

Chapter 2

Vibrational Spectroscopy

2.1 Introduction

2.1.1 Infrared (IR) Spectroscopy

The absorption of infrared (IR) radiation causes excitation of vibrations of the atoms of a molecule or the crystal lattice and causes bands in the spectra which are generally presented in the unit wave number $\tilde{\nu}$ in cm^{-1} (wavelength λ was used in the older literature). Commonly, the symbol ν is used in vibrational spectroscopy instead of the symbol $\tilde{\nu}$ in the energy scale and they are sometimes named vibrational frequencies which are measured in the maxima of absorption bands whereas this is correct only for small oscillation strength.

The infrared range of the electromagnetic spectrum is divided into three regions, named after their relation to the visible spectrum:

- *Near-infrared* (NIR) (wave number ranges from 14,000 to 4,000 cm^{-1} and wavelength ranges from 0.8 to 2.5 μm) lying adjacent to the visible region excites so-called overtone or higher harmonic vibrations (*higher harmonics*).
- *Mid-infrared* (wave number ranges from approximately 4,000 to 400 cm^{-1} and wavelength ranges from 2.5 to 25 μm) excites mainly fundamental vibrations. This part of the infrared range may be used to study the structure of molecules that we shall be concerned with in this book. In general, the name “IR-spectroscopy” conventionally refers to the mid-IR region.
- *Far-infrared* (wave number ranges from approximately 400 to 10 cm^{-1} and wavelength ranges from 25 to 1,000 μm) is the lowest-energy region which excites mainly lattice vibrations or can be used for rotational spectroscopy.

A molecule can vibrate in many ways, and each way is called a *vibrational mode*. Let us start with a simple diatomic molecule A–B, such as CO or HCl. The wave number of absorbance ν can be calculated by Eq. 2.1 derived by the model of the harmonic oscillator

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{f}{\mu}} \quad (2.1)$$

in which c is the light velocity, f is the force constant in the atomic scale and the spring constant for the macroscopic model, respectively, and μ is the reduced mass defined by Eq. 2.2

$$\mu = \frac{m_A \cdot m_B}{m_A + m_B}. \quad (2.2)$$

Note that the force constant is a criterion for the strength of the chemical bond in the molecule A–B. Therefore, the stronger the chemical bond (electronic effect) and the smaller the reduced mass μ (mass effect), the higher the wave number of the absorption band ν .

The relation in Eq. 2.1 can be applied not only for the simple diatomic molecule but also for some structural moieties in more complex molecules as long as coupling between the atoms can be neglected, in other words, at so-called *characteristic vibrations* which are explained in Sect. 2.3.2. Such vibrations are provided, for example, by multiple bonds in the neighborhood of single bonds.

Electronic effects on the position of the absorption band

The force constant increases with the bonding order, for example, $f_{C-X} < f_{C=X} < f_{C\equiv X}$. Therefore, the vibrational frequencies increase for vibrations of equal atoms X according to Eq. 2.1:

$$\begin{aligned} \nu(C-C) &\approx 1,000 \text{ cm}^{-1} < \nu(C=C) \approx 1,650 \text{ cm}^{-1} < \nu(C\equiv C) \approx 2,250 \text{ cm}^{-1} \\ \nu(C-O) &\approx 1,100 \text{ cm}^{-1} < \nu(C=O) \approx 1,700 \text{ cm}^{-1}. \end{aligned}$$

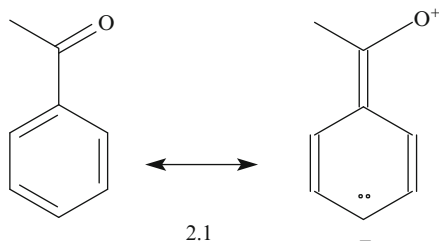
Note that Eq. 2.1 enables the recognition of the real strength of a chemical bond. For example, the hydrocarbon bond C–H is famously a *single* bond, but this is only a generalization. The neighborhood of oxygen at the carbon atom diminishes the electron density and, hence, the force constant and bonding strength, resulting in a smaller vibrational frequency according to Eq. 2.1. This is true for the following structural moieties: $\nu(\text{AlkylC-H}) \approx 3,000 \text{ cm}^{-1}$ and $\nu(\text{O=C-H}) \approx 2,750 \text{ cm}^{-1}$. Thus, the C–H-bond is slightly stronger in the alkyl group.

Let us now consider *I*- and *M*-effects on the vibrational frequencies.

The vibrational frequencies of the C=O double bond, $\nu(C=O)$ of compounds of the type $\text{CH}_3\text{C}(\text{C=O})\text{-X}$ are: $1,742 \text{ cm}^{-1}$ (for X = H), $1,750 \text{ cm}^{-1}$ (for X = Cl), and $1,685 \text{ cm}^{-1}$ (for X = phenyl). Thus, there are differences concerning the strength of the C=O bond due to the nature of the chemical bond: The –I-effect of the Cl atom diminishes the electron density at the C atom which is equalized by contribution of electron density from the free electron pair at the neighboring O atom. Thus, the bond order for the C=O bond is increased as is shown by the resonance structures $\text{C-C(=O)Cl} \leftrightarrow \text{C-C}\equiv\text{O}^+\text{Cl}^-$ which increases the force

constant and, hence, a higher vibrational frequency is observed in carboxylic acid chlorides.

Otherwise, a substituent with a + M-effect (phenyl) causes conjugation of the C=O group as Structure 2.1 shows



resulting in a smaller force constant and, hence, a smaller vibrational frequency.

Conjugation increases the thermodynamic stability of the molecule but decreases the bond strength and, hence, the force constant which results in smaller vibrational frequencies.

Conversely, the vibrational frequency obtained experimentally by the infrared spectrum provides hints to the strength of the chemical bond.

Note that coupling of various vibrations results in absorption bands of higher and lower frequency in the spectrum which are not caused by electronic effects. The transitions 3 and 4 caused by coupling of transitions 1 and 2 are shown in a simple energy diagram in Fig. 2.1.

Mass effects on the position of the absorption band

The smaller the mass of the atoms the higher the vibrational frequency, which is demonstrated by the C–H and C–D stretching frequencies,

$$\nu(\text{C} - \text{H}) \approx 3,000 \text{ cm}^{-1}; \quad \nu(\text{C} - \text{D}) \approx 2,120 \text{ cm}^{-1}.$$

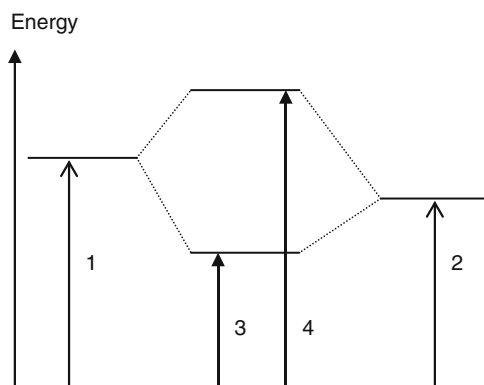


Fig. 2.1 Schematic energy diagram for the coupling of transitions 1 and 2 resulting in the transitions 3 and 4 with corresponding absorption bands in the infrared spectrum

The vibrational frequencies of heavier isotopes can markedly differ and they can occur with proper intensities for atoms with abundant isotopes.

As mentioned above, Eq. 2.1 is approximately valid for characteristic vibrations in multiatomic molecules. For such a structural moiety AB, for example, the C=O group of a carbonyl compound, the force constant f can be calculated according to the so-called “two-mass model” by Eq. 2.3

$$f \text{ in N}^{-1} = \frac{5.891 \cdot 10^{-5} \cdot \nu^2}{M_A^{-1} + M_B^{-1}} \quad (2.3)$$

in which ν is the wave number of the corresponding experimentally observed absorption band in cm^{-1} , and M_A and M_B are the relative atomic masses of the atoms A and B, respectively.

Challenge 2.1

Calculate the force constant of the P=O group in OPCl_3 . The strong infrared absorption band of the P=O stretching vibration is observed at $1,290 \text{ cm}^{-1}$.

Solution to Challenge 2.1

The force constant is $f(\text{P=O}) = 1,035 \text{ N m}^{-1}$ calculated by Eq. 2.1 with $\nu = 1,290 \text{ cm}^{-1}$, $M_P = 31$, and $M_O = 16$.

In the same manner the force constants can be calculated for carbon–carbon bonds and bonds in inorganic species resulting in the following rules:

- The relation of the force constants of the single, double, and triple bonds $f(\text{C–C}) \approx 500 \text{ N m}^{-1}$, $f(\text{C=C}) \approx 1,000 \text{ N m}^{-1}$, $f(\text{C}\equiv\text{C}) \approx 1,500 \text{ N m}^{-1}$ is 1:2:3.
- The force constant increases with increasing effective nuclear charge, for example, $f_{\text{S-O}}(\text{SO}_3^{2-}) = 552 \text{ N m}^{-1} < f_{\text{S-O}}(\text{SO}_4^{2-}) = 715 \text{ N m}^{-1}$.
- The force constant increases with increasing s -character of the hybrid orbital: $f_{\text{C-H}}(\text{sp}^3\text{C–H}) < f_{\text{C-H}}(\text{sp}^2\text{C–H}) < f_{\text{C-H}}(\text{spC–H})$.

It is well known, however, that not all aspects of the atomic level can be described by the macroscopic ball-and-spring model. Instead the quantum mechanical formalism must be applied resulting in discrete energy levels

$$E_n = h \cdot \nu \cdot \left(\nu + \frac{1}{2} \right) \quad (2.4)$$

in which ν is the vibrational quantum number. According to this selection rule, only transitions are allowed with $\Delta\nu = \pm 1$. Because for most vibrations of organic

molecules nearly exclusively the ground state $v = 0$ is occupied at ambient temperatures, the experimentally observed infrared absorption band of a two-atomic molecule is caused by the transition $v = 0 \rightarrow v = 1$ which is named the *fundamental vibration*.

Furthermore, the harmonic oscillator should be substituted by the *anharmonic oscillator model*. This substitution leads to a shape of the potential curve which is asymmetric and the right part of which converges to the dissociation energy. Therefore, the energy levels are no longer equidistant but decrease with increasing vibrational quantum number v . Moreover, the selection rule for the harmonic oscillator is no longer strongly valid; transitions with $\Delta v = \pm 2, \pm 3 \dots$ can additionally occur, albeit with lower intensity, which are named *overtones* or *higher harmonics*. Thus, overtones are, in a first approximation, the whole number multiples of the fundamentals. Because of the anharmonicity of vibration the first overtone is somewhat smaller in frequency than the double value of the corresponding fundamental and so on.

The intensity of an absorption band is determined by the strength of the electromagnetic absorption process which is mainly caused by the change of the electric dipole moment for a vibrational transition induced by infrared radiation. Note that the probability of a transition with $\Delta v = \pm 2$ is approximately tenfold smaller than that with $\Delta v = \pm 1$. The absorption coefficients α of fundamentals are in the range $1\text{--}100 \text{ L mol}^{-1} \text{ cm}^{-1}$, therefore, overtones appear with low intensities or are missing in a routine spectrum.

In molecules with more than two atoms anharmonicity can additionally lead to *combination modes* which refer to the simultaneous excitation of two vibrational modes at one frequency which can lead to additional peaks and further complicate infrared spectra. Some of them are meaningful for structural analysis, for example, for the determination of aromatic substituent types (see Sect. 2.3).

Challenge 2.2

For solutions to Challenge 2.2, see *extras.springer.com*.

1. The experimentally observed $\text{N}=\text{O}$ fundamentals $\nu(\text{N}=\text{O})$ of nitrosyl compounds $\text{O}=\text{NX}$ are: $1,800 \text{ cm}^{-1}$ (for $\text{X} = \text{Cl}$, gaseous state), $1,948 \text{ cm}^{-1}$ (for $\text{X} = \text{Cl}$, solid state), and $2,387 \text{ cm}^{-1}$ (for $\text{X} = \text{BF}_4^-$). Characterize the chemical bonding in these compounds and formulate the structure.
2. Calculate the force constants $f(\text{C}=\text{X})$ according to the two-mass model for the $\text{C}=\text{X}$ bond for $\text{X} = \text{C}$ and $\text{X} = \text{O}$, on the basis of the experimentally observed fundamentals: $\text{H}_2\text{C}=\text{O}$: $\nu(\text{C}=\text{O}) = 1,742 \text{ cm}^{-1}$, $\text{H}_2\text{C}=\text{CH}_2$: $\nu(\text{C}=\text{C}) = 1,645 \text{ cm}^{-1}$.
3. Calculate the force constant by means of the simple two-mass model for the $\text{C}-\text{H}$ and $\text{C}\equiv\text{C}$ bonds in $\text{H}-\text{C}\equiv\text{N}$ with the experimentally observed fundamentals $\nu(\text{C}-\text{H}) = 3,311 \text{ cm}^{-1}$ and $\nu(\text{C}\equiv\text{C}) = 2,097 \text{ cm}^{-1}$, respectively. The exact values obtained by a normal mode analysis are

(continued)

$f(\text{C-H}) = 582 \text{ N m}^{-1}$ and $f(\text{C}\equiv\text{C}) = 1,785 \text{ N m}^{-1}$. What is the percentage deviation between the exact and the approximate values? What knowledge can be gained from this result?

4. The stretching frequency of the ^{16}O -isotope is experimentally determined to be $\nu(^{16}\text{O}-^{16}\text{O}) = 832 \text{ cm}^{-1}$. At which wave number can the stretching frequency for the ^{18}O -isomer, $\nu(^{18}\text{O}-^{18}\text{O})$ be expected?

2.1.2 Raman Spectroscopy and Some Applications

Raman spectra result from inelastic scattering of monochromatic light, usually from a laser in the visible, near-infrared, and near-ultraviolet range. Such lasers are for example: Ar ion with wavelengths at 514, 488, and 458 nm, He/Ne with wavelengths at 628, 578, and 442 nm, or Nd/YAG with wavelengths at 523 and 1,052 nm. Note that the last wavelength lies in the NIR range.

The Raman effect occurs when monochromatic light impinges upon a molecule and interacts with the electron cloud and the bonds of this molecule. For the spontaneous Raman effect to take place the molecule is excited by a photon from the ground state to a virtual energy state. The molecule can relax and return to the ground state by emission of a photon whose energy is the same as that of the exciting radiation resulting in elastic *Rayleigh* scattering. But a very small part of the scattered light can also have frequencies that are smaller than those of the elastically scattered part because a part of the energy of the incoming photons was employed to excite molecules to a higher vibrational state $\nu = 1$. As a result, the emitted photons will be shifted to lower energy, i.e., light with a lower frequency. This shift is designated the *Stokes shift*. The difference in energy between the original state and the final state corresponds to a vibrational mode far from the excitation wavelength.

If the process starts from a vibrationally excited state $\nu = 1$ and relaxes to the ground state $\nu = 0$, then the emitted photons will be shifted to higher frequency which is designated the *Anti-Stokes shift*. Compared with the Stokes-shifted light the Anti-Stokes shifted radiation has a lower intensity because of the small population of the vibrationally excited state compared to that of the ground state of the molecule at ambient temperatures. These processes are illustrated in a simple energy level diagram in Fig. 2.2. As Fig. 2.2 shows, the infrared absorption yields similar, but often complementary information. However, whereas the vibrational frequency directly corresponds to the absorption band in the infrared spectrum the vibrational frequency in the Raman spectra corresponds to the *difference* between Rayleigh and Stokes lines in the Raman spectrum. Note that the Raman effect is a scattering phenomenon and may not be confused with fluorescence whose emission starts from a discrete and not a virtual energy level (see Sect. 3.7).

Besides spontaneous Raman spectroscopy there are a number of advanced types of Raman spectroscopy, for example, surface-enhanced Raman (SERS), resonance

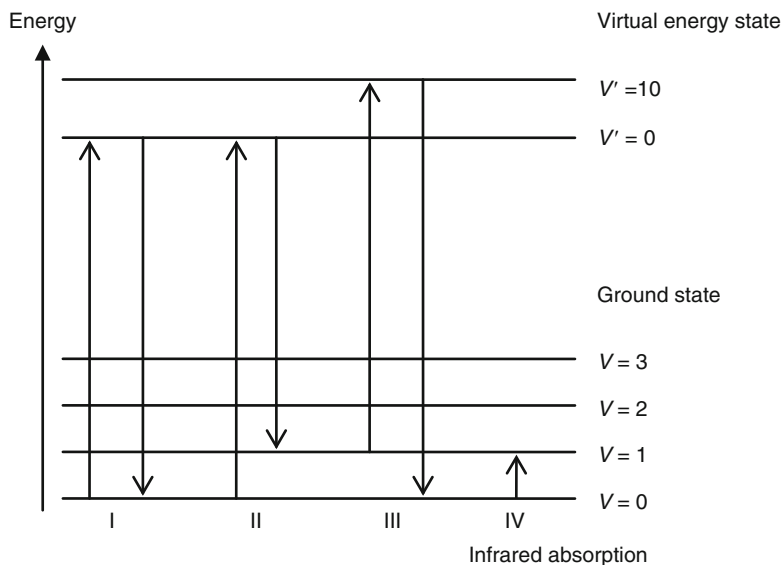


Fig. 2.2 Energy level diagram showing Rayleigh (I), Stokes (Raman) (II), and anti-Stokes (Raman) (III) scattering as well as IR-absorption (IV)

Raman spectroscopy (RRS), coherent anti-Stokes Raman spectroscopy (CARS), and others which are far beyond the scope of this book.

In principle, the registration of a Raman spectrum is simple: The sample is illuminated with an appropriate laser beam. The stray light is collected by a lens and sent through a monochromator. The elastic Rayleigh scattering light is filtered out while the rest of the collected light is dispersed onto a detector.

Although, in general, the organic chemist will prefer infrared spectroscopy for the registration of vibrational spectra, spontaneous Raman spectroscopy has a number of advantages; some of them will be given in the following text.

- The frequency of the excitation light can be chosen arbitrarily (within the limits of available laser frequencies). Thus, glass cuvettes can be applied for excitation with visible light instead of the expensive alkali discs used in infrared spectroscopy.
- Whereas the excitation of vibrations by infrared radiation is connected with changing the *electrical dipole moment*, in Raman spectroscopy only such vibrations are active that change the *induced dipole moment* (polarizability). Thus, polar bonds provide intense absorption bands whereas intense Raman lines are commonly observed from *nonpolar* bonds, such as C–C, C=C, C≡C, S–S, N=N, and others.
- Infrared and Raman spectroscopy are complementary for the investigation of symmetrical species, mostly present in inorganic chemistry, for the determination of *all* modes whereas there are also modes that cannot be excited either in IR or in Raman spectroscopy. Note that, according to the selection rules explained

in Sect. 2.1.3, symmetrical modes can only be observed in the Raman spectrum if the molecule possesses an inversion center.

- Because of the small intensities of the H–O stretching modes of water and alcohols, Raman spectroscopy is excellently suitable for alcoholic or aqueous solutions which is important, for example, in biological systems, such as the determination of the presence of S–S bridges in proteins, the symmetrical O–P–O mode of nuclear acids, or for the *in vivo* denaturation of proteins by means of Raman microscopy.
- C–C modes in rings can be better recognized and assigned because of their higher intensity in comparison to the infrared absorption bands.
- Raman spectra mostly show simpler patterns because of often-missing overtones and combination modes.
- Note that the Raman spectrum presents the *whole* range of molecular and lattice modes including those at low frequency $\nu < 200\text{ cm}^{-1}$ for which an extra setup (far-infrared spectrometer with PE cuvette) may be necessary in infrared spectroscopy.

Examples for applications in the far-infrared range are investigations of:

- The low-frequency vibrations of metal–metal modes, such as, for example $\nu(\text{Hg–Hg}) = 169\text{ cm}^{-1}$ in $\text{Hg}_2(\text{NO}_3)_2$, and $\nu(\text{Mn–Mn}) = 157\text{ cm}^{-1}$ in $\text{Mn}_2(\text{CO})_{10}$;
- Lattice modes in solids in order to characterize or to distinguish polymorphic forms;
- Stretching (ν) and deformation (δ) modes of heavy atoms, for example, $[\text{CdI}_4]^{2-}$: 145 (ν_{as}), 117 (ν_{s}), 44 (δ_1), 23 (δ_2).
- The polarization of Raman scattered light also contains important information. This property can be measured using plane-polarized laser excitation and a polarization analyzer as shown in Fig. 2.3.

z-polarized excitation light induces a dipole moment in the molecule. Scattered light travelling in the x-direction is also z-polarized light I_{\parallel} (a).

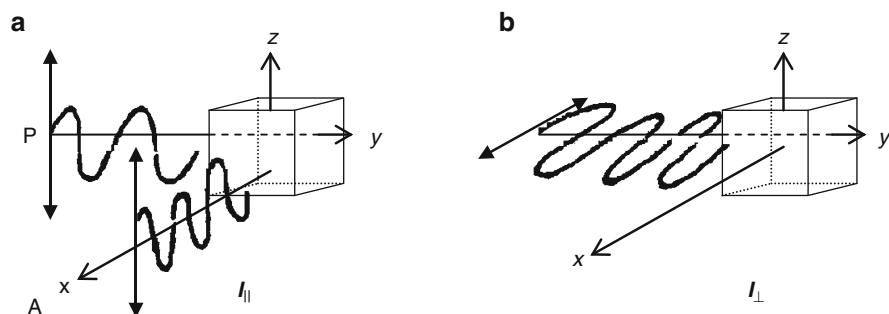


Fig. 2.3 Arrangement for measuring the polarization ratio of Raman scattered light. *P* polarizer, *A* analyzer, I_{\parallel} , I_{\perp} intensity of Raman scattered light with the analyzer set parallel and perpendicular to the excitation plane, respectively

The polarization plane of the excitation laser light as well as the direction of the induced dipole is rotated around 90° in **(b)**. Thus, in case of fully symmetric modes of optically isotropic substances, no z -polarized light is emitted travelling in the x -direction which means, the intensity I_\perp is approximately zero.

Spectra acquired with an analyzer set both parallel **(a)** and perpendicular **(b)** to the excitation plane (P) can be used to calculate the *polarization ratio*, which is appropriate to experimentally recognize modes that are totally symmetrical (see Sect. 2.1.3). The degrees of polarization ρ are calculated by the ratio of the intensities measured employing the perpendicular and parallel analyzer set according to Eq. 2.5

$$\rho = \frac{I_\perp}{I_\parallel}. \quad (2.5)$$

Totally symmetrical modes provide polarized (p) Raman lines for which $0 < \rho < \frac{3}{4}$ is valid. All other modes are depolarized (dp) with $\rho \approx \frac{3}{4}$.

Figure 2.4 shows the Raman spectra of carbon tetrachloride measured with an analyzer set both parallel (I_\parallel) and perpendicular (I_\perp) to the excitation plane and the polarization state is denoted by p and dp , respectively. As the degrees of polarization suggest, the Raman line at approximately 470 cm^{-1} is polarized. Thus, it must be assigned to the symmetric C–Cl stretching vibration. The connection between symmetry of modes, Raman activity, and the Raman spectra is the subject of the next section.

In addition to polarized IR spectroscopy, polarized Raman spectroscopy also can be used for example, in solid-state physics to determine the orientation of the crystallographic orientation of an anisotropic crystal and to understand macromolecular orientations in crystal lattices and liquid crystals. In most cases, however,

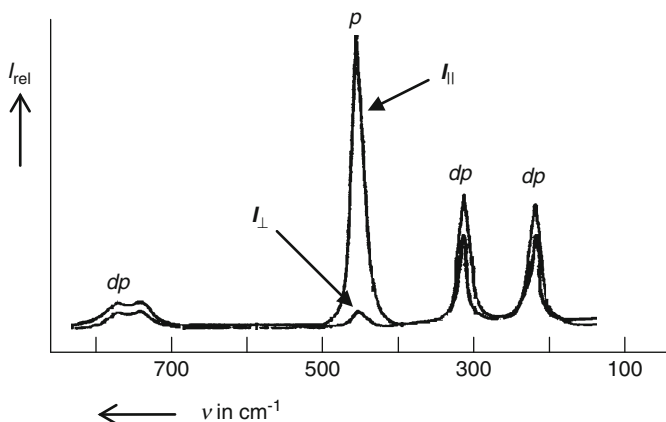


Fig. 2.4 The polarized Raman spectra of carbon tetrachloride measured with an analyzer set both parallel (I_\parallel) and perpendicular (I_\perp) to the excitation plane. p polarized Raman lines, dp depolarized Raman lines

the application is more complex than in IR spectroscopy. Both methods have their merits in polymorph analysis.

2.1.3 Symmetry, Selection Rules, and Applications

A nonlinear molecule with N atoms has $3 \cdot N - 6$ normal modes also called degrees of freedom in contrast to when the molecule is linear. Then only $3 \cdot N - 5$ normal modes are possible. As an example, the nonlinear molecule BF_3 has $3 \cdot 4 - 6 = 6$ degrees of freedom or normal modes while the linear CO_2 has $3 \cdot 3 - 5 = 4$ degrees of freedom.

There are two principal types of molecular vibrations: stretching modes and bending modes. A *stretching* vibration is characterized by movement along the bond axis with increasing and decreasing of the interatomic distance. Stretching vibrations are designated by the symbol ν . A *bending* vibration consists of a change of the bond angle between bonds or the movement of a group of atoms with respect to the remainder of the molecule with an accompanying change of bond angle. A movement *in-plane* is designated by the symbol δ and γ is used for *out-of-plane* movements (δ_{oop} vibrations). Note that normal mode vibrations may not change the center of gravity in the molecule.

The number of possible stretching vibrations is equal to the number of bonds and the number of bending vibrations is the difference of the total $3 \cdot N - 6(5)$ and the number of stretching modes.

Note that not only the “nonoscillating” molecule but also all modes of the molecule have a *symmetry* which means that they can be assigned to one of the symmetry classes of the point group to which every molecule belongs (for details, see the specialized literature on group theory). The algorithm for the determination of the point group of any molecule is presented in Table 6.7 and the symmetry classes of the normal modes are listed in Table 6.9 for the most important symmetry groups.

