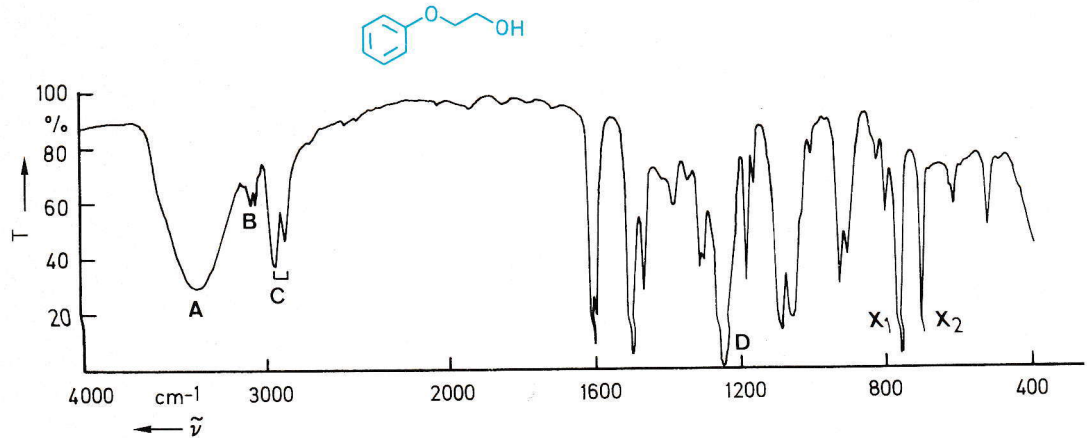


Fig. 2.18 2-Phenoxyethanol (as liquid film)
This example shows characteristic bands for an alcohol, an ether, and a monosubstituted aromatic ring

A ≈ 3350 cm^{-1} *hydrogen bonded (O–H) stretching vibration*
B (C–H) stretching vibration of the benzene ring
C (C–H) stretching vibration of the CH_2 groups
D 1250 cm^{-1} (C–O) stretching vibration in aryl alkyl ethers; dialkyl ether bands lie at lower frequency (Tab. 2.19)
X_1 760 cm^{-1} monosubstituted aromatic, i.e. five neighbouring H-atoms
X_2 695 cm^{-1} (cf. toluene, Fig. 2.23)

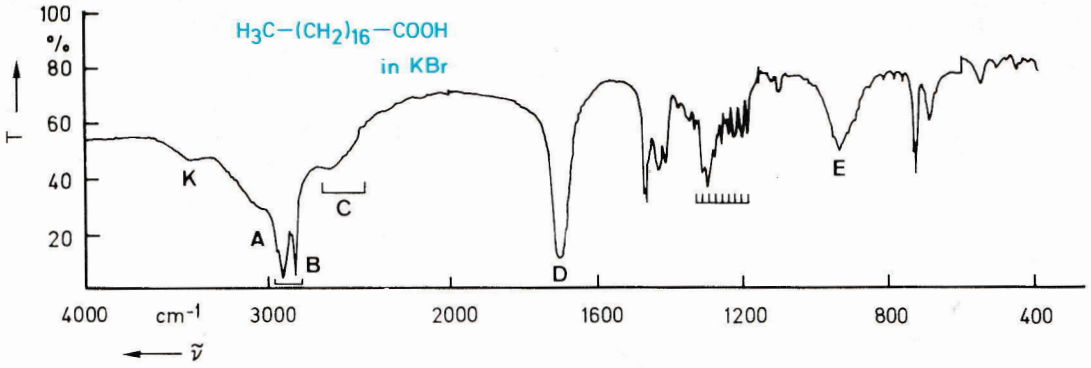


Fig. 2.19 Octadecanoic acid (stearic acid; in KBr)
Carboxylic acids associate by formation of hydrogen bonds (broad band for the dimeric form at 3000 cm^{-1}). The bending vibration of the hydrogen bonded complex at 930 cm^{-1} is also characteristic. In longer chains ($> C_{12}$) **progression bands** are observed in the solid state; these are equidistant bands between 1350 and 1200 cm^{-1}, which arise from the (*E*)-oriented CH_2 groups (**twisting** and **rocking** vibrations).

A	≈3000 cm^{-1}	very broad OH band from hydrogen bonds
B		overlapping (C–H) stretching vibrations $\nu_{as,s}(CH_2, CH_3)$
C	2700 to 2500 cm^{-1}	characteristic shoulders, arising from overtones and combination vibrations
D	1700 cm^{-1}	(C=O) stretching vibration
E	930 cm^{-1}	(O–H) bending vibration from hydrogen bonds
		O–H from traces of water in the KBr

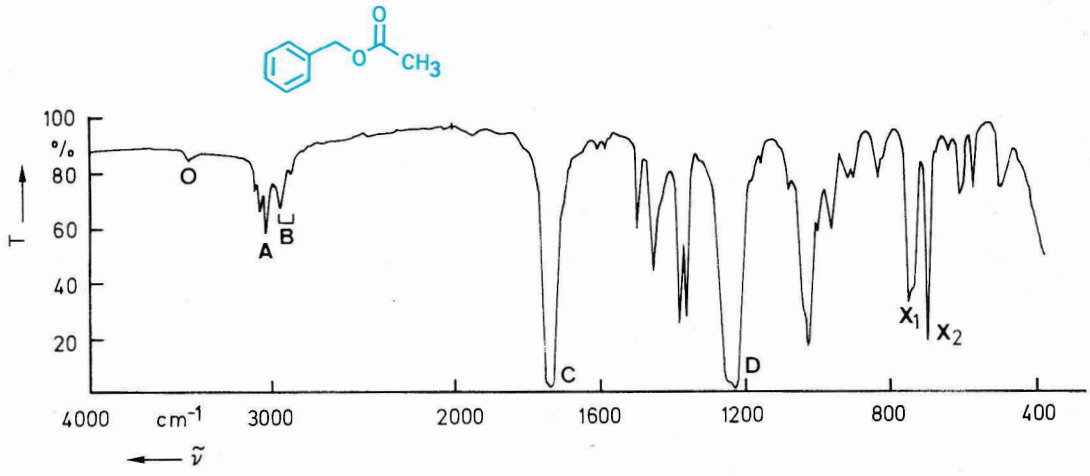


Fig. 2.20 Benzyl acetate (as liquid film)

O	3450 cm^{-1}	probably not traces of water, but overtone vibration of the carbonyl group (cf. Fig. 2.17)
A	3050 to 3020 cm^{-1}	(C–H) stretching vibration of the benzene ring
B	2960 to 2880 cm^{-1}	(C–H) stretching vibration of the CH_3 group
C	1740 cm^{-1}	(C=O) stretching vibration
D	1230 cm^{-1}	(C–O) stretching vibration; position is characteristic for the acetyl group
X_1	750 cm^{-1}	monosubstituted aromatic
X_2	700 cm^{-1}	(cf. toluene, Fig. 2.23)

