Spectra–Structure Correlations in the Mid- and Far-infrared

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1 INTRODUCTION AND GROUP FREQUENCIES

1.1 Introduction

An infrared (IR) spectrum provides a rapid and simple method for obtaining preliminary information on the identity or structure of a molecule. The spectrum is a plot of the amount of IR radiation that passes through the sample (transmittance T) versus the wavelength, λ (or wavenumber, ν) of the radiation. An example is shown in Figure 1. The sample absorbs IR radiation at various wavelengths (or wavenumbers) and the positions of the absorptions give clues to the structure of the molecule, as indicated in Figure 1. The spectra may also be exhibited in absorbance ($A = \log_{10} 1/T$) versus wavenumber units. Absorption maxima (or transmission minima) are referred to as peaks, bands, or absorptions. The wavenumber (cm^{-1}) is the reciprocal of the wavelength (cm) of the IR radiation. This unit is also a frequency (s^{-1}) divided by the velocity of light, c (cm s^{-1}). Vibrational spectroscopists often use the word frequency instead of wavenumber (with the division by c assumed). This is logical, because the frequency of an IR absorption is numerically the same as the frequency of a molecular vibration.

IR spectra are usually obtained using Fourier transform infrared (FT-IR) spectrometers. Earlier spectra were obtained using dispersive IR spectrometers and the early literature and spectral libraries are based on spectra recorded on these instruments. Instrumentation and sample preparation techniques for transmission IR and other techniques for obtaining IR spectra such as reflection, attenuated total reflection (ATR) and IR microscopy are presented elsewhere in this Handbook.

Information on the structure of a molecule is obtained from a detailed study of those bands in the spectrum that are characteristic of certain functional groups. Some of these bands are indicated in Figure 1. The IR spectrum also can be used as a *fingerprint* for molecule identification. A computer can be used to search a database of spectra digitally to find a number of spectra that most closely match that of the "unknown". The final identification is then made by visual comparison with spectra in a collection of spectra such as the Aldrich Library of FT-IR Spectra.

Characteristic group frequencies and the various factors that affect their location in the IR spectrum are discussed in detail in this section. How spectra-structure correlations

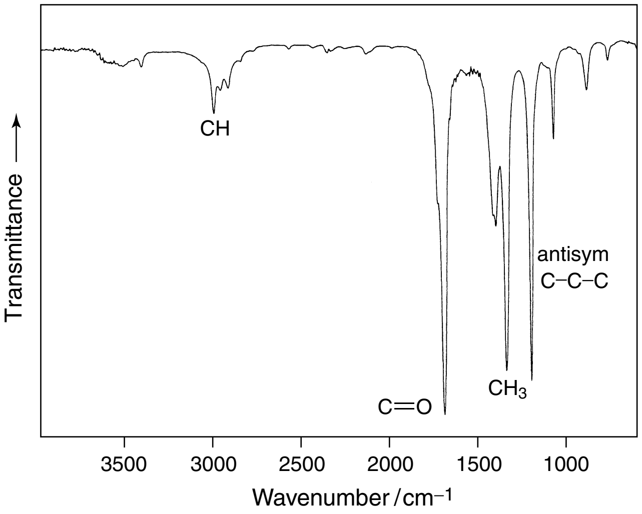

Figure 1. The IR spectrum of acetone.

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may be used to identify a compound is the subject of Section 2.

The material for these sections is based on Chapters 7, 8 and 9 of 'Organic Structural Spectroscopy'.[1]

1.2 Vibrations of molecules

IR spectroscopy gives information on molecular structure through the frequencies of the normal modes of vibration of the molecule. A normal mode is one in which each atom executes a simple harmonic oscillation about its equilibrium position. All atoms move in phase with the same frequency, while the center of gravity of the molecule does not move. There are $3N - 6$ normal modes of vibration (known as fundamentals) of a molecule ($3N - 5$ for linear molecules), where N is the number of atoms. For a molecule with no symmetry, all $3N - 6$ fundamental modes are *active* in the IR and may give rise to absorptions. There is also the possibility of overtones and combinations of the fundamentals, some of which may absorb (usually weakly) and thereby increase the total number of peaks in the IR spectrum.

Vibrations of certain functional groups such as OH, NH, CH_3, C=O, C_6H_5, and so on always give rise to bands in the IR spectrum within well-defined frequency ranges regardless of the molecule containing the functional group. The exact position of the group frequency within the range gives further information on the environment of the functional group. As an example, we might take the carbonyl stretching band ($\nu_{C=O}$) of simple aliphatic aldehydes or ketones as the standard ($1730\,cm^{-1}$). Acid chlorides, carboxylic acid (monomers) and esters have their ($\nu_{C=O}$) bands at higher frequencies, while amides and aromatic ketones have lower C=O stretching frequencies. This is illustrated in Figure 2.

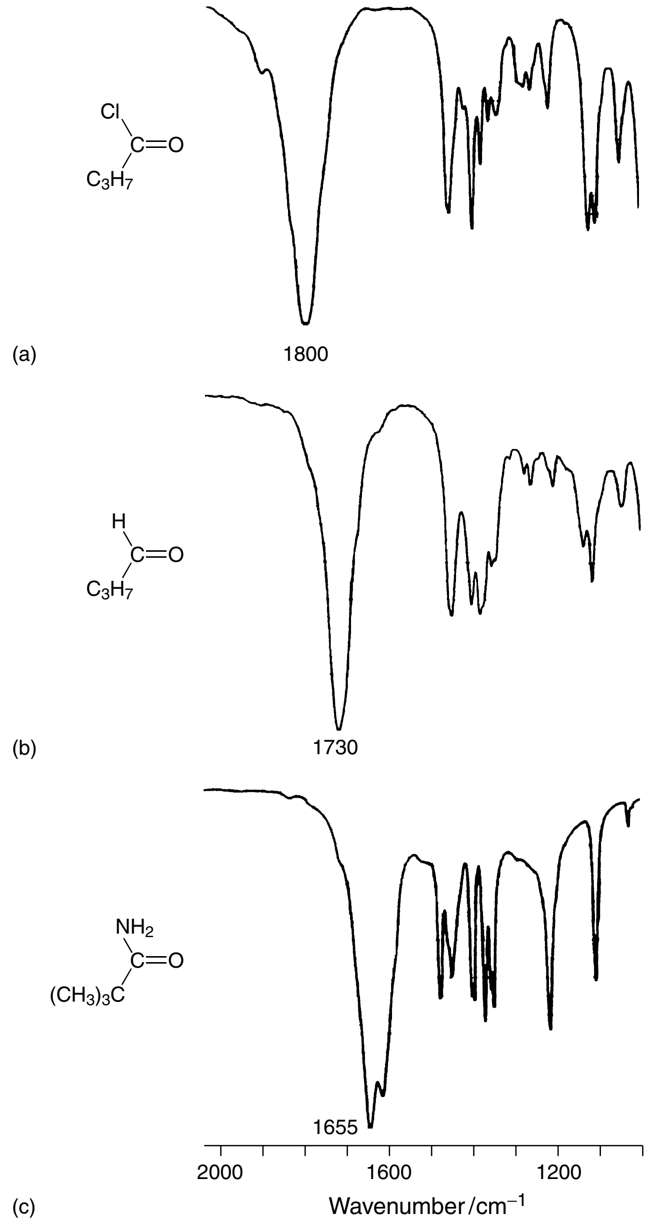

Figure 2. The carbonyl stretching bands of (a) an acid chloride, (b) an aldehyde and (c) an amide. (Reproduced by permission from Sigma-Aldrich Co.)

The observation of a band in the spectrum within an appropriate frequency range can indicate the presence of one or more different functional groups in the molecule, because there is considerable overlap of the ranges of many functional groups. It is therefore necessary to examine other regions of the spectrum for confirmation of a particular group. Examples of this procedure are given in Section 2.

Comparison of the spectrum of an unknown material with a reference spectrum, or with the spectrum of a known compound, can provide absolute proof of the identity of the unknown substance.

1.3 The far-infrared

The spectral region called the far-infrared is not very well defined. For the present purposes the mid-infrared range will be assumed to be $4000-400\,cm^{-1}$. With the use of special beam-splitters, detectors and window materials, some IR spectrometers can be configured to cover a wider range, which extends below $400\,cm^{-1}$. The region below $400\,cm^{-1}$ down to $10\,cm^{-1}$ is defined as the far-infrared. The region below $200\,cm^{-1}$ is not readily accessible and there are not many useful spectra-structure correlations in this region. However, compounds containing halogen atoms, organometallic compounds and inorganic compounds absorb in the far-infrared and torsional vibrations and hydrogen bond stretching modes are found in this region. The far-infrared also is important for studies of external (lattice) modes of crystalline solids.

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A useful discussion of some spectra-structure correlations in the far-infrared is given by Stewart.[2]

1.4 Introduction to group frequencies

IR spectra of a large number of compounds containing a particular functional group such as carbonyl, amino, phenyl, nitro, and so on are found to have certain features that appear at more or less the same frequency for every compound containing the group. It is reasonable, then, to associate these spectral features with the functional group, provided a sufficiently large number of different compounds containing the group have been studied. For example, the IR spectrum of any compound that contains a C=O group has a strong band between 1800 and 1650 $\mathrm{cm^{-1}}$. Compounds containing –NH_2 groups have two IR bands between 3400 and 3300 $\mathrm{cm^{-1}}$. The spectrum of a compound containing the C_6H_5– group has sharp peaks near 1600 and 1500 $\mathrm{cm^{-1}}$ due to stretching modes of the benzene ring. These are just three examples of the many characteristic frequencies of chemical groups observed in IR spectra.

A simple calculation can give an idea of where to expect a band due to stretching of a bond between a pair of atoms in a molecule. The stretching frequency ($\mathrm{cm^{-1}}$) of such a diatomic group may be calculated using equation (1):

$$\nu(\mathrm{cm^{-1}}) = 130.3\frac{\sqrt{k}}{\mu} \tag{1}$$

where k is the force constant ($\mathrm{N\,m^{-1}}$) and μ is the reduced mass, $m_1m_2/(m_1+m_2)$ in atomic mass units (amu). The numerical constant $130.3 = 1/2c\pi\sqrt{N} \times 10^{-1}$ (N is Avogadro's number, 6.022×10^{23}, and c is the velocity of light, $2.998 \times 10^{8}\ \mathrm{m\ s^{-1}}$).

This simple approach gives surprisingly good results when one of the atoms of the pair is a light atom, not bonded to any other atom, for example, C–H and N–H in CH_3NH_2 or C–H and C=O in $(CH_3)_2CO$. The stretching frequencies ($\mathrm{cm^{-1}}$) of these and other diatomic groups, including C≡C and C=C can be calculated from equation (1). A band characteristic of the group will be observed in the IR spectrum in the predicted region, provided the vibrational frequency of the group is not close to that of another group in the molecule. Calculated frequencies for some diatomic groups are given in Table 1. These are all examples of characteristic group frequencies and can be used to establish the presence of the functional group in the molecule. The explanation of these characteristic diatomic group frequencies lies in the approximately constant values of the stretching force constant of a bond in different molecules.

Table 1. Calculated frequencies of some diatomic groups.

Group	Reduced mass (amu)	Force constant ($\mathrm{N\ m^{-1}}$)	Frequency ($\mathrm{cm^{-1}}$)
O–H	0.94	700	3600
N–H	0.93	600	3300
C–H	0.92	500	3000
C–C	6.00	425	1100
C=C	6.00	960	1650
C=O	6.86	1200	1725
C≡C	6.00	1600	2100
C≡N	6.46	2100	2350

It can be seen from Table 1 that the values of the force constants of double and triple bonds are approximately twice and three times those of single bonds, respectively. Carbon–carbon single bonds are included in Table 1, but C–C stretching does not usually give a well-defined group frequency. Most organic molecules contain several C–C single bonds and other groups that have similar vibrational frequencies to that of the C–C stretching mode. These vibrations interact with each other, and the simple model does not apply. Vibrational interactions can take several forms and are discussed later in this section.

When two or more identical groups are present in a molecule, one might expect to observe two or more bands in the IR spectrum at similar wavenumbers. However, if the groups are attached to the same carbon atom, or to two adjacent atoms, the observed bands may be spread over a few hundred wavenumbers by interactions between the vibrations of the groups. The four CH groups in ethylene (C_2H_4) provide an example of this behavior. The four observed CH stretching frequencies are 3270, 3105, 3020, and 2990 $\mathrm{cm^{-1}}$.

Polyatomic groups also have characteristic frequencies, which involve both stretching and bending vibrations or combinations of these. No simple equation like equation (1) can be found to calculate the bending frequencies of polyatomic groups, and the best way to establish whether or not a particular group such as –CH_2, –CH_3, –NH_2, or –C_6H_5 has characteristic bending in addition to stretching frequencies is to examine the vibrational spectra of a large number of compounds containing these groups.

1.5 Factors affecting group frequencies

1.5.1 Symmetry

The vast majority of organic molecules have little or no symmetry. Nevertheless, some knowledge of symmetry can be of considerable help in understanding the factors that affect intensities of group frequencies.

Occasionally, a group frequency is not observed in the IR spectrum. This is usually a consequence of symmetry. If a molecule possesses a center of symmetry, all vibrations

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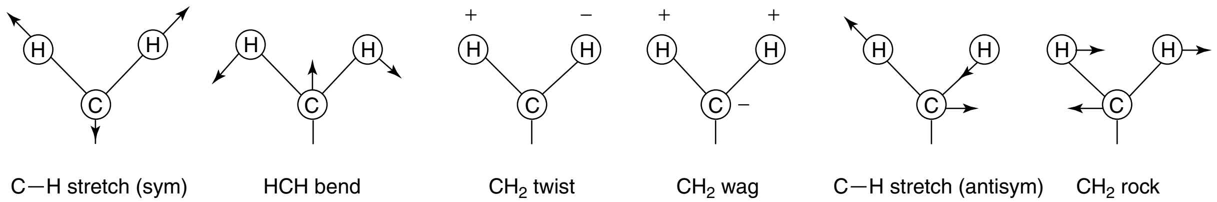

Figure 3. CH_2 group vibrations. The arrows show the direction of motion of atoms in the plane of the CH_2 group. The + and − signs denote motion above and below the plane, respectively.

that are symmetric with respect to that center are *inactive* in the IR, because they do not produce a change in the dipole moment. An example of the effect of a center of symmetry is given by the C≡C stretching mode. In methylacetylene ($CH_3C{\equiv}CH$) the vibration is IR active, and a strong IR band is observed at $2150\,cm^{-1}$. On the other hand, in dimethylacetylene ($CH_3C{\equiv}CCH_3$), which has a center of symmetry, no band is observed in the IR near $2150\,cm^{-1}$.

In larger, more complicated molecules, a local symmetry may exist for a homonuclear diatomic group such as C=C or S–S, so that the IR absorption from the group vibration may be weak or absent.

Molecules of high symmetry have simple IR spectra. As an example consider the benzene molecule. It has 12 atoms and therefore has $3N - 6 = 30$ normal modes of vibration. The first effect of the high symmetry is to make 10 pairs of these vibrations have identical frequencies (degenerate modes). This leaves 20 different normal frequencies. The second effect of the high symmetry is to reduce the number of modes for which there is a change in dipole moment (*IR active*). In fact, the IR spectrum of benzene contains only four bands due to fundamentals. When the symmetry of benzene is reduced, as in 1,3,5-trichlorobenzene, the number of IR active modes increases, but there are still some degenerate modes and the spectra are relatively simple. When the symmetry is completely removed, as in 1-chloro-2-bromobenzene, all 30 normal modes are active. However, because of the residual symmetry of the benzene ring, some of these vibrations, although allowed, appear only very weakly and are hard to distinguish from the weak bands that are due to overtones and combinations.

Vibrations of the methyl group (–CH_3) in an unsymmetrical molecule can be described in terms of the local symmetry of the free group, which has a threefold axis and three planes of symmetry. A free methyl group would have $3N - 6 = 6$ normal modes of vibration comprising symmetric and degenerate antisymmetric (with respect to the threefold axis) stretching and bending modes. When the methyl group is attached to a molecule, three new modes appear, a torsional mode and a degenerate pair of rocking vibrations. These motions would be rotations in the free methyl group. Thus, there are four regions of the spectrum where we expect to find group vibrations of the methyl group. This conclusion is amply supported experimentally. The presence of the methyl group also contributes three skeletal modes to the vibrations of the molecule. These correspond to translations of the free methyl group.

When the methyl group is part of a molecule with lower symmetry, the degeneracies are removed, leading to the observation of doublets in some of the regions of the spectrum where the methyl group frequencies are expected. The torsional mode is actually inactive in the IR, because it produces no change in dipole moment. However, it may be allowed by the low symmetry of the whole molecule and, in fact, methyl torsions are sometimes observed as weak bands in the far-infrared.

The vibrations of a methylene group (CH_2) can also be described in terms of the local symmetry of the group, which has a twofold axis and two planes of symmetry. Figure 3 shows the vibrations associated with a CH_2 group, when it is attached to a molecule. The free CH_2 group would have three modes, symmetric and antisymmetric (with respect to the twofold axis) stretching and the bending (scissors) vibration. When the group is part of a larger molecule, three additional modes described as twisting, wagging and rocking are produced. Of these, the twisting mode produces no change in dipole moment and hence is not allowed in the IR. However, it can give rise to a very weak band in the spectrum of an unsymmetrical molecule.

The terms twofold and threefold axis, plane of symmetry, and center of symmetry are examples of symmetry elements. The collection of all symmetry elements that a molecule possesses is known as a point group and provides a way of classifying the symmetry of the molecule. This, in turn, leads to an understanding of the symmetry of the normal vibrations of a molecule and to a prediction of the number of frequencies expected in the IR spectrum.

1.5.2 Mechanical coupling of vibrations

Two completely free identical diatomic molecules will, of course, vibrate with identical frequencies. When the two diatomic groups are part of a molecule, however, they can no longer vibrate independently of each other because the vibration of one group causes displacements of the other atoms in the molecule. These displacements

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are transmitted through the molecule and interact with the vibration of the second group. The resulting vibrations appear as in-phase and out-of-phase combinations of the two diatomic vibrations. When the groups are widely separated in the molecule, the coupling is very small and the two frequencies may not be resolved.

Consider the two C–H stretching modes in acetylene (H–C≡C–H). These occur at $3375\,\mathrm{cm}^{-1}$ (in-phase) and $3280\,\mathrm{cm}^{-1}$ (out-of-phase). In diacetylene (H–C≡C–C≡C–H), the two C–H stretching vibrations have closer frequencies, near 3330 and $3295\,\mathrm{cm}^{-1}$. The vibrations of two different diatomic groups are not coupled unless the uncoupled frequencies are similar as the result of a combination of mass and force constant effects. For example, in thioamides and xanthates, the C=S group has a force constant of about $650\,\mathrm{N\,m}^{-1}$ and the reduced mass is 8.72 amu, so that the vibrational frequency calculated from equation (1) is approximately $1120\,\mathrm{cm}^{-1}$. The C–N and C–O groups have force constants of about 480 and $510\,\mathrm{N\ m}^{-1}$, respectively, and the reduced masses are 6.46 and 6.86 amu. The calculated frequencies are both approximately $1120\,\mathrm{cm}^{-1}$. Consequently, in any compound containing a C=S group adjacent to a C–O or C–N group, there may be an interaction between the stretching vibrations of the groups. In compounds such as thioamides and xanthates, where the carbon atom is common to both groups, the coupling is large and the two vibrations interact with each other to produce two new frequencies, neither of which is in the expected region of the spectrum.

