13.15: Some Vibrations Are Infrared Inactive

13.15: Some Vibrations Are Infrared Inactive

Infrared spectroscopy is the study of the interaction of infrared light with matter. The fundamental measurement obtained in infrared spectroscopy is an infrared spectrum, which is a plot of measured infrared intensity versus wavelength (or frequency) of light.

Introduction

In infrared spectroscopy, units called wavenumbers are normally used to denote different types of light. The frequency, wavelength, and wavenumber are related to each other via the following equation(1):

$$c = v\lambda$$

c = the speed of light (cm/sec)
v = frequency in Hertz (sec^{-1})
λ = wavelength in cm

$$W = 1/\lambda$$

W = wavenumber in cm^{-1}
λ = wavelength in cm

(1)

These equations show that light waves may be described by their frequency, wavelength or wavenumber. Here, we typically refer to light waves by their wavenumber, however it will be more convenient to refer to a light wave's frequency or wavelength. The wavenumber of several different types of light are shown in table 1.

>14,000 cm^{-1} Visible UV & X-rays	14,000 to 4000cm^{-1} Near Infrared	4000 to 400cm^{-1} Mid Infrared	400 to 4cm^{-1} Far Infrared	<4cm^{-1} Microwaves Radio Waves
Higher Wavenumber				Lower Wavenumber
Higher Frequency				Lower Frequency
Higher Energy				Lower Energy
Shorter Wavelength				Longer Wavelength

Table 1. The Electromagnetic spectrum showing the wavenumber of several different types of light.

When a molecule absorbs infrared radiation, its chemical bonds vibrate. The bonds can stretch, contract, and bend. This is why infrared spectroscopy is a type of vibrational spectroscopy. Fortunately, the complex vibrational motion of a molecule can be broken down into a number of constituent vibrations called normal modes. For example, when a guitar string is plucked, the string vibrates at its normal mode frequency. Molecules, like guitar strings, vibrate at specfic frequencies so different molecules vibrate at different frequencies because their structures are different. This is why molecules can be distinguished using infrared spectroscopy. The first necessary condition for a molecule to absorb infrared light is that the molecule must have a vibration during which the change in dipole moment with respect to distance is non-zero. This condition can be summarized in equation(2) form as follows:

$$\frac{\partial \mu}{\partial x} \neq 0$$

$\partial \mu$ = change in dipole moment
∂x = change in bond distance

(2)

Vibrations that satisfy this equation are said to be infrared active. The H-Cl stretch of hydrogen chloride and the asymmetric stretch of CO_2 are examples of infrared active vibrations. Infrared active vibrations cause the bands seen in an infrared spectrum.

The second necessary condition for infrared absorbance is that the energy of the light impinging on a molecule must equal a vibrational energy level difference within the molecule. This condition can be summarized in equation(3) form as follows:

$$\Delta E_{vib} = hcW$$

ΔE_{vib} = vibrational energy level difference in a molecule
h = Planck's Constant (Joule-sec)
c = the speed of light (cm/sec)
W = wavenumber in cm^{-1}

(3)

If the energy of a photon does not meet the criterion in this equation, it will be transmitted by the sample and if the photon energy satisfies this equation, that photon will be absorbed by the molecule.(See Infrared: Theory for more detail)

As any other analytical techniques, infrared spectroscopy works well on some samples, and poorly on others. It is important to know the strengths and weaknesses of infrared spectroscopy so it can be used in the proper way. Some advantages and disadvantages of infrared spectroscopy are listed in table 2.

Advantages	Disadvantages
Solids, Liquids, gases, semi-solids, powders and polymers are all analyzed

The peak positions, intensities, widths, and shapes all provide useful information

Fast and easy technique

Sensitive technique (Micrograms of materials can be detected routinely)

Inexpensive | Atoms or monatomic ions do not have infrared spectra

Homonuclear diatomic molecules do not posses infrared spectra

Complex mixture and aqueous solutions are difficult to analyze using infrared spectroscopy |

Origin of Peak Positions, Intensities, and Widths

Peak Positions

The equation(4) gives the frequency of light that a molecule will absorb, and gives the frequency of vibration of the normal mode excited by that light.