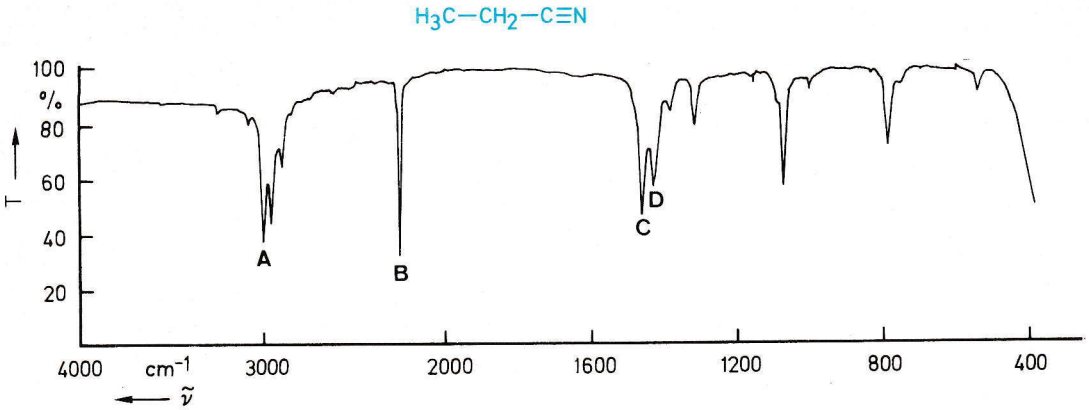


Fig. 2.21 Propionitrile (as liquid film)
Absorption bands in the region 2300–2000 cm^{-1} are almost certain indicators of triple bonds (see Tab. 2.8, p. 47)

A (C–H) stretching vibrations $\nu_{as,s}(CH_2, CH_3)$
B 2250 cm^{-1} (C≡N) stretching vibration
C 1460 cm^{-1} (C–H) bending vibration
D 1430 cm^{-1} (C–H) bending vibration next to C≡N

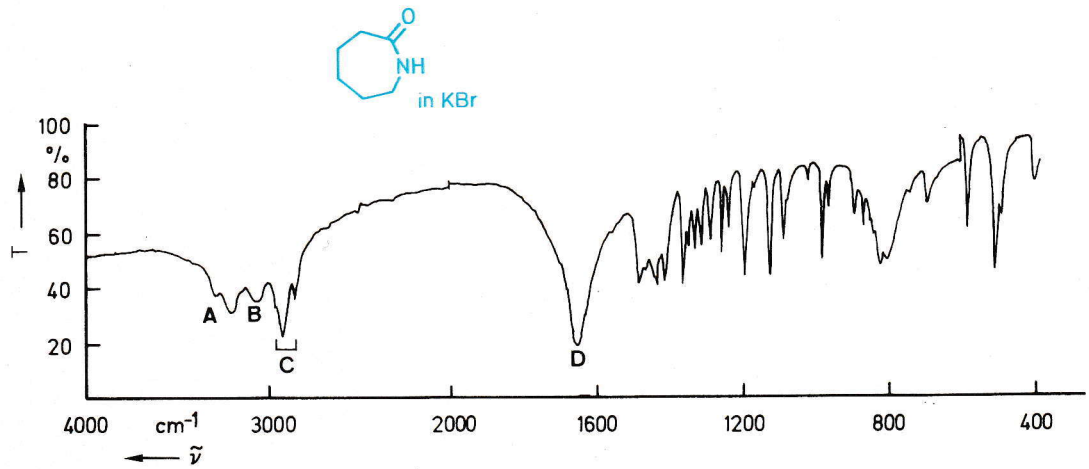


Fig. 2.22 ε-Caprolactam (hexahydro-2*H*-azepin-2-one) (in KBr)
Example of a cyclic carboxylic acid amide with absence of the amide II band (cf. Fig. 2.28a, p. 62). The many sharp bands in the fingerprint region are typical for aliphatic rings

A 3295 cm^{-1} (N–H) stretching vibrations in N-monosubstituted amides
3210 cm^{-1}
B 3100 cm^{-1} combination band ν(C=O) + δ (N–H)
C (C–H) stretching vibration $\nu_{as,s}(CH_2)$
D 1660 cm^{-1} (C=O) stretching vibration

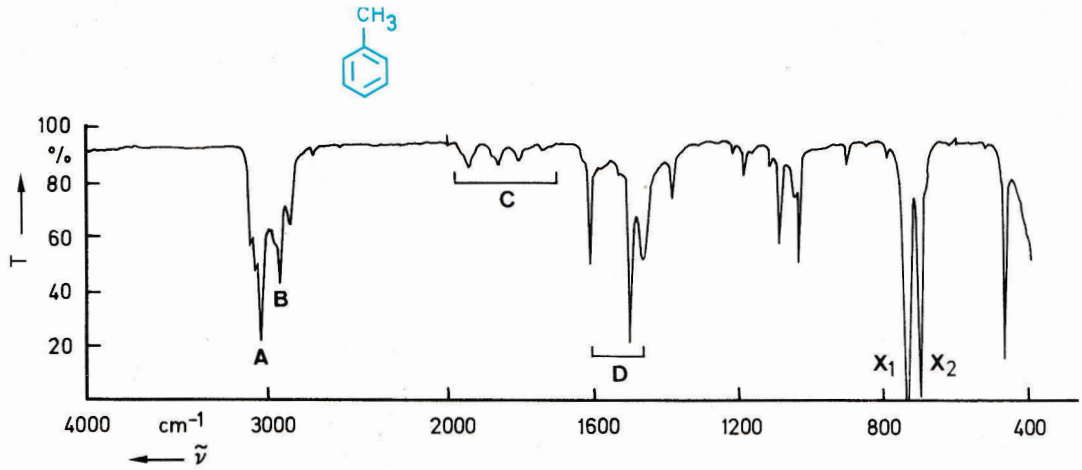


Fig. 2.23 Toluene (as liquid film)

A		aromatic (C–H) stretching vibrations
B		aliphatic (C–H) stretching vibrations
C		overtones and combination vibrations of aromatics
D		(C=C) stretching vibrations, typical of aromatics
$\mathbf{X}_1$	730 cm^{-1}	monosubstituted aromatic (five neighbouring H-atoms); H bending vibration (out of plane); (see Tab. 2.16, p. 53)
$\mathbf{X}_2$	695 cm^{-1}	ring bending vibration, also characteristic for a monosubstituted benzene