The way in which such mechanical coupling occurs can be illustrated for the case of two C=C groups coupled through a common atom, as in the allene molecule, CH_2=C=CH_2. In the absence of strong coupling one might expect to observe a band in the IR spectrum near $1600\,\mathrm{cm}^{-1}$ due to the antisymmetric (out-of-phase) combination of the vibrations of the two C=C groups. For the 1,3-butadiene molecule (CH_2=CH–CH=CH_2), this vibration gives rise to a band at $1640\,\mathrm{cm}^{-1}$. However, for allene the observed frequency is near $1960\,\mathrm{cm}^{-1}$. This result can be understood in terms of mechanical coupling of the two C=C group vibrations. When such coupling occurs, it is usually found that the antisymmetric (out-of-phase) vibration occurs at a higher frequency and is IR *active*, while the symmetric (in-phase) vibration occurs at lower frequency and is IR *inactive*.

It is possible for coupling to occur between dissimilar modes such as stretching and bending vibrations, when the frequencies of the vibrations are similar and the two groups involved are adjacent in the molecule. An example is found in secondary amides, in which the C–N stretching vibration is of a similar frequency to that of the NH bending mode. Interaction of these two vibrations gives rise to two bands in the spectrum, one at a higher and one at a lower frequency than the uncoupled frequencies. These bands are known as *amide II* and *amide III* bands. (The C=O stretching mode is known as the *amide I* band.)

Singly bonded carbon atom chains are, of course, not linear, so that the simple model used for the allene molecule would have to be modified. In addition, we were able to ignore the bending of the C=C=C group in allene, which cannot couple with the stretching modes, because it takes place at right angles to the stretching vibrations. Mechanical coupling will always occur between C–C single bonds in an organic molecule, so that there is no simple C–C group stretching frequency. One can expect that there will always be several bands in the IR spectra in the $1200-800\,\mathrm{cm}^{-1}$ range in compounds containing saturated carbon chains.

1.5.3 Fermi resonance

A special case of mechanical coupling, known as Fermi resonance, often occurs. This phenomenon, which results from coupling of a fundamental vibration with an overtone or combination, can shift group frequencies and introduce extra bands. For a polyatomic molecule there are $3N-6$ energy levels for which only one vibrational quantum number (v_1) is 1 when all the rest are zero. These are called the fundamental levels and a transition from the ground state to one of these levels is known as a *fundamental*. In addition, there are the levels for which one v_1 is 2, 3, and so on (overtones) or for which more than one v_1 is nonzero (combinations). There are therefore a very large number of vibrational energy levels, and it quite often happens that the energy of an overtone or combination level is very close to that of a fundamental. This situation is termed accidental degeneracy, and an interaction known as Fermi resonance can occur between these levels provided that the symmetries of the levels are the same. Since most organic molecules have no symmetry, all levels have the same symmetry and Fermi resonance effects occur frequently in vibrational spectra.

Normally, an overtone or combination band is very weak in comparison with a fundamental, because these transitions are not "*allowed*". However, when Fermi resonance occurs there is a sharing of intensity and the overtone can be quite strong. The result is the same as that produced by two identical groups in the molecule. As an example, two peaks are observed in the carbonyl stretching band of benzoyl chloride, near 1760 and $1720\,\mathrm{cm}^{-1}$ (Figure 4). If this were an unknown compound, one might be tempted to suggest that there were two nonadjacent carbonyl groups in the molecule. However, the lower frequency band is due to the overtone of the CH out-of-plane bending mode at $865\,\mathrm{cm}^{-1}$ in Fermi resonance with the C=O stretching fundamental.

Numerous other well-characterized examples of Fermi resonance are known. The N–H stretching mode of the

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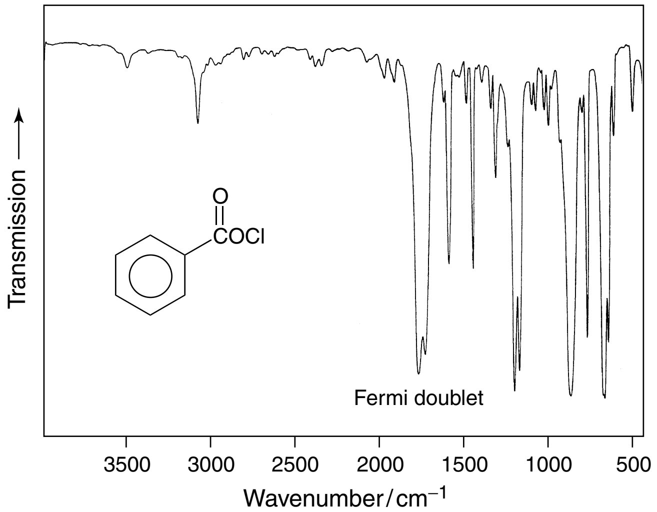

Figure 4. The IR spectrum of benzoyl chloride showing the Fermi doublet at 1760 cm^{-1} and 1720 cm^{-1}.

–CO–NH– group in polyamides (nylons), peptides, proteins, appears as two bands near 3300 and 3205 cm^{-1}. The N–H stretching fundamental and the overtone of the N–H deformation mode near 1550 cm^{-1} combine through Fermi resonance to produce the two observed bands. The CH stretching region of the –CHO group in aldehydes provides another example of Fermi resonance. Two bands are often observed near 2900 and 2700 cm^{-1} in the IR spectra of aldehydes. This doublet is attributed to Fermi resonance between the overtone of the C–H deformation mode, which occurs near 1400 cm^{-1}, and the C–H stretching mode, which would also occur near 2800 cm^{-1} in the absence of Fermi resonance.

In many molecules, mechanical coupling of the group vibrations is so widespread that there are few, if any, frequencies that can be assigned to functional groups. Many such examples are found in aliphatic fluorine compounds, in which the CF and CC stretching modes are coupled with each other and with FCF and CCF bending vibrations. The presence of fluorine can be deduced from several very strong IR bands in the region between 1400 and 900 cm^{-1}.

1.5.4 Chemical and environmental effects

Hydrogen bonding, electronic and steric effects, physical state, and solvent and temperature effects all contribute to the position, intensity, and appearance of the bands in the IR spectrum of a compound. Lowering the temperature usually makes the bands sharper and shifts them to higher frequencies. There is also a possibility of splittings arising due to crystal effects, which must be considered when examining the spectra of solids under moderately high resolution. Polar solvents can cause significant shifts of group frequencies through solvent–solute interactions, such as molecular association through hydrogen bonding.

1.5.5 Hydrogen bonding

Hydrogen bonding (written X–H$\cdots$Y) occurs between the hydrogen atom of a donor X–H group such as OH or NH and an acceptor atom Y which is usually O or N. The main effects are broadening of bands in the IR spectra and shifts of group frequencies. X–H stretching frequencies are lowered by hydrogen bonding, and X–H bending frequencies are raised. Hydrogen bonding also affects the frequencies of the acceptor group, but the shifts are less than those of the X–H group. Inert solvents can reduce the extent of hydrogen bonding and even eliminate the effect in very dilute solutions.

A very broad band centered near 3100 cm^{-1} in the spectrum of pure carboxylic acids is due mainly to OH stretching of hydrogen-bonded carboxylic acid polymers. In the solution spectra of these compounds the bands are sharper. However, hydrogen-bonding persists even in dilute solution and the carboxylic acid is present mainly as a cyclic dimer. Hydrogen bonding manifests itself in very broad OH and NH stretching bands at frequencies considerably lower than normal. Changes in the intensity of these bands can be brought about by changes in temperature and concentration.

Stretching of the hydrogen bond itself (XH$\cdots$Y) has been observed in the far IR in many cases between 200 and 50 cm^{-1}, and bending of the hydrogen bond occurs at very low frequencies, usually below 50 cm^{-1}.

Intramolecular hydrogen bonding can occur between OH groups in alcohols or phenols and halogen atoms. In 2-chloroethanol, for example, an intramolecular hydrogen bond stabilizes the gauche rotational isomer. The free ν_{OH} in the trans conformation absorbs at 3623 cm^{-1}, whereas for the hydrogen-bonded isomer the frequency is 3597 cm^{-1}. Halophenols also show two ν_{OH} bands separated by 50–100 cm^{-1} due to bonded and nonbonded conformations. IR spectra also indicate that intermolecular OH$\cdots$halogen bonding occurs between alkyl halides and phenols or alcohols.

1.5.6 Steric effects

Ring strain increases the frequency of the carbonyl stretching frequency in alicylic ketones. For cyclohexanone, cyclopentanone, and cyclobutanone, the observed carbonyl stretching frequencies are 1714, 1746, and 1783 cm^{-1}, respectively. This increase in frequency with increasing angle strain is generally observed for double bonds directly attached (exocyclic) to rings. Similar frequency changes are observed in the series of compounds, methylenecyclohexane, methylenecyclopentane, and methylenecyclobutane, in which a C=CH$_2$ group replaces the C=O group in the ring. The observed C=C stretching frequencies are 1649, 1656, and 1677 cm^{-1}, respectively.

When the double bond is a part of the ring, a decrease in the ring angle causes a lowering of the C=C stretching frequency. The observed frequencies for cyclohexene, cyclopentene, and cyclobutene are 1650, 1615, and 1565 cm^{-1}, respectively.

1.5.7 Electronic effects

Effects arising from the change in the distribution of electrons in a molecule produced by a substituent atom or group can often be detected in the vibrational spectrum. There are several mechanisms such as inductive and resonance effects, which can be used to explain observed shifts and intensity changes in a qualitative way. These effects involve changes in electron distribution in a molecule and cause changes in the force constants that are, in turn, responsible for changes in group frequencies. Inductive and resonance effects have been used successfully to explain the shifts observed in C=O stretching frequencies produced by various substituent groups in compounds such as acid chlorides and amides. High C=O stretching frequencies are usually attributed to inductive effects and low frequencies arise when delocalized structures are possible. For example, in acid chlorides the C=O frequency is near 1800 cm^{-1}, which is high compared with a normal C=O frequency such as that observed for aldehydes or ketones (near 1730 cm^{-1}). On the other hand, in amides the carbonyl frequency is lower (near 1650 cm^{-1}). In acid chlorides the electronegative chlorine atom adjacent to the carbonyl group causes the increase in frequency, whereas in amides the delocalized electronic structure lowers the C=O stretching frequency.

Conjugation of double bonds tends to lower the double bond character and increase the bond order of the intervening single bond. For compounds in which a carbonyl group can be conjugated with an ethylenic double bond, the C=O stretching frequency is lowered by 20–30 cm^{-1}.

1.5.8 Structural isomerism

Structural (constitutional) isomers often differ in the functional groups present, and their vibrational spectra then differ considerably. Some examples are the α-amino acid alanine, the ester ethyl carbamate (urethane), and the nitro compound 1-nitropropane. All three compounds have the empirical formula $C_3H_7O_2N$. IR spectra of these three compounds are shown in Figure 5.

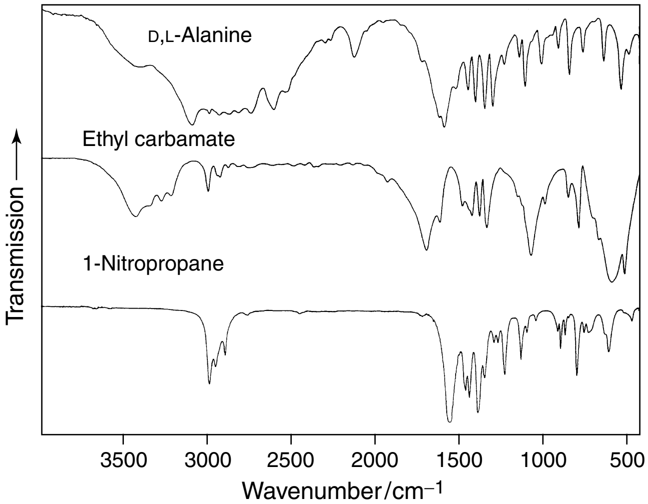

Figure 5. IR spectra of three compounds with the empirical formula $C_3H_7O_2N$.

A good example of the importance of vibrational spectra in differentiating between structural isomers is found in *ortho*-, *meta*-, and *para*-disubstituted benzenes. The CH out-of-plane deformation patterns in the 850–700 cm^{-1} region are different for each isomer. Substituted pyridines, pyrimidines, and other heterocyclic compounds provide further examples of structural isomers that can be distinguished by their vibrational spectra.

*1.5.9 Geometrical (*cis–trans*) isomerism*

IR spectroscopy is useful in distinguishing between cis and trans isomers. Absorption of IR radiation by a molecule can only occur if there is a change of dipole moment accompanying a vibration. For cis isomers a dipole moment change occurs for most of the normal vibrations. However, trans isomers usually have higher symmetry, which leads to a zero or very small dipole moment change for some vibrations, so that they are not observed in the IR spectrum. Thus, we can conclude that trans compounds often have simpler IR spectra than their cis isomers.

1.5.10 Rotational isomerism

In open chain compounds, the barriers to internal rotation about one or more carbon–carbon single bonds may be too high for rapid interconversion between different configurations. In such cases, two or more different isomers can exist and their presence may be detected in the IR spectrum. The restriction of rotation about double bonds can be thought of as an extension of the above concept. In this case, very high barriers are involved and cis and trans compounds result. The axial-equatorial conformations of cyclohexane and cyclopentane derivatives are examples of another kind of conformational (rotational) isomerism.

In noncyclic structures, rotation about a single bond can produce an infinite number of configurations. Some of

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these are energetically favored (energy minima). The simplest examples are the substituted ethanes, CH_2XCH_2Y, for which there are several preferred staggered conformations. When there is a stabilizing interaction, the eclipsed form may be one of the stable conformations. Many such examples can be found in α-halo ketones, esters, acid halides, and amides. In these compounds, the halogen atom is believed to be either cis (eclipsed) or gauche (staggered) with respect to the carbonyl group. Two C=O stretching bands are observed in such cases. One is at higher frequencies, owing to the eclipsed interaction between the halogen atom and the C=O group. The other is found at the normal frequency. For α-halocarboxylic acids, multiple carbonyl bands are not usually observed because of complications from hydrogen bonding.

In cyclic compounds, the possibility of axial and equatorial conformations exists. For example, in α-chloro substituted cyclopentanones or cyclohexanones, two distinct carbonyl stretching frequencies can be observed. One band is found near $1745\,\mathrm{cm}^{-1}$, due to the equatorial conformation, in which interaction between the Cl and C=O groups can occur. A second band near $1725\,\mathrm{cm}^{-1}$ is attributed to the axial isomer, in which interaction is minimized. The relative proportions of axial and equatorial forms change with phase, temperature, and solvent, and such changes can be readily followed in the vibrational spectra.

Ortho-halogenated benzoic acids also show two carbonyl stretching frequencies, due to the two rotational isomers, which could be described as cis and trans with respect to the halogen and C=O groups.

Vinyl ethers show a doublet for the C=C stretching mode at 1640–1620 and $1620-1610\,\mathrm{cm}^{-1}$. These bands correspond to rotational isomers about the C=C bond. The two bands show variations in intensity with temperature. The CH_2 deformation band also is found to be a doublet due to the two different rotational isomers.

1.5.11 *Tautomerism*

IR spectroscopy offers a useful means of distinguishing between possible tautomeric structures. A simple example is found in β-diketones. The keto form has two C=O groups, which have separate stretching frequencies, and a doublet is often observed in the usual ketone carbonyl stretching region, near $1730\,\mathrm{cm}^{-1}$. The enol form, on the other hand, has only one carbonyl group, the frequency of which is lowered by hydrogen bonding and conjugation by $80-100\,\mathrm{cm}^{-1}$. This structure also has an alkenic double bond that should give a band between 1650 and $1600\,\mathrm{cm}^{-1}$. The C=O and C=C peaks may then appear as a doublet. An example of tautomerism is shown in Figure 6. The IR spectrum of the compound ethyl propionylacetate clearly shows both keto and enol forms.

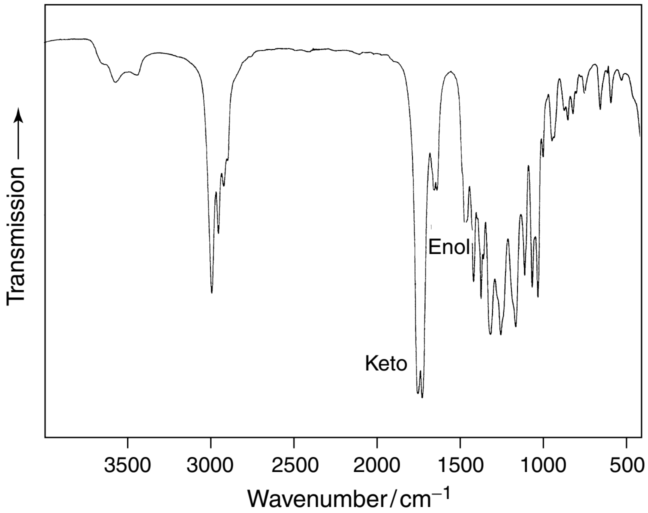

Figure 6. The IR spectrum of ethyl propionylacetate.

1.6 IR group frequencies

A good group frequency is one that falls within a fairly restricted range regardless of the compound in which the group is found. Mechanical coupling, symmetry, or other effects discussed in the previous sections may occasionally cause group frequencies to fall outside the normal range, so one should be aware of this possibility. A list of frequency ranges from 4000 down to $50\,\mathrm{cm}^{-1}$ is presented in Table 2, with possible groups that could absorb within a given range. Table 2 is by no means comprehensive and in order to make full use of the group frequency method for structure determination, the literature should be consulted.[2–9]

2 SPECTRA–STRUCTURE CORRELATIONS

2.1 Introduction

A preliminary examination of the IR spectrum of a compound will indicate the various X–H bonds present in the molecule and the presence or absence of triple or double bonds, carbonyl groups, aromatic rings, and other functional groups. This information will suggest various possible structures. The IR spectrum can then be searched in detail for bands due to the various groups in the postulated structures. Comparison with published IR spectra of compounds having the suggested or a similar structure may then be made. Published spectra are found in the literature.[10–14] Also, the computer attached to the FT-IR spectrometer usually has search software and a library of IR spectra which may be searched for spectra that most closely match the spectrum of the unknown compound.

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Table 2. Wavenumber ranges in which some functional groups and classes of compounds absorb in the mid- and far-infrared.