The principle of the determination of the symmetry properties of normal modes will be described by the example of a *planar* compound AB_3 to which belongs, for example, the molecule BF_3 or the ion NO_3^- .

According to the procedure given in Table 6.7 the triangular planar species AB_3 belongs to the point group $\text{D}_{3\text{h}}$. In order to determine the symmetry classes of the fundamental modes, expediently, the base set of the so-called *inner coordinates* are used. In distinction from the Cartesian coordinates which include the total $3 \cdot N$ modes, inner coordinates only include the possible vibrations of the molecule. The inner coordinates of the stretching vibrations should be denoted by Δr_i , those of the bending in-plane by $\Delta \alpha_i$, and the bending out-of-plane by $\Delta \gamma_i$. The coordinates are defined in such a way that all possible movements of the molecule are included with the consequence that the bending movements are over-determined. Three angles cannot be simultaneously altered; the alteration of two angles fixes the third angle. Thus, more representations are obtained as alterations of angles are possible.

Therefore, without justification, a *totally symmetrical representation* Γ_1 must be eliminated.

Next, only the *character of the transformational matrix* has to be determined for the base set of the inner coordinates. The following rule should be applied:

Only that coordinate of the base set provides a contribution to the character of the transformational matrix that does not change its position at the execution of the respective symmetry operation.

By applying this procedure, one obtains a reducible base set of the transformation matrix which can be decomposed into the set of irreducible representations Z_i by means of the reduction formula (Eq. 2.6)

$$Z_i = 1/h \cdot \sum g_k \cdot \chi_r(K) \cdot \chi_{irr}(K) \quad (2.6)$$

in which h is the order of the group (which is equal to the number of all symmetry operations), g_k is the number of the elements in each class K , and $\chi_r(K)$ and $\chi_{irr}(K)$ are the number of reducible and irreducible representations of the class K , respectively. The symmetry operations are listed in the *character table* which is given in Table 6.8 for some symmetry groups.

Let us now continue the problem for AB_3 given above. The molecule AB_3 has six normal modes: As the molecule has three bonds three stretching vibrations result. Therefore, three normal modes remain belonging to the bending modes which can be divided into in-plane (δ) and out-of-plane (γ) bending modes for a planar molecule. The base set of the inner coordinates divided as described are presented in Fig. 2.5.

The characters of the transformational matrix assigned to the three types of modes according to Fig. 2.5 are listed in Table 2.1. They are obtained by applying the rules given above.

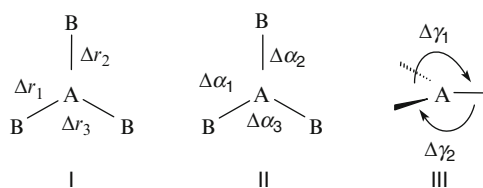


Fig. 2.5 Base set for the stretching (I), bending in-plane (II), and bending out-of-plane vibrations, for the triangular planar molecule AB_3 of the point group D_{3h}

Table 2.1 Characters of the transformational matrix assigned to the three types of modes (Fig. 2.5) for a triangular plane molecule AB_3 belonging to the point group D_{3h}

D_{3h}	E	2 C_3	3 C'_2	σ_h	2 S_3	σ_v	Symmetry classes
$\chi(\Delta r_i)$	3	0	1	3	0	1	$\Rightarrow A'_1 + E'$
$\chi(\Delta \alpha_i)$	3	0	1	3	0	1	$\Rightarrow A'_1 + E'(-A'_1)$
$\chi(\Delta \gamma_i)$	2	2	0	0	0	2	$\Rightarrow A'_1 + A_2''(-A'_1)$

The last column contains the irreducible representations calculated by Eq. 2.6 with the reducible ones given in columns 2–7. A totally symmetrical class A_1' must be eliminated for the bending modes as explained above.

As Table 2.1 shows, the following six vibrations are obtained for a triangular planar molecule AB_3 with the symmetry D_{3h} . (Note that the symbol Γ is commonly used for the representation of a class).

$$\text{Stretching vibrations:} \quad \Gamma_v = A_1' + E' \quad (2.7)$$

$$\text{Bending vibrations in-plane:} \quad \Gamma_\delta = E' \quad (2.8)$$

$$\text{Bending vibrations out-of-plane:} \quad \Gamma_\gamma = A_2'' \quad (2.9)$$

Although six vibrations are theoretically possible only four vibrations can be experimentally observed. The reason is that modes of the symmetry class E are twofold degenerated which means that both of the degenerated modes are observed as a *single* infrared absorption band or Raman line. Modes belonging to the symmetry class E consist of two energetic modes perpendicular to each other. Considering this fact, there are three stretching (Eq. 2.7), two bending in-plane (Eq. 2.8), and one bending out-of-plane (Eq. 2.9) vibrations, in summary six vibrations as calculated by $3 \cdot 4-6$.

The fundamental modes can be illustrated by so-called distortion vectors as is shown in Fig. 2.6 for the D_{3h} molecule AB_3 . Note that the sum of these vectors may not change the center of gravity of the molecule as this would be caused by a translational motion.

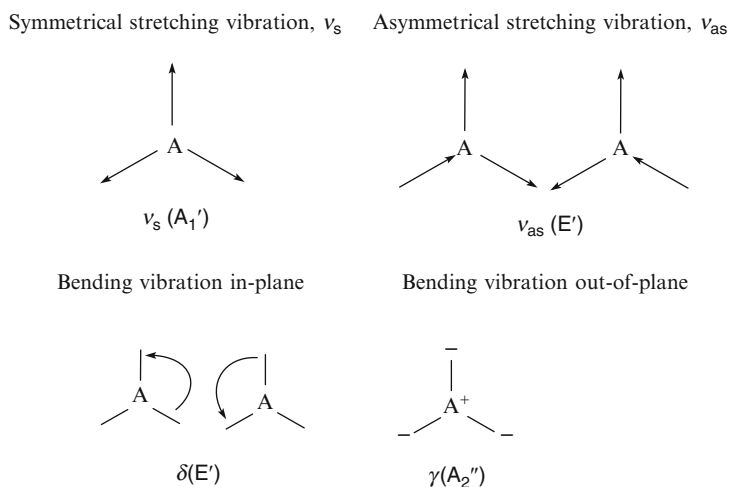


Fig. 2.6 Diagram of the fundamental modes of a molecule AB_3 with D_{3h} symmetry

The symmetry properties of molecules/ions of other symmetry groups can be obtained by the same procedure. The results for the most important structures are summarized in Table 6.9. Thus, the symmetry properties of the fundamental modes of a *pyramidal* molecule AB_3 , for example NH_3 , with the symmetry group C_{3v} are:

$$\text{Stretching vibrations:} \quad \Gamma_v = A_1 + E \quad (2.10)$$

$$\text{Bending vibrations:} \quad \Gamma_\delta = A_1 + E. \quad (2.11)$$

The question at hand is the following: Can one experimentally decide which of the two possible structures of the molecule AB_3 is present by means of the infrared and Raman spectroscopy: a planar structure with D_{3h} or pyramidal structure with C_{3v} symmetry? In order to answer this question the *selection rules* of vibrational spectroscopy must be employed.

2.1.3.1 Selection Rules in Vibrational Spectroscopy

A vibration is only infrared active, i.e., it can only be observed as an infrared absorption band if the corresponding vibration changes the electric dipole moment μ (note that a dipole moment need not exist in the equilibrium structure, but must then be built up by the vibration). For such a transition the intensity is determined by Einstein's transition moment \vec{M} which is proportional to the transition moment integral in the volume $d\tau$

$$\vec{M} \sim \int \Psi_0 \vec{\mu} \Psi_e d\tau \quad (2.12)$$

in which Ψ_0 and Ψ_e are the wave functions of the ground and the excited state, respectively and $\vec{\mu}$ is the dipole moment operator. The transition moment integral in Eq. 2.12 does not equal zero and hence, the transition has a certain probability if the integrand of the transition moment integral belongs to or contains the totally symmetric representation Γ_I .

In vibrational spectroscopy transitions are observed between different vibrational states. In a fundamental vibration the molecule is excited from its ground state ($v = 0$) to the first excited state ($v = 1$). Because the ground state belongs to the totally symmetrical representation the integrand of the transition moment integral contains only the totally symmetrical representation Γ_I if the symmetry of the excited state wave function is the same as the symmetry of the transition moment operator. This fact gives rise to the selection rule in infrared spectroscopy.

2.1.3.2 Selection Rule for Infrared Spectroscopy

A vibration can be observed in the infrared spectrum, i.e., a vibration is infrared active, if the vibration is accompanied by a change in the electric dipole moment. This is the case if the symmetry of the respective vibration belongs to the same symmetry class as one of the dipole moment operators. Vibrations are infrared inactive if there is no change of the dipole moment with changing bond distance or angle.

The symmetry classes of the dipole moment operators are listed by x , y , and z , in the second to last column of the character table (Table 6.8) for the point group belonging to the molecule.

2.1.3.3 Selection Rule for Raman Spectroscopy and Alternative Forbiddance

The Raman effect requires a changing *induced dipole moment*, i.e., the electric polarizability which is the relative tendency of a charge distribution, like the electron cloud of an atom or molecule, to be distorted from its normal shape by an external electric field, while the molecule undergoes a vibration. The symmetry of the induced dipole moment components are listed as the binary products in the last column of the character table.

Raman active vibrations, i.e., vibrations which can be observed as Raman lines in the spectrum can only be such modes which are accompanied by a change of the induced dipole moment or the polarizability. Such vibrations belong to the same symmetry classes as the polarizability tensors listed in the last column of the character table as binary products.

Alternative Forbiddance

Vibrations of molecules or ions having an inversion center i are either infrared (asymmetric modes) or Raman active (symmetric modes).

2.1.3.4 Application of the Selection Rules

After having discussed the selection rules we can come back to the question if one can distinguish between the D_{3h} and C_{3v} structures for an AB_3 molecule using vibrational spectroscopy.

Table 2.2 shows the results of the application of the selection rules for both structures of AB_3 -type molecules with D_{3h} and C_{3v} symmetry. The sign (+) means, that the vibration is allowed and (−) means that the vibration is forbidden.

According to Table 2.2, all six fundamental modes are active both in the IR- and the Raman spectrum for a molecule with pyramidal structure (C_{3v} symmetry). But

Table 2.2 Application of the selection rules to the vibrations of a molecule AB_3 having a triangular plane (D_{3h}) and a pyramidal structure (C_{3v}). The signs mean: (+): The transition is allowed and the vibration is observed, (−): the transition is forbidden and the vibration cannot be observed, and (p): the Raman line is polarized

D_{3h}	IR	Raman	C_{3v}	IR	Raman
$\nu_s(A_1')$	—	+ (p)	$\nu_s(A_1)$	+	+ (p)
$\nu_{as}(E')$	+	+	$\nu_{as}(E)$	+	+
$\delta(E')$	+	+	$\delta_s(A_1)$	+	+ (p)
$\gamma(A_2'')$	+	—	$\delta_{as}(E)$	+	+

only three bands and lines are observed in the infrared and Raman spectra, respectively for the planar structure D_{3h} where only two vibrations coincide. Thus, the application of vibrational spectroscopy can help to unambiguously distinguish between D_{3h} and C_{3v} symmetry of an AB_3 molecule or ion.

Note that sometimes the numbers of active vibrations are equal in the infrared and Raman spectra. In this case, the numbers of *polarized* Raman lines can be helpful in order to differentiate between possible structures. Bear in mind, only totally symmetrical vibrations of the symmetry classes A_1 or A'_1 provide polarized Raman lines.

Challenge 2.3

For solutions to Challenge 2.3, see *extras.springer.com*

Determine the symmetry properties of the fundamental vibrations of molecules BAX_2 (for example, $O=CCl_2$ or $O=SCl_2$) with a planar and an angled structure. Apply the selection rules and answer whether both structures can be distinguished by means of vibrational spectroscopy.

2.1.4 Fermi Resonance

Most bands in the infrared spectrum arise from fundamental modes $\nu = 0 \rightarrow \nu = 1$, from overtones $\nu = 0 \rightarrow \nu = 2$, or from combination modes which involve more than one normal mode. There exist, however, absorption bands caused by a special combination, namely the Fermi resonance. The phenomenon of Fermi resonance can arise when two modes are similar in energy resulting in an unexpected shift in energy and intensity of absorption bands.

Two conditions must be satisfied for Fermi resonance:

- The two vibrational states of a molecule transform according to the same irreducible representation of the point group of the molecule.
- The transitions have accidentally almost the same energy.

Fermi resonance causes the high-energy mode to shift to higher energy and the low-energy mode to shift to even lower energy. Furthermore, the weaker mode gains intensity and the intensity of the more intense band decreases accordingly.

Thus, Fermi resonance results in a linear combination of parent modes and does not lead to additional bands in the spectrum.

Infrared absorption bands caused by Fermi resonance can be valuable for structural analysis. For example, two intense bands between 2,850 and 2,700 cm^{-1} are typical for the formyl group $\text{O}=\text{C}-\text{H}$ caused by Fermi resonance of the overtone of the weak $\text{H}-\text{C}=\text{O}$ bending mode at approximately 1,390 cm^{-1} with the $\text{H}-\text{C}$ stretching mode. The occurrence of two (sometimes only one) bands in this region unambiguously indicates the presence of a formyl group in the molecule.

A further example is the double infrared absorption band of the $\text{C}=\text{O}$ stretching vibration of aryl acid chlorides, $\text{Aryl}-\text{C}(=\text{O})\text{Cl}$ caused by coupling of the $\text{C}=\text{O}$ stretching vibration with the overtone of the $\text{Cl}-\text{C}=\text{O}$ bending modes, $\delta(\text{Cl}-\text{C}=\text{O})$ which lies in the same range. Thus, aryl acid chlorides can be distinguished from alkyl acid chlorides by Fermi resonance. Further examples for Fermi resonances will be found in Sect. 2.3.

2.2 Interpretation of Vibrational Spectra of *Small Molecules and Ions*

The objective of the interpretation of vibrational spectra of small molecules and ions differs from that of organic molecules and can be mainly divided into three problems.

2.2.1 *Determination of the Structure (Symmetry Group) of Molecules and Ions*

The vibrational spectroscopic determination of the structure of a molecule or ion is realized by the following steps:

1. Determination of the symmetry (or point) group of a postulated structure by means of the algorithm given in Table 6.7.
2. Application of the selection rules on the fundamental modes the symmetries of which are taken from Table 6.9.
3. Assignment of the experimentally observed infrared absorption bands and Raman lines by means of the following rules:
 - (a) The wave numbers of *stretching vibrations* are always higher than those of bending vibrations because the rhythmical movement along the bond axis requires higher energy than changing of the bond angle.
 - (b) Consideration of the *force constants* and bond order, as well as the masses for the assignment of the stretching modes according to the relation in Eq. 2.1.

- (c) Consideration of the *selection rules* and the *degrees of polarization* of the Raman lines.
- (d) *Comparison of the vibrational spectra* of similar molecules or ions concerning structure, force constant, and masses. These are especially neighboring species in the periodic system of elements, for example, $\text{AsCl}_3/\text{SeCl}_3^+$.
- (e) *Theoretical calculation* of the vibrational modes but this is outside the scope of this book.

When the experimentally observed data cannot be reasonably assigned to the possible fundamental modes a new structure must be postulated and the procedure described must be repeated.

Challenge 2.4

Let us turn again to a molecule of type AB_3 . The infrared absorption bands and Raman lines listed in Table 2.3 are gathered from the respective spectra for the ions SO_3^{2-} and NO_3^- .

Table 2.3 Experimental IR-absorption bands and Raman lines of the ions SO_3^{2-} and NO_3^- given in cm^{-1} (*p* polarized Raman line)

SO_3^{2-}	IR	966	935	622	470
	Raman	967 (<i>p</i>)	933	620 (<i>p</i>)	469
NO_3^-	IR	1,370		828	695
	Raman	1,390	1,049 (<i>p</i>)		716

What structure do both ions possess?

Solution to Challenge 2.4

The ion of type AB_3 can possess a triangular planar structure $\text{D}_{3\text{h}}$ or a pyramidal structure $\text{C}_{3\text{v}}$. The symmetry of the fundamental modes and the results of the selection rules are already listed in Table 2.2. As Table 2.2 shows the $\text{D}_{3\text{h}}$ and $\text{C}_{3\text{v}}$ structures can unambiguously be distinguished just on grounds of the number of the experimentally observed infrared absorption bands and Raman lines. All modes must be infrared and Raman active for the $\text{C}_{3\text{v}}$ structure. This is realized for SO_3^{2-} . The ion NO_3^- belongs to the $\text{D}_{3\text{h}}$ structure because only three infrared absorption bands and three Raman lines can be observed in the respective spectra.

But the justification of the proposed structures requires the assignment of *all* experimentally observed data. The two highest wave numbers must be assigned to the two stretching vibrations in the ions according to the rules given above. The polarized Raman line belongs to the symmetrical stretching vibration, thus the other one has to be assigned to the asymmetrical one. In the same manner, the symmetrical bending modes can be assigned by means of

(continued)

the polarization of the Raman lines. The reasonable assignment of all wave numbers summarized in Table 2.4 justifies the assumed structures for both ions.

Table 2.4 Selection rules and assignment of the infrared absorption bands and Raman lines of the experimentally observed wave numbers (cm^{-1}) to the theoretically possible vibrations of the ions SO_3^{2-} and NO_3^-

SO_3^{2-}				NO_3^-			
C_{3v}	IR	Raman	Assignment (IR/Raman)	D_{3h}	IR	Raman	Assignment (IR/Raman)
Stretching vibrations				Stretching vibrations			
$\nu_s(\text{A}_1)$	+	+	966/967	$\nu_s(\text{A}'_1)$	—	+	—/1,049
$\nu_{as}(\text{E})$	+	+	935/933	$\nu_{as}(\text{E}')$	+	+	1,390/1,390
Bending vibrations				Bending vibrations			
$\delta_s(\text{A}_1)$	+	+	622/620	$\gamma(\text{A}''_2)$	+	—	828/—
$\delta_{as}(\text{E})$	+	+	470/469	$\delta(\text{E}')$	+	+	695/716

Vibrational spectra of materials in the *solid state* are determined by the symmetry of the crystal. When the symmetry of the crystal is lower than that of the free ion, then the following alterations are observed:

1. Splitting up of degenerate vibrations
2. Occurrence of modes that are symmetry-forbidden in the free ion.

Furthermore, interionic and intermolecular interactions in the crystal lattice cause shifts in comparison with free molecules and ions, respectively and additional translational and rotational modes of the lattice components appear in the lower frequency region ($\nu < 300 \text{ cm}^{-1}$) and overtones as well as combination vibrations are observed in the general middle region. Thus, the spectra of solids are mostly characterized by more infrared absorption bands than observed for the free molecule and ion. The selection rules for vibrational spectra of solids are determined by the *site-symmetry* (see specialized literature). Band-rich infrared absorption spectra are provided by many inorganic salts with highly symmetrical ions, such as sulfates or carbonates.

Challenge 2.5

Note that the solutions can be found in *extras.springer.com*.

The sign “p” means that the respective Raman line is polarized and “Ra” is the abbreviation for Raman.

1. The structure of the molecules and ions is to be determined with the presented data (given in cm^{-1}) gathered from the infrared and Raman spectra following the steps explained above.

(continued)

(a)	BF ₃	Ra	1,506	888 <i>p</i>	482			
		IR	1,505	719	480			
(b)	NO ₂ [−]	Ra	1,323 <i>p</i>	1,296	827			
		IR	1,323	1,296	825			
(c)	NO ₂ ⁺	Ra	1,296 <i>p</i>					
		IR	2,360	570				
(d)	VOCl ₃	Ra	1,035 <i>p</i>	504	409 <i>p</i>	249	164 <i>p</i>	131
		IR	All vibrations are infrared active					
(e)	AlCl ₄ [−]	Ra	498	348 <i>p</i>	182	119		
		IR	496	FIR:	180			
(f)	SO ₃ (g)	Ra	1,390	1,065 <i>p</i>	530			
		IR	1,391	529	495			
(g)	AsF ₅	Ra	809	733 <i>p</i>	642 p	388	366	123
		IR	810	784	400	365	FIR:	122
(h)	S ₂ O ₃ ^{2−}	Ra	1,123	995 <i>p</i>	669 p	541	446 <i>p</i>	
		IR	1,122	995	667	543	445	
(i)	HSO ₃ [−]	Ra	2,588 <i>p</i>	1,200	1,123	1,038 <i>p</i>	629 <i>p</i>	509
		IR	2,585	1,201	1,122	1,038	628	510

2. The stretching modes of [PtCl₄]^{2−} are (given in cm^{−1}):

Ra	330 <i>p</i>	312
IR	313	

Explain why this ion cannot have a tetrahedral structure? What structure can be proposed from these data?

3. Determine the structure of the ion [AsF₄][−] and assign the infrared absorption bands and Raman lines (given in cm^{−1}):

Ra	829	745 <i>p</i>	272	213
IR	830	270		

4. Deduce the structure of PCl₅ in the gaseous and solid state and assign all infrared absorption bands and Raman lines (given in cm^{−1}).

Solid state

Ra	662	458 <i>p</i>	360 <i>p</i>	283	255	238	178
IR	661	444	285	254			

Gaseous state and in a nonaqueous solution

Ra	580	392 <i>p</i>	281 <i>p</i>	272	261	102
IR	583	443	300	272	101	

(continued)

5. Derive the structure of PF_5 from the data obtained by the infrared and Raman spectra (given in cm^{-1}). Assign all infrared absorption bands and Raman lines.

Ra	1,026	817 <i>p</i>	640 <i>p</i>	542	514	300
IR	1,025	944	575	533	302	

6. Develop a proposal for the structure of the ion $\text{O}_2\text{PH}_2^{2-}$ based on the data (given in cm^{-1}) gathered from the Raman spectrum. Assign the Raman lines to the theoretical modes if this is unambiguously possible. Note that the vibration that corresponds to the Raman line at 930 cm^{-1} is infrared inactive.

Ra	2,365 <i>p</i>	2,308	1,180	1,160 <i>p</i>	1,093	1,046 <i>p</i>	930	820	470 <i>p</i>
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7. What structure can be derived from the data of the Raman spectrum (given in cm^{-1}) for NSF_3 ? Note that all vibrations are also infrared active. Assign the Raman lines to the corresponding modes of the molecule.

Ra (liquid)	1,523 <i>p</i>	815	773 <i>p</i>	525 <i>p</i>	432	346
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8. The reaction of PCl_5 with AlCl_3 gives rise to a product for which the atomic ratio $\text{Al} : \text{P} : \text{Cl} = 1 : 1 : 8$ is analytically obtained. The structure is to be derived on the basis of the data gathered from the infrared and Raman spectra (given in cm^{-1}). Assign all bands and lines.

Ra	662	498	458 <i>p</i>	348 <i>p</i>	255	182	178	120
IR	665	497	258		FIR:	181		

9. Derive the structure of an arsenic compound with the sum formula AsCl_2F_3 and assign the infrared absorption bands and Raman lines (given in cm^{-1}).

Ra	689 <i>p</i>	573	500	422 <i>p</i>	375	187	157
IR	700	500	385		FIR:	186	

10. The addition of a solution of SeCl_4 in dioxane to a solution of AlCl_3 in dioxane gives rise to a solid product for which the atomic ratio $\text{Al} : \text{Se} : \text{Cl} = 1 : 1 : 7$ is analytically obtained. Derive the structure of this reaction product from the data of the infrared and Raman spectra (given in cm^{-1}). Assign the infrared bands and Raman lines. Note that KAlCl_4 shows lines at 182 and 119 cm^{-1} in the region $\nu < 200 \text{ cm}^{-1}$ in the Raman spectrum.

Ra	498	416 <i>p</i>	395	348 <i>p</i>	294 <i>p</i>	186	182	119
IR	497	415	396	296	FIR:	Not detected		

(continued)

11. A platinum compound has the analytical composition $\text{PtCl}_4 \cdot 2\text{H}_2\text{O} \cdot 2\text{HCl}$. Develop a proposal for the structure of this solid reaction product on the basis of the infrared absorption bands and the Raman lines (given in cm^{-1}). Assign the corresponding bands to the theoretical modes.

Ra	3,226 <i>p</i>	2,825	1,695	1,070 <i>p</i>	348 <i>p</i>	318	171
IR	3,225	2,825	1,694	1,068	342	183	

12. Compose a table with the results of the selection rules for the infrared absorption bands and Raman lines of the fundamental modes of the structural moiety $\text{X}-\text{CH}_3$. Assign the experimentally observed data for $\text{X} = \text{Cl}$ (given in cm^{-1}).

Ra	3,041	2,966 <i>p</i>	1,456	1,355 <i>p</i>	1,017	734 <i>p</i>
IR	3,042	2,967	1,455	1,354	1,015	732

Which modes will provide relatively constant values of the wave numbers at variation of X and which modes will show a great range for the observed wave numbers? Explain your findings.

13. Derive the structure of the two compounds OXCl_2 with $\text{X} = \text{C}$ and $\text{X} = \text{S}$, based on the data of the vibrational spectra. Assign the infrared absorption bands and Raman lines (given in cm^{-1}) to the respective modes of each molecule.