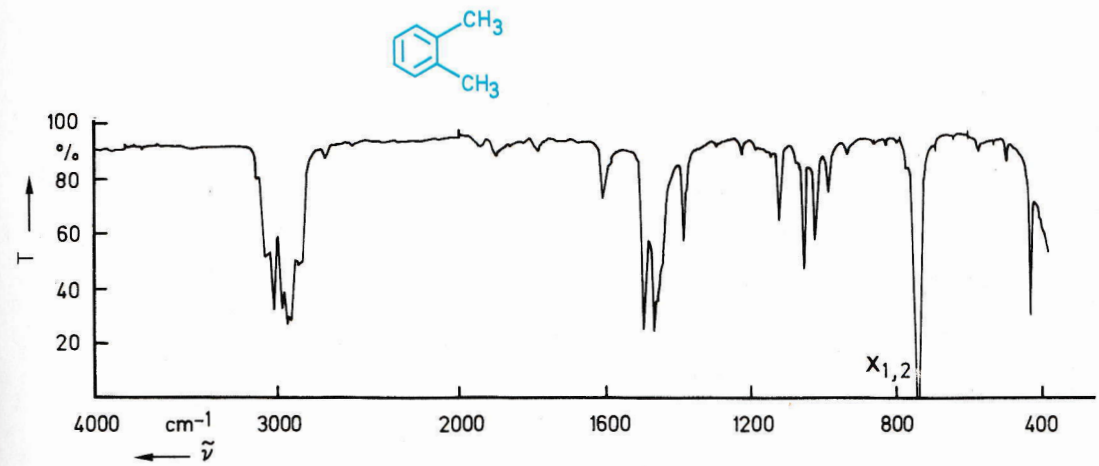


Fig. 2.24a 1,2-Dimethylbenzene (*o*-xylene) (as liquid film)

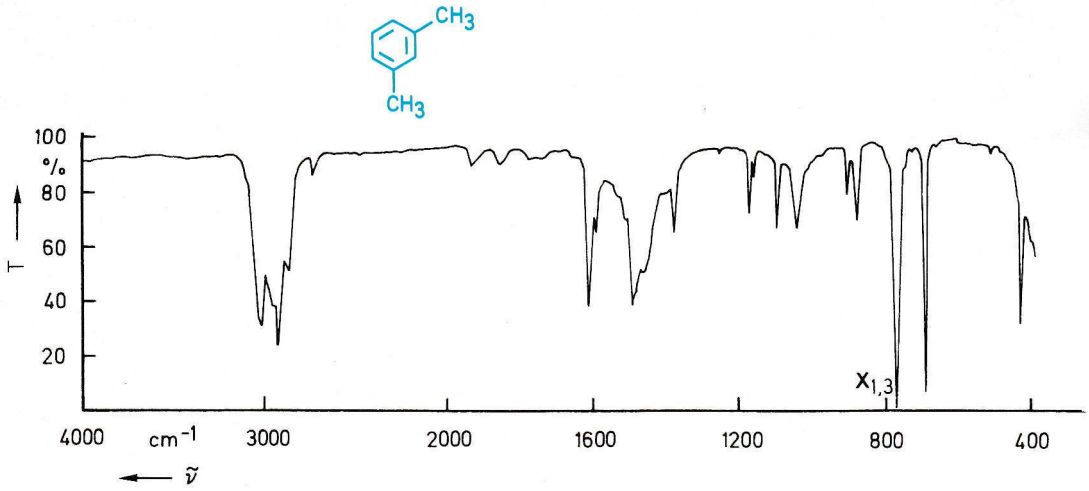


Fig. 2.24b 1,3-Dimethylbenzene (*m*-xylene) (as liquid film)

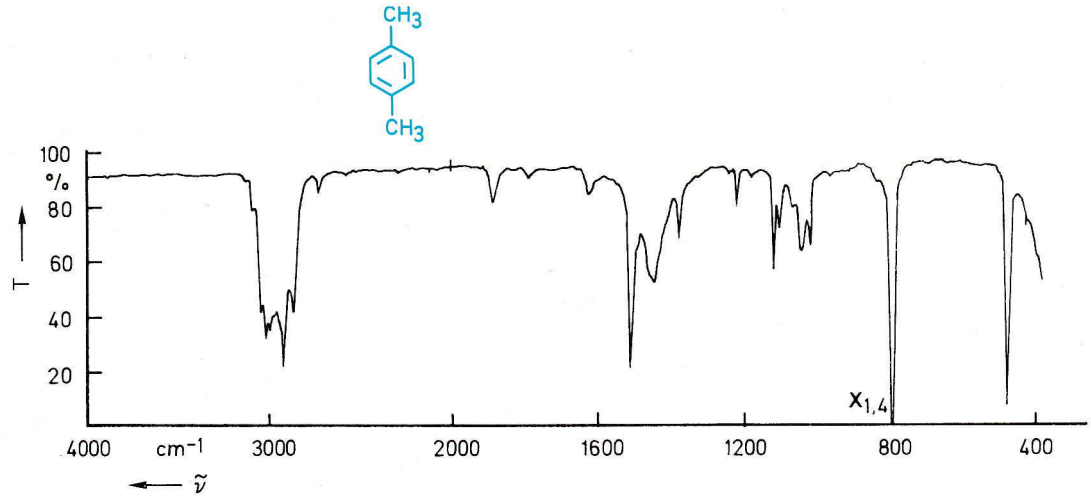


Fig. 2.24c 1,4-Dimethylbenzene (*p*-xylene) (as liquid film)

Determination of the substitution pattern from Tab. 2.16 (p. 53)

$\mathbf{X_{1,2}}$ 740 cm^{-1} typical of four neighbouring H on an aromatic (1,2-disubstitution)
$\mathbf{X_{1,3}}$ 770 cm^{-1} three neighbouring H (1,3-disubstitution)
$\mathbf{X_{1,4}}$ 770 cm^{-1} two neighbouring H (1,4-disubstitution)
For the assignment of the remaining bands compare with the spectrum of toluene (see Fig. 2.23)

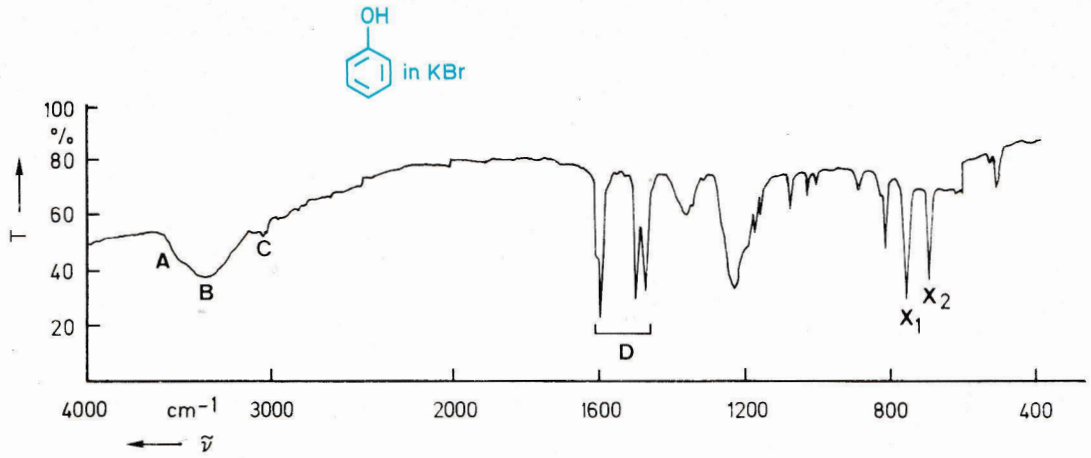


Fig. 2.25 Phenol (in KBr)