Range (cm^{-1}) and intensity[a]	Group and class	Assignment and remarks
3700–3600 (s)	–OH in alcohols and phenols	OH stretch; (dilute solution)
3520–3320 (m-s)	$-NH_2$ in aromatic amines, primary amines and amides	NH stretch; (dilute solution)
3420–3250 (s)	–OH in alcohols and phenols	OH stretch; (solids and liquids)
3400–3300 (vs)	–OO–H in hydroperoxides	Hydrogen bonded OO–H stretch
3360–3340 (m)	$-NH_2$ in primary amides	NH_2 antisymmetric stretch; (solids)
3320–3250 (m)	–OH in oximes	O–H stretch
3300–3250 (m-s)	≡CH in acetylenes	≡C–H stretch
3300–3280 (s)	–NH in secondary amides	NH stretch; (solids); also in polypeptides and proteins
3200–3180 (s)	$-NH_2$ in primary amides	NH_2 symmetric stretch; (solids)
3200–3000 (vs)	$-NH_3^+$ in amino acids	NH_3^+ antisymmetric stretching; very broad band
3100–2400 (vs)	–OH in carboxylic acids	H-bonded OH stretch ; very broad band
3100–3000 (m)	=CH in aromatic and unsaturated hydrocarbons	=C–H stretch
2990–2850 (m-s)	$-CH_3$ and $-CH_2-$ in aliphatic compounds	CH antisymmetric and symmetric stretching
2850–2700 (m)	$-CH_3$ attached to O or N	CH stretching modes
2750–2650 (w-m)	–CHO in aldehydes	Overtone of CH bending; (Fermi resonance)
2750–2350 (br)	$-NH_3^+$ in amine hydrohalides	NH stretching modes
2720–2560 (m)	–OH in phosphorus oxyacids	Associated OH stretching
2600–2540 (w)	–SH in alkyl mercaptans	S–H stretch
2410–2280 (m)	–PH in phosphines	P–H stretch; sharp peak
2300–2230 (m)	–N≡N in diazonium salts	N≡N stretch; (in aqueous solution)
2285–2250 (s)	–N=C=O in isocyanates	N=C=O antisymmetric stretch
2260–2200 (m-s)	–C≡N in nitriles	C≡N stretch
2260–2190 (w-m)	–C≡C in disubstituted alkynes	C≡C stretch
2190–2130 (m)	–C≡N in thiocyanates	C≡N stretch
2175–2115 (s)	–N≡C in isonitriles	N≡C stretch
2160–2080 (m)	N=N=N in azides	N=N=N antisymmetric stretch
2140–2100 (w-m)	–C≡C in monosubstituted alkynes	C≡C stretch
2000–1650 (w)	Substituted benzene rings	Several bands from overtones and combinations
1980–1950 (s)	C=C=C in allenes	C=C=C antisymmetric stretch
1870–1650 (vs)	C=O in carbonyl compounds	C=O stretch
1870–1830 (s)	C=O in β-lactones	C=O stretch
1870–1790 (vs)	C=O in anhydrides	C=O antisymmetric stretch; part of doublet
1820–1800 (s)	C=O in acid halides	C=O stretch; lower for aromatic acid halides
1780–1760 (s)	C=O in γ-lactones	C=O stretch
1765–1725 (vs)	C=O in anhydrides	C=O symmetric stretch; part of doublet
1760–1740 (vs)	C=O in α-keto esters	C=O stretch; enol form
1750–1730 (s)	C=O in δ-lactones	C=O stretch
1750–1740 (vs)	C=O in esters	C=O stretch; 20 cm^{-1} lower if unsaturated
1740–1720 (s)	C=O in aldehydes	C=O stretch; 30 cm^{-1} lower if unsaturated
1720–1700 (s)	C=O in ketones	C=O stretch; 20 cm^{-1} lower if unsaturated
1710–1690 (s)	C=O in carboxylic acids	C=O stretch; fairly broad
1690–1640 (s)	C=N in oximes	C=N stretch; also imines
1680–1620 (s)	C=O and NH_2 in primary amides	Two bands; (C=O stretch and NH_2 deformation)
1680–1635 (s)	C=O in ureas	C=O stretch; (broad band)
1680–1630 (m-s)	C=C in alkenes, etc.	C=C stretch
1680–1630 (vs)	C=O in secondary amides	C=O stretch; (amide I band)
1670–1640 (s-vs)	C=O in benzophenones	C=O stretch
1670–1650 (vs)	C=O in primary amides	C=O stretch; (amide I band)
1670–1630 (vs)	C=O in tertiary amides	C=O stretch
1655–1635 (vs)	C=O in β-keto esters	C=O stretch; enol form
1650–1620 (w-m)	N–H in primary amides	NH deformation; (amide II band)
1650–1580 (m-s)	NH_2 in primary amines	NH_2 deformation
1640–1580 (s)	NH_3^+ in amino acids	NH_3^+ deformation
1640–1580 (vs)	C=O in β-diketones	C=O stretch; enol form
1620–1610 (s)	C=C in vinyl ethers	C=C stretch; doublet due to rotational isomerism

(*continued overleaf*)

Table 2. (*continued*)

Range (cm^{-1}) and intensity[a]	Group and class	Assignment and remarks
1615–1590 (m)	Benzene ring in aromatic compounds	Ring stretch; sharp peak
1615–1565 (s)	Pyridine derivatives	Ring stretch; doublet
1610–1580 (s)	NH_2 in amino acids	NH_2 deformation; broad band
1610–1560 (vs)	COO^- in carboxylic acid salts	$-COO^-$ antisymmetric stretch
1590–1580 (m)	NH_2 primary alkyl amide	NH_2 deformation; (amide II band)
1575–1545 (vs)	NO_2 in aliphatic nitro compounds	NO_2 antisymmetric stretch
1565–1475 (vs)	NH in secondary amides	NH deformation; (amide II band)
1560–1510 (s)	Triazine compounds	Ring stretch; sharp band
1550–1490 (s)	NO_2 in aromatic nitro compounds	NO_2 antisymmetric stretch
1530–1490 (s)	NH_3^+ in amino acids or hydrochlorides	NH_3^+ deformation
1530–1450 (m-s)	N=N–O in azoxy compounds	N=N–O antisymmetric stretch
1515–1485 (m)	Benzene ring in aromatic compounds	Ring stretch, sharp band
1475–1450 (vs)	CH_2 in aliphatic compounds	CH_2 bending (scissors) vibration
1465–1440 (vs)	CH_3 in aliphatic compounds	Antisymmetric CH_3 deformation
1440–1400 (m)	OH in carboxylic acids	In-plane OH bending
1420–1400 (m)	C–N in primary amides	C–N stretch; (amide III band)
1400–1370 (m)	*tert*-Butyl group	Symmetric CH_3 deformations; (two bands)
1400–1310 (s)	COO^- group in carboxylic acid salts	COO^- symmetric stretch; (broad band)
1390–1360 (vs)	SO_2 in sulfonyl chlorides	SO_2 antisymmetric stretch
1380–1370 (s)	CH_3 in aliphatic compounds	CH_3 symmetric deformation
1380–1360 (m)	Isopropyl group	CH_3 symmetric deformations; (two bands)
1375–1350 (s)	NO_2 in aliphatic nitro compounds	NO_2 symmetric stretch
1360–1335 (vs)	SO_2 in sulfonamides	SO_2 antisymmetric stretch
1360–1320 (vs)	NO_2 in aromatic nitro compounds	NO_2 symmetric stretch
1350–1280 (m-s)	N=N–O in azoxy compounds	N=N–O symmetric stretch
1335–1295 (vs)	SO_2 in sulfones	SO_2 antisymmetric stretch
1330–1310 (m-s)	CF_3 attached to a benzene ring	CF_3 antisymmetric stretch
1300–1200 (vs)	N–O in pyridine *N*-oxides	N–O stretch
1300–1175 (vs)	P=O in phosphorus oxyacids and phosphates	P=O stretch
1300–1000 (vs)	C–F in aliphatic fluoro compounds	C–F stretch
1285–1240 (vs)	Ar–O in alkyl aryl ethers	C–O stretch
1280–1250 (vs)	Si–CH_3 in silanes	CH_3 symmetric deformation
1280–1240 (m-s)	C–O–C in epoxides	C–O stretch
1280–1180 (s)	C–N in aromatic amines	C–N stretch
1280–1150 (vs)	C–O–C in esters, lactones	C–O–C antisymmetric stretch
1255–1240 (m)	*tert*-Butyl in hydrocarbons	Skeletal vibration; second band near 1200 cm^{-1}
1245–1155 (vs)	SO_3H in sulfonic acids	S=O stretch
1240–1070 (s-vs)	C–O–C in ethers	C–O–C stretch; also in esters
1230–1100 (s)	C–C–N in amines	C–C–N bending
1225–1200 (s)	C–O–C in vinyl ethers	C–O–C antisymmetric stretch
1200–1165 (s)	SO_2Cl in sulfonyl chlorides	SO_2 symmetric stretch
1200–1015 (vs)	C–OH in alcohols	C–O stretch
1170–1145 (s)	SO_2NH_2 in sulfonamides	SO_2 symmetric stretch
1170–1140 (s)	SO_2– in sulfones	SO_2 symmetric stretch
1160–1100 (m)	C=S in thiocarbonyl compounds	C=S stretch
1150–1070 (vs)	C–O–C in aliphatic ethers	C–O–C antisymmetric stretch
1120–1080 (s)	C–OH in secondary or tertiary alcohols	C–O stretch
1120–1030 (s)	C–NH_2 in primary aliphatic amines	C–N stretch
1100–1000 (vs)	Si–O–Si in siloxanes	Si–O–Si antisymmetric stretch
1080–1040 (s)	SO_3H in sulfonic acids	SO_3 symmetric stretch
1065–1015 (s)	CH–OH in cyclic alcohols	C–O stretch
1060–1025 (vs)	CH_2–OH in primary alcohols	C–O stretch
1060–1045 (vs)	S=O in alkyl sulfoxides	S=O stretch
1055–915 (vs)	P–O–C in organophosphorus compounds	P–O–C antisymmetric stretch
1030–950 (w)	Carbon ring in cyclic compounds	Ring breathing mode

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Table 2. (*continued*)

Range (cm^{-1}) and intensity[a]	Group and class	Assignment and remarks
1000–950 (s)	CH=CH$_2$ in vinyl compounds	=CH out-of-plane deformation
980–960 (vs)	CH=CH– in trans disubstituted alkenes	=CH out-of-plane deformation
950–900 (vs)	CH=CH$_2$ in vinyl compounds	CH$_2$ out-of-plane wag
900–865 (vs)	CH$_2$=CRR′ in vinylidenes	CH$_2$ out-of-plane wag
890–830 (w)	Peroxides	O–O stretch
890–805 (vs)	1,2,4-Trisubstituted benzenes	CH out-of-plane deformation (two bands)
860–840 (w)	Hydroperoxides	O–OH stretch
860–760 (vs)	R–NH$_2$ primary amines	NH$_2$ wag; broad band
860–720 (vs)	Si–C in organosilicon compounds	Si–C stretch
850–830 (vs)	1,3,5-Trisubstituted benzenes	CH out-of-plane deformation
850–810 (vs)	Si–CH$_3$ in silanes	Si–CH$_3$ rocking
850–790 (m)	CH=C in trisubstituted alkenes	CH out-of-plane deformation
850–550 (m)	C–Cl in chloro compounds	C–Cl stretch
830–810 (vs)	*p*-Disubstituted benzenes	CH out-of-plane deformation
825–805 (vs)	1,2,4-Trisubstituted benzenes	CH out-of-plane deformation
820–800 (s)	Triazines	CH out-of-plane deformation
815–810 (s)	CH=CH$_2$ in vinyl ethers	CH$_2$ out-of-plane wag
810–790 (vs)	1,2,3,4-tetrasubstituted benzenes	CH out-of-plane deformation
800–690 (vs)	*m*-Disubstituted benzenes	CH out-of-plane deformation (two bands)
785–680 (vs)	1,2,3-Trisubstituted benzenes	CH out-of-plane deformation (two bands)
775–650 (m)	C–S in sulfonyl chlorides	C–S stretch; strong in Raman
770–690 (vs)	Monosubstituted benzenes	CH out-of-plane deformation (two bands)
760–740 (s)	*o*-Disubstituted benzenes	CH out-of-plane deformation
760–510 (s)	C–Cl alkyl chlorides	C–Cl stretch
740–720 (w-m)	–(CH$_2$)$_n$– in hydrocarbons	CH$_2$ rocking in methylene chains; intensity depends on chain length
730–665 (s)	CH=CH in cis disubstituted alkenes	CH out-of-plane deformation
720–600 (s)	Ar–OH in phenols	OH out-of-plane deformation; broad band
710–570 (m)	C–S in sulfides	C–S stretch
700–590 (s)	O–C=O in carboxylic acids	O–C=O bending
695–635 (s)	C–C–CHO in aldehydes	C–C–CHO bending
680–620 (s)	C–OH in alcohols	C–O–H bending
680–580 (s)	C≡C–H in alkynes	C≡C–H bending
650–600 (w)	S–C≡N in thiocyanates	S–C stretch
650–600 (s)	NO$_2$ in aliphatic nitro compounds	NO$_2$ deformation
650–500 (s)	Ar–CF$_3$ in aromatic trifluoro-methyl compounds	CF$_3$ deformation (two or three bands)
650–500 (s)	C–Br in bromo compounds	C–Br stretch
645–615 (m-s)	Naphthalenes	In-plane ring deformation
645–575 (s)	O–C–O in esters	O–C–O bend
640–630 (s)	=CH$_2$ in vinyl compounds	=CH$_2$ twisting
635–605 (m-s)	Pyridines	In-plane ring deformation
630–570 (s)	N–C=O in amides	N–C=O bend
630–565 (s)	C–CO–C in ketones	C–CO–C bend
615–535 (s)	C=O in amides	C=O out-of-plane bend
610–565 (vs)	O$_2$ in sulfonyl chlorides	SO$_2$ deformation
610–545 (m-s)	SO$_2$ in sulfones	SO$_2$ scissoring
600–465 (s)	C–I in iodo compounds	C–I stretch
580–530 (m-s)	C–C–CN in nitriles	C–C–CN bend
580–520 (m)	NO$_2$ in aromatic nitro compounds	NO$_2$ deformation
580–430 (s)	Ring in cycloalkanes	Ring deformation
580–420 (m-s)	Ring in benzene derivatives	In-plane and out-of-plane ring deformations (two bands)
570–530 (vs)	SO$_2$ in sulfonyl chlorides	SO$_2$ rocking
565–520 (s)	C–C=O in aldehydes	C–C=O bend
565–440 (w-m)	C$_n$H$_{2n+1}$ in alkyl groups	Chain deformation modes (two bands)
560–510 (s)	C–C=O in ketones	C–C=O bend

(*continued overleaf*)

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Table 2. (*continued*)

Range (cm^{-1}) and intensity[a]	Group and class	Assignment and remarks
560–500 (s)	CO_2^- in amino acids	CO_2^- rocking
555–545 (s)	$=CH_2$ in vinyl compounds	$=CH_2$ twisting
550–465 (s)	C–C=O in carboxylic acids	C–C=O bend
545–520 (s)	Naphthalenes	In-plane ring deformation
530–470 (m-s)	NO_2 in nitro compounds	NO_2 rocking
520–430 (m-s)	C–O–C in ethers	C–O–C bend
510–400 (s)	C–N–C in amines	C–N–C bend
490–465 (variable)	Naphthalenes	Out-of-plane ring bending
440–420 (s)	Cl–C=O in acid chlorides	Cl–C=O in-plane deformation
405–400 (s)	S–C=N in thiocyanates	S–C=N bend
395–360 (variable)	C–S–O in sulfoxides	Symmetric C–S–O bend
385–355 (m-s)	Nitriles	C–C≡N bend
380–330 (m-s)	Secondary amides	C–C=O bend
360–305 (m-s)	Primary amides	C–C=O bend
355–330 (variable)	Alkynes	C–C≡C bend
330–230 (variable)	Halogenated aromatic compounds	In plane phenyl-halogen bend (Cl and Br)
330–175 (variable)	Halogenated aromatic compounds	Out-of-plane phenyl-halogen bend (Cl and Br)
270–220 (w)	$C–CH_3$, $O–CH_3$, $N–CH_3$	Methyl torsion
265–180 (variable)	Dichloro alkenes	Two bands due to $=CCl_2$ deformation and rocking
200–50 (w)	Hydrogen-bonded OH group	OH . . . Y stretch (Y is the hydrogen acceptor atom)
185–160 (variable)	Aliphatic halogeno acetylenes	C≡C–X bend (X = Cl, Br, I)

[a] s, strong; m, medium; w, weak; v, very; br, broad.

Table 3. Regions of the IR spectrum for preliminary analysis.

Region (cm^{-1})	Group	Possible compounds present (or absent)
3700–3100	–OH	Alcohols, aldehydes, carboxylic acids
	–NH	Amides, amines
	≡C–H	Alkynes
3100–3000	=CH	Aromatic compounds
	$=CH_2$ or –CH=CH–	Alkenes or unsaturated rings
3000–2800	–CH, $–CH_2$, or $–CH_3$	Aliphatic groups
2800–2600	–CHO	Aldehydes (Fermi doublet)
2700–2400	–POH	Phosphorus compounds
	–SH	Mercaptans and thiols
	–PH	Phosphines
2400–2000	–C≡N	Nitriles
	–N=N=N	Azides
	–C≡C–	Alkynes[a]
1870–1650	C=O	Acid halides, aldehydes, amides, amino acids, anhydrides, carboxylic acids, esters, ketones, lactams, quinones
1650–1550	C=C, C=N, NH	Unsaturated aliphatics,[a] aromatics, unsaturated heterocycles, amides, amines, amino acids
1550–1300	NO_2	Nitro compounds
	CH_3 and CH_2	Alkanes, alkenes, etc.
1300–1000	C–O–C and C–OH	Ethers, alcohols, sugars
	S=O, P=O, C–F	Sulfur, phosphorus, and fluorine compounds
1100–800	Si–O and P–O	Organosilicon and phosphorus compounds
1000–650	=C–H	Alkenes and aromatic compounds
	–NH	Aliphatic amines
800–400	C–halogen	Halogen compounds
	Aromatic rings	Aromatic compounds

[a] Band may be absent owing to symmetry.

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2.2 Preliminary analysis

The IR spectrum can be arbitrarily divided into the regions shown in Table 3. The presence of bands in these regions gives immediate information on structural groups in the compound. The *absence* of bands in these regions is also important information, since many groups can be excluded from further consideration, provided the factors affecting group frequencies (Section 1.5) have been considered.

Certain types of compounds give strong broad absorptions, which are very prominent in the IR spectrum. The hydrogen-bonded OH stretching bands of alcohols, phenols, and carboxylic acids are easily recognized at the high frequency end of the spectrum (3600–3200 cm^{-1}). The stretching of the NH_3^+ group in amino acids gives a very broad asymmetric band, which extends over several hundred wavenumbers (3300–2300 cm^{-1}). Broad bands associated with bending of NH_2 or NH groups of primary or secondary amines are found at the low frequency end of the spectrum (850–650 cm^{-1}). Amides also give a broad band in this region. Some examples of these characteristic broad absorptions are illustrated in Figure 7. These and other broad bands are listed in Table 4.

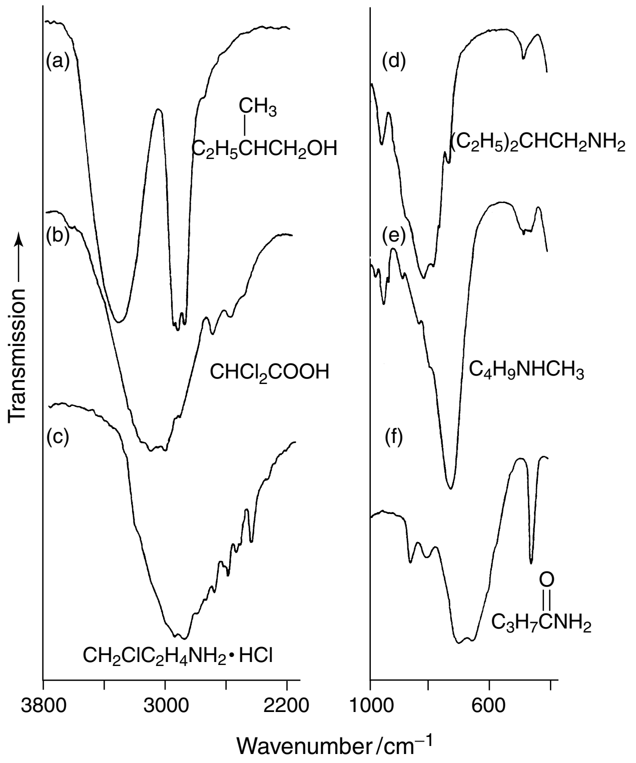

Figure 7. Some characteristic broad IR bands.