(a) $\text{X} = \text{C}$

Ra	1,827 <i>p</i>	849	580	569 <i>p</i>	440	285 <i>p</i>
IR	1,826	849	568	441	284	

(b) $\text{X} = \text{S}$

Ra	1,251 <i>p</i>	492 <i>p</i>	455	344 <i>p</i>	284	194 <i>p</i>
IR	1,250	490	454	342	284	FIR: Not detected

14. The totally symmetrical vibration ν_1 in the fluoric complexes of the third main group of the type $[\text{MeF}_6]^{3-}$ with $\text{Me} = \text{Al}, \text{Ga}, \text{In}, \text{Tl}$ is observed in the Raman spectrum at 478, 498, 535, and 541 cm^{-1} , respectively ordered according to increasing wave numbers. Assign ν_1 to the respective $\text{Me}-\text{X}$ mode. Why is the totally symmetrical vibration at best suitable in order to evaluate the bond strength via the force constant?
15. The totally symmetric vibration ν_1 in the fluoric complexes of vanadium of the type $[\text{VF}_6]^n$ with $n = 1, 2$, and 3 is observed at 533, 584, and 676 cm^{-1} , respectively. Assign ν_1 to the respective complex ion and justify your decision.
16. Perovskites of the type A_2BMO_6 can be divided according to their $[\text{MO}_6]$ -structure moiety into three groups:
- Perovskites with an undistorted $[\text{MO}_6]$ -octahedron
 - Perovskites with two different undistorted $[\text{MO}_6]$ -octahedrons
 - Perovskites with a distorted $[\text{MO}_6]$ -octahedron.

(continued)

Fig. 2.7 Line diagram of the Raman spectrum of three perovskites. “*p*” means that the respective Raman line is polarized

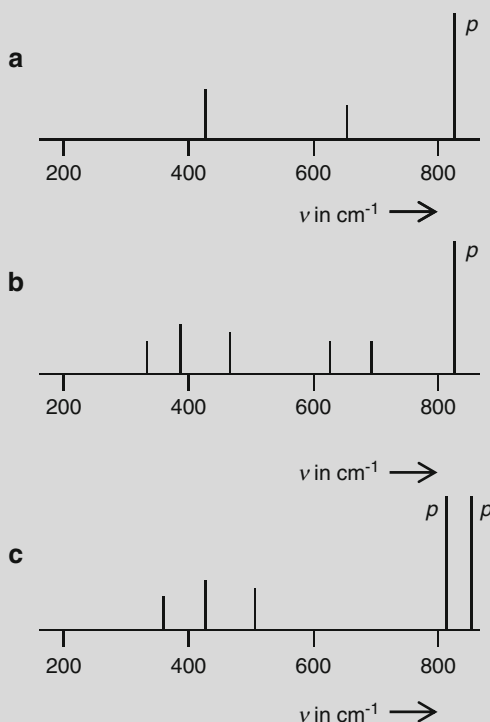
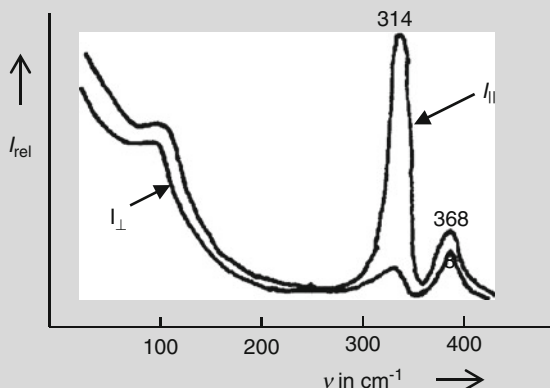


Fig. 2.8 Raman spectra of the $[\text{FeS}_4]$ structural moiety in a peptide obtained by polarized light



Assign the line diagrams of the Raman lines for three perovskites shown in Fig. 2.7 to the three types of perovskites and justify your decision.

17. The $[\text{FeS}_4]$ structure moiety of a ferric-containing peptide can be *planar* or *tetrahedral*. Explain why *Raman* spectroscopy must be applied for solving this problem. The Raman spectra obtained by polarized light are presented in Fig. 2.8. What structure has the $[\text{FeS}_4]$ moiety? Assign the stretching

(continued)

Table 2.5 Infrared absorption bands and Raman lines of the polymorphic forms of CaCO_3 : Calcite and Aragonite

<i>Calcite</i>						
IR	$\approx 1,460$ (broad)	879	706			
Ra	1,432	1,087	714			
<i>Aragonite</i>						
IR	1,504	1,492	1,080	866	711	706
Ra	The lines correspond to the IR absorption bands.					

vibrations. Note the empirical fact that $\nu_s > \nu_{as}$ is valid for the D_{4h} structure, for the tetrahedral structure the reverse relation is observed.

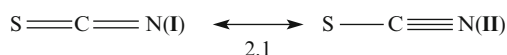
18. The two degenerated bending vibrations of the *free* SCN^- ion are observed at 470 cm^{-1} in solutions as an asymmetrical absorption band. The same mode is split into two absorption bands at 486 and 471 cm^{-1} in the infrared spectrum of *solid* KSCN . What is the reason behind this?
19. There are two structures for CaCO_3 : Calcite and aragonite. The data obtained from the vibrational spectra in the region above 400 cm^{-1} are listed in Table 2.5.

Assign the infrared absorption bands and Raman lines. Compare qualitatively both polymorphic forms of CaCO_3 .

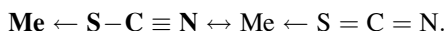
2.2.2 Coordination of Bifunctional Ligands at the Central Atom in Complex Compounds

The thiocyanate ion SCN^- is a bifunctional ligand because it can be coordinated via the S and the N atom to a central atom in a complex compound. Vibrational spectroscopy can help to distinguish between both structures and this is explained in the following.

A linear three-atomic ion provides $3 \cdot 4 - 5 = 4$ fundamental modes, which are divided into two stretching and two bending vibrations. But the infrared spectrum of the free SCN^- ion only has three absorption bands because the two bending modes at 470 cm^{-1} are degenerated. The infrared absorption bands at $2,053\text{ cm}^{-1}$ and that at 748 cm^{-1} can be roughly assigned to $\nu(\text{C}\equiv\text{N})$ and $\nu(\text{C}-\text{S})$, respectively. But the “real” $\nu(\text{C}\equiv\text{N})$ obtained for nitriles lies in the range from $2,260$ to $2,240\text{ cm}^{-1}$ and the “real” C–S stretching vibration is observed at approximately 680 cm^{-1} , see Sect. 2.3. This means, the $\text{C}\equiv\text{N}$ bond is weaker than a threefold bond and the C–S bond is stronger than a single bond; thus, the chemical structure must be described by two resonance structures I and II, respectively (see Structure 2.1):

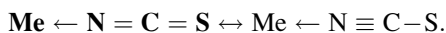


Coordination to the *S* atom favors the resonance structure II in Structure 2.1:



The wave numbers of $\nu(\text{C}-\text{S})$ should be smaller and that of $\nu(\text{C}\equiv\text{N})$ should be higher in a complex of the type $\text{Me}\leftarrow\text{S}-\text{C}\equiv\text{N}$ in comparison to the free ligand.

However, coordination to the *N* atom favors resonance structure I in Structure 2.1:

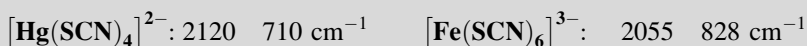


The wave number of $\nu(\text{C}-\text{S})$ should be increased and the wave number of $\nu(\text{C}\equiv\text{N})$ should be decreased in a complex of the type $\text{Me}\leftarrow\text{N}=\text{C}=\text{S}$ in comparison to the free ligand.

Deviations from these rules can be caused by coupling of vibrations.

Challenge 2.6

The stretching modes of the SCN^- ligand in two thiocyanate complexes are:



Judge whether the ligand coordinates via S or N to the central atom.

Solution to Challenge 2.6



Because the wave number of $\nu(\text{C}\equiv\text{N})$ for the complex is higher than that for the SCN^- ion and the wave number of $\nu(\text{C}-\text{S})$ for the complex is smaller than that for the SCN^- ion the coordination occurs via **S**: **Hg** \leftarrow **SCN**.



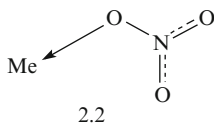
Because the following facts are valid: $\nu(\text{C}\equiv\text{N})$ (complex) $<$ $\nu(\text{C}\equiv\text{N})$ (SCN^-) and $\nu(\text{C}-\text{S})$ (complex) $>$ $\nu(\text{C}-\text{S})$ (SCN^-) the coordination occurs via **N**: **Fe** \leftarrow **SCN**.

2.2.3 Investigations of the Strength of Chemical Bonds

Vibrational spectroscopy offers the possibility to investigate chemical bond strengths because the stretching modes are determined by the force constant according to Eq. 2.1 which is proportional to the bond order. This fact will be explained employing the example of nitrate complexes $[\text{Me}(\text{NO}_3)_n]^{m-}$.

The free ligand NO_3^- shows two stretching vibrations, the symmetrical $\nu_s(\text{N-O})$ which is infrared inactive and the degenerated asymmetrical $\nu_{as}(\text{N-O})$ which is observed at $1,390\text{ cm}^{-1}$ in the infrared spectrum. Coordination of the ligand to the metal ion via O diminishes the D_{3h} symmetry of the free NO_3^- ion with the result that the degenerated stretching mode is split. Furthermore, the symmetrical stretching mode is no longer forbidden. Thus, the following stretching modes are infrared active for a metal complex with a structure moiety shown in Structure 2.2

$$\nu(\text{N-O}) = \nu_1, \nu_s(\text{NO}_2) = \nu_2, \text{ and } \nu_{as}(\text{NO}_2) = \nu_3.$$



The equality of the three N-O bonds in the free NO_3^- ion is no longer present because of the metal-oxygen bond $\text{Me}-\text{O}-\text{NO}_2$. Thus, the chemical bond in the ligand can be described by a (mainly) single N-O bond and two equal N=O bonds with conjugated double bonds which provide strongly coupled symmetrical, $\nu_s(\text{NO}_2)$ and asymmetrical, $\nu_{as}(\text{NO}_2)$ modes, respectively. Because the delocalization of the electrons is diminished to only two bonds the strength of the chemical N=O bond and hence, the wave numbers of the stretching modes of the NO_2 group increase more, the stronger the bond of the ligand to the metal ion is. In general, the mean value of the frequencies of the symmetrical and asymmetrical NO_2 stretching modes is used to qualitatively evaluate the strength of the chemical bond of the ligand to the metal ion. Furthermore, the splitting up of the degenerate N=O stretching mode will be all the greater the stronger the complex bond is. The maximum value is achieved at a “real” covalent bond, i.e., if the metal ion is substituted by H or an alkyl group; see, for example, the vibrational frequencies of HNO_3 in Table 2.6.

The comparison of stretching modes of the free ligand with those of a compound possessing a covalent bond of the ligand and those of the complex compound enables the evaluation of the strength of the chemical bond of the ligand to the central atom.

Challenge 2.7

Table 2.6 presents the stretching modes of two nitrate complexes and HNO_3 .

Decide whether NO_3^- coordinates to each of the metal ions. If this is correct, evaluate qualitatively the strength of the $\text{Me} \leftarrow \text{O} - \text{NO}_2$ bond.

Table 2.6 Stretching modes of two nitrate complexes and HNO_3

	ν_1	$\nu_2 = \nu_s(\text{NO}_2)$	$\nu_3 = \nu_{as}(\text{NO}_2)$	$\Delta\nu = \nu_3 - \nu_2$	$\bar{\nu}(\nu_2, \nu_3)$
$[\text{Cu}(\text{NO}_3)_4]^{2-}$	1,013	1,290	1,465	175	1,377.5
$[\text{Zr}(\text{NO}_3)_6]^{2-}$	1,016	1,294	1,672	378	1,428.5
HONO_2	920	1,294	1,672	378	1,483

Solution to Challenge 2.7

The degeneration of the asymmetrical stretching vibration of the free NO_3^- ion is no longer valid. Instead it is split into the symmetrical and asymmetrical NO_2 stretching vibrations. Furthermore, IR-forbidden symmetrical stretching is allowed in both complexes. Thus, the D_{3h} symmetry is no longer given because of coordination of the NO_3^- ligand to the metal ions.

To qualitatively evaluate the coordinative bond strength the mean values calculated by the wave number of the symmetrical and asymmetrical N–O stretching modes are compared with that of HNO_3 in which the H–O bond is a “true” covalent one. As the wave numbers in the last column of Table 2.6 show the coordinative bond is stronger in the Zr complex than in the Cu one because the mean value of the NO_2 stretching modes of the Zr complex is higher than that of the Cu complex and is closer to the value for a strong covalent bond.

Note that the procedure for the qualitative evaluation of the strength of a coordinative chemical bond described above can only be applied with true characteristic vibrations whose vibrational frequencies are influenced solely by electronic effects and not by couplings of vibrations.

Challenge 2.8

For solutions to Challenge 2.8, see *extras.springer.com*.

1. $\text{K}_3[\text{Co}(\text{CN})_5(\text{NCS})]$ can appear in two isomeric forms which give rise to the following infrared absorption bands:

Isomer I, ν in cm^{-1}	2,065	810	Isomer II, ν in cm^{-1}	2,110	718
-------------------------------------	-------	-----	--------------------------------------	-------	-----

Draw up and justify a proposal of the structure for the two isomeric forms of the Co(III) complex.

(continued)

2. The following infrared absorption bands are observed for the complex Pd (bipyr)(NSC)₂ in the region of the NCS stretching modes:

2,117	2,095	842	700	cm ⁻¹
-------	-------	-----	-----	------------------

Draw up and justify a proposal of the coordinative chemical bond in this complex compound.

3. Figures 2.9 and 2.10 show sections of the infrared spectra of the selenium compounds (C₆H₅)₂Se(NO₃)₂ and (C₆H₅)₃SeNO₃, respectively. Investigate whether nitrate is preferably covalently bonded to the selenium atom or whether an ionic structure with an NO₃⁻ ion is valid.
4. The mean values of the symmetrical and asymmetrical stretching vibrations of NO₂, NO₂⁺, and NO₂⁻ ordered according to increasing wave numbers are: 1,307, 1,468, and 1,878 cm⁻¹. Assign and justify the wave numbers to the corresponding nitrogen compounds.
5. Evaluate the strength of the coordinative chemical bond of the oxalate ligand to the metal ions Pt and Cu on the basis of the C=O stretching vibrations. The observed infrared absorption bands of these complex compounds as well as those of the noncoordinate, free oxalate ion and covalently bonded oxalic acid dimethyl ester are summarized in Table 2.7.
6. The stretching frequencies of manganese compounds of the type K_nMnO₄ with *n* = 1, 2, and 3 are arbitrarily listed in Table 2.8. Assign the infrared absorption bands and Raman lines to the respective manganese compounds. Explain why one can recognize a relation between the wave

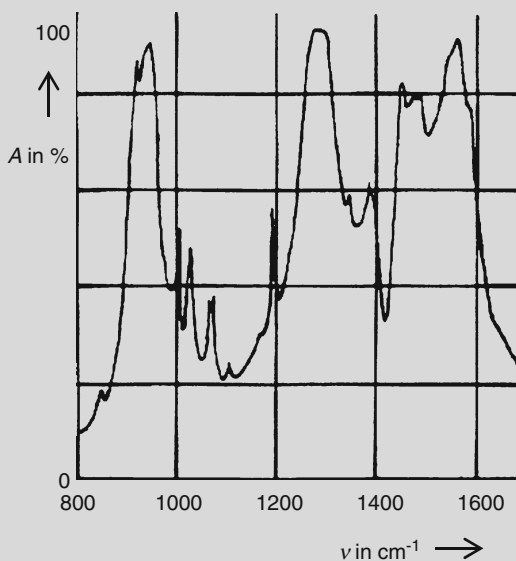


Fig. 2.9 Infrared spectrum in the range of the NO stretching modes of (C₆H₅)₂Se(NO₃)₂; sampling technique: Nujol mull

(continued)

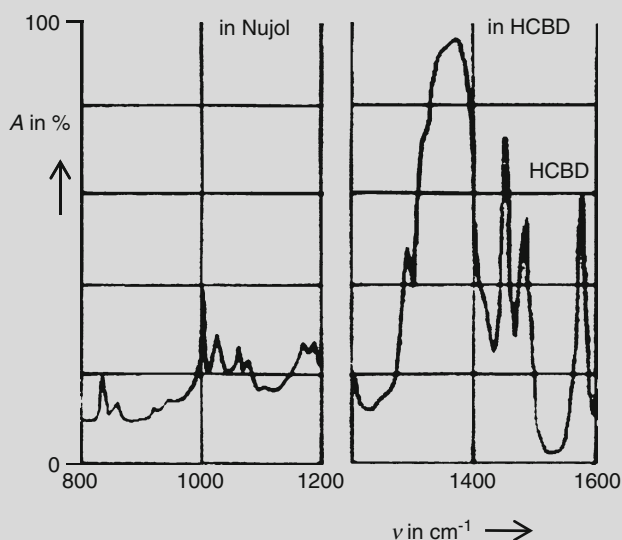


Fig. 2.10 Infrared spectrum in the range of the NO stretching modes of $(\text{C}_6\text{H}_5)_3\text{Se}(\text{NO}_3)$; sampling techniques used: Nujol mull (*left*) and hexachlor-butadiene (HCBD) (*right*)

Table 2.7 C=O stretching frequencies of the oxalate ion, oxalic acid dimethyl ester, and some oxalate complexes (given in cm^{-1})

$\text{C}_2\text{O}_4^{2-}$	1,640	1,650	$\text{C}_2\text{O}_4(\text{CH}_3)_2$	1,770	1,796
$[\text{Pt}(\text{C}_2\text{O}_4)_4]^{2-}$	1,674	1,709	$[\text{Cu}(\text{C}_2\text{O}_4)_4]^{2-}$	1,645	1,672

Table 2.8 Arbitrarily ordered infrared absorption bands and Raman lines of manganese compounds of the type K_nMnO_4

Compound I:	Raman:	820	812	332	325	cm^{-1}
	IR:	821	333			cm^{-1}
Compound II:	Raman:	902	834	386	346	cm^{-1}
	IR:	901	384			cm^{-1}
Compound III:	Raman:	789	778	332	308	cm^{-1}
	IR:	779	331			cm^{-1}

number of the symmetrical stretching modes and the effective charge of the Mn atom?

- The CO stretching vibration of $\text{C}\equiv\text{O}$ can be found at $2,155\text{ cm}^{-1}$ but it lies in the range from $2,100$ to $1,800\text{ cm}^{-1}$ in metal carbonyl compounds. The chemical bond in metal carbonyl compounds is a superposition of a σ -Me-C bond and a Me-(CO)- π back donation. What information is obtained by the mean values of the C=O stretching modes according to the part of both contributions to the chemical bond in the following charged

(continued)

metal carbonyl ions? The wave number of Ni(CO)_4 may be used as the reference compound. All values are given in cm^{-1} .

Ni(CO)_4 (2094), $[\text{Co(CO)}_4]^-$ (1946), $[\text{Fe(CO)}_4]^{2-}$ (1788), $[\text{Pt(CO)}_4]^{2+}$ (2258).

2.3 Interpretation of Vibrational Spectra of *Organic* Molecules

2.3.1 Objectives and Special Features

The interpretation of vibrational spectra mainly includes the following objectives

- Determination of *structural moieties* (alkyl, alkenyl-, alkin-, and aryl groups)
- Determination of *functional groups*
- Determination of *isomers*
- Investigation of *conformers*
- Investigation of *hydrogen bridges* (which is only possible by means of infrared spectroscopy)

In contrast to the interpretation of vibrational spectra of inorganic species symmetry properties of modes are, generally, not of interest.

The occurrence of overtones and combination vibrations increases whereas randomly degenerated vibrations decrease the number of the $3 \cdot N - 6$ possible modes. Unlike the degeneration of modes on the basis of symmetry, *randomly degenerated* vibrations are caused if two or more atomic groups accidentally possess the same vibrational frequency. This is the case, for example, for acetone, $\text{CH}_3\text{-C=O-CH}_3$. The *inner* vibrations of the two CH_3 groups accidentally possess the same vibrational frequencies resulting in *one* symmetrical $\nu_s(\text{CH}_3)$, (degenerated) asymmetrical $\nu_{\text{as}}(\text{CH}_3)$ stretching modes, symmetrical $\delta_s(\text{CH}_3)$, and (degenerated) asymmetrical $\delta_{\text{as}}(\text{CH}_3)$ bending modes, respectively for both CH_3 groups. Whereas almost *all* infrared absorption bands and Raman lines can be assigned to the respective vibrations for small inorganic species the assignment is restricted only to a *few* for organic molecules. The extensive coupling of vibrations of the atoms of similar masses (C, O, N) linked with similar bond strength (C-C, C-O, C-N) give rise to many absorption bands whose source is mostly unknown. Thus, such absorption bands cannot be assigned to the vibration of a certain atomic group.

The following vibrations are meaningful for the interpretation of the vibrational spectra of organic molecules:

- Characteristic vibrations
- Structure-specific coupled vibrations
- The fingerprint region

2.3.2 Characteristic Vibrations

2.3.2.1 Definition

Characteristic vibrations of a multiatomic molecule are present if nearly the whole potential energy is localized in the movement of a certain atomic group of the molecule with the consequence that coupling of vibrations is negligible. Thus, characteristic vibrations give rise to infrared absorption bands at about the same wave numbers, regardless of the structure of the rest of the molecule.

These site-stable infrared absorption bands are called *group wave numbers* (also called *group frequencies*) because the absorption band can be unambiguously assigned to the vibration of certain atomic groups; therefore, they provide information about the absence or presence of specific atomic groups. Thus, they are valuable diagnostic markers for the recognition of functional groups. Group wave numbers are listed in tables and they are the basis for vibrational spectra interpretation.

2.3.2.2 Criteria for Characteristic Vibrations

Characteristic vibrations can occur if

1. The force constants of neighbored bonds are different (greater 25%).
2. The mass of neighbored atoms are strongly different (greater 100%).
3. The vibration is not accidentally in the same region as another vibration.

The first and second criteria are very well fulfilled by, for example, $\text{H-C}\equiv\text{N}$. Infrared radiation at $3,311\text{ cm}^{-1}$ excites the vibration of only the H-C group because, according to calculations, 95% of the absorbed energy is utilized for the movement of this atomic group. However, 95% of the absorbed energy at $2,097\text{ cm}^{-1}$ is used for the vibration of the $\text{C}\equiv\text{N}$ group. Because both stretching vibrations fulfill the criteria for characteristic vibrations the region between $3,300$ and $3,320\text{ cm}^{-1}$ and at $\approx 2,100\text{ cm}^{-1}$ are the group wave numbers for the C-H stretching vibration with a *sp*-hybridized C atom and the $\text{C}\equiv\text{N}$ stretching one, respectively. Note that the group wave numbers of the $\text{C}\equiv\text{N}$ and $\text{C}\equiv\text{C}$ groups are nearly the same because of the similar bond order and the approximately similar reduced masses.

According to the first criterion the stretching vibrations of nonconjugated multiple bonds provide characteristic vibrations whose group wave numbers are diagnostically valuable for the unambiguous recognition of the structural groups $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$, $\text{C}=\text{O}$, $\text{C}=\text{N}$, or $\text{C}\equiv\text{N}$.

The first criterion is also fulfilled for the $\text{C}=\text{S}$ group. Therefore, the $\text{C}=\text{S}$ group should provide a characteristic vibration and the wave number range of this group should be consistent in analogy to the $\text{C}=\text{O}$ group. Unfortunately this is not the case. Because of the greater mass of S the stretching frequency is diminished and

lies in the range of the bending vibrations of the CH skeleton. Thus, criterion 3 is not fulfilled and the C=S stretching vibrations cannot be assumed to be a characteristic vibration with a small range of group wave numbers. According to calculations a large amount of the absorbed energy of the expected range of the C=S stretching vibration is distributed to bending vibrations of the CH skeleton, in other words, the C=S stretching vibration is a strongly coupled one and the denotation $\nu(\text{C}=\text{S})$ for an intense absorption band in the relatively large range of the C=S stretching vibrations is only approximately valid.

Because, in general, low-energy bending vibrations are strongly coupled the presence of characteristic vibrations is limited to stretching vibrations except for the *inner* bending vibrations of the CH_3 and CH_2 group.

The respective *inner* vibrations of the CH_3 and CH_2 groups are characterized by the fact that the vibration is mainly limited to the movement of CH atoms whereas outer vibrations also include movements of the neighbored atoms which are named *rocking* (ρ), *wagging* (ω), and *twisting* (τ). It is clear that these vibrations are not characteristic and do not provide group frequencies. Therefore, they are not of interest for structural analysis.

2.3.2.3 Examples of Characteristic Vibrations (Group Wave Numbers) According to Criterion 1 ($f_1 \neq f_2$)

Examples are listed in Table 2.9.

2.3.2.4 Examples of Characteristic Vibrations (Group Wave Numbers) According to Criterion 2 ($m_1 \neq m_2$)

Examples are listed in Table 2.10.

2.3.2.5 Internal and External Influences on Characteristic Vibrations

Because of negligible coupling of characteristic vibrations their group wave numbers should be observed in a narrow range. But this is not the case as is shown, for

Table 2.9 Examples of group wave numbers (in cm^{-1}) of compounds with multiple bonds

$\begin{array}{c} f_1 \quad f_2 \\ \text{—C—C= X} \end{array}$	X = O	Carbonyls	$\nu(\text{C}=\text{O}) \approx 1,850\text{--}1,650$
	X = N	Azomethine	$\nu(\text{C}=\text{N}) \approx 1,650$
	X = C	Alkene	$\nu(\text{C}=\text{C}) \approx 1,640$
$\begin{array}{c} f_1 \quad f_2 \\ \text{—C—C}\equiv\text{X} \end{array}$	X = N	Nitrile	$\nu(\text{C}\equiv\text{N}) \approx 2,260\text{--}2,200$
	X = C	Alkyne	$\nu(\text{C}\equiv\text{C}) \approx 2,260\text{--}2,100$

Table 2.10 Examples of group wave numbers (in cm^{-1}) of compounds with the $-\text{C}-\text{X}-\text{H}$ structural moiety

$\text{---C---}\overset{m_1}{\text{X}}\text{---}\overset{m_2}{\text{H}}$	$\text{X} = \text{O}$	Alcohol, phenol	$\nu(\text{OH})_{\text{free}} \approx 3,650$
		Not associated	$\nu(\text{OH})_{\text{ass}} \approx 3,200$
		Associated	$\nu(\text{NH}) \approx 3,400$
	$\text{X} = \text{N}$	Amine, amide	2 IR-absorption bands
		Primary	1 IR-absorption band
		Secondary	$\nu(\text{CH}) \approx 3,300\text{--}2,850$
	$\text{X} = \text{C}$	Hydrocarbon	
		$\equiv\text{C}(\text{sp})\text{---H}$	$\nu(\text{CH}) \approx 3,300$
		$=\text{C}(\text{sp}^2)\text{---H}$	$\nu(\text{CH}) \approx 3,100\text{--}3,000$
		$-\text{C}(\text{sp}^3)\text{---H}$	$\nu(\text{CH}) \approx 3,000\text{--}2,850$

example, for the group wave numbers of the C–H stretching vibrations (see Tables 2.10). The reason for this fact is that characteristic vibrations are influenced by internal and external effects. Knowledge of the correlation between peak position and these effects is valuable to recognize functional groups and structural moieties.