A 3500 cm^{-1} (O–H) stretching vibration in hydrogen bonded dimer
B 3360 cm^{-1} (O–H) stretching vibration in hydrogen bonded polymer
C 3040 cm^{-1} (C–H) stretching vibration in aromatic
D (C=C) stretching vibrations, typical of aromatics (cf. Fig. 2.33)
X_1 755 cm^{-1}
X_2 690 cm^{-1} monosubstituted aromatic (see Tab. 2.16, p. 53)

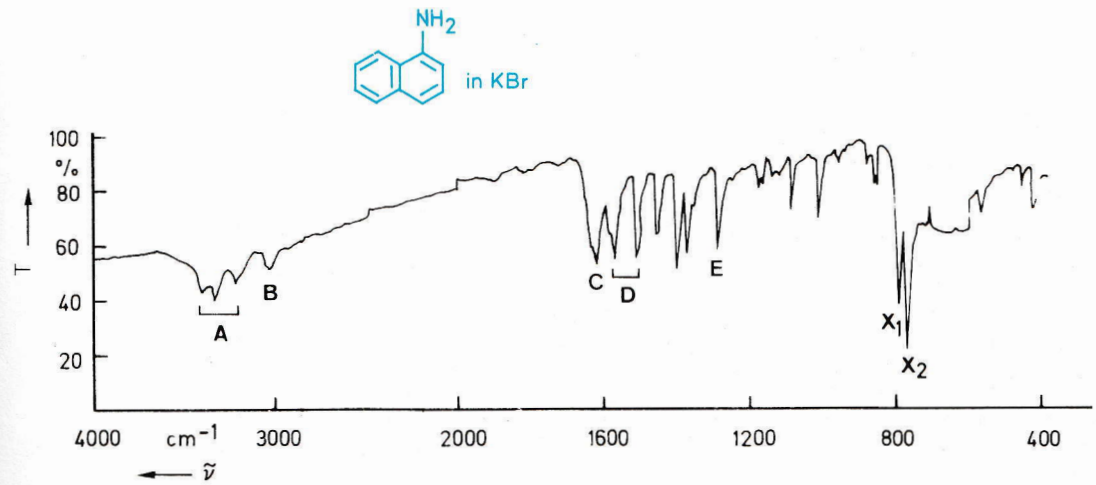


Fig. 2.26 1-Naphthylamine (in KBr)

A (N–H) stretching vibration (various degrees of association)
B 3040 cm^{-1} (C–H) stretching vibration in aromatic
C 1620 cm^{-1} (N–H) bending vibration
D 1570 cm^{-1} aromatic (C=C) stretching vibrations
1510 cm^{-1}
E 1290 cm^{-1} (C–N) stretching vibration
X_1 795 cm^{-1} monosubstituted aromatic (the values in Tab. 2.16 apply approximately to naphthalenes)
X_2 770 cm^{-1}

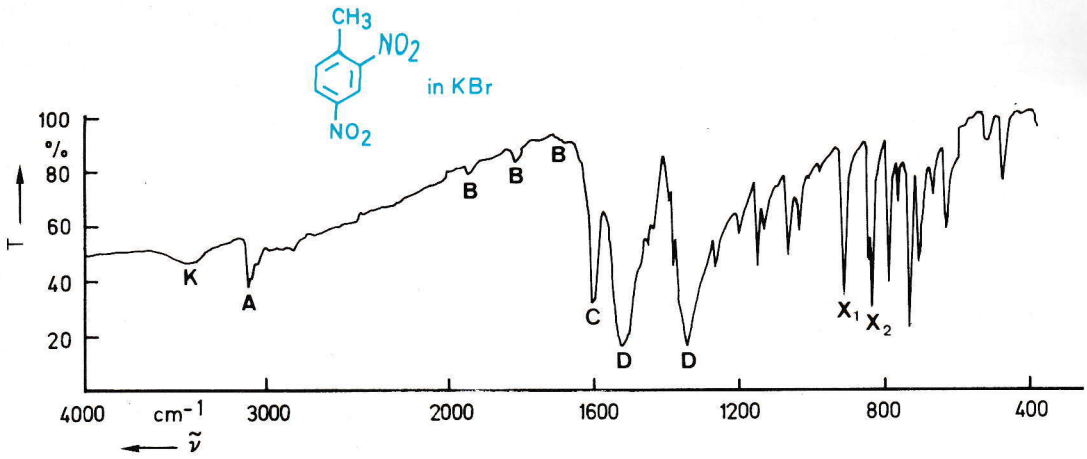


Fig. 2.27 2,4-Dinitrotoluene (in KBr)

A	3100 cm^{-1}	aromatic (C–H) stretching vibration
B		aromatic overtone vibrations
C	1600 cm^{-1}	aromatic (C=C) stretching vibrations
D	1520 cm^{-1}	asymmetric and symmetric N=O stretching vibration
	1340 cm^{-1}	(conjugated to aromatic system)
X_1	915 cm^{-1}	probably the two bands of the out-of-plane (C–H) bending vibrations
X_2	840 cm^{-1}	indicative of 1,2,4-substitution
K		traces of water in the KBr disc

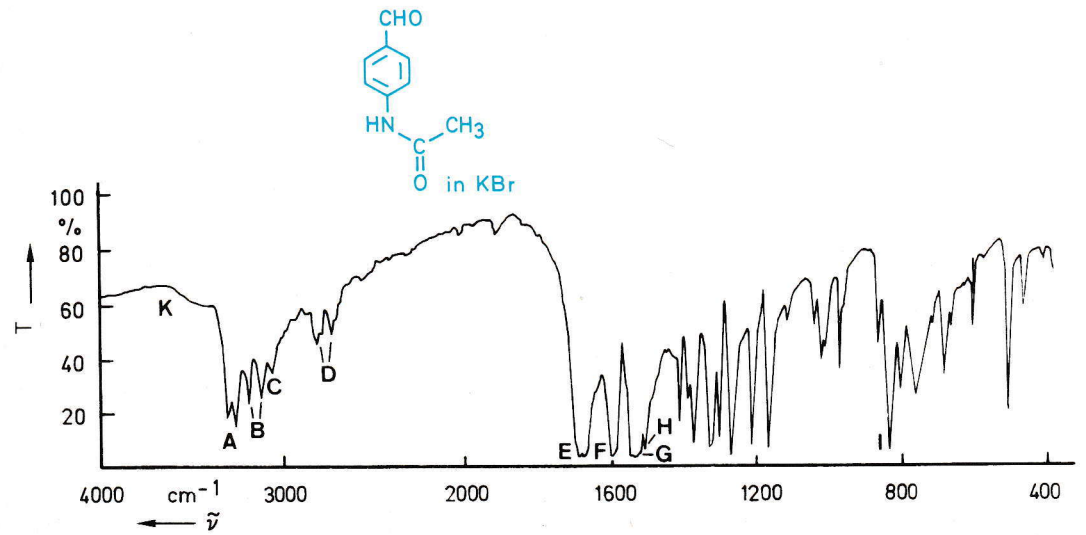


Fig. 2.28a 4-Acetylaminobenzaldehyde (in KBr)

