

Course: B.Sc. (P) Analytical Chemistry

Subject: Instrumental Methods of Analysis

Semester: VI

Preparation of Samples for Infrared Spectroscopy

To determine the infrared spectrum of a compound, one must place the compound in a sample holder, or cell. In infrared spectroscopy, this immediately poses a problem. Glass and plastics absorb strongly throughout the infrared region of the spectrum. Cells must be constructed of ionic substances-typically sodium chloride or potassium bromide. Potassium bromide plates are more expensive than sodium chloride plates but have the advantage of usefulness in the range of 4000 to 400 cm^{-1} . Sodium chloride plates are used widely because of their relatively low cost. The practical range for their use in spectroscopy extends from 4000 to 650 cm^{-1} . Sodium chloride begins to absorb at 650 cm^{-1} , and any bands with frequencies less than this value will not be observed. Since few important bands appear below 650 cm^{-1} , sodium chloride plates are in most common use for routine infrared spectroscopy.

Liquids

A drop of a liquid organic compound is placed between a pair of polished sodium chloride or potassium bromide plates, referred to as **salt plates**. When the plates are squeezed gently, a thin liquid film forms between them. A spectrum determined by this method is referred to as a **neat** spectrum since no solvent is used. Salt plates break easily and are water soluble. Organic

compounds analyzed by this technique must be free of water. The pair of plates is inserted into a holder that fits into the spectrometer.

Solids

There are several methods for determining infrared spectra for solids. One method of choice has been to mix a finely ground sample with powdered potassium bromide and press the mixture under high pressure. Under pressure, the potassium bromide melts and seals the sample into a matrix. The resulting **KBr pellet** is inserted in the instrument. If a good pellet is prepared, the spectrum obtained will have no interfering bands since potassium bromide is transparent down to 400 cm^{-1} .

Another method, a **Nujol mull**, involves grinding the compound with mineral oil (Nujol) to create a suspension of the finely divided sample dispersed in mineral oil. The thick suspension is placed between two salt plates. The main disadvantage of this method is that the mineral oil obscures bands that may be present in the analyzed compound. Nujol bands appear at 2924, 1462, and 1377 cm^{-1} .

The best method of determining a spectrum of a solid is to make use of an **attenuated total reflectance (ATR) accessory**. Modern FT-IR instruments now offer this accessory along with the typical transmittance module. The ATR method provides a powerful sampling technique that virtually eliminates sample preparation with both liquids and solids, thus leading to rapid analysis of samples. Although manufacturers offer multiple crystal options, the diamond ATR offers the best option for maximum durability in the organic chemistry laboratory. With the ATR accessory, one simply places a small amount of a liquid or solid directly on the diamond without any previous preparation. The diamond is cut and mounted at precise angles so that the incoming

beam of infrared radiation bounces back and forth off the internal surfaces of the crystal. When the beam reflects off the surface where the sample has been applied, it penetrates the sample slightly, and the vibrational frequencies of the sample are somewhat absorbed, thereby “attenuating” the beam.

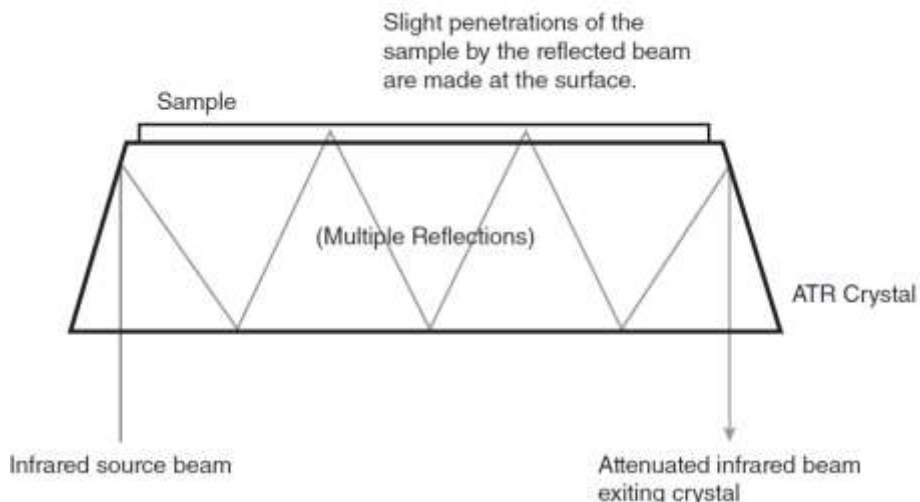


Fig. 1 Schematic diagram of IR spectroscopy

The ATR accessory has revolutionized the ease of infrared spectral analysis of solids. For example, it is often unnecessary to make use of KBr pellets and Nujol mulls. The spectrum obtained with an ATR FT-IR is nearly identical to that obtained with an FT-IR operating in the transmittance mode. One may observe some differences in the relative intensities of the peaks, but the peak position in wavenumbers is identical in both modes.² ATR FT-IR does not require a clear sample that allows light to pass through the sample, such as is common with transmittance instruments. There are some limitations with a diamond ATR instrument. Some materials such as coatings on metal and very dark samples do not analyze satisfactorily, but there are few other limitations.