Table 4. Characteristic broad absorption bands.

Range or band center (cm^{-1}) and intensity[a]	Possible compounds	Assignment and remarks
3600–3200 (vs)	Alcohols, phenols, oximes	OH stretch (hydrogen-bonded)
3400–3000 (vs)	Primary amides	NH_2 stretch; usually a doublet
3400–2400 (vs)	Carboxylic acids and other compounds with –OH groups	H-bonded OH stretch of dimers and polymers
3200–2400 (vs)	Amino acids (zwitterion), amine hydrohalides	NH_3^+ stretching; a very broad asymmetric band
3000–2800 (vs)	Hydrocarbons, all compounds containing CH_3 and CH_2 groups	CH stretch; bands due to Nujol obscure this region when spectra are obtained from Nujol mulls
1700–1250 (vs)	Amino acids	C=O stretch; a broad region of absorption with much structure
1650–1500 (vs)	Salts of carboxylic acids	$-COO^-$ antisymmetric stretch
ca 1250 (vs)	Perfluoro compounds	CF stretches; may cover the whole region from 1400–1100 cm^{-1} with several bands
ca 1200 (vs)	Esters	C–O–C stretch; ester linkage (not always broad) with much structure
ca 1200 (vs)	Phenols	C–OH stretch
ca 1150 (vs)	Sulfonic acids	S=O stretch; with structure
1150–950 (vs)	Sugars	Very broad band with structure
ca 1100 (vs)	Ethers	C–O–C stretch
1100–1000 (s)	Alcohols	C–OH stretch
ca 1050 (vs)	Anhydrides	Not always reliable
1050–950 (vs)	Phosphites and phosphates	P=O stretch; often two bands
ca 920 (ms)	Carboxylic acids	H-bonded C–OH deformation
ca 830 (vs)	Primary aliphatic amines	May cover the region 1000–700 cm^{-1}
ca 730 (s)	Secondary aliphatic amines	May cover the region 850–650 cm^{-1}
ca 650 (s)	Amides	May cover the region 750–550 cm^{-1}
800–500 (w)	Alcohols	A weak, broad band

[a] s, strong; m, medium; w, weak; v, very.

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Table 5. Some characteristic overtone or combination bands.

Range (cm^{-1})	Classes of compounds	Assignment and remarks
ca 3450	Esters	Overtone of C=O stretch
3100–3060	Secondary amides	Overtone of NH deformation
ca 2700	Aldehydes	Part of a Fermi doublet between 2800–2700 cm^{-1}
2200–2000	Amino acids and amine hydrohalides	Combination of NH_3^+ torsion and NH_3^+ antisymmetric deformation
2000–1650	Aromatic compounds	Overtones and combinations of CH out-of-plane deformations
1990–1960 and 1830–1800	Vinyl compounds	Overtones of CH and CH_2out-of-plane deformations (high frequency band is stronger)
1800–1780	Vinylidine compounds	Overtone of CH_2 wag

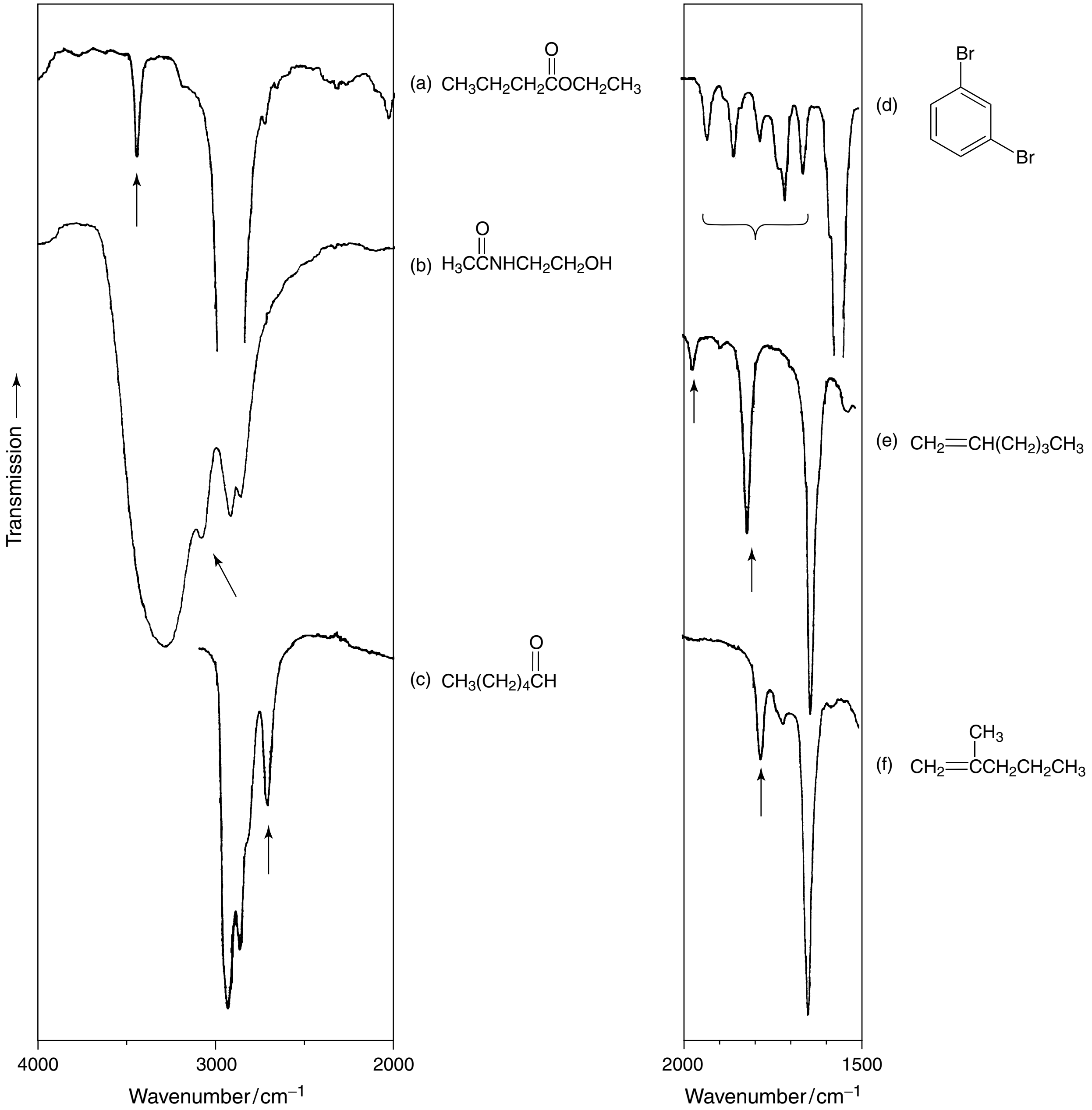

Figure 8. Some characteristic weak IR bands due to overtones or combinations: (a) an ester, (b) a secondary amide, (c) an aldehyde, (d) a substituted benzene, (e) a vinyl compound, (f) a vinylidene compound.

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In the IR spectra of certain compounds there are weak but characteristic bands that are known to be due to overtones or combinations. Some of these bands are listed in Table 5 with assignments and are shown in Figure 8.

2.3 Hydrocarbons or hydrocarbon groups

2.3.1 CH stretching bands

The nature of a hydrocarbon or the hydrocarbon part of a molecule can be identified by first looking in the region between 3100 and 2800 cm^{-1}. If there is no absorption between 3000 and 3100 cm^{-1}, the compound contains no aromatic or unsaturated aliphatic CH groups. Cyclopropanes, which absorb above 3000 cm^{-1}, are an exception. If the absorption is entirely above 3000 cm^{-1}, the compound is probably aromatic or contains =CH or $=CH_2$ groups only. Absorption both above and below 3000 cm^{-1} indicates both saturated and unsaturated or cyclic hydrocarbon moieties. This is illustrated for *sec*-butylbenzene in Figure 9.

CH stretching bands are occasionally observed outside the 3100–2800 cm^{-1} range. A band near 3300 cm^{-1} indicates the presence of an acetylenic hydrogen atom, while a band near 2710 cm^{-1} usually means that there is an aldehyde group in the molecule.

The CH stretching mode of the aldehyde group appears as a Fermi doublet (see Section 1.5.3) near 2820 and 2710 cm^{-1}. The 2710 cm^{-1} absorption is very useful and characteristic of aldehydes, but the higher frequency component often appears as a shoulder on the 2850 cm^{-1} CH_2 stretching band. In the spectrum of a purely aromatic aldehyde there is no overlap of other CH stretching bands and the doublet is clearly resolved. An example is given in Figure 10.

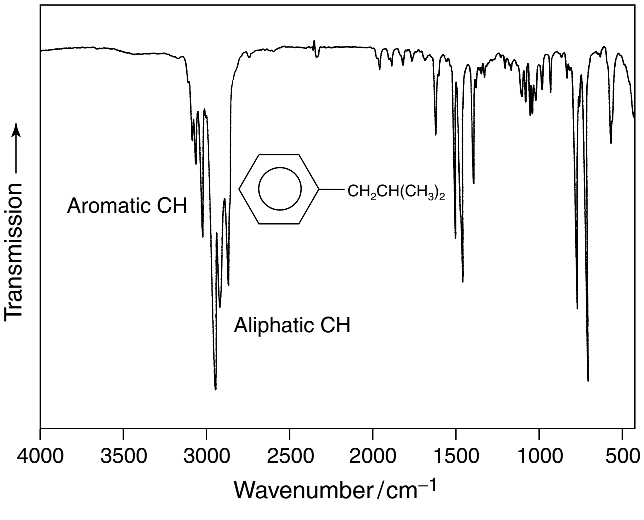

Figure 9. The IR spectrum of *sec*-butylbenzene.

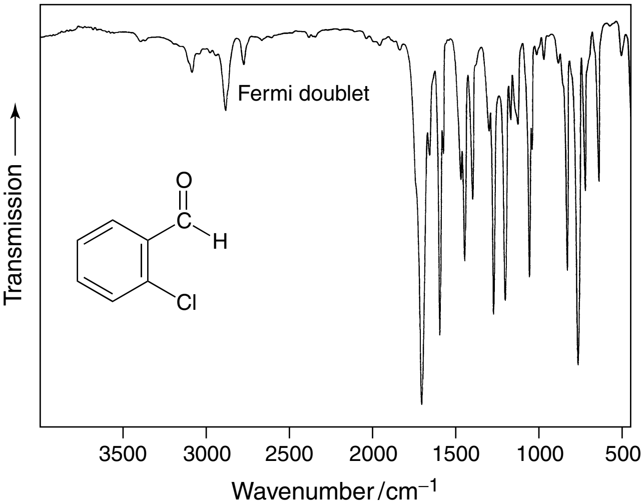

Figure 10. The IR spectrum of an aromatic aldehyde showing the Fermi doublet.

It should be noted that, when IR spectra of solids are recorded from paraffin oil mulls, the CH stretching region is obscured by strong bands from the mulling material. Other mulling materials such as hexachlorobutadiene can be used for this region, or spectra can be recorded from KBr disks.

Saturated compounds can have methyl, methylene, or methine groups, each of which has characteristic CH stretching frequencies. CH_3 groups absorb near 2960 and 2870 cm^{-1} and the CH_2 bands are at 2930 and 2850 cm^{-1}. In many cases, only one band in the 2870–2850 cm^{-1} region can be resolved when both CH_3 and CH_2 groups are present in the molecule. Figure 11 shows the CH stretching region of three normal saturated molecules.

As the carbon chain becomes longer, the CH_2 group bands increase in intensity relative to the CH_3 group absorptions. The doublet at 2960 cm^{-1} is due to the antisymmetric CH_3 stretching mode, which would be degenerate in a free CH_3 group or in a molecule in which the three-fold symmetry of the group was maintained, for example, CH_3Cl. The degeneracy is removed in the saturated molecules, and consequently two individual antisymmetric CH_3 stretching bands are observed. The methine CH stretch can only be observed (as a weak peak near 2885 cm^{-1}) when CH_3 and CH_2 groups are absent. The methoxy group CH_3O– has a characteristic sharp band of medium intensity near 2830 cm^{-1} separate from other CH stretching bands. Saturated cyclic hydrocarbon groups also have characteristic CH stretching bands in their IR spectra. The frequencies range from 3100 cm^{-1} in cyclopropanes down to 2900 cm^{-1} in cyclohexanes and larger rings.

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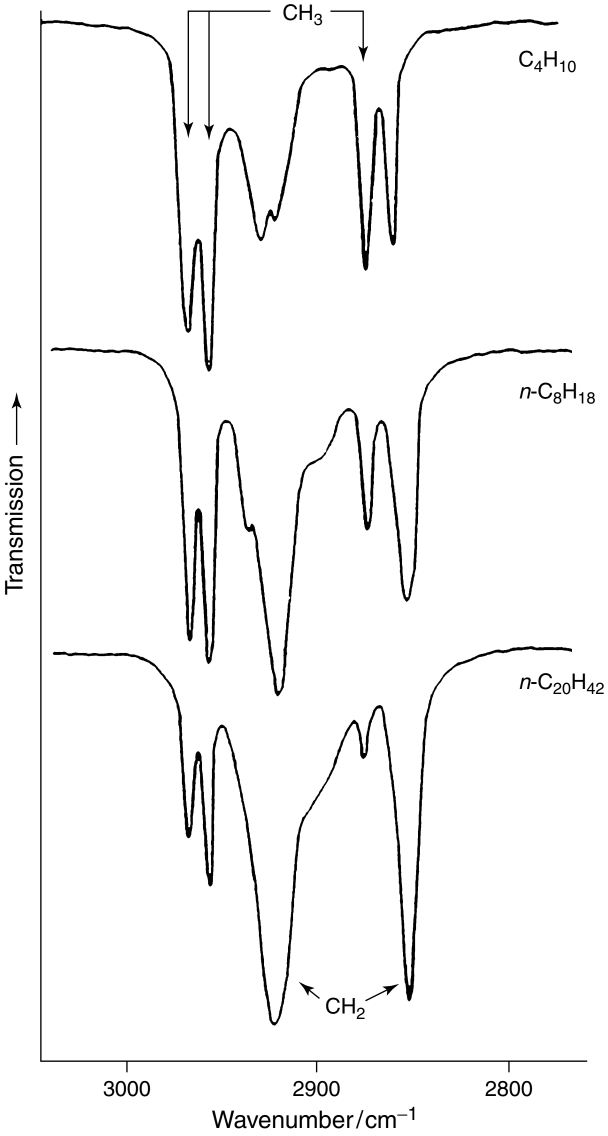

Figure 11. The C–H stretching region of n-C_4H_{10}, n-C_8H_{18}, and n-$C_{20}H_{42}$.

2.3.2 *Methyl groups*

The vibrations of a methyl group: stretching, bending (deformation), rocking, and torsion give rise to IR absorption in four different regions of the spectrum. The frequencies of CH stretching vibrations of methyl groups have been discussed above. Antisymmetric deformation of the HCH angles of a CH_3 group gives rise to very strong IR absorption in the 1470–1440 cm^{-1} region. Bending of methylene (–CH_2–) groups also gives rise to a band in the same region. The symmetric CH_3 deformation gives a strong, sharp IR band between 1380 and 1360 cm^{-1}. This band appears as a doublet when more than one CH_3 group is attached to the same carbon atom and gives a good indication of the presence of isopropyl or *tert*-butyl groups (see Section 2.3.3). When the methyl group is attached to an atom other than carbon, there is a significant shift in the symmetric CH_3 deformation frequency. Table 6 lists some typical wavenumber ranges.

Table 6. Frequencies of the symmetric CH_3 deformation vibration in various compounds.

Compounds	Group	Range (cm^{-1})
Esters, ethers, etc.	O–CH_3	1460–1430
Amines, amides	N–CH_3	1440–1410
Hydrocarbons	C–CH_3	1380–1360
Sulfoxides, thiophenes, etc.	S–CH_3	1330–1290
Phosphines	P–CH_3	1310–1280
Silanes	Si–CH_3	1280–1250
Organomercury compounds	Hg–CH_3	1210–1190

The CH_3 rocking vibrations are usually coupled with skeletal modes and may be found anywhere between 1240 and 800 cm^{-1}. Medium to strong bands in the IR spectrum may be observed, but these are of little use for structure determination. The methyl torsion vibration has a frequency in the far-infrared between 200 and 50 cm^{-1}, but is often not observed. In cases where torsional frequencies can be observed or estimated, information on rotational isomerism, conformation, and barriers to internal rotation can be obtained.

2.3.3 *Isopropyl and* tert-*butyl groups*

Isopropyl and tertiary butyl groups give characteristic doublets in the symmetric CH_3 deformation region of the IR spectrum. The isopropyl group gives a strong doublet at 1385/1370 cm^{-1}, while the *tert*-butyl group gives a strong band at 1370 cm^{-1} with a weaker peak at 1395 cm^{-1}. Examples of these doublets are seen in Figure 12.

2.3.4 *Methylene groups*

There are two kinds of methylene groups, the –CH_2– group in a saturated chain and the terminal =CH_2 group in vinyl, allyl, or vinylidene compounds. Diagrams of stretching, bending, wagging, twisting, and rocking motions of a CH_2 group were given in Figure 3. The CH stretching vibrations were covered in Section 2.3.1. However, bending, wagging and rocking modes of CH_2 groups also give rise to important group frequencies.

CH_2 bending (scissoring). The bending (sometimes called scissoring) motion of saturated –CH_2– groups gives a band of medium to strong intensity between 1480 and 1440 cm^{-1}. When the –CH_2– group is adjacent to a carbonyl or nitro

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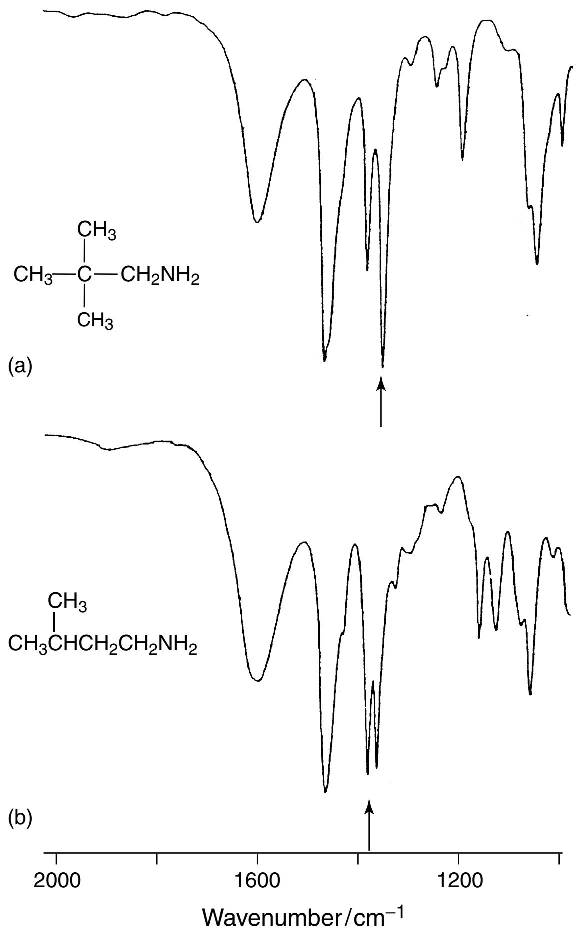

Figure 12. Examples of the doublets observed in the symmetric CH_3 deformation region for (a) an isopropyl group and (b) a *tert*-butyl group. (Reproduced by permission from Sigma-Aldrich Co.)

group, the frequency is lowered to 1430–1420 cm^{-1}. A vinyl $=CH_2$ group gives a band of medium intensity between 1420 and 1410 cm^{-1}. This band is sometimes assigned as an in-plane deformation, since the two hydrogen atoms are in the same plane as the C=C group.