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2}$$

ν = frequency in cm^{-1}

k = force constant in N/cm

μ = reduced mass in Kg

(4)

Only two variables in equation(4) are a chemical bond's force constant and reduced mass. Here, the reduced mass refers to $(M_1M_2)/(M_1+M_2)$ where M_1 and M_2 are the masses of the two atoms, respectively. These two molecular properties determine the wavenumber at which a molecule will absorb infrared light. No two chemical substances in the universe have the same force constants and atomic masses, which is why the infrared spectrum of each chemical substance is unique. To understand the effect of atomic masses and force constant on the positions of infrared bands, table 3 and 4 are shown as an example, respectively.

Table 3. An Example of an Mass Effect

Bond	C-H Stretch in cm^{-1}
$C-^1H$	~3000
$C-^2D$	~2120

The reduced masses of $C-^1H$ and $C-^2D$ are different, but their force constants are the same. By simply doubling the mass of the hydrogen atom, the carbon-hydrogen stretching vibration is reduced by over $800cm^{-1}$.

Table 4. An Example of an electronic Effect

Bond	C-H Stretch in cm^{-1}
C-H	~3000

H-C=O	~2750

When a hydrogen is attached to a carbon with a C=O bond, the C-H stretch band position decrease to ~2750cm^{-1}. These two C-H bonds have the same reduced mass but different force constants. The oxygen in the second molecule pulls electron density away from the C-H bond so it makes weaken and reduce the C-H force constant. This cause the C-H stretching vibration to be reduced by ~250cm^{-1}.

The Origin of Peak Intensies

The different vibrations of the different functional groups in the molecule give rise to bands of differing intensity. This is because $\frac{\partial \mu}{\partial x}$ is different for each of these vibrations. For example, the most intense band in the spectrum of octane shown in Figure 3 is at 2971, 2863 cm^{-1} and is due to stretching of the C-H bond. One of the weaker bands in the spectrum of octane is at 726cm^{-1}, and it is due to long-chain methyl rock of the carbon-carbon bonds in octane. The change in dipole moment with respect to distance for the C-H stretching is greater than that for the C-C rock vibration, which is why the C-H stretching band is the more intense than C-C rock vibration.

Another factor that determines the peak intensity in infrared spectra is the concentration of molecules in the sample. The equation(5) that relates concentration to absorbance is Beer's law,

$$A = \varepsilon lc \qquad A = \text{absorbance}$$
$$\varepsilon = \text{absorptivity}$$
$$l = \text{pathlength}$$
$$c = \text{concentration}$$

(5)

The absorptivity is the proportionality constant between concentration and absorbance, and is dependent on $(\partial\mu/\partial x)^2$. The absorptivity is an absolute measure of infrared absorbance intensity for a specific molecule at a specific wavenumber. For pure sample, concentration is at its maximum, and the peak intensities are true representations of the values of $\partial\mu/\partial x$ for different vibrations. However, in a mixture, two peaks may have different intensities because there are molecules present in different concentration.

The Orgins of Peak Widths

In general, the width of infrared bands for solid and liquid samples is determined by the number of chemical environments which is related to the strength of intermolecular interactions such as hydrogen bonding. Figure 1. shows hydrogen bond in water molecules and these water molecules are in different chemical environments. Because the number and strength of hydrogen bonds differs with chemical environment, the force constant varies and the wavenumber differs at which these molecules absorb infrared light.
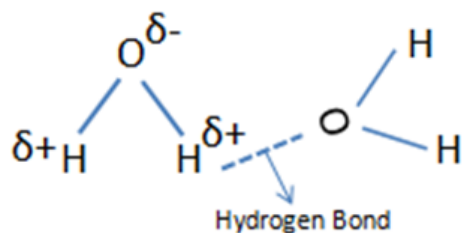
Figure 1. Hydrogen Bonding in water molecules

In any sample where hydrogen bonding occurs, the number and strength of intermolecular interactions varies greatly within the sample, causing the bands in these samples to be particularly broad. This is illustrated in the spectra of ethanol(Fig7) and hexanoic acid(Fig11). When intermolecular interactions are weak, the number of chemical environments is small, and narrow infrared bands are observed.