2.3.2.6 Inductive Effects

Increasing of the $-\text{I}$ effect increases the bond order and, hence, the force constant in carbonyl compounds. Therefore, the wave number of the C=O stretching vibrations increases with the strength of the $-\text{I}$ effect of X which is shown by the following examples:

$\text{CH}_3(\text{C}=\text{O})\text{---X}$	$\text{X} = \text{H}$	$\nu(\text{C}=\text{O}): 1,740 \text{ cm}^{-1}$	$\text{X} = \text{Cl}$	$\nu(\text{C}=\text{O}): 1,800 \text{ cm}^{-1}$
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2.3.2.7 Mesomeric Effects

Mesomerism diminishes the bond order and, hence, the force constant resulting in lower wave numbers of the stretching vibration. Examples are:

$\text{CH}_3(\text{C}=\text{O})\text{---X}$	$\text{X} = \text{H}$	$\nu(\text{C}=\text{O}): 1,740 \text{ cm}^{-1}$
	$\text{X} = \text{Aryl}$	$\nu(\text{C}=\text{O}): 1,685 \text{ cm}^{-1}$
$-\text{C}=\text{C}\text{---X}$	$\text{X} = \text{H}$	$\nu(\text{C}=\text{C}): \approx 1,645\text{--}1,640 \text{ cm}^{-1}$
	$\text{X} = \text{Aryl}$	$\nu(\text{C}=\text{C}): \approx 1,600\text{--}1,450 \text{ cm}^{-1}$

2.3.2.8 Intermolecular Effects

Autoassociation, hydrogen bridges, interactions with the solvent and further effects diminish the strength of the chemical bond and, hence, the respective stretching vibrations are observed at lower wave numbers as is demonstrated by the

experimentally observed wave numbers of the C=O stretching vibration of acetone: $\nu(\text{C}=\text{O})$, gaseous: $1,745\text{ cm}^{-1}$, $\nu(\text{C}=\text{O})$, in CCl_4 : $1,720\text{ cm}^{-1}$. Therefore, information on the preparation techniques used for the registration of the vibrational spectrum of a sample should always be given.

2.3.3 Structure-Specific Coupled Vibrations

In contrast to characteristic vibrations structure-specific coupled vibrations cannot be assigned to the vibration of certain atomic groups but they appear as a known absorption band pattern in the infrared spectrum which is specific for a certain structural moiety.

Structure-specific coupled vibrations are accompanied by the presence of certain structural moieties in the molecule. Therefore, they diagnose a certain structural type rather than a functional group in a molecule.

Examples of structure-specific coupled vibrations

1. Overtones and combination vibrations of the CH out-of-plane bending modes and ring bending modes of the CC skeleton of aromatic compounds result in absorption bands in the range from $2,000$ to $1,600\text{ cm}^{-1}$ whose pattern enables the recognition of the substitution type of the aromatic compound by comparison of the absorption band pattern with those of “ideal” ones shown in Fig. 6.1. Note that these absorption bands give rise to weak intensities. Hence, in general, they can be observed as more intense bands at higher concentrations or layer thickness of the cuvette.
2. The two intense (sometimes only one) infrared absorption bands in the range from $2,850$ to $2,700\text{ cm}^{-1}$ diagnose the presence of the formyl group CHO in the molecule. As explained above these absorption bands specific for a formyl group are caused by Fermi resonance.
3. The weak infrared absorption band in the range from $1,840$ to $1,800\text{ cm}^{-1}$ due to a combination of the two out-of-plane bending vibrations at ≈ 990 and $\approx 910\text{ cm}^{-1}$ diagnose the vinyl-group, $-\text{CH}=\text{CH}_2$.

2.3.4 The Fingerprint Region

The absorption bands in the range $<1,500\text{ cm}^{-1}$ mostly result from strongly coupled vibrations that cannot be assigned to movements of certain atomic groups. Therefore, their position in the spectrum is determined by a certain structure of the molecule and only small structural changes in the molecule will markedly alter the pattern of these coupled vibrations. Whereas characteristic vibrations provide group wave numbers for functional groups and structure moieties regardless of the structure of the rest of the molecule the strongly coupled vibrations with absorption

bands $<1,500\text{ cm}^{-1}$ are specific for a *single* molecule. Therefore, this region is named the *fingerprint* region.

Whereas characteristic vibrations diagnose only functional groups and structure moieties the fingerprint region facilitates the identification of an individual compound.

The *identification of substances* is realized by visual or computer-aided comparison of the infrared absorption spectrum of the sample with that of a reference sample and a reference spectrum from a spectroscopic library, on condition that both spectra were measured under the same conditions. Especially, the pattern of the fingerprint region is valuable to recognize an individual compound crystallized in a special lattice. Bands of residual solvents or the habit of the crystal can give rise to additional, but weakly intense bands and slightly change the position of bands in the spectrum, respectively. But the most intense absorption bands may not differ more than $\pm 1\text{ cm}^{-1}$.

Additional infrared absorption bands or Raman lines or changed band positions, especially observed in the low wave number range, can be caused by different crystal structures, i.e., *polymorphic forms*. Most of the organic compounds crystallize in polymorphic forms. Because vibrational spectra can be easily obtained from solids, vibrational spectroscopy is an excellent and simple method in order to determine polymorphic structures in routine analysis. Thus, such investigations are included, for example, in the regulations (Pharmacopeia) for pharmaceutical analysis. Note that polymorphic forms differ in physical properties such as solubility and stability. Therefore, the determination of the correct polymorphic form is an important condition to apply a compound as an active pharmaceutical ingredient. Besides vibrational spectroscopy, X-ray diffraction, thermal analytical methods, photoacoustic spectroscopy, and solid-state NMR spectroscopy are further methods to investigate polymorphism.

Because Raman spectroscopy, in contrast to routine infrared spectroscopy, also allows recording of the low-frequency range of lattice vibrations which are valuable for recognition of polymorphic forms, Raman spectroscopy is an excellent method for the investigation of polymorphism whereas Raman microscopy enables the investigation of single crystallites. But thermal transformation of polymorphic forms during the measurement must be considered.

2.3.5 Interpretation of Vibrational Spectra of Hydrocarbons

Vibrational spectra provide information about

1. The structural type of hydrocarbons (alkanes, alkenes, alkynes, aromatic hydrocarbons),
2. Branching of the carbon-carbon chains,
3. Structures of branch points,
4. Bonding geometry around the C=C-bond of alkenes,
5. Substitution pattern of aromatic compounds.

Table 2.11 Diagnostic information (wave numbers in cm^{-1}) for **alkanes** ($sp^3\text{C-H}$)

<i>CH stretching vibrations, $\nu_{CH} < 3,000$</i>			
CH₃	$\nu_{as}(E): \approx \mathbf{2,965}$	$\nu_s: 2,875$	$I(\nu_{as}) > I(\nu_s)$
CH₂	$\nu_{as}: \approx \mathbf{2,925}$	$\nu_s: 2,855$	$I(\nu_{as}) > I(\nu_s)$
CH	$\approx 2,900$ (weak intensity; mostly overlaid)		
Deviating position and intensity at CH ₃ –X and CH ₂ –X with X = O, N, Aryl			
<i>Bending vibrations</i>			
CH₃	$\delta_{as}(E) \approx 1,470$	$\delta_s \approx \mathbf{1,375}$	Splitting up at branching
CH₂	$\delta \approx \mathbf{1,455}$		

Table 2.12 Diagnostic information (wave numbers in cm^{-1}) for **alkenes** and **aromatics** ($sp^2\text{C-H}$)

<i>CH stretching vibration, $\nu_{\text{CH}} < 3,000$</i>			
Alkenes		Aromatics	
$\nu(\text{C}=\text{C})$	1,690–1,635	$\nu(\text{C}=\text{C})$	1,625–1,400
$>\text{C}=\text{C} < \text{types}$		<i>Aryl substitution types</i>	
$-\text{CH}=\text{CH}-(\text{E/Z})$	$\gamma(\text{CH})$	$\gamma(\text{CH}) + \text{ring bending at mono and meta substitution}$	850–650
$-\text{CH}=\text{CH}_2$	1,005–675	Only $\gamma(\text{CH})$ at <i>ortho</i> and <i>para</i> substitutions	2,000–1,000 Band pattern, see Fig. 6.1
$>\text{C}=\text{CH}_2$		Overtone and combination vibrations	

Table 2.13 Diagnostic information (wave numbers in cm^{-1}) for **alkynes** ($sp\text{C-H}$)

<i>CH stretching vibration, ν_{CH}</i>	3,340–3,250
	Sharper than $\nu(\text{OH})$ and $\nu(\text{NH})$
<i>$\text{C}\equiv\text{C}$ stretching vibration, $\nu_{\text{C}\equiv\text{C}}$</i>	2,260–2,100
	Intensity is small to missing
<i>Bending vibration, $\delta_{\text{C}\equiv\text{CH}}$</i>	$\nu \approx \mathbf{650}$ with an overtone at $\nu \approx 1,250$

The most useful diagnostic bands to determine these structural alterations are the C-H , $\text{C}=\text{C}$, and $\text{C}\equiv\text{C}$ stretching vibrations, the internal bending vibrations of the CH_3 and CH_2 groups, the out-of-plane bending modes of alkenes and aromatic compounds $\gamma(\text{CH})$ or δ_{oop} , the out-of-plane bending modes of the CC skeleton of the aromatics and their over and combination tones which are summarized in Tables 2.11, 2.12 and 2.13 and in detail in Table 6.15.I. Note that the $\delta_{\text{in-plane}}$ of alkenes and aromatics are meaningless for structural determinations.

Challenge 2.9

Figure 2.11 shows the infrared absorption spectrum of a synthetic product. Justify that the spectrum can be assigned to *para*-methyl styrene (Structure 2.3).

(continued)

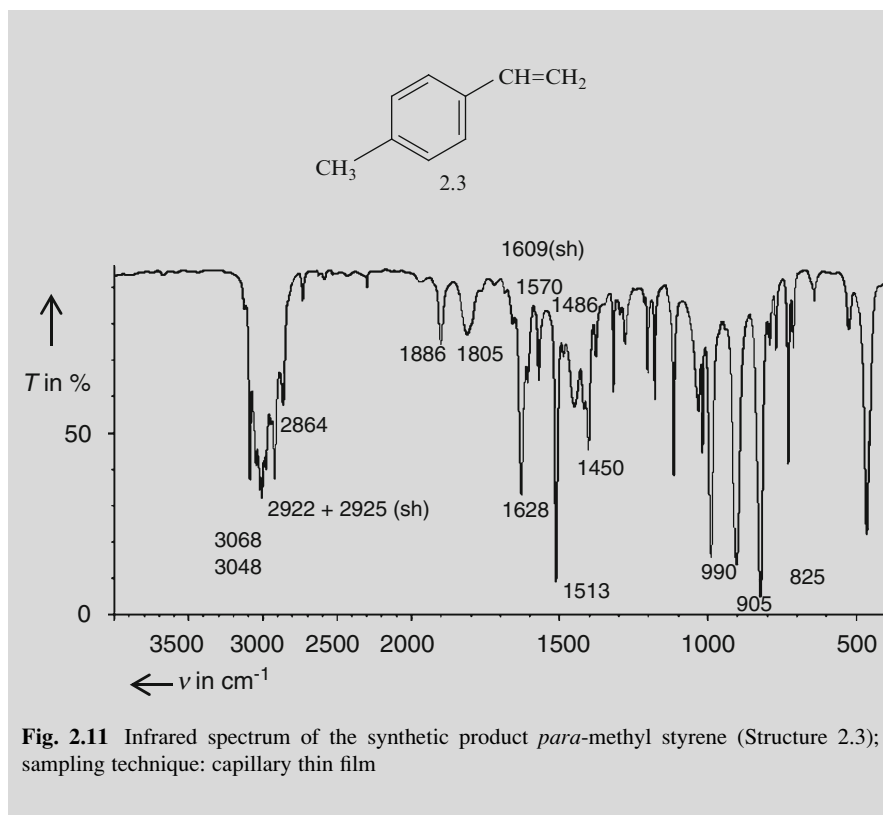


Fig. 2.11 Infrared spectrum of the synthetic product *para*-methyl styrene (Structure 2.3); sampling technique: capillary thin film

Solution to Challenge 2.9

The structural moieties that can be spectroscopically justified by infrared spectroscopy are summarized in Table 2.14.

Table 2.14 Assignment of the IR-absorption bands to *para*-methyl styrene (Structure 2.3)

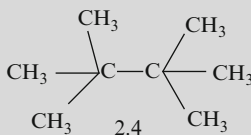
Structural moiety	Wave numbers in cm^{-1}	Assignment of the infrared absorption bands
Aromatic compounds	3,070–3,010	$\nu(\text{sp}^2\text{C-H})$
	1,570 w, 1,513 s, 1,486 w	$\nu(\text{sp}^2\text{C}=\text{C})$, Aryl
$-\text{CH}=\text{CH}_2$	3,070–3,010	$\nu(\text{sp}^2\text{C-H})$
	1,628 m	$\nu(\text{C}=\text{C})$, in conjugation
	990 s + 905 s	$\gamma(\text{CH})$ for $-\text{CH}=\text{CH}_2$
$\text{CH}_3\text{-aryl}$	2,922 m + 2,864 m	$\nu_s(\text{CH}_3)$ + Fermi resonance, Aryl- CH_3
	2,925 (sh), w	$\nu_{\text{as}}(\text{CH}_3)$ for aryl- CH_3
<i>para</i> -substitution	825 s	$\gamma(\text{CH})$, Aryl (No ring bending!)
	2,000–1,650	Pattern of overtones and combination vibrations

Challenge 2.10

For solutions to Challenge 2.10, see *extras.springer.com*.

1. Figures 2.12, 2.13, 2.14 and 2.15 present infrared spectra of hydrocarbons. Assign the infrared absorption bands to the vibration of alkanes, alkenes, alkynes, and aromatic compounds. What structural moieties can and cannot be reliably recognized? The relevant wave numbers for the structure determination of the respective compounds are marked in bold.

a



Assign the following infrared bands:

2,971; 2,875; 1,480; 1,448; 1,380/1,365; 1,180 cm^{-1}

What spectroscopic information gives rise to the evidence for

- (1) The absence of a CH_2 group,
- (2) The presence of the tertiary butyl group?

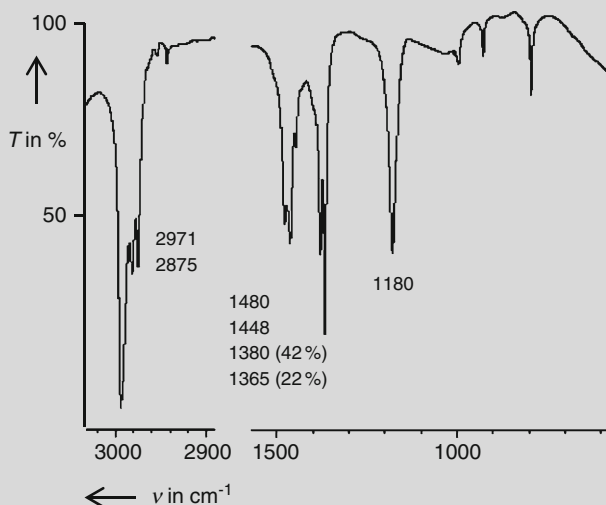


Fig. 2.12 Infrared spectrum of 2,2,3,3-tetra-methyl butane (Structure 2.4); sampling technique: capillary thin film

(continued)

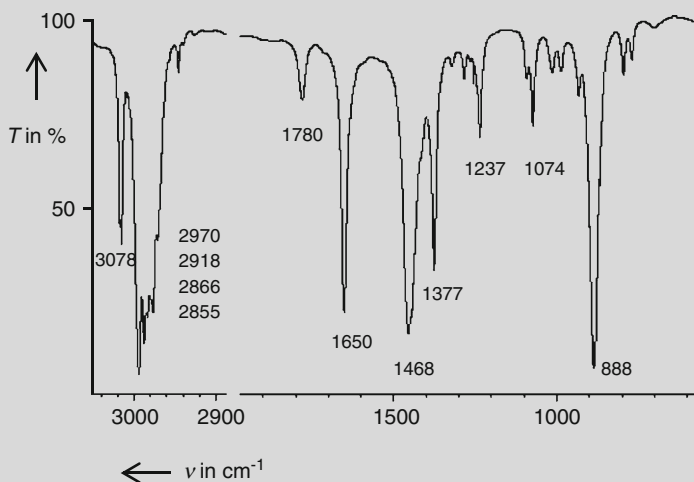


Fig. 2.13 Infrared spectrum of 2-methyl buten-1 (Structure 2.5); sampling technique: capillary thin film

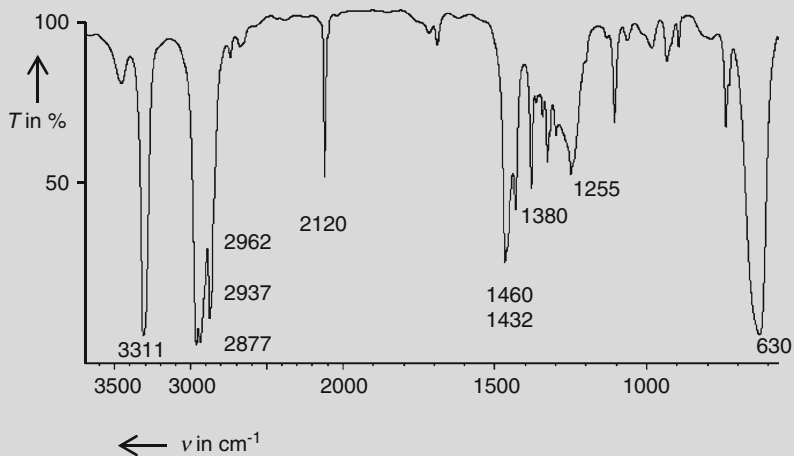
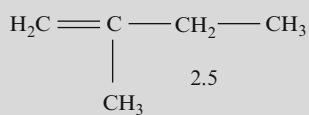


Fig. 2.14 Infrared spectrum of hexin-1 (Structure 2.6); sampling technique: capillary thin film

b



(continued)

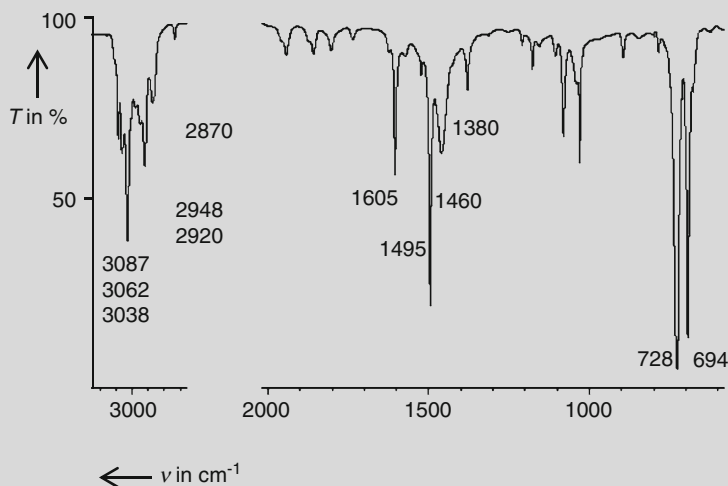


Fig. 2.15 Infrared spectrum of toluene (Structure 2.7); sampling technique: capillary thin film

Assign the following infrared bands:

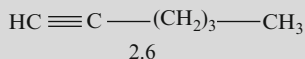
3,078; 2,970; 2,918; 2,866; 2,855; **1,780**; **1,650**; 1,468; 1,377; **888** cm^{-1} .

The bold wave numbers belong to the alkene.

What spectroscopic information provides evidence for

- (a) The presence of a $\text{CH}_2=\text{CR}_1\text{R}_2$ moiety,
- (b) An unbranched C–C chain?

c



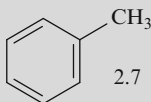
Assign the following infrared bands:

3,311; 2,962; 2,937; 2,877; **2,120**; 1,460; 1,432; 1,380; **1,255**; **630** cm^{-1}

The bold wave numbers belong to the alkyne.

What spectroscopic information provides evidence for an unbranched C–C chain?

d



Assign the following infrared absorption bands:

3,087; **3,062**; **3,038**; 2,948; 2,920; 2,870; **2,000–1,650**; **1,605–1,495**; 1,460; 1,380; **728**; **694** cm^{-1}

(continued)

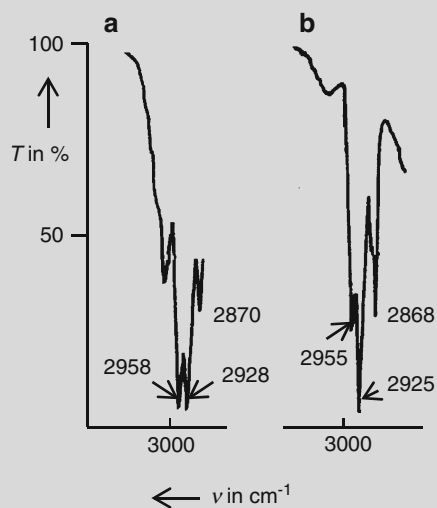


Fig. 2.16 (a, b) Infrared spectra of hydrocarbons extracted from seepage water; sampling technique: capillary thin film

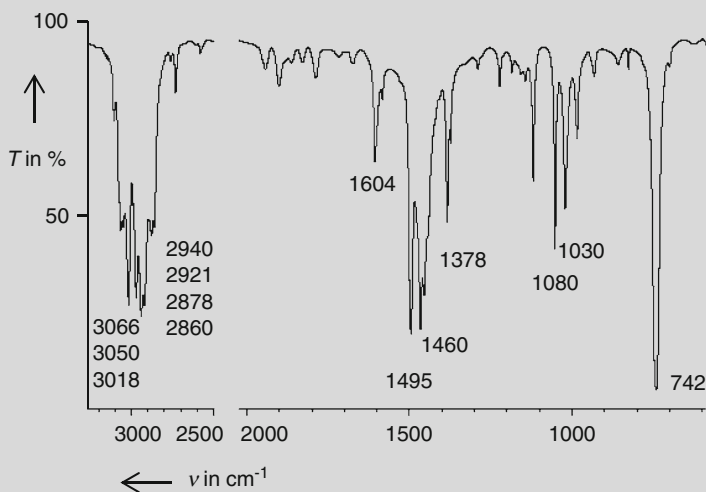


Fig. 2.17 Infrared spectrum of a liquid hydrocarbon compound; sampling technique: capillary thin film. **MS** : $m/z(I_{\text{rel}} \text{ in } \%)$: 106(68) $M^{\bullet+}$; 107(6.0)

The bold wave numbers belong to the aromatic part of the molecule.

What spectroscopic information gives rise to the evidence for

- The presence of an aromatic and the absence of a C=C group,
- The *mono*-substitution of the aromatic compound.
- The presence of the CH₃-aryl structural moiety?

(continued)

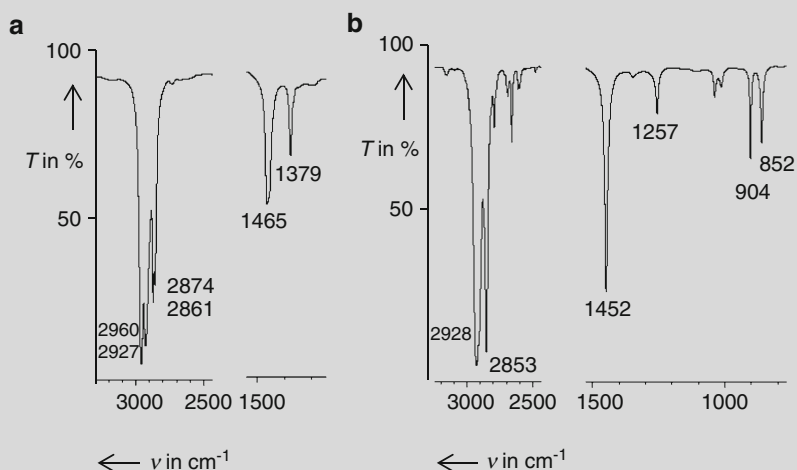


Fig. 2.18 (a, b) Infrared spectra of two C_6 -hydrocarbon compounds; sampling technique: (a) in CCl_4 ; (b) capillary thin film

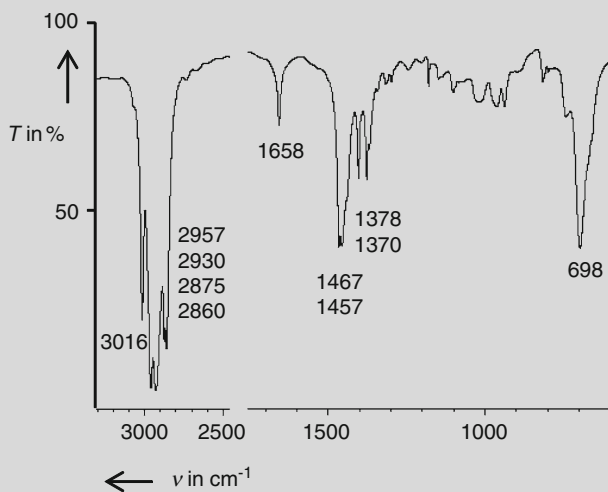


Fig. 2.19 Infrared spectrum of a liquid hydrocarbon compound; sampling technique: capillary thin film. $h - MS : m/z = 98.1097 \text{ amu } M^{+\bullet}$

- Seepage water of two retention basins at the interstate was extracted by $C_2Cl_3F_3$. The infrared spectra measured in the range of the C–H stretching vibrations after removal of the extraction solvent are shown in Fig. 2.16a, b.