CH_2 wagging and twisting. The $–CH_2–$ wagging and twisting frequencies in saturated groups are observed between 1350 and 1150 cm^{-1}. The IR bands are weak unless an electronegative atom such as a halogen or sulfur is attached to the same carbon atom. The CH_2 twisting modes occur at the lower end of the frequency range and give very weak IR absorption.

CH_2 rocking. A small band is observed near 725 cm^{-1} in the IR spectrum when there are four or more $–CH_2–$ groups in a chain. The intensity increases with the increasing chain length. This band is assigned to the rocking of the CH_2 groups in the chain. However, many compounds have bands in this region, so the CH_2 rocking band is only useful for aliphatic molecules. The band will always be present in spectra recorded from Nujol mulls.

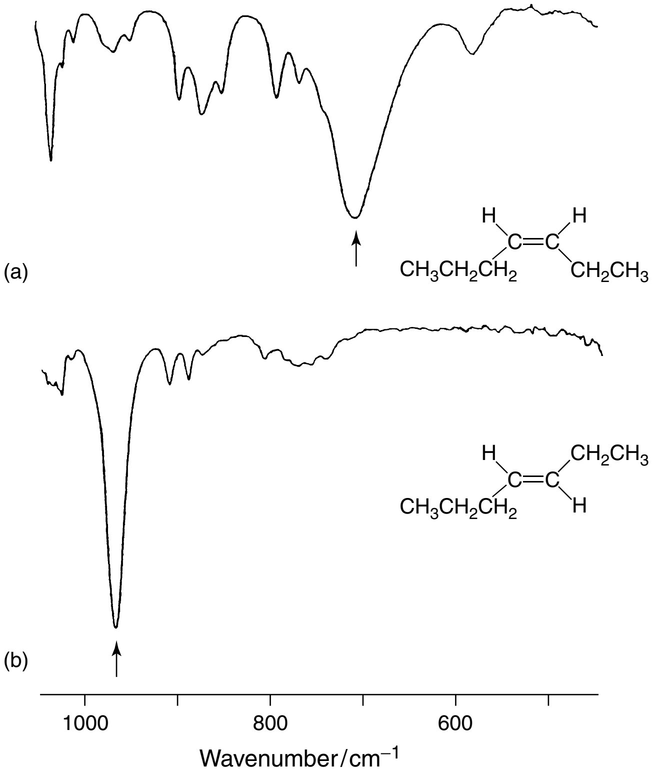

Figure 13. Portions of IR spectra of (a) *cis*- and (b) *trans*-disubstituted alkenes showing the out-of-plane CH bending bands. (Reproduced by permission from Sigma-Aldrich Co.)

$=CH$ and $=CH_2$ bending modes. The CH and CH_2 wagging or out-of-plane bending modes are very important for structure identification in unsaturated compounds. They occur in the region between 1000 and 650 cm^{-1}. The *trans*-CH bending of a vinyl group gives rise to a strong IR band between 1000 and 980 cm^{-1}, while a *trans*-disubstituted alkene is characterized by a very strong band in the 980–950 cm^{-1} frequency range. Electronegative groups tend to lower this frequency. The *cis* disubstituted alkenes give a medium to strong, but less reliable band between 750 and 650 cm^{-1}. IR spectra of *trans*- and *cis*-disubstituted alkenes are shown in Figure 13.

CH_2 wagging in vinyl and vinylidene compounds. The CH_2 wagging modes in vinyl and vinylidene compounds are found at much lower frequencies than in the saturated groups. In vinyl compounds, a strong band is observed in the IR spectrum between 910 and 900 cm^{-1}. For vinylidene compounds the frequency range is 10 cm^{-1} lower. The overtone of the CH_2 wag often can be clearly seen as a band of medium intensity near 1820 cm^{-1} for vinyl

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Table 7. CH_2 wagging and out-of-plane bending frequencies of alkenes.

Range (cm^{-1}) and intensity[a]	Group or class	Assignment and remarks
1000–980 (s)	Vinyl group ($-CH{=}CH_2$)	*trans* CH=CH bending (lower in vinyl ethers)
980–950 (vs)	*trans*-Disubstituted alkenes (vinylenes)	CH=CH bending (frequency lowered by halogen substituents)
920–900 (s)	Vinyl group ($-CH{=}CH_2$)	$=CH_2$ out-of-plane wagging (frequency higher in vinyl ketones but lower in vinyl ethers)
900–880 (s)	Vinylidene group ($C{=}CH_2$)	Terminal $=CH_2$ out-of-plane wagging
750–650 (m-s)	*cis*-Disubstituted and cyclic alkenes	*cis* CH=CH bending

[a] s, strong; m, medium; v, very.

and 1780 cm^{-1} for vinylidene compounds. These frequencies are raised above the normal range by halogens or other functional groups on the carbon atom.

The CH_2 out-of-plane wagging vibration of vinyl and vinylidene compounds gives a strong band between 910 and 890 cm^{-1}. This band coupled with the *trans* CH bending mode gives a very characteristic doublet (1000 and 900 cm^{-1}) and distinguishes the vinyl group from the vinylidene group (900 cm^{-1} only). Examples of IR spectra of vinyl and vinylidene compounds are seen in Figure 14. The overtones of the out-of-plane CH bend and the CH_2 wagging modes give weak but characteristic bands near 1950 and 1800 cm^{-1}, respectively. These are clearly seen in Figure 14 and provide a useful confirmation of the structural grouping. The unsaturated $=CH_2$ stretch can be observed near 3100 cm^{-1}.

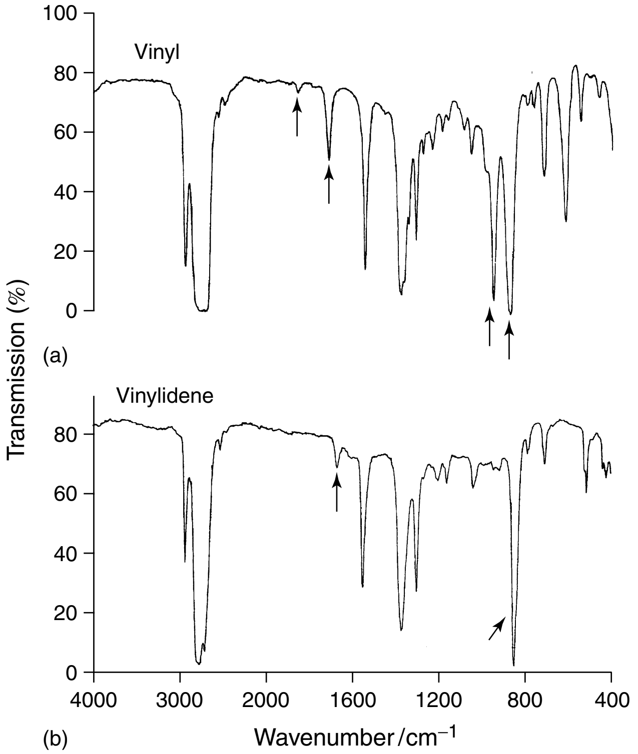

Figure 14. IR spectra of (a) 3,4-dimethyl-1-hexene, a compound containing a vinyl group, and (b) 2,3-dimethyl-1-pentene, a compound containing a vinylidene group.

CH_2 vibrations in cyclic alkenes. Cyclic alkenes usually have a strong band between 750 and 650 cm^{-1} due to out-of-plane bending of the two CH groups in a cis arrangement. However, when another group such as methyl substitutes one of these hydrogens, the band between 750 and 650 cm^{-1} is absent. There are always several bands of medium intensity between 1200 and 800 cm^{-1} in the IR spectra of cycloalkyl and cycloalkene compounds due to $-CH_2-$ rocking. A summary of the out-of-plane CH_2 bending or wagging modes in alkenic compounds is given in Table 7.

2.4 Aromatic compounds

Bands characteristic of aromatic compounds can be found in five regions of the IR spectrum. These are 3100–3000 cm^{-1} (CH stretching), 2000–1700 cm^{-1} (overtones and combinations), 1650–1430 cm^{-1} (C=C stretching), 1275–1000 cm^{-1} (in-plane CH deformation) and 900–690 cm^{-1} (out-of-plane CH deformation). Examples of IR spectra of three aromatic compounds can be seen in Figures 9, 10 and 15. In these spectra, there are bands in all five regions. However, the intensities of the bands vary widely.

The intensities of the CH stretching bands range from medium, to weak. Occasionally, these bands are seen only as shoulders on a strong aliphatic CH stretching band. There are usually sharp bands near 1600, 1500, and 1430 cm^{-1} in benzene derivatives. The 1600 cm^{-1} absorption can be hidden by a strong C=O stretching band in some carbonyl compounds, or an NH deformation band in amines. There are also several sharp bands between 1275 and 1000 cm^{-1} in aromatic compounds. In the 900–690 cm^{-1} region, one or two strong bands are observed. These bands, together with the pattern of weak bands between 2000 and

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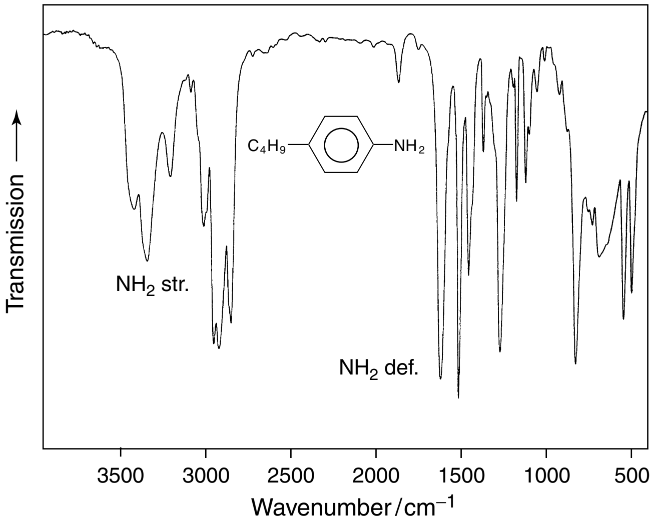

Figure 15. The IR spectrum of an aniline derivative, *p*-butylaniline.

1700 cm^{-1}, give an indication of the type of substitution on the benzene ring.

2.4.1 Substituted aromatic compounds

The monosubstitution pattern is easily recognized by two very strong bands near 750 and 700 cm^{-1} in the IR spectrum due to out-of-plane CH bending. These are very prominent in the spectrum of Figure 9, which will now be recognized as a monosubstituted benzene derivative. In addition, monosubstitution is indicated by four weak but clear absorptions between 2000 and 1700 cm^{-1}. Again, Figure 9 illustrates this pattern. The polystyrene test film supplied by the instrument manufacturers also provides a "text book" example of monosubstitution. The patterns of bands in these two regions can also give an indication of the positions of substitution in di- and trisubstituted benzene rings. These regions are less useful for highly substituted derivatives. The characteristic bands of mono-, di-, and trisubstituted aromatic compounds are summarized in Table 8. Examples of the three disubstitution patterns are shown in Figure 16.

2.5 Compounds containing C=C and C≡C bonds

2.5.1 The C=C stretching mode

Stretching of a C=C bond gives rise to a sharp but weak peak near 1650 cm^{-1}. The corresponding IR band is often weak and sometimes is not observed at all in symmetrical molecules. Weak absorption due to overtones or combinations may occur in this region and could be mistaken for a C=C stretching mode.

The exact frequency of the C=C stretching mode gives some additional information on the environment of the double bond. Tri- or tetralkyl-substituted groups and *trans*-disubstituted alkenes have frequencies in the 1690–1660 cm^{-1}

Table 8. Absorption bands characteristic of substitution in benzene rings.

Type of substitution	Range (cm^{-1}) and intensity[a]	Remarks
Monosubstitution	770–730 (vs) and 710–690 (s)	Two bands; very characteristic of monosubstitution
	2000–1700 (w)	Four weak but prominent bands; also very characteristic of monosubstitution
Ortho-disubstitution	770–730 (vs)	A single strong band
	1950–1650 (vw)	Several bands, the two most prominent near 1900 and1800 cm^{-1}
Meta-disubstitution	810–750 (vs) and 725–680 (s)	Two bands similar to monosubstitution, but the higher frequency band is 50 cm^{-1} higher, and the lower is more variable in position and intensity than in monosubstituted benzenes
	1930–1740 (vw)	Three weak but prominent bands; the lowest frequency band may be broader with some structure
Para-disubstitution	860–800 (vs)	A single strong band, similar to *ortho*-disubstitution, but 50 cm^{-1} higher in frequency
	1900–1750 (w)	Two bands; the higher frequency one is usually stronger
1,3,5-Trisubstitution	865–810 (s) and 765–730 (s)	Two bands with wider separation than mono- or *m*-disubstitution
	1800–1700 (w)	One fairly broad band with a much weaker one near 1900 cm^{-1}
1,2,3-Trisubstitution	780–760 (s) and 745–705 (s)	Two bands, similar to *m*-disubstitution, but closer in frequency
	2000–1700 (w)	Similar to monosubstitution, but only three bands
1,2,4-Trisubstitution	885–870 (s) and 825–805 (s)	Two bands at higher frequencies than mono-, *m*-di-, and the other trisubstituted compounds
	1900–1700 (w)	Two prominent bands near 1880 and 1740 cm^{-1} with a much weaker one between

[a] s, strong; m, medium; w, weak; v, very.

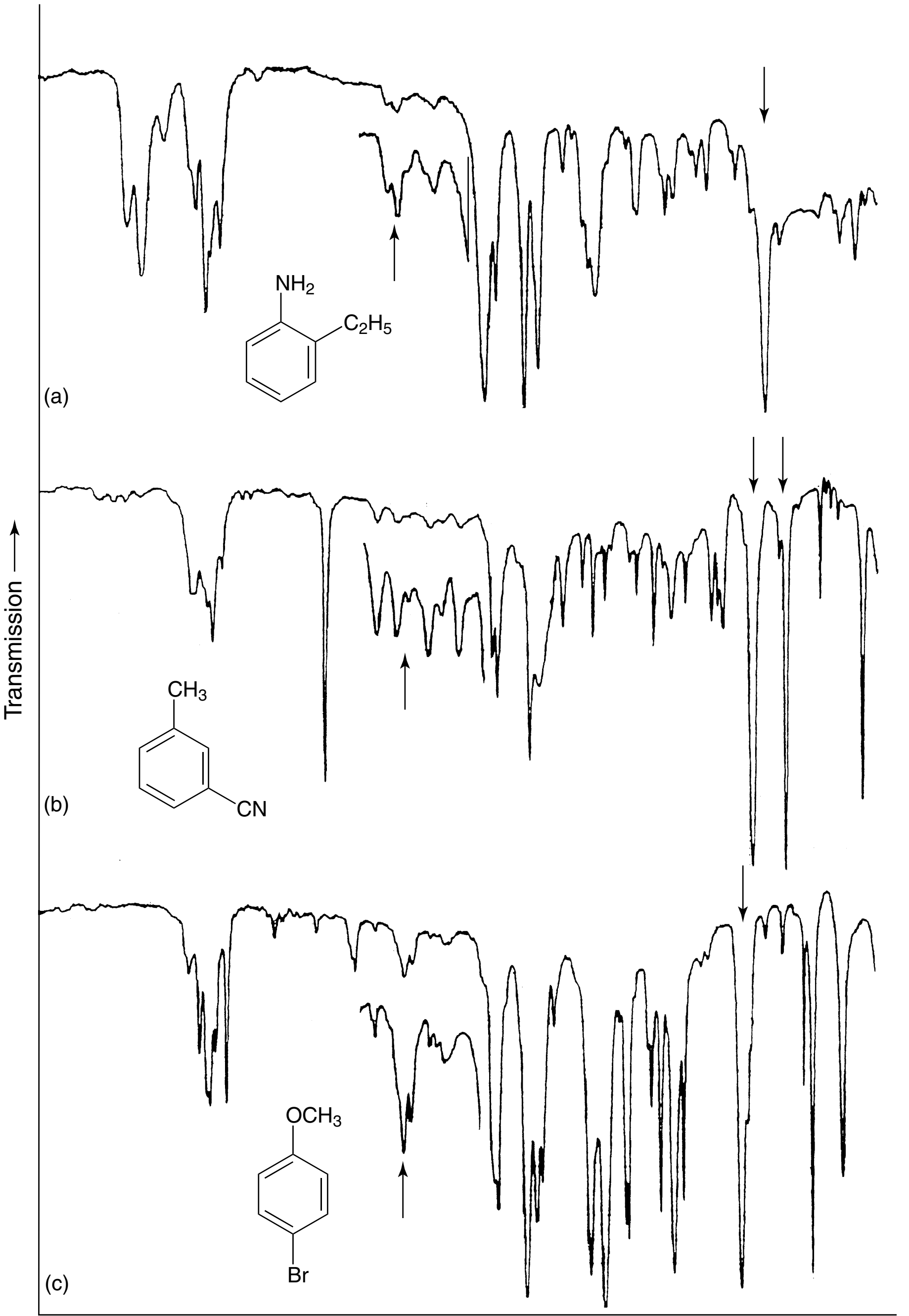

Figure 16. IR spectra showing characteristic substitution patterns in (a) *ortho*-, (b) *meta*-, and (c) *para*-disubstituted benzenes.

range. Vinyl and vinylidene compounds as well as *cis*-alkenes absorb between 1660 and 1630 cm^{-1}. Substitution by halogens may shift the C=C stretching band out of the usual range. Fluorinated alkenes have very high C=C stretching frequencies (1800–1730 cm^{-1}). Chlorine and other heavy substituents, on the other hand, usually lower the frequency.

The C=C stretching frequencies of cyclic unsaturated compounds depend on ring size and substitution. Cyclobutene, for example, has its C=C stretching mode at 1565 cm^{-1}, whereas cyclopentene, cyclohexene, and cycloheptene have C=C stretching frequencies of 1610, 1645, and 1655 cm^{-1}, respectively. These frequencies are increased by substitution.

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2.5.2 The C≡C stretching mode

A small sharp peak due to C≡C stretching is observed in the IR spectra of terminal alkynes near 2100 cm^{-1}. In substituted alkynes the band is shifted by 100–150 cm^{-1} to higher frequencies. If the substitution is symmetric, no band is observed in the IR because there is no change in dipole moment during the C≡C stretching vibration. Even when substitution is unsymmetrical, the band may be very weak in the IR and could be missed.

2.6 Compounds containing oxygen

There are three regions of the IR spectrum that may contain bands due to oxygen-containing functional groups. A strong broad band between 3500 and 3200 cm^{-1} is likely due to the hydrogen-bonded OH stretching mode of an alcohol or a phenol (water also absorbs in this region). If hydrogen bonding is absent, the OH stretching band will be sharp and at higher frequencies (3650–3600 cm^{-1}). Carboxylic acids give very broad OH stretching bands between 3200 and 2700 cm^{-1}. Several sharp peaks may be seen on this broad band near 3000 cm^{-1} due to CH stretching vibrations.