The Origin of Group Frequencies

An important observation made by early researchers is that many functional group absorb infrared radiation at about the same wavenumber, regardless of the structure of the rest of the molecule. For example, C-H stretching vibrations usually appear between 3200 and 2800cm^{-1} and carbonyl(C=O) stretching vibrations usually appear between 1800 and 1600cm^{-1}. This makes these bands diagnostic markers for the presence of a functional group in a sample. These types of infrared bands are called group frequencies because they tell us about the presence or absence of specific functional groups in a sample.
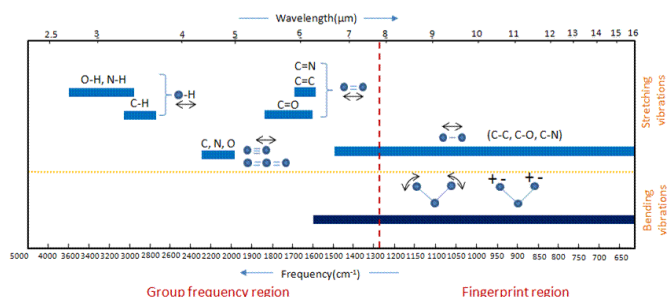
Figure 2. Group frequency and fingerprint regions of the mid-infrared spectrum

The region of the infrared spectrum from 1200 to 700 cm^{-1} is called the fingerprint region. This region is notable for the large number of infrared bands that are found there. Many different vibrations, including C-O, C-C and C-N single bond stretches, C-H bending vibrations, and some bands due to benzene rings are found in this region. The fingerprint region is often the most complex and confusing region to interpret, and is usually the last section of a spectrum to be interpreted. However, the utility of the fingerprint region is that the many bands there provide a fingerprint for a molecule.

Spectral Interpretation by Application of Group Frequencies

Organic Compounds

One of the most common application of infrared spectroscopy is to the identification of organic compounds. The major classes of organic molecules are shown in this category and also linked on the bottom page for the number of collections of spectral information regarding organic molecules.

Hydrocarbons

Hydrocarbons compounds contain only C-H and C-C bonds, but there is plenty of information to be obtained from the infrared spectra arising from C-H stretching and C-H bending.

In alkanes, which have very few bands, each band in the spectrum can be assigned:

- C–H stretch from 3000–2850 cm^{-1}
- C–H bend or scissoring from 1470-1450 cm^{-1}
- C–H rock, methyl from 1370-1350 cm^{-1}
- C–H rock, methyl, seen only in long chain alkanes, from 725-720 cm^{-1}

Figure 3. shows the IR spectrum of octane. Since most organic compounds have these features, these C-H vibrations are usually not noted when interpreting a routine IR spectrum. Note that the change in dipole moment with respect to distance for the C-H stretching is greater than that for others shown, which is why the C-H stretch band is the more intense.
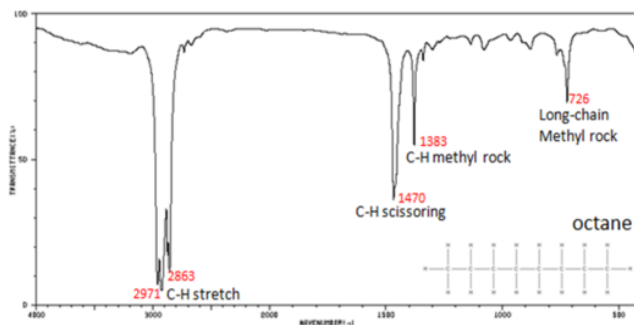
Figure 3. Infrared Spectrum of Octane

In alkenes compounds, each band in the spectrum can be assigned:

- C=C stretch from 1680-1640 cm^{-1}
- =C–H stretch from 3100-3000 cm^{-1}
- =C–H bend from 1000-650 cm^{-1}