(continued)

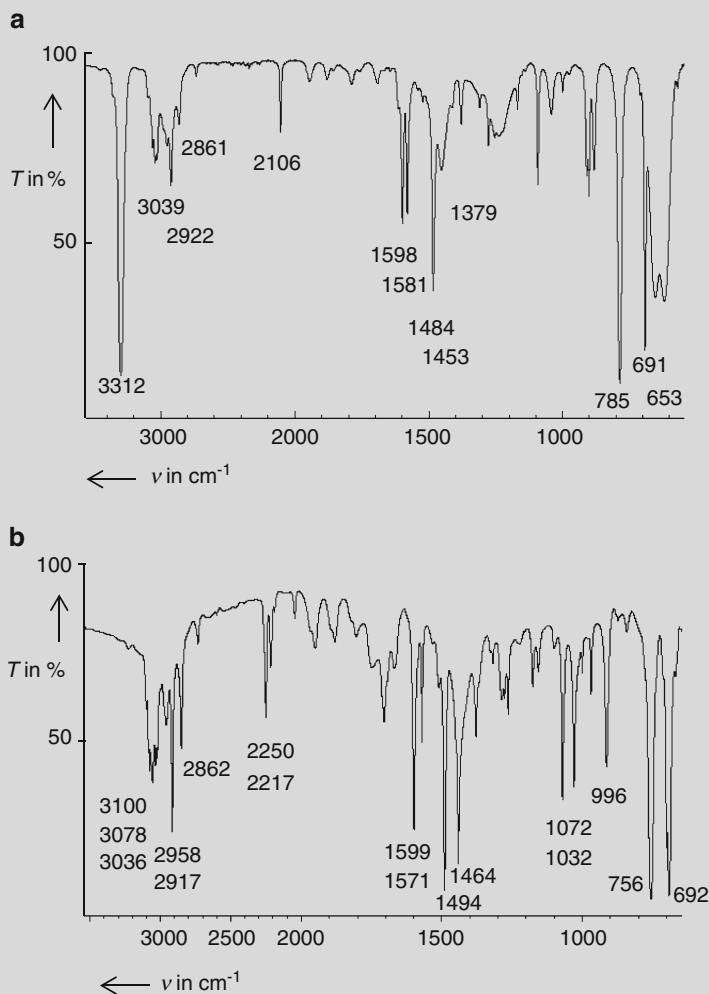


Fig. 2.20 (a, b) Infrared spectra of two structurally isomeric hydrocarbon compounds; sampling technique: capillary thin film. **h** – MS : $m/z = 116.0627$ amu $M^{\bullet+}$

Determine and justify whether the infrared spectra belong to gasoline or diesel oil.

3. Figures 2.17, 2.18, 2.19, and 2.20 present the infrared spectra of hydrocarbons. Determine structural moieties of these compounds and propose a structure for these with the aid of the additional information given.

(continued)

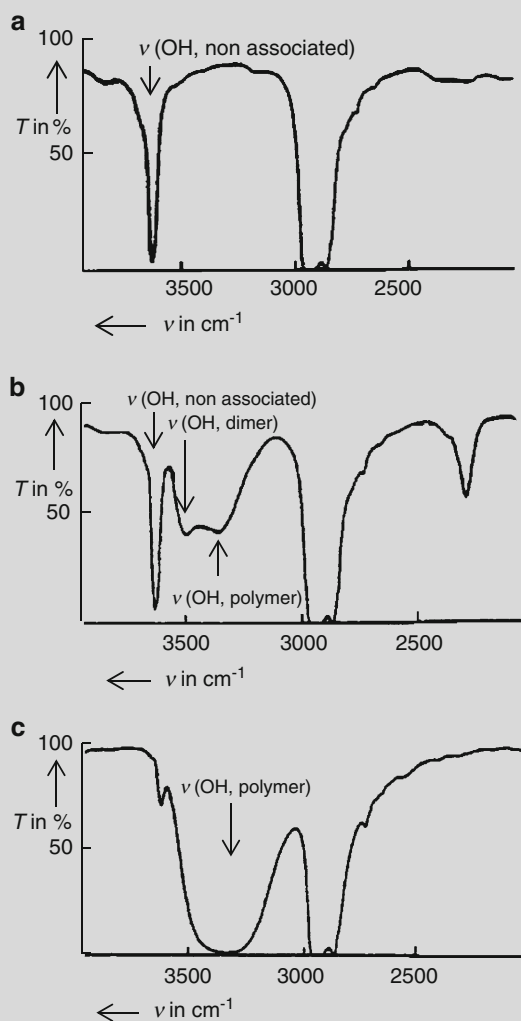


Fig. 2.21 (a–c) Infrared spectra of the O–H stretching vibrations of solutions of *n*-butanol in CCl_4 with various concentrations (in mol L^{-1}) and thicknesses of the cuvettes, l (in mm): (a) $c = 0.005$, $l = 50$; (b) $c = 0.125$, $l = 2$ mm; (c) $c = 2$, $l = 0.05$ mm

2.3.6 Interpretation of Vibrational Spectra of Compounds Containing the Functional Group C–X–R with X = O, N, and S

2.3.6.1 Alcohols and Phenols, C–O–H

The diagnostically valuable vibrations are:

H–O stretching vibrations

Wave number range:

$$\nu(\text{OH})_{\text{free}} \quad 3650 - 3585 \text{ cm}^{-1} \text{ (sharp and intense)}$$

$$\nu(\text{OH})_{\text{associated}} \quad 3550 - 3200 \text{ cm}^{-1} \text{ (very broad and very intense).}$$

The intense and sharp O–H stretching frequency of the nonassociated O–H group $\nu(\text{OH})_{\text{free}}$ is observed in the gaseous state, in very dilute solutions, or in the case of substances that cannot associate for steric reasons.

Association due to hydrogen bridges gives rise to a *decrease of the wave number* and an *increase of the intensity* of the O–H...O stretching vibration.

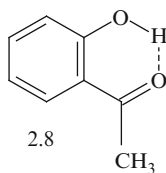
The influence of the concentration on the O–H stretching vibrations in the range from 3,650 to 3,000 cm^{-1} is shown in Fig. 2.21a–c.

Only nonassociated species are present in strongly diluted solutions as can be concluded from the absence of the broad absorption bands of dimeric and higher associated species at shorter wave numbers as shown in the infrared spectra of Fig. 2.21a, b. In contrast only polymeric species are present in highly concentrated solutions or in liquid samples as Fig. 2.21c shows by missing O–H stretching frequencies for the monomeric and dimeric species.

The stronger the hydrogen bonding the greater is the shift to lower wave numbers. For example, a shift up to $\approx 2,200 \text{ cm}^{-1}$ is observed for inorganic compounds with the strongest hydrogen bridges. Thus, the *wave number shift* is a semiquantitative indicator to evaluate the *strength of hydrogen bridges*.

The *broadness* of the infrared bands caused by association through hydrogen bridges is determined by the degree of association. The broader the infrared bands the higher the degree of association. Because the hydrogen bridge in N–H compounds is weaker, only dimeric species are formed and the N–H stretching vibrations give rise to narrower bands which is evidence in order to distinguish N–H and O–H stretching vibrations in a given infrared spectrum.

Intramolecular hydrogen bridges are marked by a broad and flat pattern which is independent from the concentration; see, for example, the O–H stretching band for *o*-hydroxy acetophenone (Structure 2.8) in Fig. 2.22a, b. The *intermolecular* hydrogen bridge is caused by equilibrium; therefore, the pattern is determined by the concentration (see Fig. 2.21a–c).



The strong intramolecular hydrogen bridges of diketones provide *very flat* and *very broad* bands in the range from approximately $3,200$ to $2,000\text{ cm}^{-1}$ which is demonstrated by the very strong chelate bridge band of acetylacetone (Structure 2.9) in Fig. 2.23.

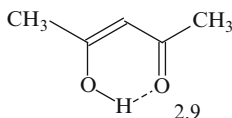


Fig. 2.22 (a, b) Infrared spectrum in the range of O–H stretching vibration of *o*-hydroxy-acetophenone (Structure 2.8) in CCl_4 : (a) $c = 0.025\text{ mol L}^{-1}$, $l = 0.5\text{ mm}$; (b) $c = 0.5\text{ mol L}^{-1}$, $l = 0.025\text{ mm}$

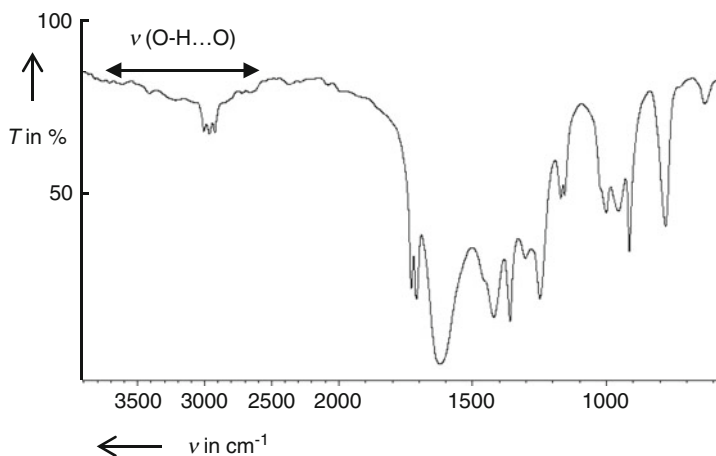
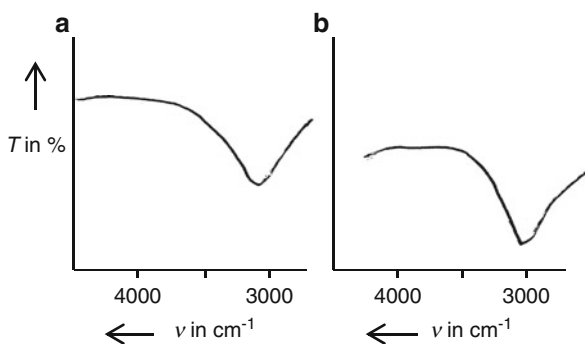


Fig. 2.23 Infrared spectrum of acetylacetone (Structure 2.9) containing a very strong chelate bridge; cuvette: $l = 0.01\text{ mm}$

Bending deviations of the C–O–H group

Wave number range: $\delta_{\text{in-plane}}$: **$1375 \pm 45 \text{ cm}^{-1}$** $\delta_{\text{out-of-plane}}$: **$650 \pm 50 \text{ cm}^{-1}$**

The two types of bending deviations of the C–O–H group give rise to very broad absorption bands; thus, they can easily be distinguished by C–H bending modes of alkyl and aromatic structures. The in-plane bending vibration of primary and secondary alcohols couples with the C–H wagging mode resulting in two bands at $\approx 1,420 \text{ cm}^{-1}$ and $\approx 1,330 \text{ cm}^{-1}$, respectively. Such coupling is not achievable for tertiary alcohols; therefore, in general, only one band is observed in this range. This evidence can be used to recognize tertiary alcohols.

The bending vibrations of phenols – $\delta_{\text{in-plane}}$ and $\delta_{\text{out-of-plane}}$ – are observed in the same range as those of the alcohols. The $\delta_s(\text{CH}_3)$ band, valuable for the recognition of the presence of a CH_3 group, can be distinguished from the $\delta_{\text{in-plane}}$ by its greater broadness.

“C–O” stretching vibrations

Wave number range: $\nu(\text{“C–O”})$: **$1,280\text{--}980 \text{ cm}^{-1}$** (very intense bands)

The very intense bands in the range from $1,280$ to 980 cm^{-1} are generally assigned to the stretching vibration of the C–O group, but these bands are caused by coupling with the neighboring C–C bond, especially in primary alcohols. Therefore, these bands should be named more precisely asymmetrical C–C–O stretching vibration $\nu_{\text{as}}(\text{C–C–O})$. The bands are diagnostically very valuable because they enable the recognition of the alcohol type because of their various positions in the infrared spectrum. They are observed in the ranges from $1,075$ to $1,000 \text{ cm}^{-1}$ for primary (1°), from $1,150$ to $1,075 \text{ cm}^{-1}$ for secondary (2°), and from $1,210$ to $1,100 \text{ cm}^{-1}$ for tertiary (3°) alcohols, respectively. As one can see, the wave numbers of secondary and tertiary alcohols partially overlap which prevents the recognition of the alcoholic type. Sometimes, the *symmetrical* C–C–O stretching vibration $\nu_s(\text{C–C–O})$ can be helpful which is observed between 900 and 800 cm^{-1} in 1° and 2° alcohols and lies at $\approx 1,000 \text{ cm}^{-1}$ in 3° alcohols, respectively.

The C–O stretching vibration of phenols lies in the range from $1,260$ to $1,200 \text{ cm}^{-1}$ which is approximately the same range as for 3° alcohols. However, the distinction between both structures should not be difficult because of the characteristic pattern of the aromatic moiety.

Let us now turn to the problem of the occurrence of absorption bands of *water*. Water is contained in many compounds, even if only in traces, or it is incorporated during the sample preparation. Water provides stretching vibrations that overlap with those of alcohols. Therefore, the recognition of the O–H group of an alcohol can be complicated. However, in contrast to alcohols water provides a bending vibration at $\approx 1,650 \text{ cm}^{-1}$ which is demonstrated by the infrared spectrum of a hydrocarbon which is contaminated with water, shown in Fig. 2.24.

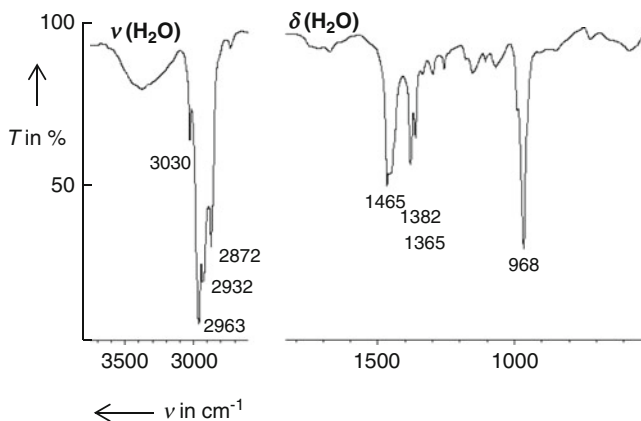


Fig. 2.24 Infrared spectrum of a hydrocarbon compound which is contaminated with water

2.3.6.2 Ethers, C–O–C(α)

Saturated ethers or such containing a *nonbranched* α -C atom provide a strongly asymmetric C–O–C stretching vibration in the range from 1,150 to 1,080 cm^{-1} (mostly at $\approx 1,125 \text{ cm}^{-1}$) and a symmetric C–O–C stretching vibration with medium intensity which lies in the range from 890 to 820 cm^{-1} . Ethers with a *branched* α -C atom show two or more absorption bands with approximately equal intensity in the range from 1,210 to 1,070 cm^{-1} because of coupling of vibrations of the C–O with the neighboring C–C group.

Note that the range of the stretching vibrations of ethers overlaps with those of alcohols (and also carboxylic acid esters, see below), but the presence of an alcohol requires additionally a very intense O–H stretching vibration as explained above (and esters are characterized by intense C=O stretching vibrations).

For other types of ethers intense absorption bands are observed in the following ranges:

Aryl alkyl ether: $\nu_{\text{as}}(\text{C–O–C})$: 1,275 – 1,200 cm^{-1} ; $\nu_{\text{s}}(\text{C–O–C})$: $\approx 1,210 \pm 10 \text{ cm}^{-1}$;

Di-aryl ethers: $\nu_{\text{as}}(\text{C–O–C})$: 1,300 – 1,200 cm^{-1} .

A representative infrared spectrum employing the example di-*sec*-butyl ether (Structure 2.10) is shown in Fig. 2.25. The bands assigned to the vibration of the ether group are marked in bold.

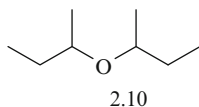
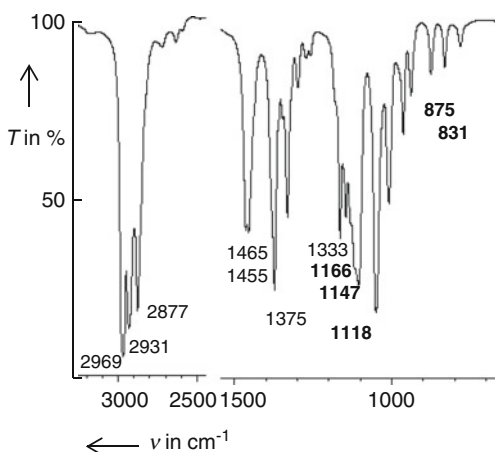


Fig. 2.25 Infrared spectrum of di-*sec*-butyl ether (Structure 2.10); sampling technique: capillary thin film

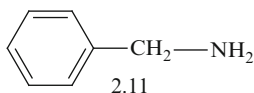


2.3.6.3 Amines, C-NHR (R = H, Alkyl, Aryl)

N-H stretching vibrations, $\nu(\text{N-H})$

Wave number range: **3500 – 3280 cm^{-1}**

Primary (1°) amines show two IR-absorption bands: $\nu_{\text{as}}(\text{N-H})$ at 3,380–3,350 cm^{-1} and 3,500–3,420 cm^{-1} for *saturated* and *aromatic* amines, respectively, and $\nu_{\text{s}}(\text{N-H})$ at lower wave numbers. The intensities of $\nu(\text{N-H})$ are weaker than those of $\nu(\text{O-H})$ because of the weaker hydrogen bridges in amines in contrast to alcohols and phenols. Thus, only dimer species are formed resulting in narrower bands as is shown in the infrared spectrum of benzyl amine (Structure 2.11) presented in Fig. 2.26.



Secondary (2°) amines give rise to only *one* N-H stretching vibration which lies in the range of 3,320–3,280 cm^{-1} and at $\approx 3,400 \text{ cm}^{-1}$ for saturated and aromatic amines, respectively.

Tertiary (3°) amines do not show any N-H stretching vibration.

Bending vibrations

Wave number range: $\delta_{\text{in-plane}}(\text{NH}_2)$: **1650 – 1580**; $\delta_{\text{oop}}(\text{NH}_2)$: **850 – 700 cm^{-1}**

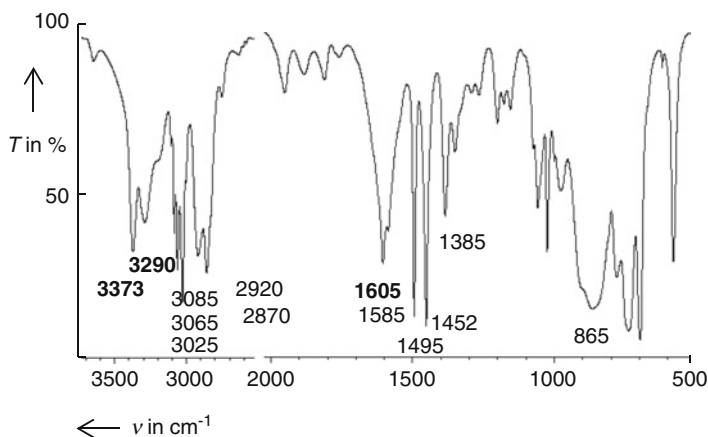


Fig. 2.26 Infrared spectrum of benzyl amine (Structure 2.11); sampling technique: capillary thin film

The medium intense scissoring $\delta_{\text{in-plane}}(\text{NH}_2)$ is observed as a relatively broad band. Thus, it can be distinguished from other vibrations in this range and is important in order to distinguish primary amines and alcohols.

The out-of-plane bending vibration lies in the range from 850 to 750 cm^{-1} and from 750 to 700 cm^{-1} for primary and secondary amines, respectively. Sometimes, this difference may be used to distinguish both types of amines.

C–N stretching vibrations, $\nu(\text{C–N})$

Wave number range: **$1350 - 1020\text{ cm}^{-1}$**

The medium intense $\nu(\text{C–N})$ lies in the range from $1,250$ to $1,020\text{ cm}^{-1}$ and from $1,350$ to $1,250\text{ cm}^{-1}$ for saturated and aromatic amines, respectively. Because of its lower intensity it can be easily distinguished from the very intense C–O bending vibration provided it is not superimposed by a $\nu(\text{C–O})$. Primary amines containing a branched αC atom show new bands due to coupling of vibrations but they cannot be reasonably assigned.

The asymmetrical C–N–C stretching vibration of secondary amines can be used to distinguish saturated and aromatic secondary amines: Saturated secondary amines show bands at $1,180$ – $1,130\text{ cm}^{-1}$ and those of aromatic ones are observed in the range from $1,350$ to $1,250\text{ cm}^{-1}$.

2.3.6.4 Thiols, C–S–H

Wave number range: $\nu(\text{S–H})$: **$2600 - 2550\text{ cm}^{-1}$**

The S–H stretching frequency lies in a range which is not occupied by other fundamentals; hence, the functional group S–H can be well recognized using infrared spectroscopy. Note that the intensity of $\nu(\text{S–H})$ is low because of the small dipole moment change during vibration of this group.

Challenge 2.11

Justify the structure of *N*-methyl *p*-toluidine (Structure 2.12) by assignment of the marked bold infrared absorption bands in Fig. 2.27.

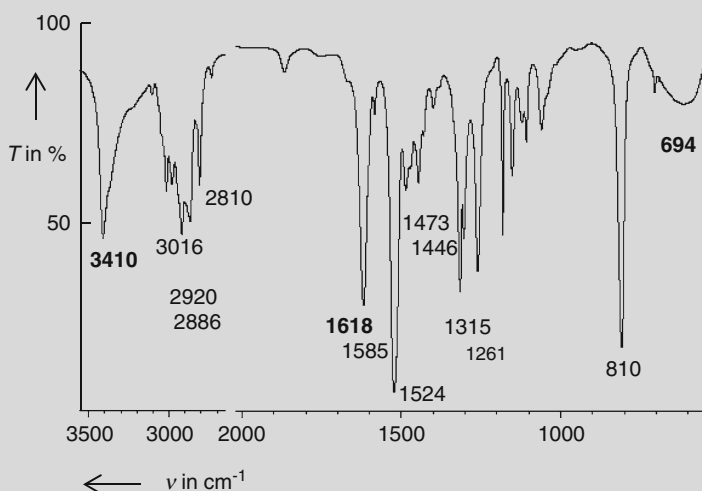
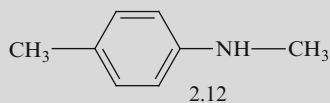


Fig. 2.27 Infrared spectrum of *N*-methyl *p*-toluidine (Structure 2.12); sampling technique: capillary thin film

Solution to Challenge 2.11

The assignment of the absorption bands of the infrared spectrum in Fig. 2.27 is summarized in Table 2.15.

(continued)

Table 2.15 Assignment of infrared absorption bands of N-methyl *p*-toluidine (Structure 2.12)

ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment
3,410 vs	$\nu(\text{N-H}), 2^\circ$ Amine	1,473 m	$\delta_{\text{as}}(\text{CH}_3)$
		1,446 m	
3,016 m	$\nu(\text{sp}^2\text{C-H})$, Aryl	1,315 w	$\delta_{\text{s}}(\text{CH}_3)$
2,920 m	$\nu_{\text{s}}(\text{CH}_3)$ + Fermi	1,261 m	$\nu(\text{C-N-C})$, N-aryl
2,886 m	resonance		
2,810 m	$\nu_{\text{s}}(\text{CH}_3)$, N-aryl	810 s	$\gamma(\text{C-H})$, 1,4-disubstituted
1,618 s-, 524	$\nu(\text{C=C})$, Aryl	694 m	$\delta_{\text{oop}} 2^\circ$ Amine
		2,000–1,650 w	Overtone and combination vibrations for aryl 1,4-disubstituted

The following structural moieties can be justified according to results in Table 2.15:

1. The *aromatic* structure is recognized by $\nu(\text{sp}^2\text{C-H})$ in the range from 3,100 to 3,000 cm^{-1} in addition to $\nu(\text{C=C})$ at $\approx 1,600\text{--}1,490\text{ cm}^{-1}$. Note that there are no hints of an alkene because of the missing absorption band $\nu > 1,600\text{ cm}^{-1}$.
The *para*-substitution is proposed by $\gamma(\text{C-H})$ at 810 cm^{-1} in combination with the missing ring bending vibration. Note that the latter fact is also valid for a 1,2-disubstitution, but the pattern of the weak overtone and combination vibrations in the range from 2,000 to 1,650 cm^{-1} indicate the *para*-substitution rather than the *ortho*-one (see Fig. 6.1).
2. The presence of the secondary amine structure is indicated by the intense single band at 3,410 cm^{-1} which belongs to $\nu(\text{N-H})$ and, additionally, by δ_{oop} at $\approx 700\text{ cm}^{-1}$.
3. Alkyl groups are indicated by $\nu(\text{sp}^3\text{C-H})$ in the range from 3,000 to 2,800 cm^{-1} as well as the asymmetric and symmetric bending vibrations at 1,473, 1,446, and 1,315 cm^{-1} .

The stretching vibrations of a CH_3 group which is directly linked to aryl or N are diminished and are observed for the N-aryl structure at $2,925 \pm 5$, $2,865 \pm 5$, and $2,815 \pm 5\text{ cm}^{-1}$, which is experimentally justified by the respective absorption band.