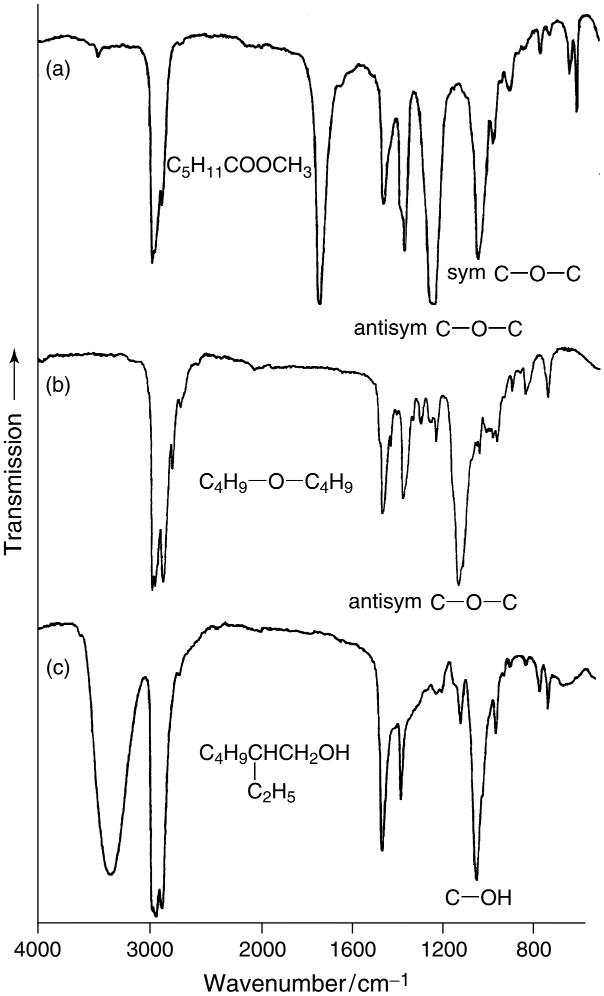

Figure 17. The IR spectra of (a) an ester, (b) an ether, and (c) an alcohol, showing the C–O stretching bands between 1300 and 1000 cm^{-1}.

A very strong band between 1850 and 1650 cm^{-1} is almost certainly due to the C=O stretching of a carbonyl group. (Poly(vinyl alcohol) has a band in this region, but this is probably due to the presence of the precursor polymer, poly(vinyl acetate), which has not been fully hydrolyzed). The CO_3^{2-} antisymmetric stretching mode in carbonates gives rise to a very strong broad band near 1450 cm^{-1}. Some examples of C=O stretching bands were shown earlier in Figure 2. The third region is between 1300 and 1000 cm^{-1}, where bands due to C–OH stretching of alcohols and carboxylic acids and C–O–C stretching modes of ethers and esters are observed. Some examples of C–O stretching bands are shown in Figure 17.

The presence or absence of the bands due to OH, C=O, and C–O stretching gives a good indication of the type of oxygen-containing compound. IR spectra of aldehydes and ketones show only the C=O band, while spectra of ethers have only the C–O–C band. Esters have bands due to both C=O and C–O–C groups, but none due to the OH group. Alcohols have bands due to both OH and C–O groups, but no C=O stretching band. Spectra of carboxylic acids contain bands in all three regions mentioned above.

2.6.1 The carbonyl stretching region (1850–1650 cm^{-1})

A very important region of the spectrum for structural analysis is the carbonyl stretching region. If we were to include metal carbonyls and salts of carboxylic acids, the region of the C=O stretching mode would extend from 2200 cm^{-1} down to 1350 cm^{-1}. However, most organic compounds containing the C=O group show very strong IR absorption in the range 1850–1650 cm^{-1}. The actual position of the peak (or peaks) within this range is characteristic of the type of compound. At the upper end of the range are found bands due to anhydrides (two bands) and four-membered rings (β-lactones), while acyclic amides and substituted ureas absorb at the lower end of the range. In compounds that have two interacting carbonyl groups out-of-phase and in-phase (antisymmetric and symmetric) C=O stretching vibrations can occur (see Section 1.5.2). Usually, the out-of-phase mode is found at higher frequencies than the in-phase mode.

The type of functional group usually cannot be identified from the C=O stretching band alone, because there may be several carbonyl-containing functional groups that absorb within a given frequency range. However, an initial

Table 9. Carbonyl stretching frequencies for compounds having one carbonyl group.

Range (cm^{-1}) and intensity[a]	Classes of compounds	Remarks
1840–1820 (vs)	β-Lactones	Four-membered ring
1810–1790 (vs)	Acid chlorides	Saturated aliphatic compounds
1800–1750 (vs)	Aromatic and unsaturated esters	The C=C stretch is longer than normal
1800–1740 (s)	Carboxylic acid monomer	Only observed in dilute solution
1790–1740 (vs)	γ-Lactones	Five-membered ring
1790–1760 (vs)	Aromatic or unsaturated acid chlorides	Second weaker band near 1740 cm^{-1} due to Fermi resonance (see text)
1780–1700 (s)	Lactams	Position of band depends on ring size
1770–1745 (vs)	α-Halo esters	Higher frequency due to electronegative halogen
1750–1740 (vs)	Cyclopentanones	Unconjugated structure
1750–1730 (vs)	Esters and δ-lactones	Aliphatic compounds
1750–1700 (s)	Urethanes	R–O–(C=O)–NHR compounds
1745–1730 (vs)	α-Halo ketones	Noncyclic compounds
1740–1720 (vs)	Aldehydes	Aliphatic compounds
1740–1720 (vs)	α-Halo carboxylic acids	20 cm^{-1} higher frequency if halogen is fluorine
1730–1705 (vs)	Aryl and α, β-unsaturated aliphatic esters	Conjugated carbonyl group
1730–1700 (vs)	Ketones	Aliphatic and large ring alicyclic ketones
1720–1680 (vs)	Aromatic aldehydes	Also α, β-unsaturated aliphatic aldehydes
1720–1680 (vs)	Carboxylic acid dimer	Broader band
1710–1640 (vs)	Thiol esters	Lower than in normal esters
1700–1680 (vs)	Aromatic ketones	Position affected by substituents on ring
1700–1680 (vs)	Aromatic carboxylic acids	Dimer band
1700–1670 (s)	Primary and secondary amides	Observed in dilute solution
1700–1650 (vs)	Conjugated ketones	Check C=C stretch region
1690–1660 (vs)	Quinones	Position affected by substituents on ring
1680–1630 (vs)	Amides (solid state)	Note second peak due to NH deformation near 1625 cm^{-1}
1670–1660 (s)	Diaryl ketones	Position affected by substituents on ring
1670–1640 (s)	Ureas	Second peak due to NH deformation near 1590 cm^{-1}
1670–1630 (vs)	Aromatic ketones with ortho –OH or –NH_2 group	C=O frequency has been lowered by chelation with the ortho –OH or –NH_2 group

[a] s, strong; m, medium; v, very.

separation into possible compounds can be achieved using Tables 9 and 10. For example, a single carbonyl peak in the region 1750–1700 cm^{-1} could indicate an ester, an aldehyde, a ketone (including cyclic ketones), a large ring lactone, a urethane derivative, an α-halo ketone, or an α-halo carboxylic acid. The presence of the halogen could be checked from the elemental analysis, an aldehyde would have a peak near 2700 cm^{-1} and esters and lactones give a strong band near 1200 cm^{-1}, which is often quite broad in esters. Urethanes would have an NH stretching band near 3300 cm^{-1} if hydrogen bonding is present or near 3400 cm^{-1} if it is absent.

2.6.2 The C–O–C and C–OH stretching region (1400–900 cm^{-1})

Carboxylic acids and anhydrides, alcohols, phenols, and carbohydrates all give strong, often broad IR absorption bands somewhere between 1400 and 900 cm^{-1}. These bands are associated with stretching of the C–O–C or C–OH bonds or bending of the C–O–H group. The position and multiplicity of the absorption together with evidence from other regions of the spectrum can help to distinguish the particular functional group. The usual frequency ranges for these groups in various compounds are summarized in Table 11.

2.6.3 Ethers

The simplest structure with the C–O–C link is the ether group. Aliphatic ethers absorb near 1100 cm^{-1}, while alkyl aryl ethers have a very strong band between 1280 and 1220 cm^{-1} and another strong band between 1050 and 1000 cm^{-1}. In vinyl ethers the C–O–C stretching mode is found near 1200 cm^{-1}. Vinyl ethers can be further distinguished by a very strong C=C stretching band and the out-of-plane CH bending and CH_2 wagging bands, which are observed near 960 and 820 cm^{-1}, respectively. These frequencies are below the usual ranges discussed in Section 2.3.4. Examples of these three types of ether

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Table 10. Carbonyl stretching frequencies for compounds having two interacting carbonyl groups.

Range (cm^{-1}) and intensity[a]	Classes of compounds	Remarks
1870–1840 (m-s) and 1800–1770 (vs)	Cyclic anhydrides	Two bands, low-frequency band is stronger
1825–1815 (vs) and 1755–1745 (s)	Non-cyclic anhydrides	Two bands, high-frequency band is stronger
1780–1760 (m) and 1720–1700 (vs)	Imides	Two bands, low frequency band is broad; high frequency band may be obscured
1760–1740 (vs)	α-Keto esters	Usually only one band
1740–1730 (vs)	β-Keto esters (keto form)	May be a doublet due to two C=O groups
1660–1640 (vs)	β-Keto esters (enol form)	May be a doublet due to a C=O and a C=C group
1710–1690 (vs) and 1640–1540 (vs)	Diketones	Two bands, high-frequency band due to keto form; low-frequency band due to enol form
1690–1660 (vs)	Quinones	Frequency depends on substituents
1650–1550 (vs) and 1440–1350 (s)	Carboxylic acid salts	Two broad bands due to antisymmetric and symmetric –COO$^-$ stretches

[a]s, strong; m, medium; v, very.

Table 11. C–O–C and C–O–H group vibrations.

Range (cm^{-1}) and intensity[a]	Group or class	Assignment and remarks
1440–1400 (m)	Aliphatic carboxylic acids	C–O–H deformation; may be obscured by CH_3 and CH_2 deformation bands
1430–1280 (m)	Alcohols	C–O–H deformation; broad band
1390–1310 (m-s)	Phenols	C–O–H deformation
1340–1160 (vs)	Phenols	C–O stretch; broad band with structure
1310–1250 (vs)	Aromatic esters	C–O–C antisymmetric stretch
1300–1200 (s)	Aromatic carboxylic acids	C–O stretch
1300–1100 (vs)	Aliphatic esters	C–O–C antisymmetric stretch
1160–1000 (s)	Aliphatic esters	C–O–C symmetric stretch
1280–1220 (vs)	Alkyl aryl ethers	Aryl C–O stretch; a second band near 1030 cm^{-1}
1270–1200 (s)	Vinyl ethers	C–O–C stretch; a second band near 1050 cm^{-1}
1265–1245 (vs)	Acetate esters	C–O–C antisymmetric stretch
1250–900 (s)	Cyclic ethers	C–O–C stretch, position varies with compound
1230–1000 (s)	Alcohols	C–O stretch; see below for more specific frequency ranges
1200–1180 (vs)	Formate and propionate esters	C–O–C stretch
1180–1150 (m)	Alkyl-substituted phenols	C–O stretch
1150–1050 (vs)	Aliphatic ethers	C–O–C stretch; usually centered near 1100 cm^{-1}
1150–1130 (s)	Tertiary alcohols	C–O stretch; lowered by chain branching or adjacent unsaturated groups
1110–1090 (s)	Secondary alcohols	C–O stretch; lowered 10–20 cm^{-1} by chain branching
1060–1040 (s-vs)	Primary alcohols	C–O stretch; often fairly broad
1060–1020 (s)	Saturated cyclic alcohols	C–O stretch; not cyclopropanol or cyclobutanol
1050–1000 (s)	Alkyl aryl ethers	Alkyl C–O stretch
960–900 (m-s)	Carboxylic acids	C–O–H deformation of dimer

[a]s, strong; m, medium; v, very.

are compared in Figure 18. Cyclic saturated ethers such as tetrahydrofuran have a strong antisymmetric C–O–C stretching band in the range 1250–1150 cm^{-1}, while unsaturated cyclic ethers have their C–O–C stretching modes at lower frequencies.

2.6.4 Alcohols and phenols

Alcohols and phenols in the pure liquid or solid state have broad bands due to hydrogen-bonded OH stretching. For alcohols, this band is centered near 3300 cm^{-1}, while in phenols the absorption maximum is 50–100 cm^{-1} lower. A sterically hindered OH group will give rise to a sharp band in the free OH stretching region near 3600 cm^{-1}. Phenols absorb near 1350 cm^{-1} due to the OH deformation and give a second broader, stronger band due to C–OH stretching near 1200 cm^{-1}. This second band often has fine structure due to underlying aromatic CH in-plane deformation vibrations. IR spectra of an alcohol and a phenol are compared in Figure 19.

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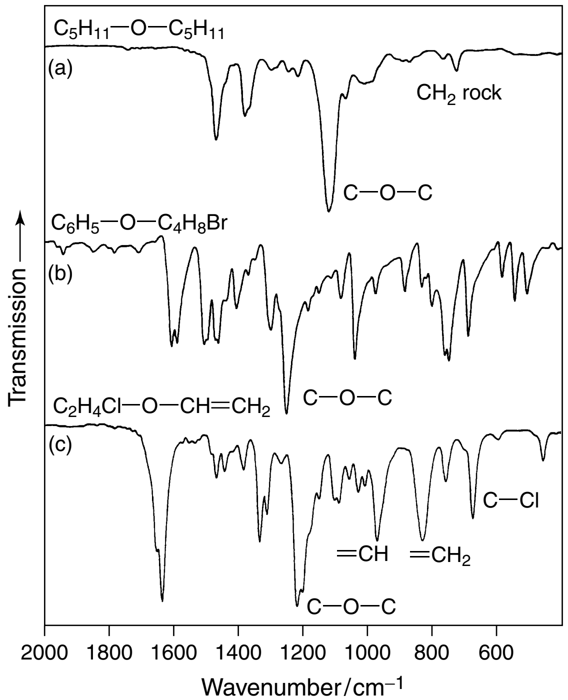

Figure 18. The IR spectra of three types of ethers: (a) a simple aliphatic ether; (b) an alkyl aryl ether; and (c) a vinyl ether.

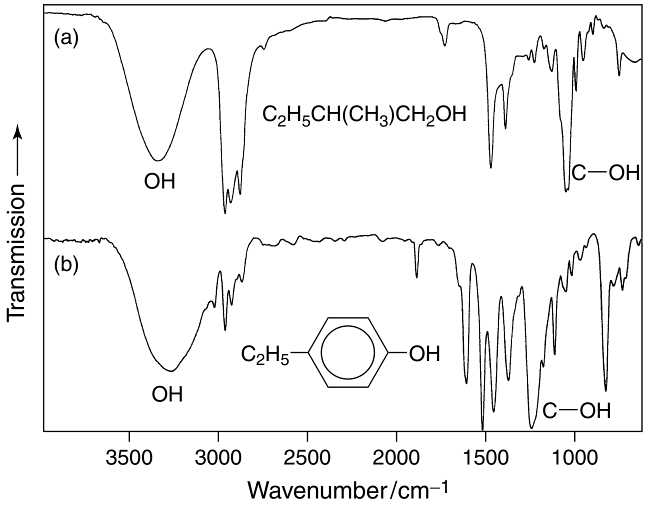

Figure 19. IR spectra of (a) an alcohol, 2-methyl-1-pentanol, and (b) a phenol, 4-ethylphenol.

In simple alcohols the frequency of the C–OH stretch is raised by substitution on the C–OH carbon atom. Sugars and carbohydrates give very broad absorption bands centered near 3300 cm^{-1} (OH stretching), 1400 cm^{-1} (OH deformation) and 1000 cm^{-1} (C–OH stretching).

2.6.5 *Carboxylic acids and anhydrides*

Carboxylic acids usually exist as dimers except in dilute solution. The carbonyl stretching band of the dimer is found near 1700 cm^{-1}, while in the monomer spectrum the band is located at higher frequencies (1800–1740 cm^{-1}). In addition to the very broad OH stretching band mentioned in Section 2.2, there are three vibrations associated with the C–OH group in carboxylic acids: a band of medium intensity near 1430 cm^{-1}, a stronger band near 1240 cm^{-1}, and another band of medium intensity near 930 cm^{-1}. The presence of an anhydride is detected by the characteristic absorption in the C=O stretching region. This consists of a strong sharp doublet with one band at unusually high frequency (1840–1800 cm^{-1}) and a second band at about 60 cm^{-1} lower (1780–1740 cm^{-1}). The C–O–C stretch gives rise to a broad band near 1150 cm^{-1} in open chain anhydrides and at higher frequencies in cyclic structures.

2.6.6 *Esters*

The antisymmetric C–O–C stretching mode in esters gives rise to a very strong and often quite broad band near 1200 cm^{-1}. The actual frequency of the maximum of this band can vary from 1290 cm^{-1} in benzoates down to 1100 cm^{-1} in aliphatic esters. There may be structure on this band due to CH deformation vibrations that absorb in the same region. The band may be even stronger than the C=O stretching band near 1750 cm^{-1}. The symmetric C–O–C stretch also gives a strong band at lower frequencies between 1160 and 1000 cm^{-1} in aliphatic esters.

2.6.7 *Peroxides and hydroperoxides*

Ethers slowly form hydroperoxides (–OOH) on standing in contact with air. These compounds are often dangerously unstable and suppliers usually add small amounts of inhibitors to prevent the formation of hydroperoxides. The dominant feature of the IR spectra of hydroperoxides is a very strong broad band centered near 3350 cm^{-1}, which is assigned to the hydrogen bonded OO–H stretching mode. The O–O stretching vibration gives rise to a weak absorption near 850 cm^{-1}.

The O–O stretching vibration in hydrogen peroxide occurs at 877 cm^{-1}. A band in the range 890–830 cm^{-1} often is observed in the spectra of organic peroxides. However the band is weak and difficult to differentiate from skeletal frequencies in large molecules.

2.7 Compounds containing nitrogen

In an examination of the IR spectrum of a compound known to contain nitrogen, one or two bands in the region 3500–3300 cm^{-1} indicate primary or secondary amines or amides. These bands may be confused with OH stretching bands. Amides may be identified by a strong doublet in the IR spectrum centered near 1640 cm^{-1}. These bands are associated with the stretching of the C=O group and bending of the NH_2 group of the amide. A sharp band near 2200 cm^{-1} is characteristic of a nitrile.

When both nitrogen and oxygen are present, but no NH groups are indicated, two very strong bands near 1560 and 1370 cm^{-1} provide evidence of the presence of nitro groups. An extremely broad band with some structure centered near 3000 cm^{-1} and extending as low as 2200 cm^{-1} is indicative of an amino acid or an amine hydrohalide, while a broad band between 850 and 650 cm^{-1} suggests an amine or an amide. Figure 7 shows examples of these broad bands.