A	3300 and 3260 cm^{-1}	N–H in N-monosubstituted amides
B	3190 and 3110 cm^{-1}	amide bands of unknown origin
C	3060 cm^{-1}	aromatic C–H
D	2810 and 2730 cm^{-1}	C–H in aldehydes
E	1690 and 1670 cm^{-1}	aldehyde-carbonyl and amide I
F	1600 cm^{-1}	benzene ring
G	1535 cm^{-1}	amide II
H	1515 cm^{-1}	benzene ring
I	835 cm^{-1}	*p*-disubstituted benzene ring
K		shoulder of an OH band from traces of water in the KBr disc

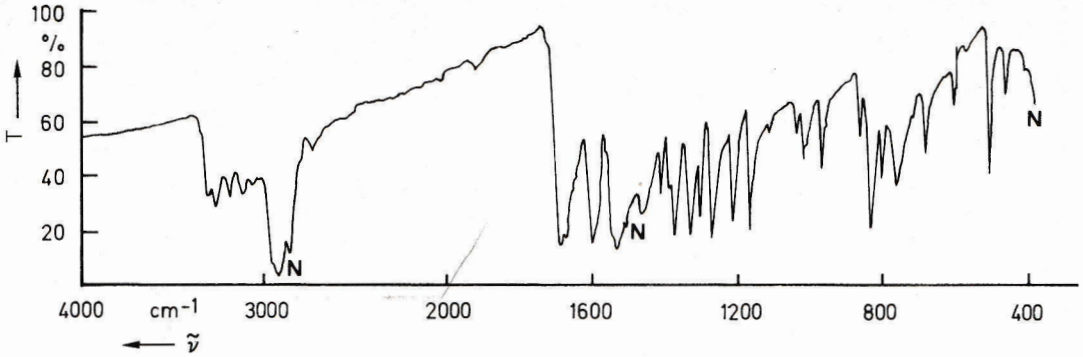


Fig. 2.28b 4-Acetylaminobenzaldehyde (in Nujol)

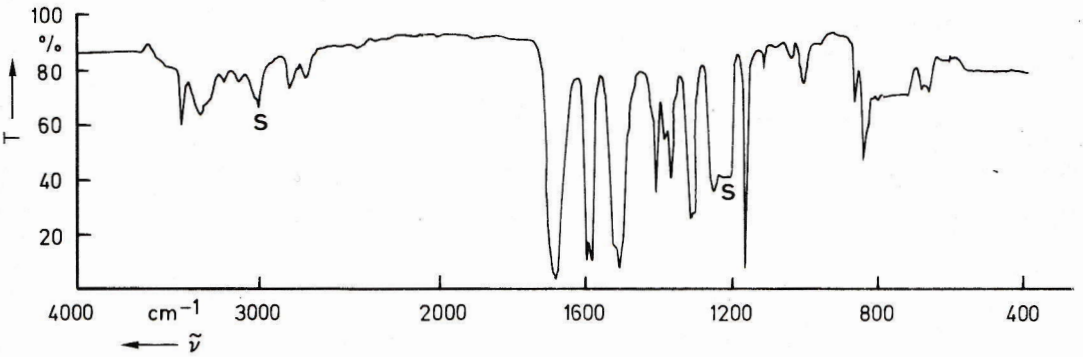


Fig. 2.28c 4-Acetylaminobenzaldehyde (in $CHCl_3$)

The spectrum in Fig. 2.28a shows a multiplicity of bands which is typical for N-monosubstituted amides. The appearance of so many bands in the spectra of amides is presumably due to the many possibilities for association, of which only one is shown on p. 47.

In contrast to Fig. 2.28a, the spectrum in Fig. 2.28b was measured in Nujol. As a result, the aldehyde (C–H) band (**D** in Fig. 2.28a) is obscured by the strong Nujol band (marked with **N**). On the other hand the absorption marked **K** has disappeared, since it was due to the traces of moisture in the KBr disc.

The spectrum in Fig. 2.28c shows the same compound in solution. This causes several changes: the region of the (N–H) vibration is much different, and the amide I band is somewhat shifted to higher frequency. This leads to overlap with the aldehyde (C=O) absorption. Such differences are generally to be expected on going from the crystalline state to solution, since the latter leads to a reduction in the **inter**molecular interactions. The change is most apparent for the vibration frequencies of those functional groups which are most strongly involved in the association.

The benzene absorption at 1600 cm^{-1} is now split into two separate bands, i.e. spectra in solution are often better resolved than solid state spectra. On the other hand solid state spectra show considerably more bands in the fingerprint region.

The bands marked **S** originate from the solvent, which is not totally compensated for by the double beam technique.

Amino acids (Fig. 2.30) show spectra of zwitterionic groups. The (N–H) absorption of the primary ammonium group (NH_3^+) is overlayed by the bands of the saturated C–H bonds. The two bands at 2500 and 2000 cm^{-1} are often seen when an $-NH_3^+$ group is present, and are due to overtones and combination vibrations. In the double bond region there are several bands of which at least one arises from the ionised carboxyl group.

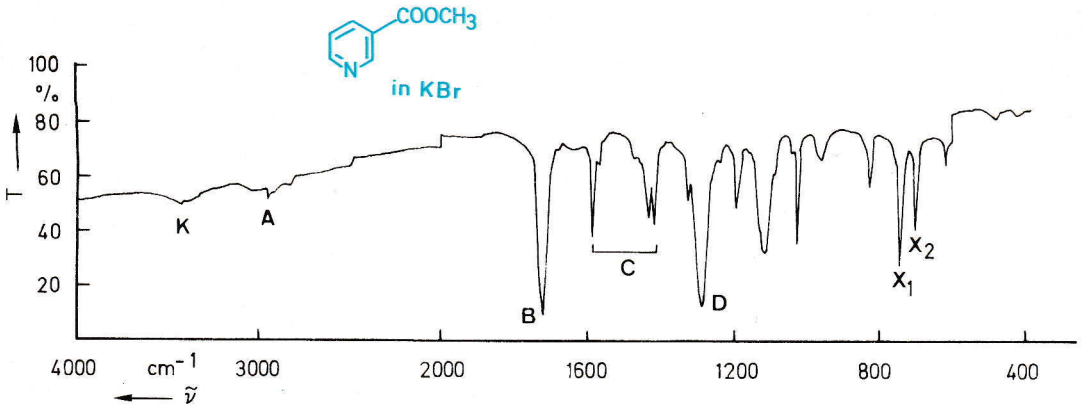


Fig. 2.29 Nicotinic acid methyl ester (in KBr)