The CH_2 group cannot be recognized by its respective vibrations because the position of its sole indication, namely the presence of $\nu_{\text{as}}(\text{C-H})$ at $\approx 2,925\text{ cm}^{-1}$ (see Table 2.11), is overlaid by the shifted stretching vibrations of the N- CH_3 group. Note that recognition number and types of alkyl groups are not the subject of infrared spectroscopy.

Challenge 2.12

For solutions to Challenge 2.12, see *extras.springer.com*.

1. Assign the given absorption bands of the infrared spectrum of di-*sec*-butyl ether (Structure 2.10) in Fig. 2.25. The wave numbers that are important for the ether group are marked in bold.
2. Assign the given absorption bands of the infrared spectrum of benzylamine (Structure 2.11) in Fig. 2.26. The wave numbers that are important for the amine group are marked in bold.
3. An unknown compound with the sum formula $C_4H_{11}N$ give rise to the infrared spectrum shown in Fig. 2.28. Derive the structure.
4. The infrared spectra of three structurally isomeric compounds are presented in Fig. 2.29a–c. Derive the structure of each compound. The sum formula can be determined by the spectrometric data of the isomer **B**; m/z (I_{rel} in %): 108 (83.5) M^{+} , 109 (6.8).

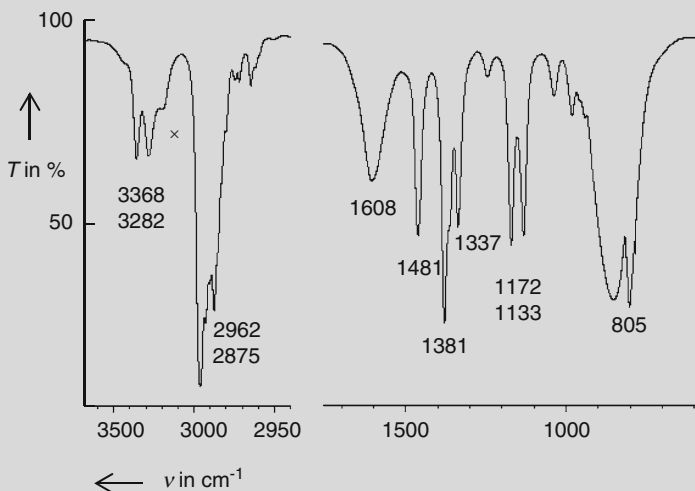


Fig. 2.28 Infrared spectrum of an unknown liquid compound; sampling technique: capillary thin film; × - Fermi resonance: Overtone of $\delta(NH_2) + \nu(NH)$

(continued)

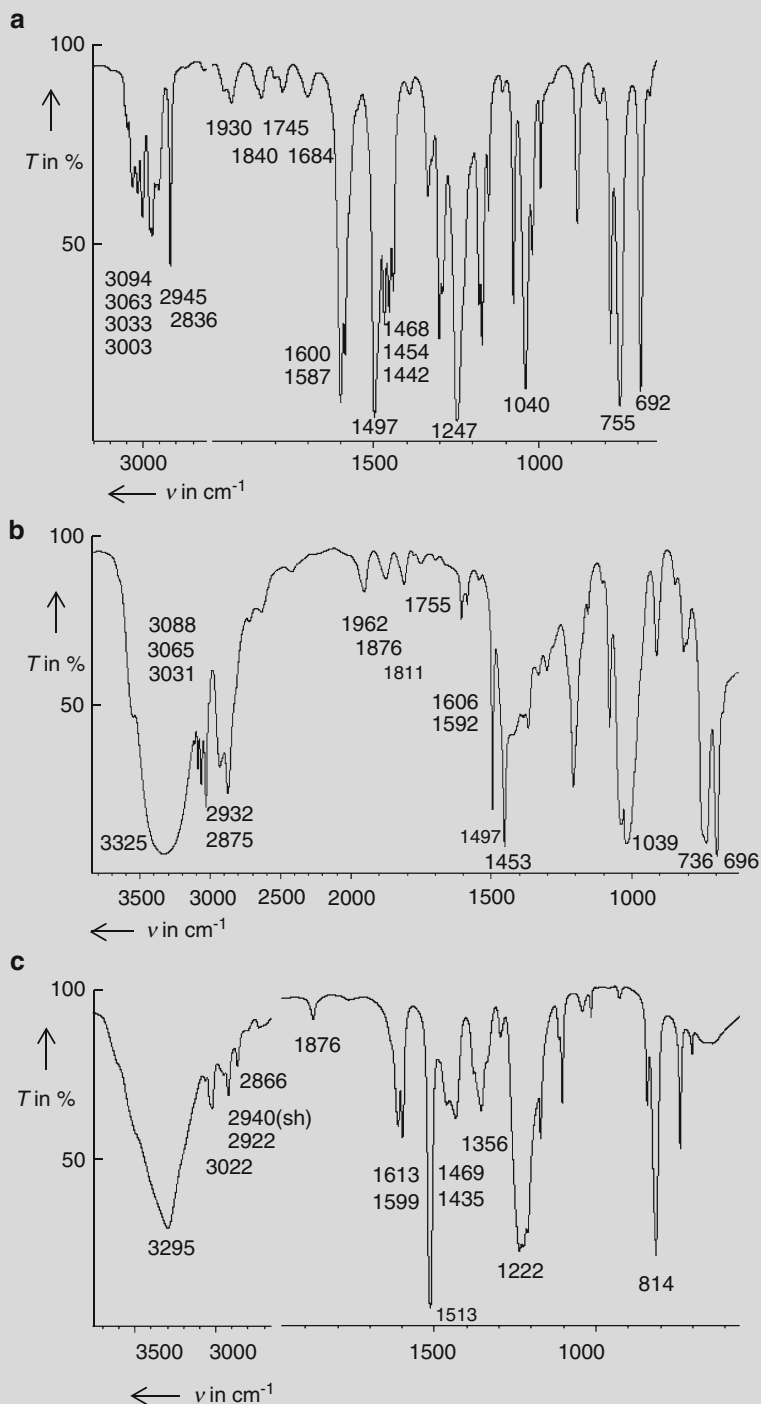


Fig. 2.29 (a–c) Infrared spectra of unknown liquid compounds; sampling technique: capillary thin film

2.3.7 Interpretation of Vibrational Spectra of Carbonyl Compounds Containing the Functional Group $-(C=O)-X$ with $X = H, C, OH, OR, O(C=O)R, NR_2$, and Cl

Wave number range: $\nu(C=O)$: **1,850 – 1,650 cm^{-1}**

As explained above, the $C=O$ stretching mode is a very characteristic vibration. However, its range of 200 cm^{-1} is relatively large for a characteristic vibration. Electronic effects are the main reasons for this, as explained in Sect. 2.3.2. Knowledge of these relations, in combination with further information, is the basis for recognition of the substituent X linked at the $C=O$ group which is summarized in this section. Note that a weak band mostly occurs in the range $\nu \approx 3,400\text{--}3,650\text{ cm}^{-1}$ which is the overtone of the intense $C=O$ stretching vibration. Although this overtone coincides with the $O-H$ stretching vibration it can be unambiguously assigned by its low intensity and the missing broadness.

2.3.7.1 Ketones, $X = C$

Wave number ranges for diagnostically important vibrations of ketones are listed in Table 2.16.

Decreasing of $\nu(C=O)$ is observed by branching at the αC atom.

Ketones can be recognized by the combination of $\nu(C=O)$ and $\nu(C-C-C)$. In contrast to $\nu(C-C)$ of the alkyl chain the intense asymmetrical stretching vibration of the $C-C(=O)-C$ skeleton indicates a ketone provided that functional groups of the aldehyde, ester, and carbonic acids are not present in the molecule. Figure 2.30 shows the IR-spectrum of acetophenone (Structure 2.13). The bold IR-bands belong to the vibration of the carbonyl group.

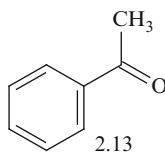


Table 2.16 Wave number ranges of important vibrations of ketones in cm^{-1}

	Saturated ketones	Aryl-alkyl-ketones	Di-aryl ketones
$\nu(C=O)$	$1,715 \pm 10$	1,700–1,670	1,680–1,650
$\nu(C-C-C)$	1,230–1,100	1,300–1,230	1,300–1,230

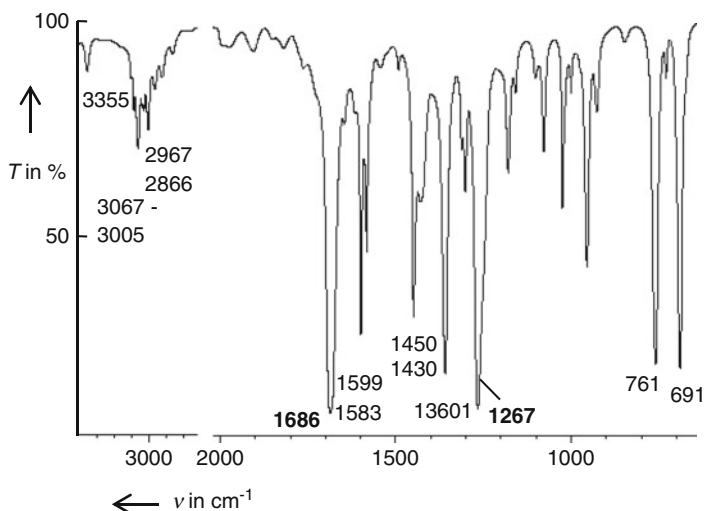


Fig. 2.30 Infrared spectrum of acetophenone (Structure 2.13); sampling technique: capillary thin film

Table 2.17 Wave number ranges of important vibrations of aldehydes in cm^{-1}

$\nu(\text{CH})$ + Fermi resonance	2,850–2,700, 1 or 2 bands
$\nu(\text{CH})$, saturated, non α -C branched	2,730–2,715
$\nu(\text{CH})$, saturated, α -C branched	2,715–2,700
$\nu(\text{C}=\text{O})$, saturated	$1,730 \pm 10$
$\nu(\text{C}=\text{O})$, aryl	$1,700 \pm 10$
$\delta(\text{CHO})$	$\approx 1,390$

2.3.7.2 Aldehydes, X = H

Wave number ranges for diagnostically important vibrations of aldehydes are listed in Table 2.17.

Although the range of the very intense $\text{C}=\text{O}$ stretching vibration lies admittedly somewhat higher, it overlaps partially with that of the corresponding ketones. Thus, this band is not an evidence to distinguish both functional groups. *However, the aldehyde can be unambiguously distinguished from the corresponding ketone by two or one intense absorption bands at $2,850 - 2,700 \text{ cm}^{-1}$ combined with $\delta(\text{CHO})$ at $\approx 1,390 \pm 10 \text{ cm}^{-1}$.* This is shown in the infrared spectrum of *n*-hexanal (Structure 2.14) presented in Fig. 2.31. Note that only the band of the Fermi resonance is well separated, whereas $\nu(\text{CH})$ is developed only as a shoulder because of overlap with the CH -stretching vibration. This fact is also to be expected for a saturated, non α -C branched aldehyde. In the case of α -branched saturated aldehydes, however, $\nu(\text{CH})$ is decreased (see Table 2.17) and hence, two separate bands will be observed in this range.

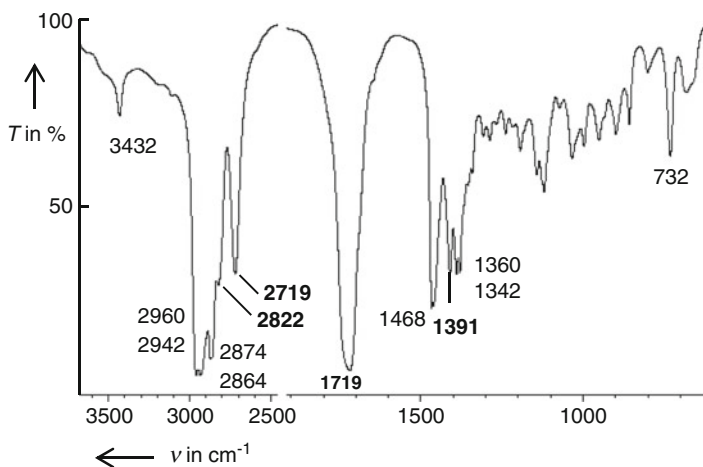


Fig. 2.31 Infrared spectrum of *n*-hexanal, $\text{CH}_3-(\text{CH}_2)_4-\text{COH}$ (Structure 2.14); sampling technique: capillary thin film

2.3.7.3 Carboxylic acids, $\text{X} = \text{OH}$

Since carboxylic acid contains a carbonyl and a hydroxyl group, bands of both functional groups can be seen in the corresponding spectra. A representative spectrum is shown in Fig. 2.32 for propionic acid.

Typical bands for the carboxylic acid groups are marked in bold.

O–H stretching vibrations

The very broad and intense infrared band in the range from 3,500 to 2,500 cm^{-1} is an unambiguous evidence for the carboxylic group. No other functional group shows such a broad and intense band, which is caused by the strong hydrogen bonding. Even in the gas state dimeric species linked by hydrogen bridges are still present. Additionally, overtone and combination modes feature bands of medium intensity on the low side of the O–H stretching up to 2,500 cm^{-1} . As shown in Fig. 2.32, the sharper C–H stretching bands are superimposed upon the broad O–H stretching band. Note that the free $\nu(\text{OH})$ stretching mode appears only in very strongly diluted solutions at $\approx 3,520 \text{ cm}^{-1}$. The broad O–H stretching bands of β -diketones caused by the strong chelate hydrogen bridge lie in the same range as those of the carboxylic group, however, the intensity is markedly lower (compare the infrared spectra of Figs. 2.23 and 2.32).

C=O stretching vibrations

The intensity of the $\text{C}=\text{O}$ stretching $\nu(\text{C}=\text{O})$ is higher than that of ketones, compare Figs. 2.30 and 2.32. Monomeric saturated carboxylic acids absorb at 1,760 cm^{-1} . The common dimeric structures feature only the asymmetrical $\text{C}=\text{O}$ stretching vibration, which lies at $1,710 \pm 10 \text{ cm}^{-1}$ for aliphatic carboxylic acids. Conjugation diminishes the band position of $\nu(\text{C}=\text{O})$ which is found at $1,700 \pm 15 \text{ cm}^{-1}$. Intramolecular hydrogen bonding can be recognized by bands

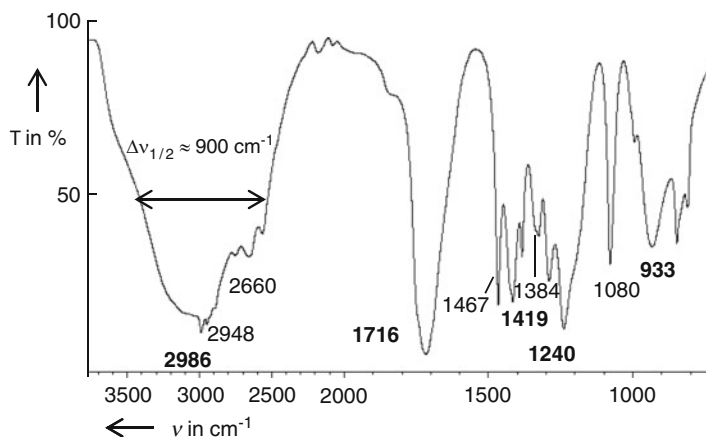


Fig. 2.32 IR-spectrum of propionic acid $\text{CH}_3\text{-CH}_2\text{-COOH}$ (Structure 2.15); sampling technique: capillary thin film

markedly shifted to lower wave numbers. Thus, the C=O stretching bands of *o*-hydroxy benzoic acid and *p*-hydroxy benzoic acid are observed in KBr at $1,667$ and $1,682\text{ cm}^{-1}$, respectively.

C–O and O–H bending vibrations

Coupling of the C–O stretching vibration $\nu(\text{C–O})$ with the in-plane bending $\delta_{\text{in-plane}}(\text{C–O–H})$ provides two bands. The bending named by “ $\delta_{\text{in-plane}}(\text{O–H})$ ” lies in the range from $1,440$ to $1,395\text{ cm}^{-1}$ and the more intense “ $\nu(\text{C–O})$ ” lies at $1,315\text{--}1,280\text{ cm}^{-1}$. The latter is split into more bands for long-chained carboxylic acids which is an evidence to recognize *fatty acids*.

Carboxylic acid salts (carboxylates)

Infrared spectra of carboxylates differ from the carboxylic acids by the lack of broad stretching and bending bands. The carboxylic group provides two bands in the range from $1,650$ to $1,350\text{ cm}^{-1}$. The more intense band at the higher wave number is assigned to the asymmetric CO_2 stretching vibration and that in the range from $1,450$ to $1,350\text{ cm}^{-1}$ to the symmetric CO_2 stretching vibration, respectively.

2.3.7.4 Carboxylic Acid Esters, $\text{X} = \text{OR}$

Aliphatic and aromatic carboxylic acid esters are characterized by three intense infrared bands which lie in the ranges $\nu \approx 1,700\text{ cm}^{-1}$, $\approx 1,200\text{ cm}^{-1}$, and $\approx 1,100\text{ cm}^{-1}$. This so-called “three band rule” is diagnostic for the carboxylic acid ester group.

The band with the highest wave number belongs to the C=O stretching vibration $\nu(\text{C=O})$. The medium band is caused by asymmetric C–C and C–O attached to the carbonyl carbon and is called $\nu_{\text{as}}(\text{C–C–O})$. The third of these bands includes the asymmetrical vibration of the ester oxygen and the next two carbon atoms in the

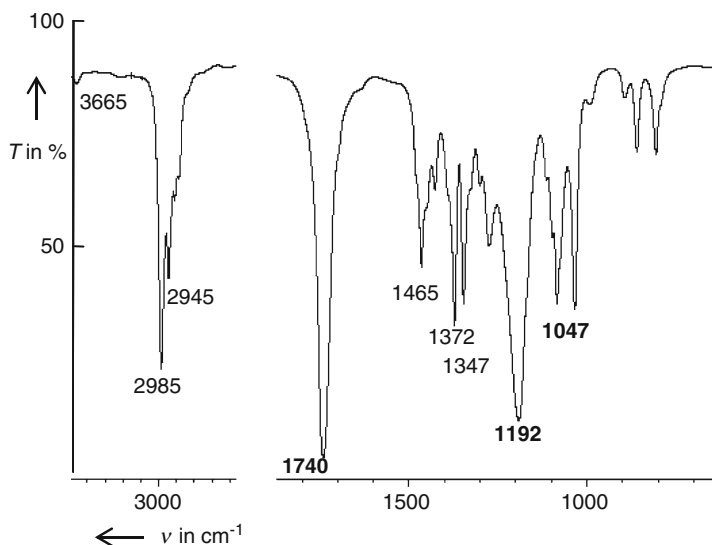


Fig. 2.33 Infrared spectrum of propionic acid ethyl ester (Structure 2.16); sampling technique: capillary thin film

Table 2.18 Wave number ranges for various types of carboxylic esters

	Saturated esters	Aromatic or α,β -nonsaturated esters
$\nu(\text{C}=\text{O})$	1,750–1,735	1,730–1,710
$\nu(\text{C}-\text{C}-\text{O})$	1,210–1,165	1,330–1,250
$\nu(\text{C}-\text{C}-\text{O})$, acetates	$\approx 1,240$	
$\nu(\text{O}-\text{C}-\text{C})$	1,100–1,030	1,130–1,000

hydrocarbon chain $\nu_{\text{as}}(\text{O}-\text{C}-\text{C})$. All of these bands can be found in the infrared spectrum of propionic acid ethyl ester $\text{C}_2\text{H}_5-\text{COO}-\text{C}_2\text{H}_5$ (Structure 2.16) shown in Fig. 2.33. The bands typical for the carboxylic acid groups are marked in bold.

Wave number ranges for various types of esters are summarized in Table 2.18.

2.3.7.5 Carboxylic Acid Anhydrides, $\text{X}=\text{O}-(\text{C}=\text{O})-\text{OR}$

C=O stretching vibrations

The coupling of the two $\text{C}=\text{O}$ groups results in two intense $\text{C}=\text{O}$ stretching vibrations of which the symmetrical vibration is observed at higher wave numbers than the asymmetrical one. The symmetrical stretching vibration provides more intense bands than the asymmetric one for noncyclic anhydrides; the reverse intensity ratio is true for cyclic anhydrides.

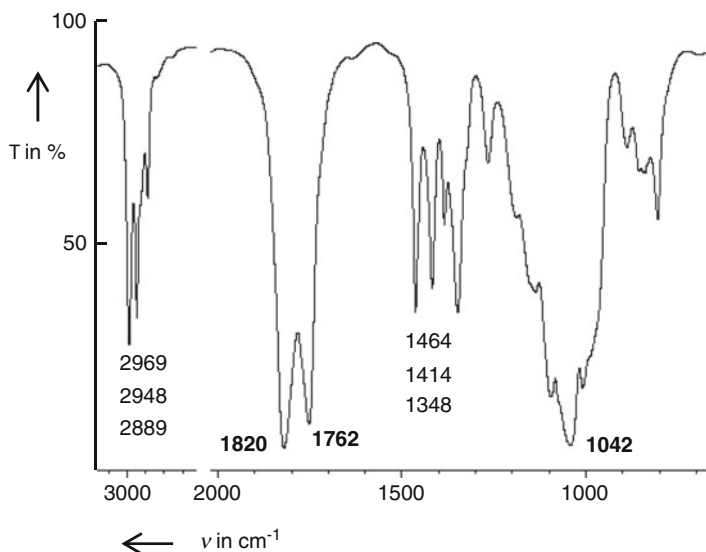
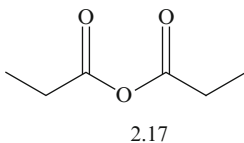


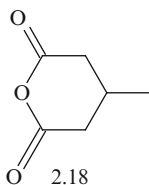
Fig. 2.34 Infrared spectrum of noncyclic propionic acid anhydride (Structure 2.17); sampling technique: capillary thin film

The intensity ratio of $\nu_s(\text{C}=\text{O})$ and $\nu_{as}(\text{C}=\text{O})$ enables us to distinguish between cyclic and noncyclic anhydrides, respectively.

In the infrared spectrum of noncyclic propionic acid anhydride (Structure 2.17) shown in Fig. 2.34 the stretching vibrations lie at $1,820\text{ cm}^{-1}$ [the more intense $\nu_s(\text{C}=\text{O})$] and $1,762\text{ cm}^{-1}$ [the weaker $\nu_{as}(\text{C}=\text{O})$]. The respective C=O stretching vibrations in the infrared spectrum of cyclic 3-methyl glutaric acid anhydride (Structure 2.18) presented in Fig. 2.35 at $\nu_s(\text{C}=\text{O}) = 1,809\text{ cm}^{-1}$ and $\nu_{as}(\text{C}=\text{O}) = 1,762\text{ cm}^{-1}$ have the reverse intensity ratio. The same result is true for five-ring anhydrides.



The infrared bands due to the anhydride group are marked in bold.



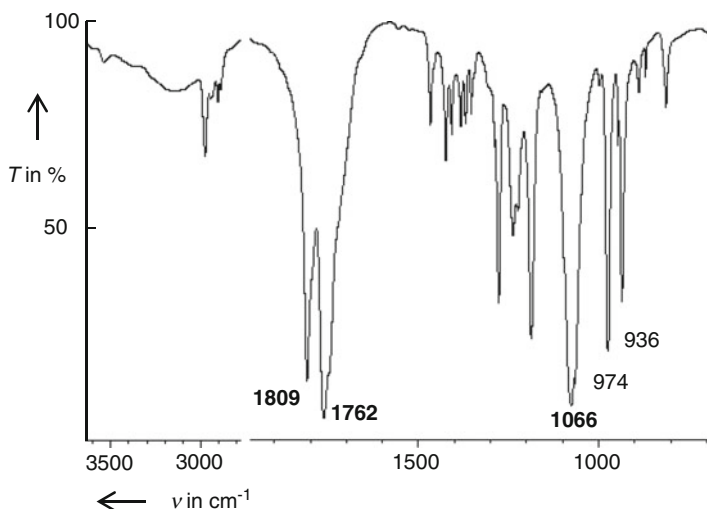


Fig. 2.35 Infrared spectrum of 3-methyl glutaric acid anhydride (Structure 2.18); sampling technique: capillary thin film

Table 2.19 Wave number ranges of the C=O and C–O stretching vibrations for some anhydride types

		Noncyclic anhydrides	Cyclic anhydrides
$\nu_s(\text{C=O})$	Saturated	$1,820 \pm 5$ (stronger)	$1,860 \pm 10$ (weaker)
	Nonsaturated	$1,775 \pm 5$ (stronger)	$1,850 \pm 10$ (weaker)
$\nu_{as}(\text{C=O})$	Saturated	$1,750 \pm 5$ (weaker)	$1,785 \pm 15$ (stronger)
	Nonsaturated	$1,720 \pm 5$ (weaker)	$1,870 \pm 10$ (stronger)
$\nu(\text{C–O})$		$1,050 \pm 10$	$1,300\text{--}1,175$ and $950\text{--}880$

C–O stretching vibrations

The C–O and C–C–O stretching vibrations, in most cases more intense than $\nu(\text{C=O})$, lie at $\nu \approx 1,050 \text{ cm}^{-1}$.

The wave number ranges of the C=O and C–O stretching vibrations are listed in Table 2.19 for some anhydride types.

2.3.7.6 Carboxylic Acid Amides, $\text{X} = \text{NR}_2$

N–H stretching vibrations

The number of N–H stretching vibrations is equal to the number of N–H bonds.

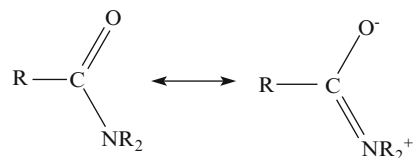
The two bands of *primary* (1°) *amides* $\text{R}-(\text{C=O})-\text{NH}_2$ are seen at $\nu \approx 3,520$ and $\approx 3,400 \text{ cm}^{-1}$ with medium intensity in the spectrum which is obtained by employing diluted solutions. In the solid state the bands are shifted to smaller wave numbers because of hydrogen bonding.