The presence of primary or secondary amines and amides can be detected by absorption due to stretching of NH_2 or NH groups between 3350 and 3200 cm^{-1}. Tertiary amines and amides, on the other hand, are more difficult to identify, because they have no N–H groups. Nitriles and nitro compounds also give characteristic IR absorption bands near 2250 and 1530 cm^{-1}, respectively. Isocyanates and carbodiimides have very strong IR bands near 2260 and 2140 cm^{-1}, respectively, where very few absorptions due to other groupings occur. Oximes, imines, and azo compounds give weak IR bands in the 1700–1600 cm^{-1} region due to stretching vibrations of the –C=N–, or –N=N– group. Some characteristic group frequencies of nitrogen-containing compounds are listed in Table 12.

2.7.1 Amino acids, amines, and amine hydrohalides

Three classes of nitrogen-containing compounds (amino acids, amines, and amine hydrohalides) give rise to very characteristic broad absorption bands. Perhaps the most striking of these are found in the IR spectra of amino acids, which contain an extremely broad band centered near 3000 cm^{-1} and often extending as low as 2200 cm^{-1}, with some structure. An example is shown in Figure 20.

Amine hydrohalides give a similar, very broad band, which has structure on the low frequency side. The center of the band tends to be lower than in amino acids, especially in the case of tertiary amine hydrohalides, the band center for which may be as low as 2500 cm^{-1}. In fact, this band gives a very useful indication of the presence of a tertiary amine hydrohalide, and an example is shown in Figure 21.

Both amino acids and primary amine hydrohalides have a weak but characteristic band between 2200 and 2000 cm^{-1}, which is believed to be a combination of the $–NH_3^+$ deformation near 1600 cm^{-1} and the $–NH_3^+$ torsion near 500 cm^{-1}.

Primary amines have a fairly broad band in their IR spectra centered near 830 cm^{-1}, whereas the frequency for secondary amines is about 100 cm^{-1} lower (see Figure 7d and e). This band is not present in the spectra of tertiary amines or amine hydrohalides.

2.7.2 Anilines

In anilines, the characteristic broad band shown by aliphatic amines in the 830–730 cm^{-1} region is not present, so that the out-of-plane CH deformations of the benzene ring can be observed. These bands permit the ring substitution pattern to be determined. Of course, when an aliphatic amine is joined to a benzene ring through a carbon chain, both the characteristic amine band and the CH deformation pattern will be present.

In Figure 15 the IR spectrum of an aniline derivative is shown. Figure 22 shows the spectrum of an aliphatic amine joined to a benzene ring. The presence of the benzene ring is identified in both compounds by CH stretching bands between 3100 and 3000 cm^{-1}, out-of-plane CH bending bands between 850 and 700 cm^{-1}, and bands diagnostic of the substitution patterns between 2000 and 1700 cm^{-1}. In the out-of-plane bending region, the single band at 825 cm^{-1} in Figure 15 indicates the presence of a *para*-disubstituted benzene ring, while the doublet at 740 and 700 cm^{-1} in Figure 22 indicates monosubstitution (see Section 2.4.1).

2.7.3 Nitriles

Saturated nitriles absorb weakly in the IR near 2250 cm^{-1}. Unsaturated or aromatic nitriles for which the double bond or ring is adjacent to the C≡N group absorb more strongly in the IR than saturated compounds, and the band occurs at somewhat lower frequencies near 2230 cm^{-1}.

2.7.4 Nitro compounds

Nitro compounds have two very strong absorption bands in the IR due to the antisymmetric and symmetric NO_2 stretching vibrations. In aliphatic compounds, the frequencies are near 1550 and 1380 cm^{-1}, whereas in aromatic compounds the bands are observed near 1520 and 1350 cm^{-1}. These frequencies are somewhat sensitive to nearby substituents. In particular, the 1350 cm^{-1} band in aromatic nitro compounds is intensified by electron-donating substituents in the ring. The out-of-plane CH bending patterns of *ortho*-, *meta*-, and *para*-disubstituted benzene rings are often perturbed in nitro compounds. Other compounds containing N–O bonds have strong characteristic IR absorption bands.

2.7.5 Amides

Secondary amides (*N*-monosubstituted amides) usually have their NH and C=O groups trans to each other. The

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Table 12. Details of IR frequencies of some nitrogen-containing groups.

Group and class	Range (cm^{-1}) and intensity[a]	Assignment and remarks
The –NH_2 group		
Primary amides (solid state)	3360–3340 (vs)	NH_2 antisymmetric stretch
	3190–3170 (vs)	NH_2 symmetric stretch
	1680–1660 (vs)	C=O stretch; (amide I band)
	1650–1620 (m)	NH_2 deformation; (amide II band)
Primary amines	3450–3250 (m)	NH_2 stretching; broad, with structure
	1650–1590 (s)	NH_2 deformation
	850–750 (s)	NH_2 wagging; broad band
The –NH– Group		
Secondary amides	3300–3250 (m)	NH stretch; solid state
	3100–3060 (w)	Overtone band
	1680–1640 (vs)	C=O stretch; (amide I band)
	1560–1530 (vs)	Coupled NH deformation and C–N stretch; (amide II band)
	750–650 (s)	NH wag, broad band
Secondary amines	3500–3300 (m)	NH stretch
	750–650 (s, br)	NH wag
The C≡N group		
Saturated aliphatic nitriles	2260–2240 (w)	C≡N stretch
Aromatic nitriles	2240–2220 (variable)	C≡N stretch; stronger than in saturated aliphatic nitriles
Isonitriles (alkyl)	2180–2110 (w-m)	–N≡C stretch
Isonitriles (aryl)	2130–2110 (w-m)	–N≡C stretch
The C=N group		
Oximes	1690–1620 (w-m)	C=NOH stretch
Pyridines	1615–1565 (s)	Two bands, due to C=C and C=N stretching in ring
The C–N group (amines and amides)		
Primary aliphatic	1140–1070 (m)	C–C–N antisymmetric stretch
Secondary aliphatic	1190–1130 (m-s)	C–N–C antisymmetric stretch
Primary aromatic	1330–1260 (s)	Phenyl-N stretch
Secondary aromatic	1340–1250 (s)	Phenyl-N stretch
The NO_2 group		
Aliphatic nitro compounds	1560–1530 (vs)	NO_2 antisymmetric stretch
	1390–1370 (m-s)	NO_2 symmetric stretch
Aromatic nitro compounds	1540–1500 (vs)	NO_2 antisymmetric stretch
	1370–1330 (s-vs)	NO_2 symmetric stretch
Nitrates R–O–NO_2	1660–1620 (vs)	NO_2 antisymmetric stretch
	1300–1270 (s)	NO_2 symmetric stretch
	710–690 (s)	NO_2 deformation
The NO groups (N=O, N–O)		
Nitrites R–O–NO	1680–1650 (vs)	N=O stretch
Oximes	965–930 (s)	N–O stretch
Nitrates R–O–NO_2	870–840 (s)	N–O stretch
Aromatic *N*-oxides	1300–1200 (vs)	N–O stretch
Aliphatic *N*-oxides	970–950 (vs)	N–O stretch
The N≡N and N=N groups		
Azides	2120–2160 (variable)	N≡N stretch
Azo compounds	1450–1400 (vw)	N=N stretch

[a] s, strong; m, medium; w, weak; v, very.

carbonyl stretching mode gives rise to a very strong IR band between 1680 and 1640 cm^{-1}. This band is known as the amide I band. A second, very strong absorption that occurs between 1560 and 1530 cm^{-1} is known as the amide II band. It is believed to be due to coupling of the NH bending and C–N stretching vibrations. The trans amide linkage also gives rise to absorption between 1300 and 1250 cm^{-1} and to a broad band centered near 700 cm^{-1} (Figure 7f). Occasionally, the amide linkage is cis in cyclic compounds such as lactams. In such cases, a strong NH stretching band

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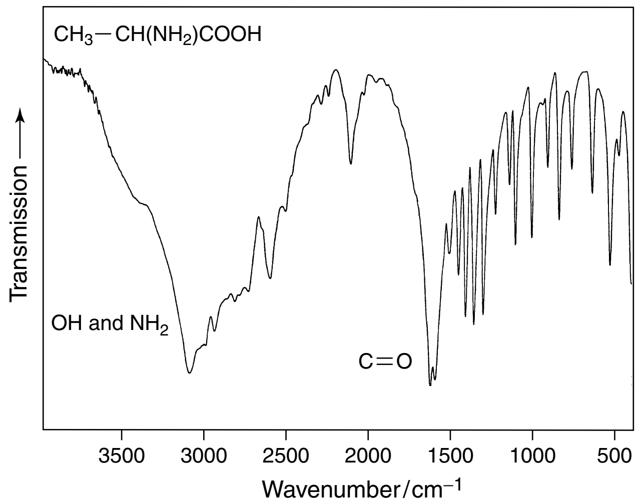

Figure 20. The IR spectrum of an amino acid, L-alanine.

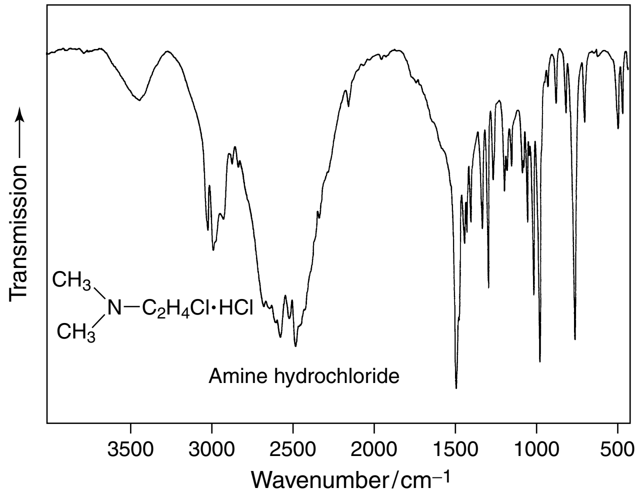

Figure 21. The IR spectrum of a tertiary amine hydrohalide, (2-chloroethyl)dimethylamine hydrochloride.

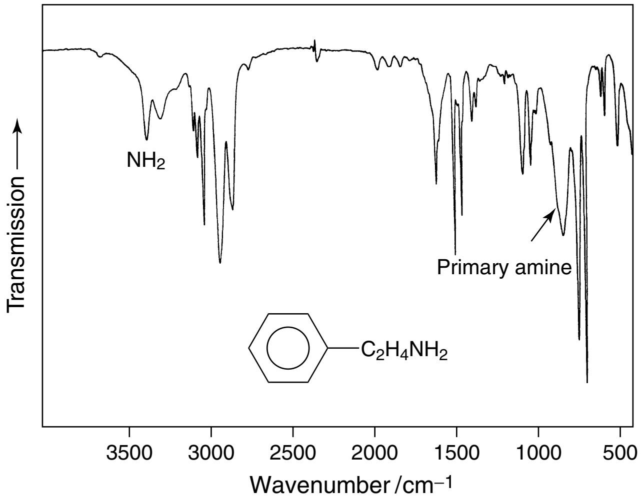

Figure 22. The IR spectrum of an aliphatic amine joined to a benzene ring, phenethylamine.

is seen near 3200 cm^{-1} and a weaker combination band near 3100 cm^{-1} involving simultaneous excitation of C=O stretching and NH bending. The amide II band is absent but a *cis* NH bending mode absorbs between 1500 and 1450 cm^{-1}. This band may be confused with the CH_2 or antisymmetric CH_3 deformation bands.

2.8 Compounds containing phosphorus and sulfur

The presence of phosphorus in organic compounds can be detected by the IR absorption bands arising from the P–H, P–OH, P–O–C, P=O, and P=S groups. A phosphorus atom directly attached to an aromatic ring is also well characterized. The usual frequencies of these groups in various compounds are listed in Table 13. Thomas[9] is a good source of information on IR spectra of organophosphorus compounds. Most of these groups absorb strongly or very strongly in the IR, with the exception of P=S. There is no characteristic P–C group frequency in aliphatic compounds.

The SO_2 and SO groups give rise to very strong IR bands in various compounds between 1400 and 1000 cm^{-1}. Other bonds involving sulfur, such as C–S, S–S, and S–H, give very weak IR absorptions. Characteristic frequencies of some sulfur-containing groups are also listed in Table 13. The C=S group has been omitted from the table because the C=S stretching vibration is invariably coupled with vibrations of other groups in the molecule. Frequencies in the 1400–850 cm^{-1} range have been assigned to this group with thioamides at the low frequency end of the range. The IR bands involving C=S groups are usually weak.

2.8.1 Phosphorus acids and esters

Phosphorus acids have P–OH groups that give one or two broad bands of medium intensity between 2700 and 2100 cm^{-1}. Esters and acid salts that have P–OH groups also absorb in this region. A small, sharp band near 2400 cm^{-1} indicates the presence of a PH group. In ethoxy and methoxy phosphorus compounds, as well as other aliphatic compounds with a P–O–C linkage, a very strong and quite broad IR band is observed between 1050 and 950 cm^{-1}. The presence of a P=O bond is indicated by a strong band close to 1250 cm^{-1}.

2.8.2 Aromatic phosphorus compounds

Aromatic phosphorus compounds have several characteristic group frequencies. A fairly strong, sharp IR peak is observed near 1440 cm^{-1} in compounds in which a phosphorus atom is attached directly to a benzene ring. A quaternary phosphorus atom attached to a benzene ring has a characteristic strong, sharp band near 1100 cm^{-1}. The

Table 13. Characteristic IR frequencies of groups containing phosphorus or sulfur.

Group and class	Range (cm^{-1}) and intensity[a]	Assignment and remarks
The P–H group		
Phosphorus acids and esters	2425–2325 (m)	P–H stretch
Phosphines	2320–2270 (m)	P–H stretch; sharp band
Phosphines	1090–1080 (m)	PH_2 deformation
Phosphines	990–910 (m-s)	P–H wag
The P–OH group		
Phosphoric or phosphorus acids	2700–2100 (w)	OH stretch; one or two broad and often weak bands
Esters and salts	1040–929 (s)	P–OH stretch
The P–O–C group		
Aliphatic compounds	1050–950 (vs)	Antisymmetric P–O–C stretch
	830–750 (s)	Symmetric P–O–C stretch (methoxy and ethoxy phosphorus compounds only)
Aromatic compounds	1250–1160 (vs)	Aromatic C–O stretch
	1050–870 (vs)	P–O stretch
The P–C group		
Aromatic compounds	1450–1430 (s)	P joined directly to a ring; sharp band
Quaternary aromatic	1110–1090 (s)	P^+ joined directly to a ring; sharp band
The P=O group		
Aliphatic compounds R–O–P(=O)–	1260–1240 (s)	Strong, sharp band
Aromatic compounds Ar–O–P(=O)–	1350–1300 (s)	Lower frequency (1250–1180 cm^{-1}) when OH group is attached to the P atom
Phosphine oxides	1200–1140 (s)	P=O stretch
The S–H group		
Thiols (mercaptans)	2580–2500 (w)	S–H stretch
The C–S group		
General	720–600 (w)	C–S stretch
The S–S group		
Disulfides	550–450 (vw)	S–S stretch
The S=O group		
Sulfoxides	1060–1020 (vs)	S=O stretch
Dialkyl sulfites	1220–1190 (vs)	S=O stretch
The SO_2 group		
Sulfones, sulfonamides, sulfonic acids, sulfonates, sulfonyl chlorides	1390–1290 (vs) 1190–1120 (vs)	SO_2 antisymmetric stretch SO_2 symmetric stretch
Dialkyl sulfates and sulfonyl fluorides	1420–1390 (vs) 1220–1190 (vs)	SO_2 antisymmetric stretch SO_2 symmetric stretch
The S–O–C group		
Dialkyl sulfites	1050–850 (vs)	S–O–C stretching (two bands)
Sulfates	1050–770 (vs)	S–O–C stretching (two or more bands)

[a] s, strong; m, medium; w, weak; v, very.

P–O group attached to an aromatic ring gives rise to two strong bands between 1250 and 1160 cm^{-1} and between 1050 and 870 cm^{-1} due to stretching of the Ar–P–O linkage. When the P–O group is attached to a ring through the oxygen atom, the Ar–O–P group again gives two strong bands, but the higher frequency of these is found between 1350 and 1250 cm^{-1}.

2.8.3 Compounds containing C–S, S–S, and S–H groups

IR spectra of compounds containing C–S and S–S bonds contain very weak bands due to these groups between 700 and 600 and near 500 cm^{-1}, respectively. The S–H stretching band near 2500 cm^{-1} is normally quite weak in the IR.

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2.8.4 Compounds containing S=O groups

The stretching vibration of the S=O group in sulfoxides gives rise to strong broad IR absorption near 1050 cm^{-1}. In the spectra of alkyl sulfites the S=O stretch is observed near 1200 cm^{-1}. Organic sulfones contain the SO_2 group which gives rise to two very strong bands due to antisymmetric (1369–1290 cm^{-1}) and symmetric (1170–1120 cm^{-1}) stretching modes.

The frequencies of the SO_2 stretching vibrations of sulfonyl halides are about 50 cm^{-1} higher than those of sulfones due to the electronegative halogen atom. In the IR spectra of sulfonic acids, very broad absorption is observed between 3000 and 2000 cm^{-1} due to OH stretching. The antisymmetric and symmetric SO_2 stretching modes give two strong bands near 1350 cm^{-1} and between 1200 and 1100 cm^{-1} respectively in both alkyl and aryl sulfonic acids and sulfonates.

2.9 Heterocyclic compounds

Heterocyclic compounds containing nitrogen, oxygen, or sulfur may exhibit three kinds of group frequencies: those involving CH or NH vibrations, those involving motion of the ring, and those due to the group frequencies of substituents on the ring. The identification of a heterocyclic compound from its IR spectrum is a difficult task. However, characteristic frequencies for some heterocyclic compounds are collected in Table 14 and the identification of a few types of compound are discussed in this section. Details of IR spectra of numerous classes of heterocyclic compounds may be found in Socrates.[4]

2.9.1 Aromatic heterocycles

Hydrogen atoms attached to carbon atoms in an aromatic heterocyclic ring such as pyridine give rise to CH stretching modes in the usual 3100–3000 cm^{-1} region, or a little higher in furans, pyrroles, and some other compounds. Characteristic ring stretching modes, similar to those of benzene derivatives, are observed between 1600 and 1000 cm^{-1}. The out-of-plane CH deformation vibrations give rise to strong IR bands in the 1000–650 cm^{-1} region. In some cases, these patterns are characteristic of the type of substitution in the heterocyclic ring. Some examples include furans, indoles, pyridines, pyrimidines, and quinolines. The in-plane CH bending modes also give several bands in the 1300–1000 cm^{-1} region for aromatic heterocyclic compounds. CH vibrations in benzene derivatives and analogous modes in related heterocyclic compounds can be correlated and may be useful in structure determination.

Overtone and combination bands are observed between 2000 and 1750 cm^{-1} in the IR spectra. These bands are similar to those observed for benzene derivatives and are characteristic of the position of substitution. In aromatic heterocyclic compounds involving nitrogen, the coupled C=C and C=N stretching modes give rise to several characteristic vibrations. These are similar in frequency to their counterparts in the corresponding nonheterocyclic compounds. Ring stretching modes are found in the 1600–1300 cm^{-1} region. Other skeletal ring modes include ring-breathing modes near 1000 cm^{-1}, in-plane ring deformation between 700 and 600 cm^{-1} and out-of-plane ring deformation modes, which may be observed between 700 and 300 cm^{-1}.