A 2950 cm^{-1} (C–H) stretching vibration $\nu(CH_3)$; the aromatic (C–H) stretching vibration is only weakly visible (above 3000 cm^{-1})
B 1725 cm^{-1} (C=O) stretching vibration; (C=C) and (C=N) stretching vibration
D 1290 cm^{-1} (C–O) stretching vibration
X_1 745 cm^{-1} monosubstituted aromatic (the values in Tab. 2.16 apply approximately to pyridines)
X_2 705 cm^{-1}
K traces of water in the KBr disc

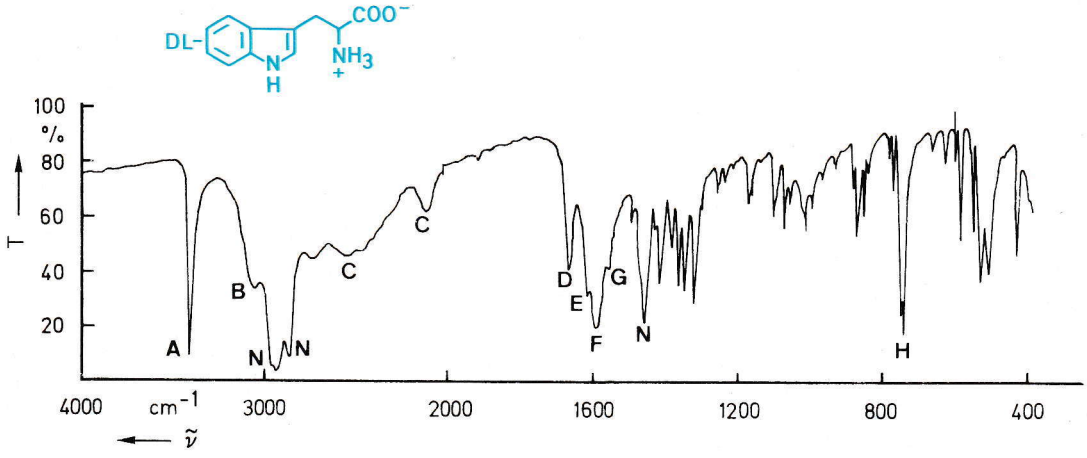


Fig. 2.30 D,L-Tryptophan (in Nujol)

A 3400 cm^{-1} indole (N–H) stretching vibration
B 3030 cm^{-1} broad "ammonium" band from $-NH_3^+$
C ≈2500 and ≈2100 cm^{-1} two bands, very common in amino acids, also appear in primary ammonium salts
D 1665 cm^{-1} amino acid I; unusually strong
E 1610 cm^{-1} probably aryl group
F 1585 cm^{-1} amino acid II; ionised carboxyl group $-COO^-$
G 1555 cm^{-1} $-NH_3^+$ bending vibration
H 755 or 745 cm^{-1} (C–H) out-of-plane bending vibrations of a 1,2-disubstituted benzene ring
N Nujol bands

13. Information Technology as an Aid to IR Spectroscopy

All modern IR spectrometers operate in on-line mode; the actual measurement device forms a unit with the computer and storage media.

IR software currently available can be divided into five categories:

1. Software for spectrometer operation (setting measurement parameters, etc.)
2. Software for spectral processing (peak recognition, expansions of sections of the spectrum, overlaying spectra for comparison purposes, etc.)
3. On-line catalogues of spectra: both general (all chemicals of a fine chemicals supplier) and specialised catalogues (e.g. spectra of active species, drugs) are available. Such software is often capable of comparing a measured spectrum with spectra from the catalogue and determine a correlation factor based on positions and intensities of the bands. The quality of the results is dependent on the quality of the digitisation and the coverage of the catalogue. Often measured spectra can be added to the catalogue, which improves the applicability of the system.
4. Software for spectral interpretation: this extends from simple systems, which make suggestions based on peak positions or list typical absorptions for a functional group, to systems employing pattern recognition and similar chemometric methods.
5. Software for the combination of spectroscopic methods (IR, NMR, MS, UV) with one another and with chemical structures, which are held in relational databases so that for a specific structural element recognised in the IR spectrum the corresponding NMR signals, fragmentations in the MS or UV bands can be shown, right through to the co-ordinated interpretation of the various spectra, using artificial intelligence methods to reproduce human skills of reasoning.

Software of types 1 and 2 is an integral component of the IR spectrometer. It is delivered by the manufacturer, as are usually spectral catalogues and simple interpretation software. More powerful software of types 3 to 5 can be purchased as accessories from the instrument manufacturers or from scientific software companies. The capabilities of such programs are constantly increasing in parallel with the increasing performance of computers; a comprehensive treatment is outside the range of this chapter.

14. Quantitative IR Spectroscopy

The quantitative determination of the concentration of a substance in a solution or mixture can be made with the assistance of IR spectroscopy. As in UV spectroscopy the Beer-Lambert law describes the relationship between absorbed light and concentration:

$$\lg \frac{I_0}{I} = \varepsilon \cdot c \cdot d = E_\lambda$$

The absorption at a specific wavelength is proportional to the concentration c and the transmission distance (cell thickness) d. The measured quantity is the ratio I_0/I of the light **before** and **after** its passage through the sample. The quantity $\lg I_0/I$ is the absorbance E_λ and ε the extinction coefficient. In the formula above there are three variables, c, d, and E_λ while ε is a constant for the substance. The aim of quantitative IR analysis is therefore to determine the concentration c from E_λ for a characteristic absorption band; d is the thickness of the cell.

The Beer-Lambert law is however only strictly valid at **low** concentration, e.g. for the very dilute solutions used for UV spectroscopy. Reflections and diffraction of the incident light also

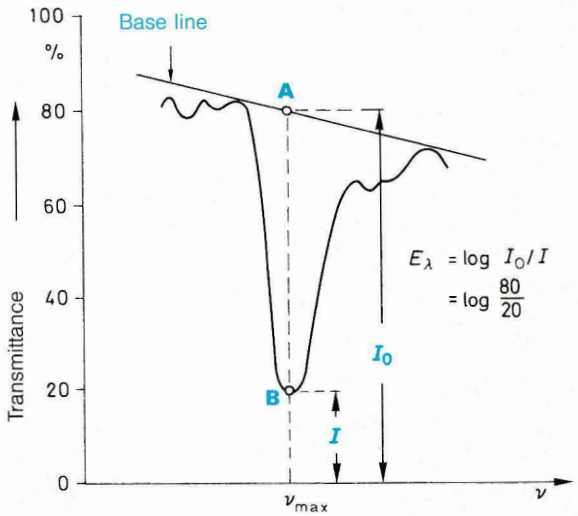


Fig. 2.31 Base line method for the determination of the absorbance E_λ

affect the determination of I_0/I. Thus KBr discs are only suitable for **semi**-quantitative IR measurements.

The quantitative determination of a sample using IR spectroscopy essentially requires the establishment of an empirical **calibration curve**. Several solutions of different concentrations are prepared and the resulting absorbances of a characteristic absorption plotted against the concentration. Since there is initially no reference point against which to measure the absorbance, the base line method is often used. This consists of using as the base line (i.e. the line of no absorbance) a straight line, often drawn as a tangent to the absorption curve as in Fig. 2.31. The ratio I_0/I can then be easily determined for each concentration.