Figure 4. shows the IR spectrum of 1-octene. As alkanes compounds, these bands are not specific and are generally not noted because they are present in almost all organic molecules.
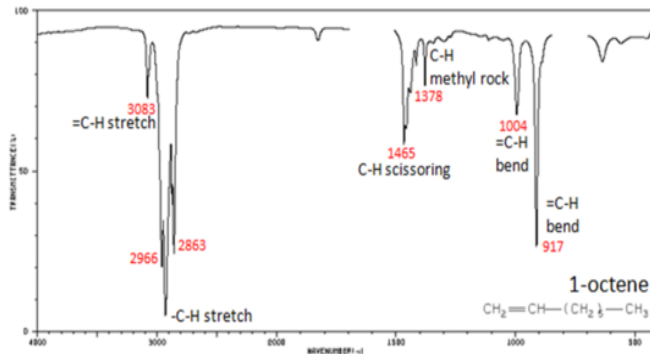

Figure 4. Infrared Spectrum of 1-Octene

In alkynes, each band in the spectrum can be assigned:

- −C?C− stretch from 2260-2100 cm^{-1}
- −C?C−H: C−H stretch from 3330-3270 cm^{-1}
- −C?C−H: C−H bend from 700-610 cm^{-1}

The spectrum of 1-hexyne, a terminal alkyne, is shown below.
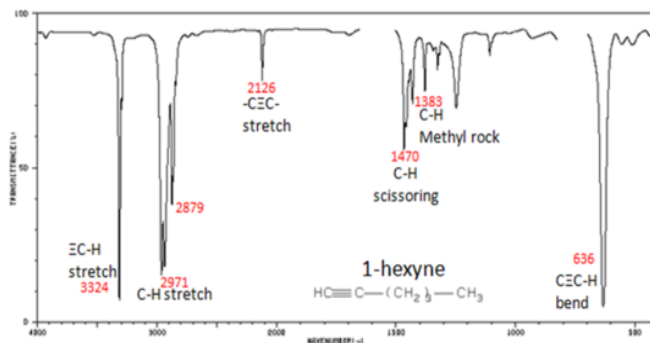
Figure 5. Infrared Spectrum of 1-Hexyne

In aromatic compounds, each band in the spectrum can be assigned:

- C−H stretch from 3100-3000 cm^{-1}
- overtones, weak, from 2000-1665 cm^{-1}
- C−C stretch (in-ring) from 1600-1585 cm^{-1}
- C−C stretch (in-ring) from 1500-1400 cm^{-1}
- C−H "oop" from 900-675 cm^{-1}

Note that this is at slightly higher frequency than is the –C–H stretch in alkanes. This is a very useful tool for interpreting IR spectra. Only alkenes and aromatics show a C–H stretch slightly higher than 3000 cm^{-1}.

Figure 6. shows the spectrum of toluene.
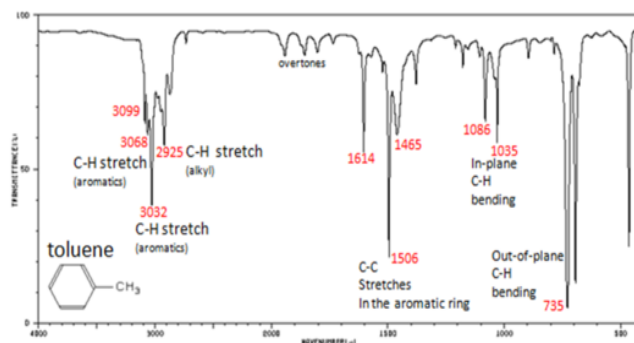
Figure 6. Infrared Spectrum of Toluene

Functional Groups Containing the C-O Bond

Alcohols have IR absorptions associated with both the O-H and the C-O stretching vibrations.