2.9.2 Pyrimidines and purines

Pyrimidines and purines absorb strongly in the IR between 1640 and 1520 cm^{-1} due to C=C and C=N stretching of the ring. A band near 1630 cm^{-1} is attributed to C=N stretching and a second band between 1580 and 1520 cm^{-1} is assigned to a C=C stretch. (The C=N stretch usually gives rise to a very strong Raman line in these and related heterocyclic compounds.) Pyrimidines and purines usually have absorption bands between 700 and 600 cm^{-1} due to CH out-of-plane bending. Nitrogen heterocycles can form *N*-oxides, which have a characteristic very strong IR band near 1280 cm^{-1}.

2.9.3 Five-membered ring compounds

Pyrroles, furans and thiophenes generally have a band in their IR spectra due to C=C stretching near 1580 cm^{-1}. A strong band is also observed between 800 and 700 cm^{-1} due to an out-of-plane deformation vibration of the CH=CH group, similar to that of *cis*-disubstituted alkenes. In the spectra of pyrroles a strong broad band is observed between 3400 and 3000 cm^{-1} due to the H-bonded N–H stretching mode. Furans have medium to strong IR bands between 1610 and 1560 cm^{-1}, 1520 and 1470 cm^{-1} and 1400 and 1390 cm^{-1} due to ring stretching vibrations. All furans have a strong absorption near 595 cm^{-1}, which is attributed to a ring deformation mode.

Thiophenes absorb in the IR between 3100 and 3000 cm^{-1} (CH stretching), 1550 and 1200 cm^{-1} (ring stretching) and 750 and 650 cm^{-1} (out-of-plane C–H bending). IR spectra of thiophenes generally have a band in the region 530–450 cm^{-1} due to an out-of-plane ring deformation.

2.9.4 NH stretching bands in heterocyclic compounds

Spectra of heterocyclic nitrogen compounds may contain bands due to a secondary or tertiary amine group. Pyrroles,

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Table 14. Characteristic IR frequencies for some heterocyclic compounds.

Classes of compounds	Range (cm^{-1}) and intensity[a]	Assignment and remarks
Azoles (imidazoles, isoxazoles, oxazoles, pyrazoles, triazoles tetrazoles)	3300–2500 (s)	Broad, H-bonded NH stretch; resembles carboxylic acids
	1650–1380 (m-s)	Three ring-stretching bands
	1040–980 (s)	Ring breathing
1,4-Dioxanes	1460–1440 (vs)	CH_2 deformation
	1400–1150 (s)	CH_2 twist and wag
	1130–1000 (m)	Ring mode
Furans	3140–3120 (m)	CH stretch; higher than most aromatics
	1600–1400 (m-s)	Ring stretching modes (three bands)
	770–720 (vs)	Band weakens as number of substituents increases
Indoles	3470–3450 (vs)	NH stretch
	1600–1500 (m-s)	Ring stretching modes (two bands)
	900–600 (vs)	Substitution patterns due to both 6- and 5-membered rings
Pyridines (general)	3080–3020 (w-m)	CH stretch; several bands
	2080–1670 (w)	Overtones and combinations, similar to substituted benzenes
	1615–1565 (s)	Two bands due to C=C and C=N stretching in ring
	1030–990 (s)	Ring-breathing
Pyridines (2-substituted)	780–740 (s)	CH out-of-plane deformation
	630–605 (m-s)	In-plane ring deformation
	420–400 (s)	Out-of-plane ring deformation
Pyridines (3-substituted)	820–770 (s)	CH out-of-plane deformation
	730–690 (s)	Ring deformation
	635–610 (m-s)	In-plane ring deformation
	420–380 (s)	Out-of-plane ring deformation
Pyridines (4-substituted)	850–790 (s)	CH out-of-plane deformation
Pyridines (disubstituted)	830–810 (s) and 740–720 (s)	CH out-of-plane deformations
Pyridines (trisubstituted)	730–720 (s)	CH out-of-plane deformation
Pyrimidines	1590–1370 (m-s)	Ring stretching; four bands
	685–660 (m-vs)	Ring deformation
Pyrroles	3480–3430 (vs)	NH stretch; often a sharp band
	3130–3120 (w)	CH stretch; considerably higher than normal
	1560–1390 (variable)	Ring stretching; usually three bands
	770–720 (s)	Broad band due to CH out-of-plane deformation
Thiophenes	1590–1350 (m-vs)	Several bands due to ring stretching modes
	810–680 (vs)	CH out-of-plane deformation; lower than in pyrroles and furans
Triazines	1560–1520 (vs) and 1420–1400 (s)	Two bands due to ring stretching modes
	820–740 (s)	Out-of-plane ring deformation

[a] s, strong; m, medium; w, weak; v, very.

indoles, and carbazoles in nonpolar solvents have their NH stretching vibrations between 3500 and 3450 cm^{-1}, and the band is very strong in the IR. In saturated heterocyclics, such as pyrrolidines and piperidines, the band is at lower frequencies. Azoles have a very broad hydrogen-bonded NH stretching band between 3300 and 2500 cm^{-1}. This band might be confused with the broad OH stretching band of carboxylic acids.

2.10 Compounds containing halogens

A halogen atom attached to a carbon atom adjacent to a functional group often causes a significant shift in the group frequency. Some examples are listed in Table 15. Fluorine is particularly important in this regard and special care must be exercised in conclusions drawn from IR (and Raman) spectra when this element is present. Carbon–fluorine stretching bands are very strong in the IR, usually between 1350 and 1100 cm^{-1}. The CF stretching band may hide other functional groups that absorb in this region of the spectrum. It should be mentioned that there are many known cases of symmetrical C–F stretching modes at frequencies much lower than the usual 1350–1100 cm^{-1}. The usual regions for the C–X stretching and bending vibrations have been given previously in Table 2.

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Table 15. The effect of halogen substituents on some group frequencies.

Group or class	Range (cm^{-1})	Assignment and remarks
Fluorine		
Fluorocarbons (–FCH– and CF_2H)	3010–2990	CH stretch; higher frequency than normal
$F_2C{=}CF$–	1870–1800	C=C stretch; much higher frequency than normal
$F_2C{=}C$	1760–1730	C=C stretch; much higher frequency than normal
Acid fluorides (F–C=O)	1900–1820	C=O stretch; very high carbonyl group frequency
Ketones (–CF_2COCH_2) and (–CD_2COCF_2)	1800–1770	C=O stretch; normal range for ketones is 1730–1700 cm^{-1}
Carboxylic acids (–CF_2–COOH)	1780–1740	C=O stretch; the normal range for carboxylic acids (dimers) is 1720–1680 cm^{-1}
Nitriles (–CF_2–C=N)	2280–2260	C=N stretch; 20 cm^{-1} higher than normal
Amides (CF_2–$CONH_2$)	1730–1700	C=O stretch; 30 cm^{-1} higher than normal
Chlorine, bromine, and iodine		
CH_2Cl	1300–1240	CH_2 wag; strong IR band
CH_2Br	1240–1190	CH_2 wag; strong IR band
CH_2I	1190–1150	CH_2 wag; strong IR band
Acid chlorides	1810–1790	C=O stretch
α-Halo esters	1770–1745	C=O stretch; 20 cm^{-1} higher than the normal range
Noncyclic halo ketones	1745–1730	C=O stretch; 15 cm^{-1} higher than the normal range
α-Halo carboxylic acids	1740–1720	C=O stretch; the normal range is 1720–1680 cm^{-1}
Chloroformates	1800–1760	C=O stretch; near 1720 cm^{-1} in formate esters
α-Chloro aldehydes	1770–1730	Higher than normal aldehydes

The CH_2 wagging mode in compounds with a CH_2X group gives rise to a strong band whose frequency depends on X. When X is Cl, the range is 1300–1250 cm^{-1}. For Br, the band is near 1230 cm^{-1}, and for I, a still lower frequency near 1170 cm^{-1} is observed.

2.11 Boron, silicon and organometallic compounds

Boron–carbon and silicon–carbon stretching modes are not usually identifiable, since they are coupled with other skeletal modes. However, the C–B–C antisymmetric stretching mode in phenylboron compounds gives a strong IR band between 1280 and 1250 cm^{-1}, and a silicon atom attached to an aromatic ring gives two very strong bands near 1430 and 1110 cm^{-1}. Metal–carbon stretching frequencies are found between 600 and 400 cm^{-1} with the lighter metals at the high frequency end of the range, as expected from equation (1). The B–O and B–N bonds in organoboron compounds give very strong IR bands between 1430 and 1330 cm^{-1}. The Si–O–C vibration gives a very strong IR absorption, which is often quite broad in the 1100–1050 cm^{-1} range. Some characteristic frequencies for boron and silicon compounds are listed in Table 16. The B–CH_3 and Si–CH_3 symmetric CH_3 deformation modes occur at 1330–1280 cm^{-1} and 1280–1250 cm^{-1}, respectively. The CH_3 deformations in metal–CH_3 groups give rise to bands between 1210 and 1180 cm^{-1} in organomercury and organotin compounds and between 1170–1150 cm^{-1} in organolead compounds.

The IR spectra of aromatic organometallic compounds usually contain a fairly strong, sharp band near 1430 cm^{-1} due to a benzene ring vibration. This band has been observed for compounds in which As, Sb, Sn, Pb, B, Si, and P atoms are attached directly to the ring.

2.12 Examples of the use of spectra structure correlations

Deducing the structure of a compound from its IR spectrum is not easy; in fact, for large complicated molecules it is not possible. The best way to obtain structural information from IR spectra is by practice. A list of sources of interpreted spectra and problems is given in the literature.[15–17]

It is useful to have a checklist of questions giving basic information on the structure. For example, which elements are present? what is the molecular mass? is the molecular formula known? what additional information is available from other instrumental or chemical methods? Then, from an IR survey spectrum, further clues can be gathered. Again, a checklist is useful. Are there any broad absorption bands? (See Table 4.) Is there an aromatic ring present? (See Section 2.4.) What kind of X–H bonds are present? (OH, NH, CH, SH, etc.) Is there a carbonyl group in the molecule? Then a systematic analysis of the bands in the IR spectrum can be made, first using Table 3,

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Table 16. Some IR group frequencies in boron and silicon compounds.

	Group	Range (cm^{-1}) and intensity[a]	Assignment and remarks
Boron	–BOH	3300–3200 (s)	Broad band due to H-bonded OH stretch
	–BH and –BH_2	2650–2350 (s)	Doublet for –BH_2 stretch
	–BH and –BH_2	1200–1150 (ms)	–BH_2 deformation, or B–H bend
	–BH_2	980–920 (m)	–BH_2 wag
	B-Benzene ring	ca 1430 (m-s)	Benzene ring vibration
	B–N	1460–1330 (vs)	B–N stretch; borazines and aminoboranes
	B–O	1380–1310 (vvs)	B–O stretch; boronates, boronic acids
	C–B–C	1280–1250 (vs)	C–B–C antisymmetric stretch
Silicon -	SiOH	3700–3200 (s)	OH stretch, similar to alcohols
	Si–OH	900–820 (s)	Si–O stretch
	–SiH, –SiH_2, and –SiH_3	2150–2100 (m)	Si–H stretch
	–SiH, –SiH_2, and –SiH_3	950–800 (s)	Si–H deformation and wag
	Si-Aromatic ring	ca 1430 (m-s)	Ring mode
	Si-Aromatic ring	1100 (vs)	Ring mode
	Si–O–C (aliphatic)	1100–1050 (vvs)	Si–O–C antisymmetric stretch
	Si–O–Aromatic ring	970–920 (vs)	Si–O stretch
	Si–O–Si	1100–1000 (s)	Si–O–Si antisymmetric stretch

[a] s, strong; m, medium; v, very.

then Table 2. Tentative assignments can be made to each band, cross-checking where possible in other regions of the spectrum. When a tentative identification has been made to a class of compounds, the IR spectrum of the "unknown" compound should be compared to spectra of similar compounds in a library of IR spectra.[10–14,18–21]

2.12.1 *Example 1. A compound containing two C=O groups*

The IR spectrum of an example of this type of compound is shown in Figure 23.

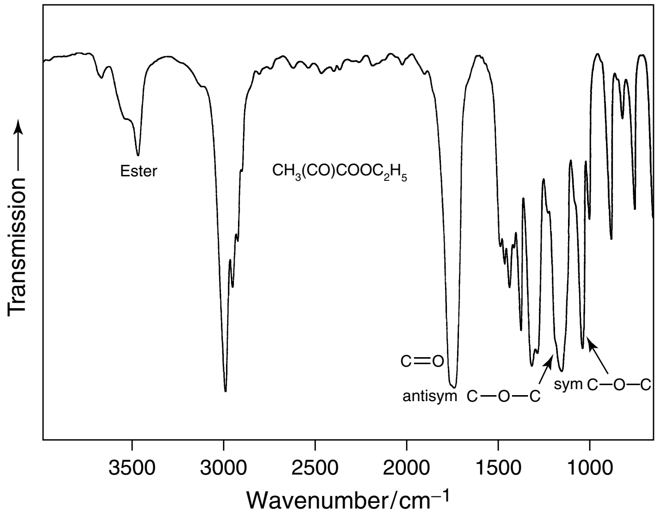

Figure 23. The IR spectrum of an α-keto ester, ethyl pyruvate.

An elemental analysis indicates that only C, H, and O are present and the molecular formula is $C_5H_8O_3$. Looking at the CH stretching region, we conclude that there is no unsaturated group present. This is confirmed by the absence of absorption between 1670 and 1540 cm^{-1}.

A CH_3 group or groups (bands at 2980 and 1355 cm^{-1}) and possibly a CH_2 group (bands at 2930 and 1415 cm^{-1}) are present. Now, turning to the carbonyl stretching region, we note from Tables 9 and 10 that the compound could be a cyclic ketone, an ester, a lactone, an aldehyde, or an α-keto ester. We can eliminate aldehyde (no band near 2700 cm^{-1}) and lactones or cyclic ketones (not possible with three oxygens and a methyl group). The bands at 1135 and 1020 cm^{-1} suggest an ester linkage. The weak band at 3440 cm^{-1} (see Table 5) supports this assignment.

Thus the IR spectrum indicates that the compound is an α-keto ester. Two α-keto esters could have the molecular formula $C_5H_8O_3$. One of these is ethyl pyruvate ($CH_3COCOOC_2H_5$). The other ($C_2H_5COCOOCH_3$) contains a methoxy group, which would give a sharp band near 2830 cm^{-1} (see Section 2.3.1).

2.12.2 *Example 2. A compound containing C, H and O*

A low-melting white solid of molecular weight 164 gave the spectrum shown in Figure 24.

The very strong broad band extending from 3500 cm^{-1} down to 2400 cm^{-1} is characteristic of a hydrogen-bonded carboxylic acid (Table 4). The weaker broad band centered near 930 cm^{-1} together with the strong carbonyl stretching

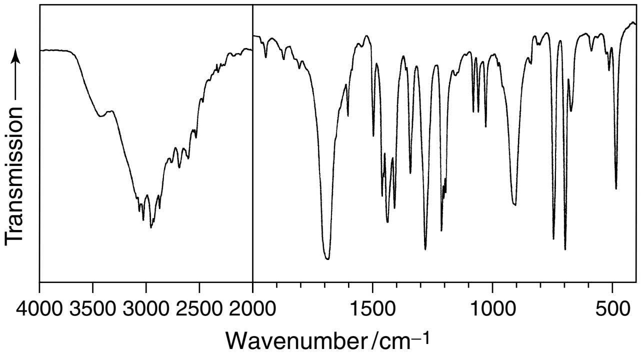

Figure 24. The IR spectrum of a solid compound of molecular weight 164.

band at 1700 cm^{-1} also indicate the presence of a COOH group (Table 9). The sharp bands near 1600 cm^{-1} (weak) and 1500 cm^{-1} (medium) suggest a benzene ring, and the doublet at 750 and 700 cm^{-1} indicates that the ring is monosubstituted (Table 8). Peaks are seen on top of the broad OH stretching band at 3035 and 2940 cm^{-1}, indicating the presence of both aromatic CH and aliphatic CH_2 or CH_3 groups.

The combined molecular weight of the C_6H_5– and –COOH groups is 122. The remaining mass of 42 could be due to C_3H_6, which would be present in any of the three structural isomers 2-, 3-, and 4-phenylbutyric acid. The absence of a band near 1375 cm^{-1} indicates that there is no methyl group in the molecule. Thus it is concluded that the compound is 4-phenylbutyric acid.

2.12.3 *Example 3. A compound containing C, H and N*

A liquid of molecular weight 101 gave the spectrum shown in Figure 25.

The most striking feature of the spectrum in Figure 25 is the strong broad band centered near 800 cm^{-1}. Examination of Table 4 indicates that the compound is probably a primary aliphatic amine. The doublet at 3380 and 3310 cm^{-1} confirms this assignment, and the absence of any CH stretching bands above 3000 cm^{-1} indicates that the molecule is saturated. Another feature is the weak band at 725 cm^{-1}, which indicates a chain of at least four –CH_2– groups. The band at 1385 cm^{-1} is due to a methyl group, so that a possible structure of molecular weight 101 is $CH_3(CH_2)_5NH_2$. The compound is hexylamine.

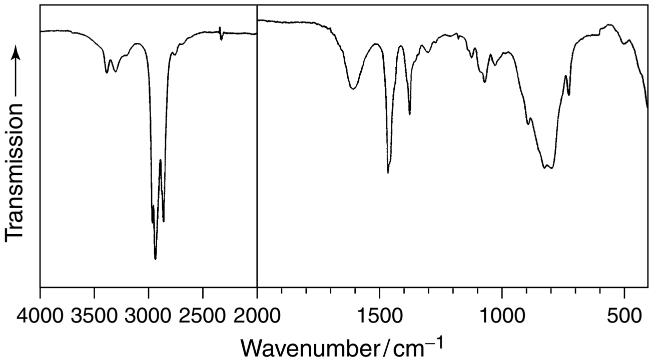

Figure 25. The IR spectrum of a liquid compound of molecular weight 101.

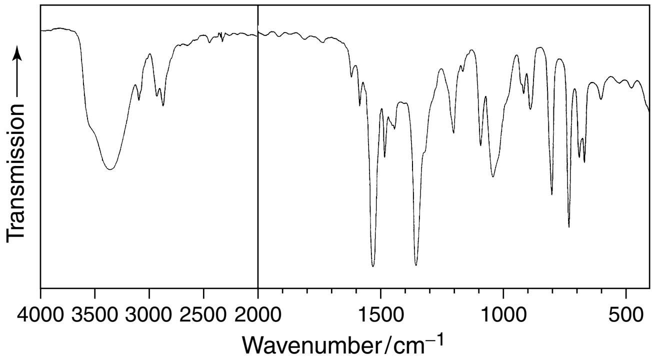

Figure 26. The IR spectrum of a compound of molecular weight 153.

2.12.4 *Example 4. A compound containing C, H, O and N*

The strongest bands in the spectrum in Figure 26 are the broad feature centered at 3400 cm^{-1} and the very strong peaks at 1530 and 1355 cm^{-1}. The first of these can be assigned to an OH group, while the other two suggest the presence of an aromatic nitro compound (Table 12). The weak peaks at 3105, 2940, and 2950 cm^{-1} suggest that both unsaturated and saturated CH groups are present. The sharp peaks at 1590 and 1485 cm^{-1} could be due to a benzene ring, and in that case the strong doublet at 810 and 730 cm^{-1} indicates a 1,3-disubstituted benzene derivative. A possible structure with the appropriate molecular weight is *m*-nitrobenzyl alcohol.

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