The calibration curve is then generated by plotting the absorbances against the concentration (Fig. 2.32). From the calibration curve an unknown concentration c_x can be determined from a measurement of E_λ.

Quantitative IR analysis nowadays finds practical application in the plastics industry and in quality control of pharmaceuticals and agricultural pesticides.

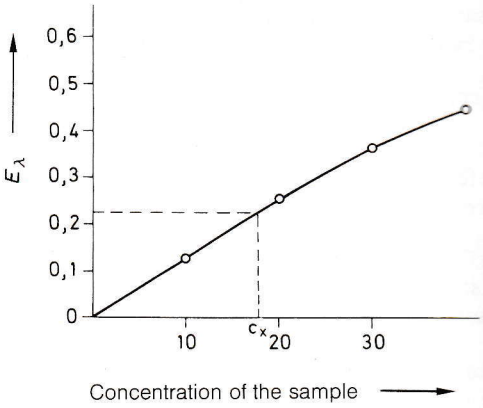


Fig. 2.32 Calibration curve

15. Raman Spectroscopy

The Raman effect was predicted theoretically by **A. Smekal** in 1923 and observed experimentally five years later by **C. V. Raman**.

Raman spectra are not normally recorded routinely, and the organic-oriented chemist seldom uses Raman spectroscopy for structural determination. Nevertheless a Raman spectrum can for certain specialised problems be a useful complement to IR spectroscopy, for example for the measurement of aqueous solutions, single crystals, and polymers. The applicability of Raman spectroscopy has also become much easier and quicker by the application of **laser technology**.

15.1 The Raman Effect

If a liquid or a concentrated solution of a substance is irradiated with monochromatic light (e.g. with an argon laser, which has a wavelength of 488 nm = 20492 cm^{-1}) then:

- the majority of the light passes through the sample unaffected (transmission)
- a small portion of the light (factor 10^{-4}) is scattered in all directions, but retains the frequency of the irradiating light; this is called **Rayleigh scattering** and can be thought of as arising from elastic impacts of the light quanta with the molecules.
- an even smaller portion of the light (factor 10^{-8}) is also scattered in all directions, but has a frequency distribution; it arises from absorption and re-emission combined with a vibrational excitation or extinction. This scattered radiation can be spectrally analysed and recorded with a photoelectric detector. The difference between the frequency of the irradiating line and a Raman line is the frequency of the relevant vibration.

The Raman effect is thus a consequence of the interaction between matter and electromagnetic radiation. The Raman spectrum is an **emission spectrum**. The frequency of the Raman lines or bands can be larger or smaller than the excitation frequency ν_0 (Rayleigh line). Characteristic for a molecule are the **differences** between the Raman frequencies and the excitation frequency ν_0. They are independent of ν_0 and can also be found in the IR spectrum as absorption bands (see selection rules).

The origin of the Raman effect can be explained as follows: when the laser beam hits molecules of the sample (and the excitation energy is insufficient for an electronic transition) the interaction either causes elastic scattering (Rayleigh scattering) or a part of the light energy is taken up by increasing the vibrational energy of the molecule, i.e. the scattered light is of **lower energy** (longer wavelength). If the excitation beam hits a molecule in an excited vibrational state, the same interaction results in the emission of light of **higher energy** (shorter wavelength). The Raman lines on the longer-wavelength side of the Rayleigh frequency are called **Stokes** lines, those on the shorter-wavelength side **anti-Stokes** lines.

15.2 Selection Rules

As explained in Sec. 2 (see p. 31) the generation of an IR absorption requires that a change in the **dipole moment** of the molecule is caused by the vibration. For the appearance of a Raman line however it is necessary that there is a change in the **polarisability** of the molecule. The polarisability is a measure of the ease of deformation of the electron cloud around an atom or molecule, e.g. greater for I^- than for Cl^- or Br^-.

These selection rules have an important consequence: in symmetrical molecules vibrations which are symmetric about the symmetry centre are IR inactive (no change of dipole moment) but Raman active. Conversely, vibrations which are not symmetric about the symmetry centre are Raman inactive (forbidden) and in the IR spectrum generally active (allowed). This can be demonstrated by the simple example of the carbon dioxide molecule (Fig. 2.33). In the symmetric stretching vibration with amplitudes **a** and **b** it is apparent that there is no change in the dipole moment. This vibration is therefore IR inactive, and causes no absorption band in the spectrum. The polarisability in the compressed state **a** is however different from that in the extended state **b**, therefore this vibration is Raman active. This underlines the importance of Raman spectroscopy for symmetrical molecules. For the antisymmetric stretching vibration (**c,d**) however the situation is reversed. The polarisability remains the same, whereas the dipole moment changes. Thus this vibration does not appear in the Raman spectrum. The changes of polarisability α and dipole moment μ for the stretching vibrations of the CO_2 molecule are also shown graphically in Fig. 2.33.

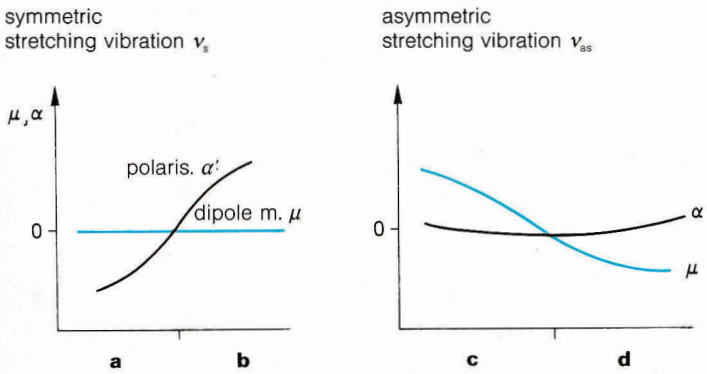


Fig. 2.33 Stretching vibrations of the CO_2 molecules and the change of polarisability α and dipole moment μ.