- O–H stretch, hydrogen bonded 3500-3200 cm^{-1}
- C–O stretch 1260-1050 cm^{-1} (s)

Figure 7. shows the spectrum of ethanol. Note the very broad, strong band of the O–H stretch.
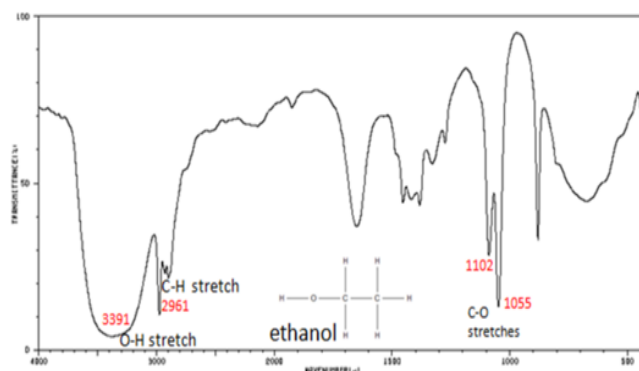
Figure 7. Infrared Spectrum of Ethanol

The carbonyl stretching vibration band C=O of saturated aliphatic ketones appears:

- C=O stretch   - aliphatic ketones 1715 cm^{-1}

    - ?, ?-unsaturated ketones 1685-1666 cm^{-1}

Figure 8. shows the spectrum of 2-butanone. This is a saturated ketone, and the C=O band appears at 1715.
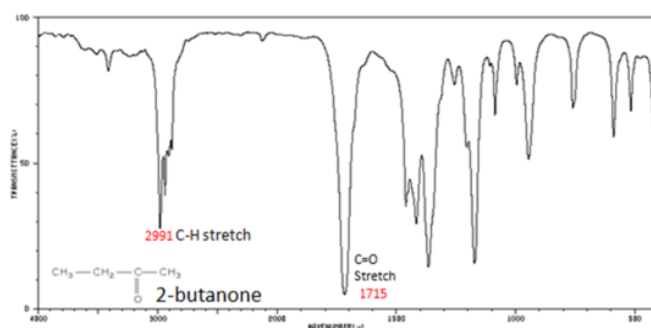
Figure 8. Infrared Spectrum of 2-Butanone

If a compound is suspected to be an aldehyde, a peak always appears around 2720 cm^{-1} which often appears as a shoulder-type peak just to the right of the alkyl C–H stretches.

- H–C=O stretch 2830-2695 cm^{-1}
- C=O stretch:
  - aliphatic aldehydes 1740-1720 cm^{-1}
  - alpha, beta-unsaturated aldehydes 1710-1685 cm^{-1}

Figure 9. shows the spectrum of butyraldehyde.
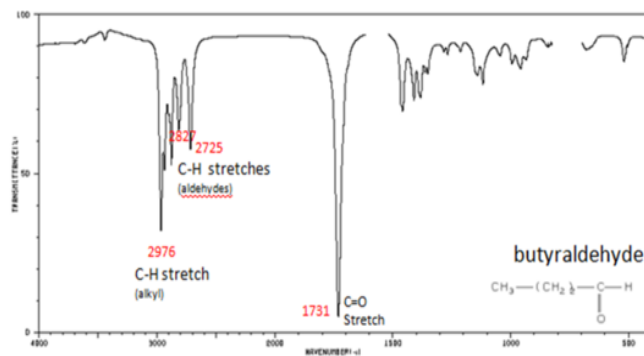
Figure 9. Infrared Spectrum of Butyraldehyde

The carbonyl stretch C=O of esters appears:

- C=O stretch
  - aliphatic from 1750-1735 cm^{-1}
  - ?, ?-unsaturated from 1730-1715 cm^{-1}
- C–O stretch from 1300-1000 cm^{-1}

Figure 10. shows the spectrum of ethyl benzoate.
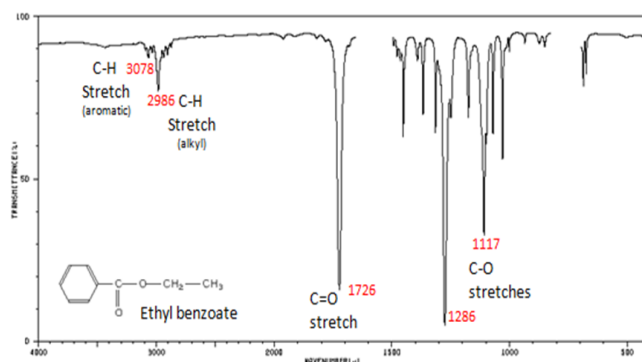
Figure 10. Infrared Spectrum of Ethyl benzoate

The carbonyl stretch C=O of a carboxylic acid appears as an intense band from 1760-1690 cm^{-1}. The exact position of this broad band depends on whether the carboxylic acid is saturated or unsaturated, dimerized, or has internal hydrogen bonding.