Secondary (2°) amides $R-(C=O)-NRH$ show only one band in the range from 3,500 to 3,400 cm^{-1} in diluted solutions. In the solid state generally several bands appear caused by various conformeric structures that are formed by hydrogen bonding.

Tertiary (3°) amides $R-(C=O)-NR_2$ do not show any bands in the range from 3,500 to 3,300 cm^{-1} .

C=O stretching vibrations

$\nu(C=O)$ is shifted to smaller wave numbers due to mesomerism as is shown by the two resonance structures:



Furthermore, the $C=O$ stretching vibration cannot be assumed to be purely $\nu(C=O)$ because of coupling with other vibrations. Therefore, “ $\nu(C=O)$ ” is named the *amide I* band. It is seen in the spectrum always below 1,700 cm^{-1} and its position is determined by the sampling technique and the amide type. The amide I band of tertiary amides is nearly independent of the physical state because of missing hydrogen bridges.

N-H bending vibrations

The NH_2 scissoring $\delta(NH_2)$ couples with the $N-C=O$ stretching vibration, because both vibrations lie in nearly the same wave number range, result in a band which is named *amide II*. In 1° amides the amide II bands mostly coincides with the amide I band or it is developed only as a shoulder but in solution both bands are separate.

Coupling of the amide II band with the $\delta(NH_2)$ band gives rise to the *amide III* band which appears at $\nu \approx 1,250 \text{ cm}^{-1}$.

Other vibrations

1° amides show a band at $\nu \approx 1,400 \text{ cm}^{-1}$ which is assigned to the $C-N$ stretching vibration.

The out-of-plane bending of the NH_2 group $\delta_{\text{oop}}(NH_2)$, also named “wagging NH_2 ,” appears as a broad band in the range from 750 to 600 cm^{-1} whose intensity is smaller for 2° amides. Typical wave numbers of various types of amides are summarized in Table 2.20.

Figure 2.36 presents the infrared spectrum of benzamide (Structure 2.19) as an example of a primary amide prepared in KBr. Typical wave numbers for the aryl-benzamides are marked in bold.

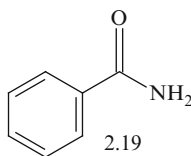
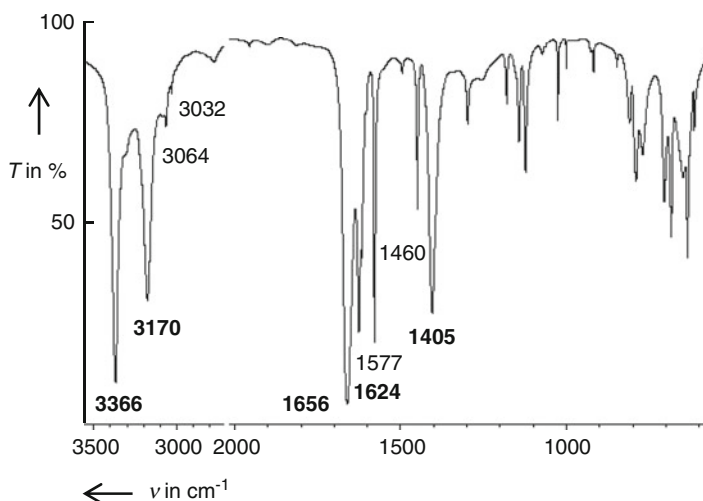


Table 2.20 Typical wave numbers (in cm^{-1}) of various types of amides

	1° amide	2° amide	3° amide
$\nu(\text{NH})_{\text{nonassociated}}$	$\nu_{\text{s}}: 3,520$ $\nu_{\text{as}}: 3,400$	3,500–3,400	No
$\nu(\text{NH})_{\text{associated}}$	$\nu_{\text{s}}: 3,350$ $\nu_{\text{as}}: 3,180$	3,300–3,060 Mostly several	No
Amide I _{nonassociated}	1,690	1,700–1,680	1,680–1,630
Amide I _{associated}	1,680–1,630	1,680–1,630	No
Amide II	1,655–1,620	1,570–1,515	No
$\nu(\text{C-N})$	Separated in diluted solutions 1,430–1,390	High intensity 1,310–1,230	$\approx 1,505$ $\text{R}=\text{CH}_3$
$\delta_{\text{oop}}(\text{O}=\text{C}-\text{NH}_2)$	750–600 (broad)	750–680 broad	No

**Fig. 2.36** Infrared spectrum of benzamide (Structure 2.19) as an example of a primary amide; sampling technique: KBr pellet

2.3.7.7 Carboxylic Acid Chlorides, $\text{X} = \text{Cl}$

Recall from the discussion in Sect. 2.3.1 that a substituent with an $-I$ effect linked at the carbonyl group decreases the wave number of $\nu(\text{C}=\text{O})$ bands. Because of the strong $-I$ effect of the Cl atom, the shift of $\nu(\text{C}=\text{O})$ towards higher wave numbers is large. Thus, $\nu(\text{C}=\text{O})$ of nonconjugated carboxylic acid chlorides appears in the high wave number range from 1,815 to 1,785 cm^{-1} . Conjugation, as discussed above, diminishes the $\nu(\text{C}=\text{O})$ band position to 1,800–1,770 cm^{-1} .

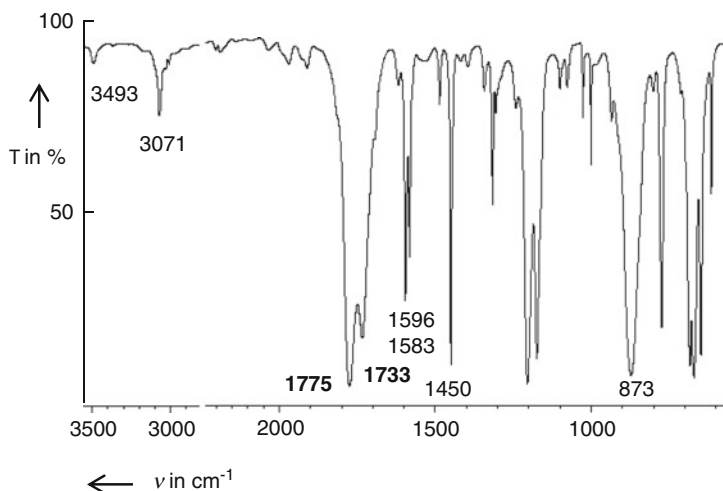
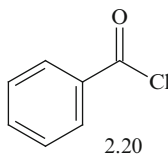


Fig. 2.37 Infrared spectrum of benzoyl chloride (Structure 2.20); sampling technique: capillary thin film using AgCl discs

The (C=O) stretching vibration of *aryl-carboxylic acid chlorides* is split into two absorption bands due to Fermi resonance as discussed in Sect. 2.1.4. This is an evidence to distinguish alkyl and aryl carboxylic acid chlorides. In general, the band at lower wave number has a lower intensity.

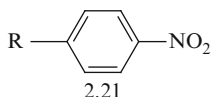
The infrared spectrum of benzoyl chloride (Structure 2.20) is shown in Fig. 2.37. The typical wave numbers for carboxylic acid chlorides are marked in bold.



2.3.8 Interpretation of Vibrational Spectra of N-Containing Compounds

2.3.8.1 NO₂ Compounds

The NO₂ group gives rise to two intense infrared bands that are easy to identify and this is demonstrated in the infrared spectrum of *p*-ethyl nitro benzene (Structure 2.21, R=C₂H₅) shown in Fig. 2.38. The group wave numbers of the NO₂ group are marked in bold in the spectrum.



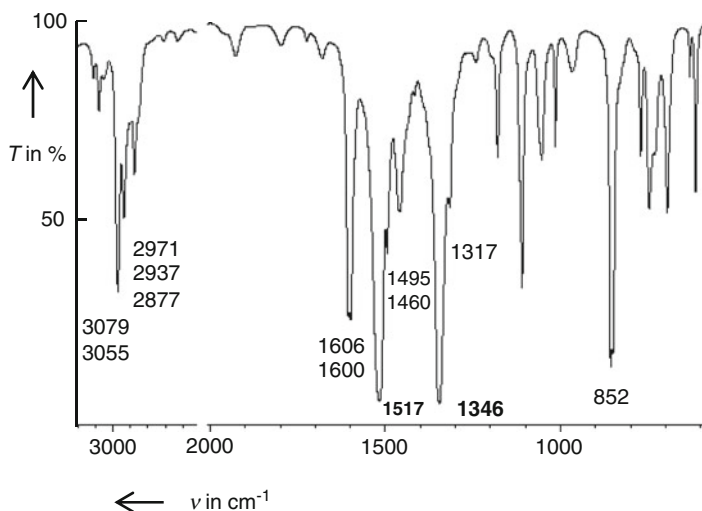


Fig. 2.38 Infrared spectrum of *p*-ethyl nitro benzene (Structure 2.21); sampling technique: capillary thin film

Table 2.21 Group wave numbers of the functional group NO_2 (in cm^{-1})

	$\nu_{\text{as}}(\text{NO}_2)$	$\nu_{\text{s}}(\text{NO}_2)$
Alkyl- NO_2	1,570–1,540 (very intense)	1,390–1,340 (intense)
Aryl- NO_2	1,560–1,500 (very intense)	1,360–1,300 (intense)

The most intense asymmetrical N–O stretching vibration $\nu_{\text{as}}(\text{NO}_2)$ appears at higher wave numbers than the less intense symmetrical one $\nu_{\text{s}}(\text{NO}_2)$. Conjugation in aryl nitro compounds shifts the wave number to somewhat smaller values, see Table 2.21.

Electron donor substituents decrease the group wave numbers and increase their intensity. Thus, $\nu_{\text{as}}(\text{NO}_2)$ and $\nu_{\text{s}}(\text{NO}_2)$ of *p*-nitro aniline (Structure 2.21, $\text{R}=\text{NH}_2$) appear at 1,475 and 1,310 cm^{-1} , respectively as very intense infrared bands.

Coupling between $\delta_{\text{oop}}(\text{NO}_2)$ and $\gamma(\text{C-H})$ of the aromatic group gives rise to new bands which alter the pattern of the infrared bands in the range from 2,000 to 1,650 cm^{-1} . Hence, the pattern cannot be used to recognize the aromatic substitution type.

2.3.8.2 N=O Compounds

Because of similar mass and bond order the N=O stretching vibration should give rise to infrared bands similar to those of the C=O group. Thus, $\nu(\text{N=O})$ is observed

as an intense infrared band at 1,585–1,540 and 1,510–1,490 cm^{-1} for alkyl-N=O and aryl-N=O compounds, respectively.

2.3.8.3 Nitriles

The $\text{C}\equiv\text{N}$ group gives rise to characteristic vibrations in a unique wave number range. The $\text{C}\equiv\text{N}$ stretching vibration is observed from 2,260 to 2,240 cm^{-1} for saturated nitriles and from 2,250 to 2,200 cm^{-1} for aromatic ones, respectively. Thus, the position of $\nu(\text{C}\equiv\text{N})$ enables us to distinguish between saturated and aromatic nitriles.

2.3.9 Interpretation of Vibrational Spectra of S–O-Containing Compounds

2.3.9.1 Structure Types $\text{RR}'\text{S}=\text{O}$, $\text{RO}-(\text{S}=\text{O})-\text{O}-\text{R}'$

Because of the larger mass of S the bands of the $\text{S}=\text{O}$ stretching vibrations are shifted to lower wave numbers compared to the respective $\text{C}=\text{O}$ ones and appear in the range from 1,225 to 980 cm^{-1} as intense infrared bands. For further information, see Sect. XIII in Table 6.15.

2.3.9.2 Structure Types $-\text{SO}_2-$

Like nitro compounds the SO_2 group gives rise to an asymmetric $\nu_{\text{as}}(\text{SO}_2)$ and a symmetric $\nu_{\text{s}}(\text{SO}_2)$ stretching vibration which can be well recognized in the infrared spectrum in the range from 1,420 to 1,000 cm^{-1} because of their high intensity. $\nu_{\text{as}}(\text{SO}_2)$ lies at a higher wave number than $\nu_{\text{s}}(\text{SO}_2)$. Note that the range of the group wave numbers of the SO_2 compounds overlap with those of other functional groups.

Challenge 2.13

Mass and infrared spectra are given for an unknown compound in Figs. 2.39 and 2.40, respectively. Create a proposal for the structure of this compound as far as it is possible. The peaks and wave numbers given in the mass and infrared spectra, respectively have to be assigned.

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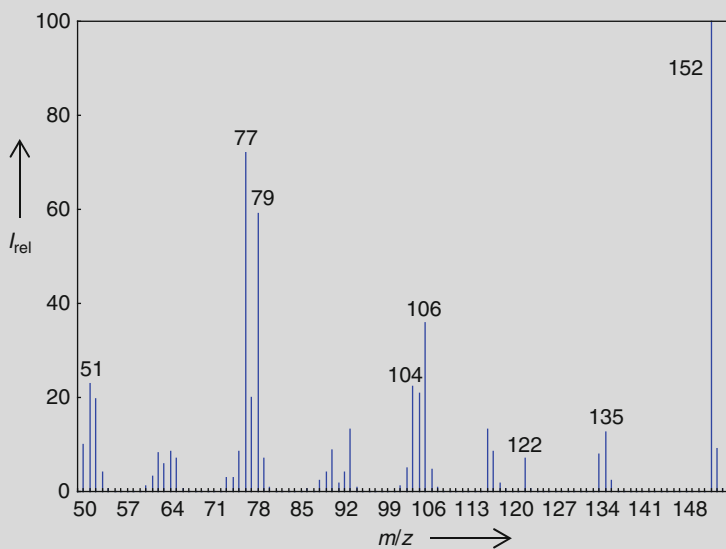


Fig. 2.39 70-eV mass spectrum of an unknown compound. m/z (I_{rel} in %): 152 (100), 153 (8.8)

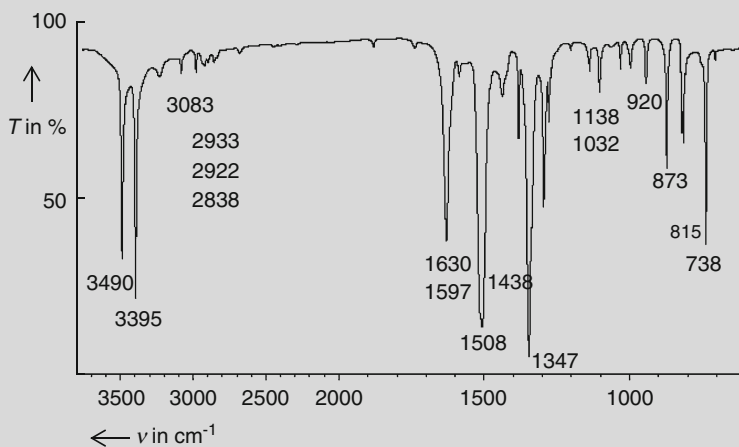


Fig. 2.40 Infrared spectrum of an unknown compound; sampling technique: KBr pellet

Solution to Challenge 2.13**Mass spectrum**

- Derivation of the *sum formula*

The results for the derivation of the sum formula are summarized in Table 2.22.

- Calculation and assignment of the *double bond equivalents* (DBE)

Transformation of the sum formula into C_nH_x according to the rules given in Sect. 1.3:



DBE = 5 calculated by Eq. 1.19.

Assignment: Aryl (4 DBE) + NO₂ (1 DBE),

\Rightarrow No further rings can be present in the molecule.

- Structural moieties determined by mass spectroscopy

Structural moiety/functional group	Recognized by
NO ₂ , NH ₂	Molpeak (N rule), (M – X) fragment peaks
Aromatic compound	DBE, specific fragment peaks: $m/z = 51$, 65, 77 amu
CH ₃	Difference to the sum formula

Table 2.22 Results for the development of the sum formula. The m/z values and differences are given in amu

Number of C and N atoms n_C , n_N				
m/z (I_{rel} in%)	Assignment	Information		
152 (100)	M ⁺⁺	$n_N = 0$ or 2		
153 (8.8)	[M + 1] ⁺⁺	$n_C = 8 \pm 1$		
Evidence of N in the molecule				
Search for N-containing fragment peaks				
m/z (start ion)	m/z (end ion)	Difference	Loss of	Hints for
152	122	30	N=O	Aryl–NO ₂
152	106	46	NO ₂	Aryl–NO ₂
106	79	27	HCN	Aryl–NH ₂ or pyridine
104	77	27	HCN	Aryl–NH ₂ or pyridine
Result	$n_N = 2$			
Search for O-containing fragment peaks				
m/z (start ion)	m/z (end ion)	Difference	Loss of	Hints for
152	136	16	O	Aryl–NO ₂
152	135	17	OH	<i>Ortho</i> -effect?
Development of the sum formula				
Summation of the atoms recognized as yet			8 ± 1 C + 2 N + 2 O	
Proposals	Mass number	Difference to M	n_H	
C ₇ N ₂ O ₂ + H _x	144 + xH	152–144 = 8	8	
C ₈ N ₂ O ₂ + H _y	156	Not possible, because larger than M		
Result	C ₇ H ₈ N ₂ O ₂	OE ⁺⁺ proved according to Eq. 1.11		

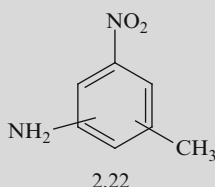
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Table 2.23 The assignment of the infrared bands obtained by the infrared spectrum shown in Fig. 2.40

ν in cm^{-1}	I	Assignment	Hints for structural moieties
3,490	vs	$\nu_{\text{as}}(\text{NH})$	
3,395	vs	$\nu_{\text{s}}(\text{NH})$	1° amine, $\text{R}-\text{NH}_2$
3,180	w	$\text{OT } \delta_{\text{as}}(\text{NH}_2) + \nu(\text{NH})$	Fermi resonance
3,083	w	$\nu(\text{sp}^2\text{CH})$	Benzene ring/alkene
2,933	w	$\nu_{\text{as}}(\text{Aryl}-\text{CH}_3)$	
2,922	w	$\nu_{\text{s}}(\text{Aryl}-\text{CH}_3)$	Aryl-CH₃
2,861	w	$\text{OT } \delta_{\text{as}}(\text{CH}_3) + \nu(\text{CH})$	Fermi resonance
1,950–1,700	vw	$\text{OT} + \text{CV}$	Pattern for 1,2,4-trisubstitution (?)
1,630	s	$\delta(\text{NH}_2)$	1° amine, NH₂
1,597	w	$\nu(\text{C}=\text{C})$ aryl	Aromatic compound
1,508	vs	$\nu_{\text{as}}(\text{NO}_2)$	
1,347	s	$\nu_{\text{s}}(\text{NO}_2)$	Aryl-NO₂
1,438	m	$\delta_{\text{as}}(\text{CH}_3)$	CH₃
1,371	m	$\delta_{\text{s}}(\text{CH}_3)$	
1,032	m	$\nu(\text{C}-\text{N})$?	
873	m	$\delta(\text{NO}_2)$	
920	m	$\gamma(\text{Aryl}-\text{CH})$	Aryl, 1 neighboring H atom?
815	m	$\gamma(\text{Aryl}-\text{CH})$	Aryl, 2 neighboring H atoms?

OT overtone, *CV* combination vibration, *I* estimated intensity

- The compound is a nitro amino toluene (Structure 2.22) whose substitution type is unknown. Remember that, in general, the recognition of aromatic isomers is not the subject of mass spectroscopy.



Infrared spectrum

The assignment of the infrared bands is listed in Table 2.23.

Structural moieties and functional groups determined by infrared spectroscopy:

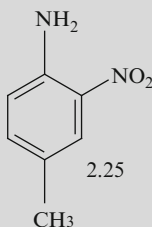
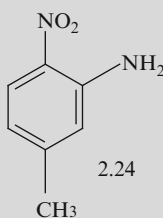
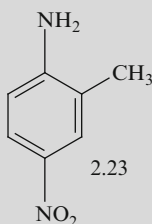
Aryl-NO₂, R-NH₂, Aryl-CH₃, 1,2,4-trisubstituted (?) aromatic compound.

Proposal for structures

The benzene ring must be trisubstituted, the substituents are NO₂, NH₂, and CH₃. *Ortho*-substitution of NO₂ and CH₃ should be excluded because of the missing $[M - 17]$ peak due to the elimination of O-H via the *ortho*-effect in the mass spectrum. Thus, Structures 2.23–2.25 come into consideration. Note that the true structure can only be established by comparison of the

(continued)

infrared spectrum with those of the respective reference spectra. But this is not the subject of this book. With the employment of further methods presented in the next chapters the evidence of the final structure will be adduced.



Challenge 2.14

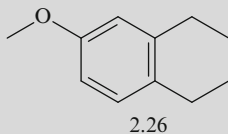
For solutions to Challenge 2.14, see *extras.springer.com*.

1. Assign the given wave numbers in the infrared spectra of Figs. 2.30, 2.31, 2.32, 2.33, 2.34, 2.35, 2.36, 2.37 and 2.38 to the respective vibrations. The wave numbers distinctive for a certain substance class are marked in bold. Assemble certain and uncertain structural moieties.
2. Carbonyl compounds can be easily recognized by the intense infrared band in the range from $1,800$ to $1,650\text{ cm}^{-1}$ but there are many substance classes containing the $\text{C}=\text{O}$ group. Show how the following substance

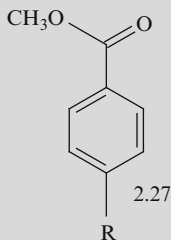
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classes can be evidenced and distinguished from the others by infrared spectroscopy: aldehydes, ketones, carboxylic acids, carboxylic acid esters, amides, and anhydrides.

3. Show how the following structures can be distinguished:
 - (a) Intra- and intermolecular hydrogen bonding
 - (b) *E/Z* isomers for compounds with the general structure $\text{RHC}=\text{CHR}$
 - (c) Substitution types of aromatic compounds
 - (d) Distinction between $\text{aryl}-\text{CH}_2-\text{CHO}$ and $\text{CH}_3-\text{aryl}-\text{CHO}$
 - (e) Distinction between primary and secondary amines
 - (f) Recognition of a tertiary carboxylic acid amide
 - (g) Distinction between $\text{CH}_3-\text{aryl}-\text{CHO}$ and $\text{aryl}-(\text{C}=\text{O})-\text{CH}_3$
 - (h) Distinction between $\text{CH}_3-\text{aryl}-(\text{C}=\text{O})-\text{Cl}$ and $\text{Cl}-\text{CH}_2-\text{aryl}-\text{CHO}$
 - (i) Distinction between $\text{R}-\text{S}-\text{H}$, $\text{R}-\text{S}-\text{R}'$, and $\text{R}-\text{S}-\text{S}-\text{R}'$.
4. The oxidation of 3-methoxy-tetraline (Structure 2.26) gives rise to the main product whose molecular peak is 16 amu greater than that of the starting compound. The infrared spectrum of a solution of the reaction product in CCl_4 shows an intense band at $1,686\text{ cm}^{-1}$. What structures can be assigned to the reaction product and what can be excluded?

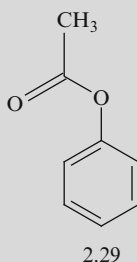
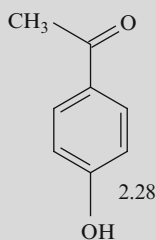


5. The following wave numbers for the $\text{C}=\text{O}$ stretching vibrations are obtained in the infrared spectrum of compounds of the structural type shown in Structure 2.27 with $\text{R} = \text{H}$, OH , $\text{N}(\text{CH}_3)_2$, NO_2 : $1,737$, $1,727$, $1,715$, and $1,685\text{ cm}^{-1}$. Assign the infrared bands to the respective carbonyl compounds and justify your decision.

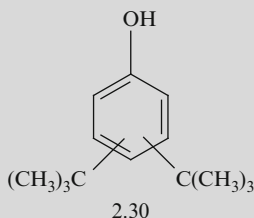


6. An intense absorption band is observed at $1,766\text{ cm}^{-1}$ in the infrared spectrum. Decide whether the infrared spectrum belongs to a compound of Structures 2.28 or 2.29.

(continued)



7. The range of the characteristic C=O stretching vibrations from $1,850$ to $1,650\text{ cm}^{-1}$ is smaller than that observed for the C=S stretching vibration ($1,275\text{--}1,030\text{ cm}^{-1}$). Explain this fact.
8. Figure 2.41 shows the infrared spectrum of a liquid compound. Develop the structure and assign the infrared bands. The molecular peak is $m/z = 128$ amu.
9. Figure 2.42 shows the infrared spectrum of a liquid compound. Develop the structure and assign the infrared bands. The molecular peak is $m/z = 78$ amu.
10. Figure 2.43 shows the infrared spectrum of a solid compound. Derive the structure and assign the infrared bands. The following information is obtained by the mass spectrum given in m/z (I_{rel} in %): 157 amu (40) M^{++} , 158 amu (3.3), 159 amu (2).
11. The infrared spectrum of a di-*tert*-butylphenol (Structure 2.30) is presented in Fig. 2.44. Develop the structure and assign the infrared bands.