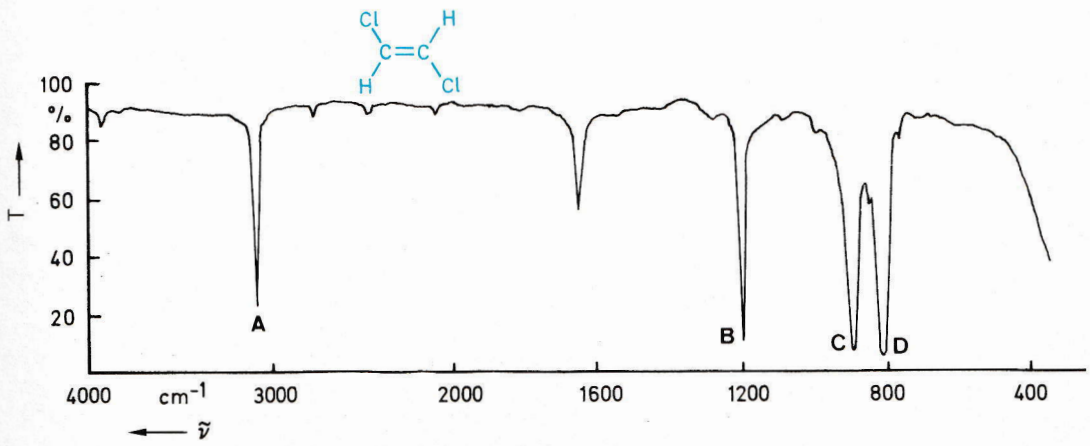


Fig. 2.34 IR spectrum of dichloroethylene

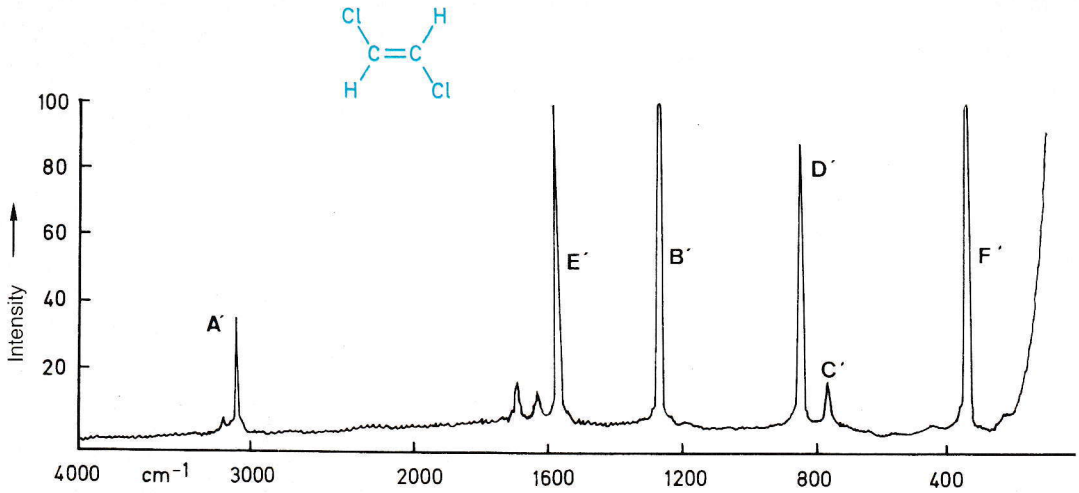
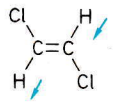
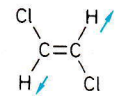
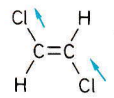
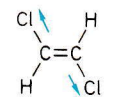
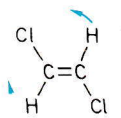
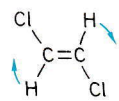
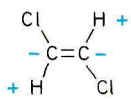
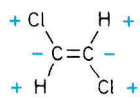
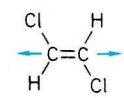
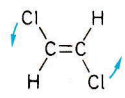


Fig. 2.35 Laser Raman spectrum of (*E*)-dichloroethylene

As an illustration the IR and Raman spectra of (*E*)-dichloroethylene (i.e. a symmetrical molecule) are shown in Figs. 2.34 and 2.35. These show clearly how IR and Raman spectroscopy yield complementary pictures of the vibrations in a molecule: in the IR spectrum the absorptions from the **antisymmetric** vibrations appear, whereas the Raman spectrum shows the emission bands of the **symmetric** vibrations. In Tab. 2.22 the individual vibrations are assigned to their respective bands.

Tab. 2.22 Assignment of the bands in Figs. 2.34 and 2.35

vibration type	anti-symmetric vibration (IR active)	IR band Fig. 2.34 (cm^{-1})	symmetric vibration (Raman active)	Raman band Fig. 2.35 (cm^{-1})
ν (C—H)		3090 (**A**)		3070 (**A'**)
ν (C—Cl)		817 (**D**)		844 (**D'**)
δ (C—H)		1200 (**B**)		1270 (**B'**)
γ (C—H)		895 (**C**)		760 (**C'**)
ν (C=C)	–	–		1576 (**E'**)
δ (C—Cl)	below 300 cm^{-1} in IR	–		350 (**F'**)

Tab. 2.17 Sulfur compounds S

Group	Band	Notes
–S–H	2600–2550 (w)	(S–H) stretching vibration; weaker than O–H and less influenced by hydrogen bonding. This absorption is strong in the Raman spectrum
	1200–1050 (s)	
	≈3400	(N–H) stretching vibration; shifted in the solid state to as low as 3150 cm^{-1}
	1550–1460 (s)	amide II
	1300–1100 (s)	amide I
	1060–1040 (s)	
sulfones		
	1350–1310 (s) 1160–1120 (s)	
sulfonamides		
	1370–1330 (s) 1180–1160 (s)	
sulfonates		
$R-SO_2-OR'$	1420–1330 (s) 1200–1145 (s)	
sulfates		
$RO-SO_2-OR'$	1440–1350 1200–1145	

Tab. 2.18 Phosphorus compounds P

Group	Band	Notes
P–H	2400–2350 (s)	sharp
P-Phenyl	1440 (s)	sharp
P–O-Alkyl	1050–1030 (s)	
P–O-Aryl	1240–1190 (s)	
P=O	1300-1250 (s)	
P–O–P	970– 910 (s)	broad
	2700–2560 1240–1180 (s)	hydrogen bonded O–H (P=O) stretching vibration

Tab. 2.19 Functional groups with C–O single bonds
This region suffers from multiple overlap! The bands are only significant in conjunction with other structural indicators

Group	Band	Notes
Alcohols		
C–OH	1250–1000 (S)	primary alcohols at the lowest, tertiary and phenols at the highest end of the region often doublet
ethers		
	1150–1070 (s) 1275–1200 (s) 1075–1020 (S)	sometimes split, see Fig. 2.18 (p. 56)
epoxides	~1250, ~900, ~800	
		
esters		
	1330–1050 (s)	2 bands $\delta_{asym.}$ stronger, and at lower wavenumbers
$CH_3CO-O-C$	~1240	asymmetric stretching vibration
$RCO-O-CH_3$	~1165	

Tab. 2.20 Halogen compounds C–Hal

Group	Alkyl–Hal	Aryl–Hal	
C–F	1365–1120 (s)	1270–1100	
C–Cl	830– 560 (s)	1100–1030	skeletal vibrations
C–Br	680– 515 (s)	1075–1030	skeletal vibrations
C–I	≈ 500 (s)	≈ 1060	skeletal vibrations

Tab. 2.21 Inorganic ions

Group	Band	Notes
ammonium	3300–3030	all bands are strong
cyanide, thiocyanate, cyanate	2200–2000	
carbonate	1450–1410	
sulfate	1130–1080	
nitrate	1380–1350	
nitrite	1250–1230	
phosphate	1100–1000	