- O–H stretch from 3300-2500 cm^{-1}
- C=O stretch from 1760-1690 cm^{-1}
- C–O stretch from 1320-1210 cm^{-1}
- O–H bend from 1440-1395 and 950-910 cm^{-1}

Figure 11. shows the spectrum of hexanoic acid.
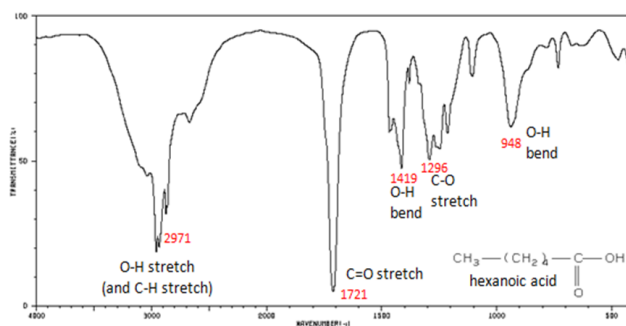
Figure 11. Infrared Spectrum of Hexanoic acid

Organic Nitrogen Compounds

- N–O asymmetric stretch from 1550-1475 cm^{-1}
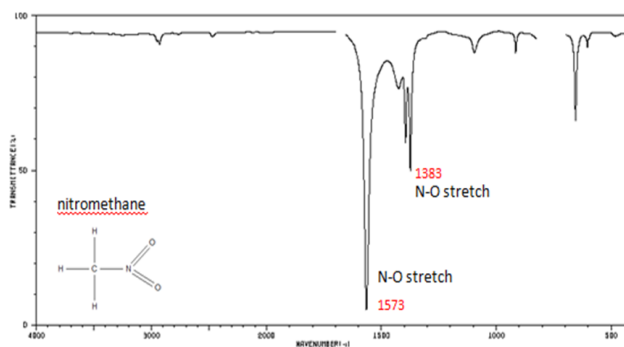- N–O symmetric stretch from 1360-1290 cm^{-1}

Figure 12. Infrared Spectrum of Nitomethane

Organic Compounds Containing Halogens

Alkyl halides are compounds that have a C–X bond, where X is a halogen: bromine, chlorine, fluorene, or iodine.

- C–H wag (-CH$_2$X) from 1300-1150 cm^{-1}
- C–X stretches (general) from 850-515 cm^{-1}
  - C–Cl stretch 850-550 cm^{-1}
  - C–Br stretch 690-515 cm^{-1}
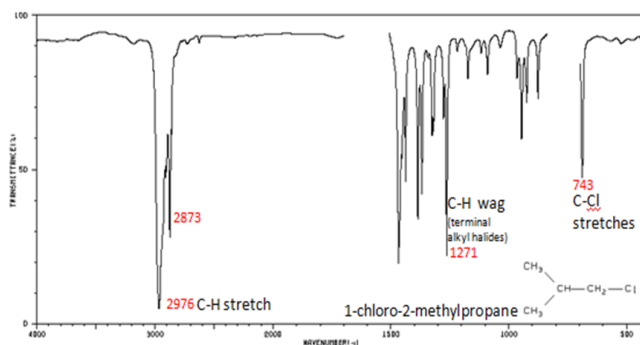
The spectrum of 1-chloro-2-methylpropane are shown below.

Figure 13. Infrared Spectrum of 1-chloro-2-methylpropane

For more Infrared spectra Spectral database of organic molecules is introduced to use free database. Also, the infrared spectroscopy correlation table is linked on bottom of page to find other assigned IR peaks.

Inorganic Compounds

Generally, the infrared bands for inorganic materials are broader, fewer in number and appear at lower wavenumbers than those observed for organic materials. If an inorganic compound forms covalent bonds within an ion, it can produce a characteristic infrared spectrum.