(continued)

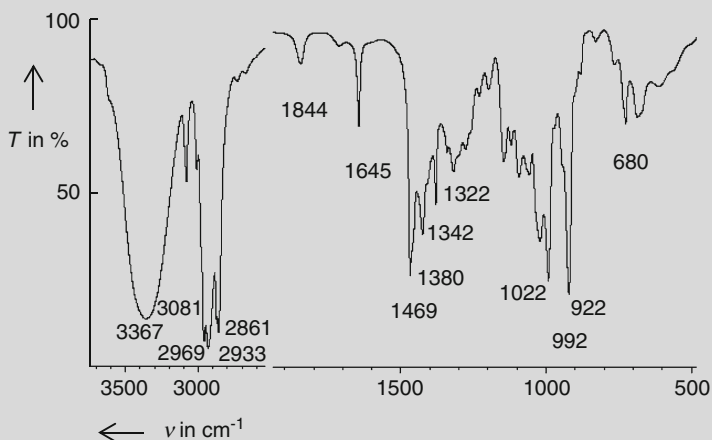


Fig. 2.41 Infrared spectrum of a liquid compound; sampling technique: capillary thin film; MS: $m/z = 128$ amu M^{+}

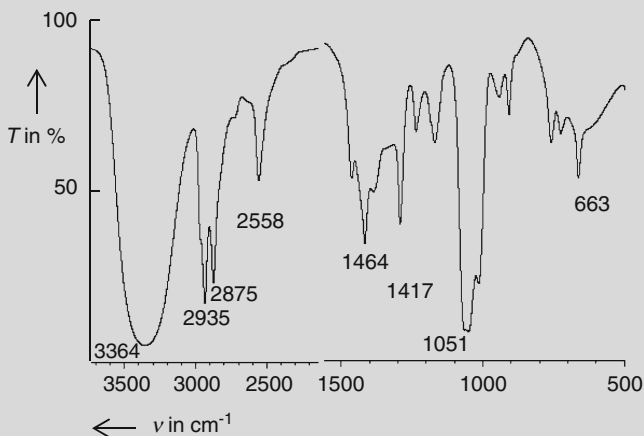


Fig. 2.42 Infrared spectrum of a liquid compound; sampling technique: capillary thin film; MS: $m/z = 78$ amu M^{+}

12. Derive the structure and assign the given wave numbers in the infrared spectrum shown in Fig. 2.44. The CI-mass spectrum (reaction gas: *iso*-butylene) shows an intense peak at $m/z = 85$ amu.
13. Dependent on the solvents the thermic decomposition of phenyl azo cyclo hexene provides the two products whose structure is given in Structure 2.31A, B. The infrared spectra feature the following bands in the range $\nu > 3,000 \text{ cm}^{-1}$:

(continued)

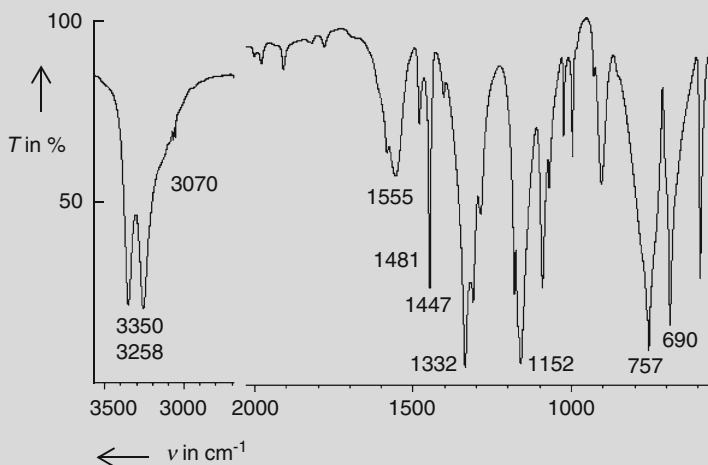


Fig. 2.43 Infrared spectrum of a solid compound; sampling technique: KBr pellet; MS: m/z (I_{rel} in %): 157 amu (40) M^{+} , 158 amu (3.3), 159 amu (2)

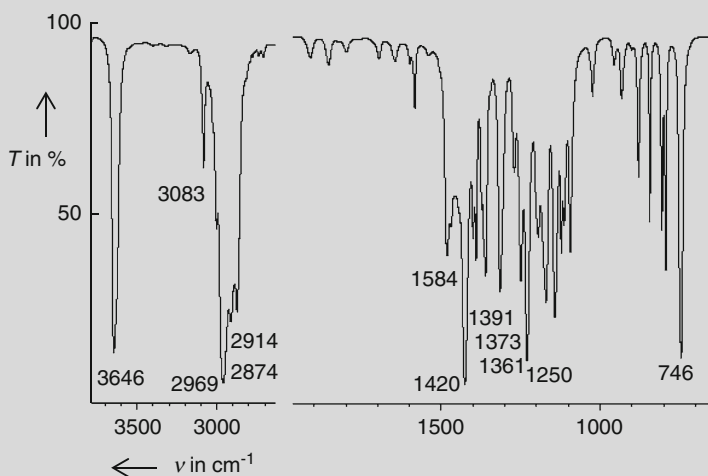


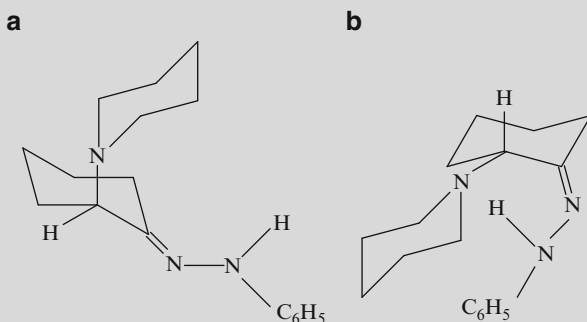
Fig. 2.44 Infrared spectrum of a di-*tert*-butylphenol (Structure 2.30); sampling technique: KBr pellet

Product I: sharp band at $3,360\text{ cm}^{-1}$,

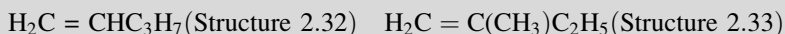
Product II: broad band centered around $3,150\text{ cm}^{-1}$.

What structures have the reaction products?

(continued)



14. Some mass spectrometric data and the infrared spectra of two isomeric liquid compounds are featured in Fig. 2.45a, b. Develop the structures and assign the given wave numbers in the infrared spectra.
15. The following bands listed in arbitrary order are observed in the infrared spectra of four isomeric pentenes possessing the structures



A: 966 (s); **B:** 1,780 (w), 887 (s); **C:** 1,826 (w), 1,643 (m), 993 (s), 912 (s);

D: 1,659 (m), 689 (m).

Which structure belongs to which infrared spectrum? Assign the infrared bands to the respective vibrations.

16. Figure 2.46a, b features the Raman (A) and the infrared spectra (B) of an aromatic C_{14} compound. Develop the structure and assign the given wave numbers in the spectra.
17. Figure 2.47a, b presents the infrared spectra of two C_8 compounds. Derive the structure and assign the given wave numbers in the spectra.
18. Some mass spectrometric data and the infrared spectra of four structurally isomeric compounds are given in Fig. 2.48a–d. Derive the structure, assign the given wave numbers in the spectra and formulate the relevant mass spectrometric fragmentation for each compound.
19. A section of an infrared spectrum in the range $1,800\text{--}1,600\text{ cm}^{-1}$ obtained by a reaction product of succinic acid is shown in Fig. 2.49. Which reaction product was obtained?

(continued)

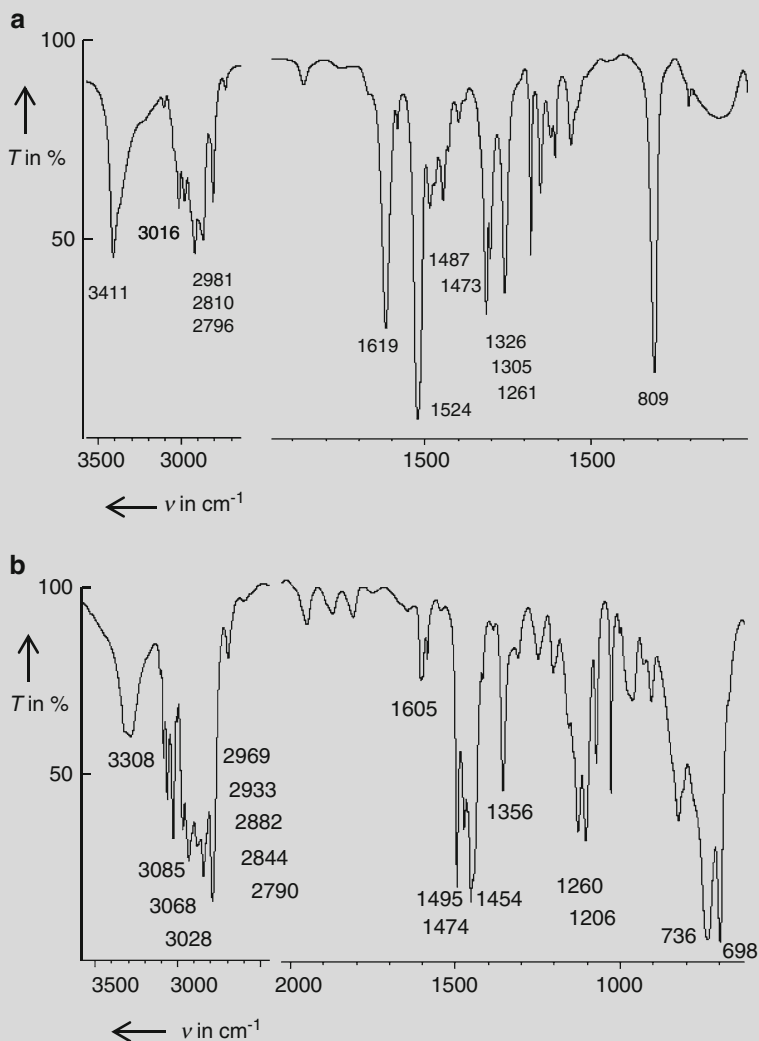


Fig. 2.45 (a, b) Infrared spectra of a two isomeric compounds; sampling technique: capillary thin film **a: h-MS**: $[M]^{+}$: $m/z = 121.0891$ amu; base peak: $m/z = 120$ amu. **b: MS**: Base peak: $m/z = 120$ amu; intense peaks: m/z (I_{rel} in %): 44 (93), 91 (68)

20. In general, the asymmetric C–O stretching vibration is observed at higher wave numbers than the corresponding symmetrical one. This order is reversed in carboxylic anhydrides. How can this fact be confirmed experimentally?

(continued)

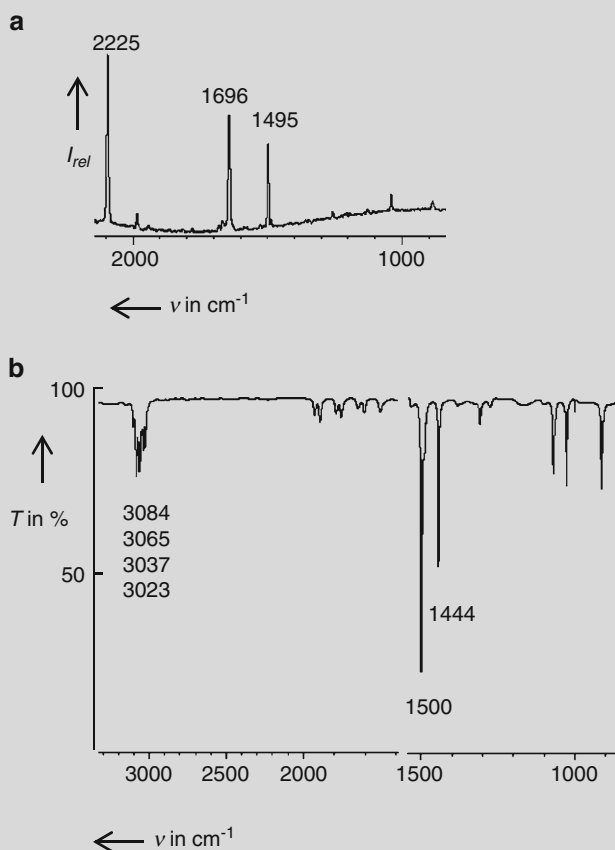


Fig. 2.46 Raman (a) and infrared spectrum (b) of an aromatic C_{14} compound; sampling technique (IR): capillary thin film

21. Figure 2.50a–e feature the infrared spectra of unknown compounds supplemented by some mass spectrometric information. Derive the structure and assign the given wave numbers in the spectra.

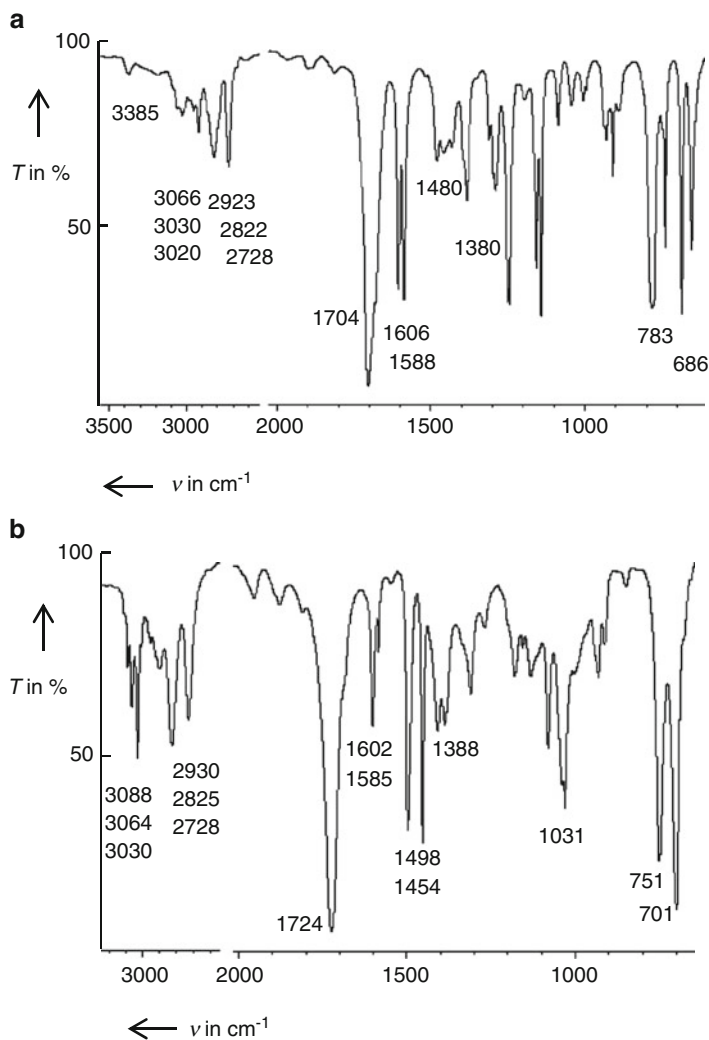


Fig. 2.47 (a, b) Infrared spectra of two C_8 compounds; sampling technique: capillary thin film.
a: MS: intense $[\text{M} - 1]^{*+}$ peak. **b:** MS: Base peak: $m/z = 91$ amu

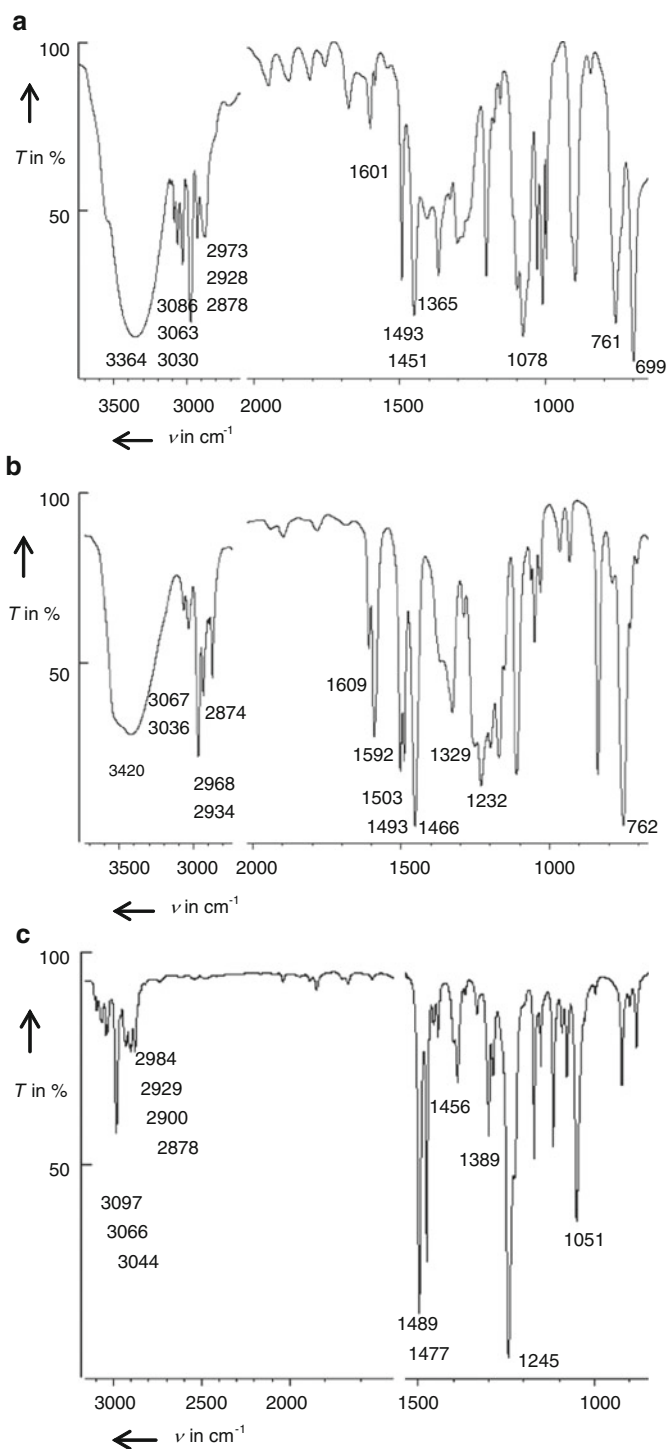


Fig. 2.48 (continued)

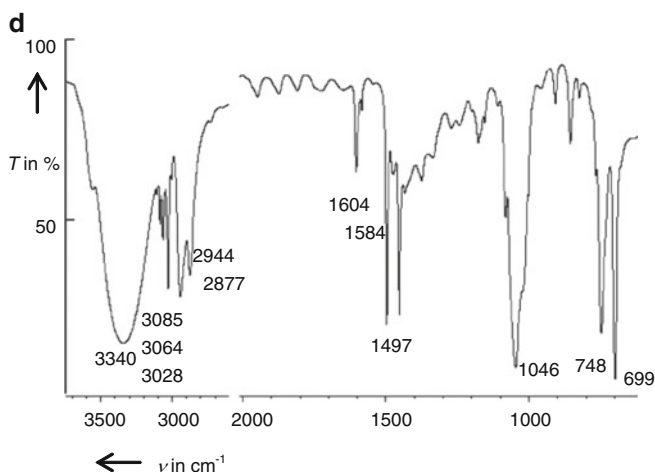


Fig. 2.48 (a–d) Infrared spectra of four structurally isomeric compounds; sampling technique for all samples: capillary thin film. **a: MS:** m/z in amu (I_{rel} in %): 107 (100), 122 M^{++} , intense peaks: 51, 77, 79. **b: MS:** m/z (I_{rel} in %): 107 (100), 122 (40) M^{++} , peaks with $I_{\text{rel}} > 10\%$: 39, 51, 77, 79, 91. **c: MS:** Base peak: $m/z = 94$ amu; peaks with $I_{\text{rel}} > 10\%$: m/z in amu = 39, 51, 65. **d: MS:** Base peak: $m/z = 91$ amu

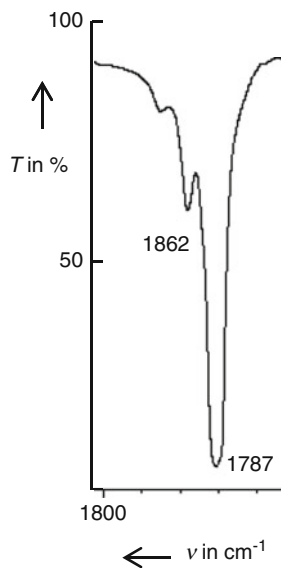


Fig. 2.49 Part of the infrared spectra of a reaction product of succinic acid; sampling technique: solution in carbon tetrachloride

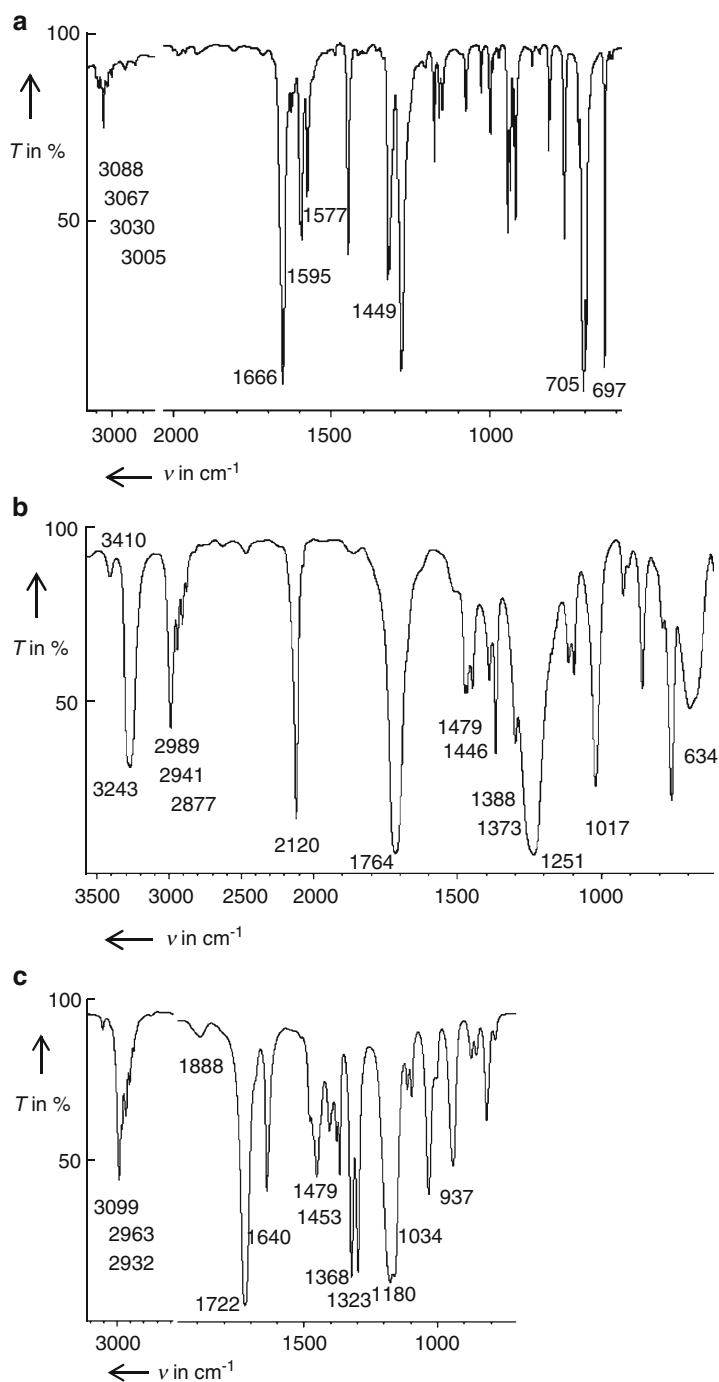


Fig. 2.50 (continued)

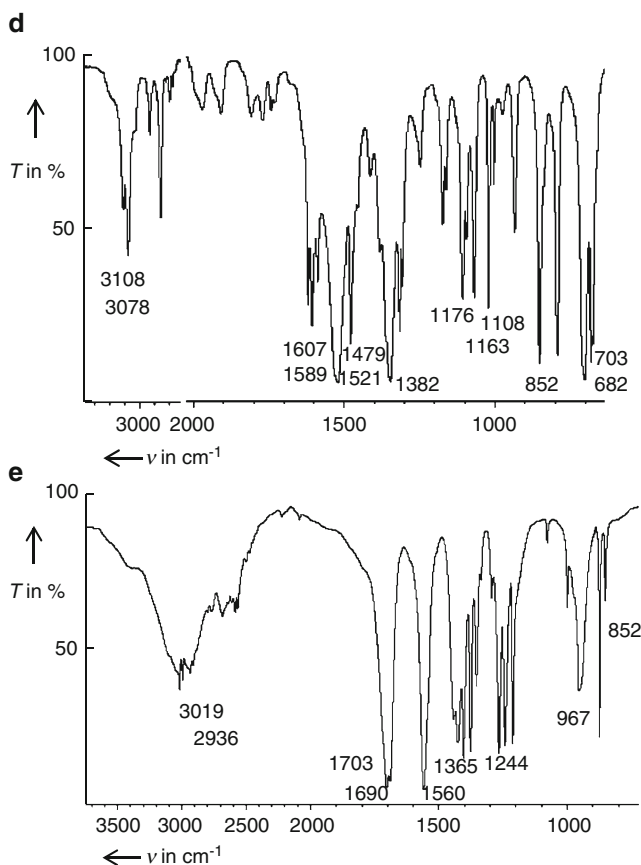


Fig. 2.50 (a–e) Infrared spectra and some mass spectrometric data of unknown compounds. **a:** Sampling technique: KBr pellet, **MS:** m/z in amu (I_{rel} in %): 51 (15), 77 (49), 105 (100), 182 (32) M^+ , 183 (4.2). **b:** Sampling technique: capillary thin film, **MS:** m/z in amu (I_{rel} in %): 53 (100), 97 (4.8), 98 (0.4) M^+ . **c:** Sampling technique: capillary thin film, **MS:** $m/z = 114$ amu $[M-1]^+$; C_6 compound. **d:** Sampling technique: KBr pellet, **MS:** m/z in amu (I_{rel} in %): 123 (85) M^+ , 124 (6). **e:** Sampling technique: KBr pellet, **MS:** m/z in amu (I_{rel} in %): 119 (< 0.1) M^+ , 45 (100), 55 (43), 73 (82)

Further Reading

1. Nakamodo K (1997) Infrared and Raman spectra of inorganic and coordination compounds. Wiley, New York
2. Smith B (1999) Infrared spectral interpretation. CRC Press, Boca Raton
3. Long DL (2001) The Raman effect. Wiley, New York
4. Colthup ND, Daly LH, Wiberley SE (1990) Introduction to infrared and Raman spectroscopy. Academic, New York

Challenges in Molecular Structure Determination

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