Main infrared bands of some common inorganic ions:

- CO_3^{2-} 1450-1410, 880-800cm^{-1}
- SO_4^{2-} 1130-1080, 680-610cm^{-1}
- NO_3^- 1410-1340, 860-800cm^{-1}
- PO_4^{3-} 1100-950cm^{-1}
- SiO_4^{2-} 1100-900cm^{-1}
- NH_4^+ 3335-3030, 1485-1390cm^{-1}
- MnO_4^- 920-890, 850-840cm^{-1}

Diatomic molecules produce one vibration along the chemical bond. Monatomic ligand, where metal s coordinate with atoms such as halogens, H, N or O, produce characteristic bands. These bands are summarized in below.

Chracteristic infrared bands of diatomic inorganic molecules: M(metal), X(halogen)

- M-H stretching   2250-1700cm^{-1}
- M-H bending   800-600cm^{-1}
- M-X stretching   750-100cm^{-1}
- M=O stretching   1010-850cm^{-1}
- M=N stretching   1020-875cm^{-1}

The normal modes of vibration of linear and bent triatomic molecules are illustrated and some common linear and bent triatomic molecules are shown below. Note that some molecules show two bands for $?_1$ because of Fermi resonance.

Characteristic infrared bands(cm^{-1}) of triatomic inorganic molecules:

Linear Molecules	OCO	HCN	NCS⁻	ClCN	MgCl₂

1388, 1286   3311   2053   714, 784   327

ν_1

667   712   486, 471   380   249

ν_{2a}

2349   2049   748   2219   842

ν_{2b}

ν_3

Bent Molecules H_2O O_3 $SnCl_2$

3675   1135   354

ν_1
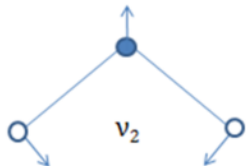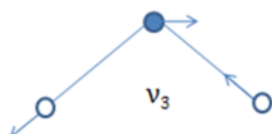
1595   716   120

ν_2

3756   1089   334

ν_3
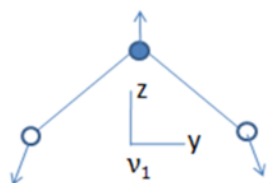
Identification

There are a few general rules that can be used when using a mid-infrared spectrum for the determination of a molecular structure. The following is a suggested strategy for spectrum interpretation:[2]

1. Look first at the high-wavenumber end of the spectrum($>1500 cm^{-1}$) and concentrate initially on the major bands
2. For each band, 'short-list' the possibilities by using a correlation table
3. Use the lower-wavenumber end of the spectrum for the confirmation or elaboration of possible structural elements
4. Do not expect to be able to assign every band in the spectrum
5. Keep 'cross-checking' wherever possible.
6. Exploit negative evidence as well as positive evidence

7. Band intensities should be treated with some caution. Under certain circumstances, they may vary considerably for the same group

8. Take care when using small wavenumber changes. If in solution, some bands are very 'solvent-sensitive'

9. Do not forget to subtract slovent bands if possible

Infrared spectroscopy is used to analyze a wide variety of samples, but it cannot solve every chemical analysis problem. When used in conjunction with other methods such as mass spectroscopy, nuclear magnetic resonance, and elemental analysis, infrared spectroscopy usually makes possible the positive identification of a sample.

References

1. Infrared Spectral Interpretation by Brian Smith, CRC Press, 1999

2. Infrared Spectroscopy: Fundamentals and Applications by Barbara Atuart, John Wiley&Sons, Ltd., 2004

3. Interpretation of Infrared Spectra, A Practical Approach by John Coates in Encyclopedia of Analytical Chemistry pp. 10815-10837, John Wiley&Sons Ltd, Chichester, 2000

Outside Links

- Spectral Database for Organic Compounds SDBS: http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology, date of access)
- Infrared Spectroscopy Correlation Table: http://en.wikipedia.org/wiki/Infrared_spectroscopy_correlation_table
- FDM Reference Spectra Databases: http://www.fdmspectra.com/index.html
- Other Usuful Web Pages:
    ◦ http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/InfraRed/infrared.htm
    ◦ Fermi resonance : http://en.wikipedia.org/wiki/Fermi_resonance