Analysis of Infrared Spectra

An infrared spectrometer determines the positions and relative sizes of all the absorptions, or peaks, in the infrared region and plots them on a piece of paper. This plot of absorption intensity versus wavenumber (or sometimes wavelength) is referred to as the infrared spectrum of the compound.

Figure 2 shows a typical infrared spectrum, that of 3-methyl-2-butanone. The spectrum exhibits at least two strongly absorbing peaks at about 3000 and 1715 cm^{-1} for the C-H and C=O stretching frequencies, respectively.

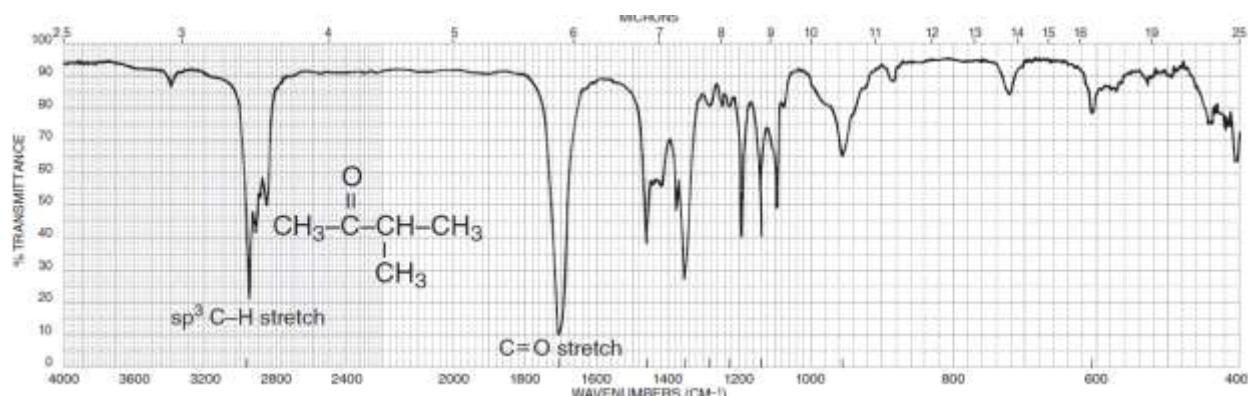


FIG. 2 The infrared spectrum of 3-methyl-2-butanone (neat liquid, KBr plates).

The strong absorption at 1715 cm^{-1} that corresponds to the carbonyl group (C=O) is quite intense. In addition to the characteristic position of absorption, the *shape* and *intensity* of this peak are also unique to the C=O bond. This is true for almost every type of absorption peak; both shape and intensity characteristics can be described, and these characteristics often enable the chemist to distinguish the peak in potentially confusing situations. For instance, to some extent C=O and C=C bonds absorb in the same region of the infrared spectrum:

C=O	1850–1630 cm^{-1}
C=C	1680–1620 cm^{-1}

However, the C=O bond is a strong absorber, whereas the C=C bond generally absorbs only weakly (Fig. 3). Hence, trained observers would not interpret a strong peak at 1670 cm^{-1} to be a C=C double bond or a weak absorption at this frequency to be due to a carbonyl group

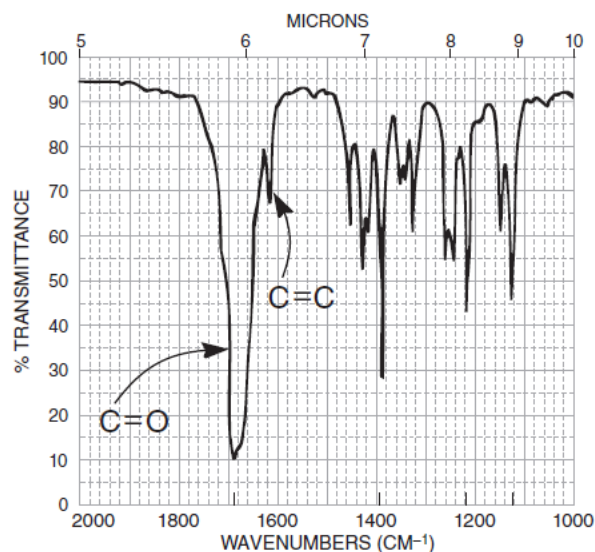


FIG. 3 A comparison of the intensities of the C=O and C=C absorption bands.

The shape and fine structure of a peak often give clues to its identity as well. Thus, although the N-H and O-H regions overlap,

O-H	$3650\text{--}3200\text{ cm}^{-1}$
N-H	$3500\text{--}3300\text{ cm}^{-1}$

the N-H absorption usually has one or two *sharp* absorption bands of lower intensity, whereas OH, when it is in the N-H region, usually gives a *broad* absorption peak. Also, primary amines give *two* absorptions in this region, whereas alcohols as pure liquids give only one (Fig. 4). Figure 4 also shows typical patterns for the C-H stretching frequencies at about 3000 cm^{-1} .

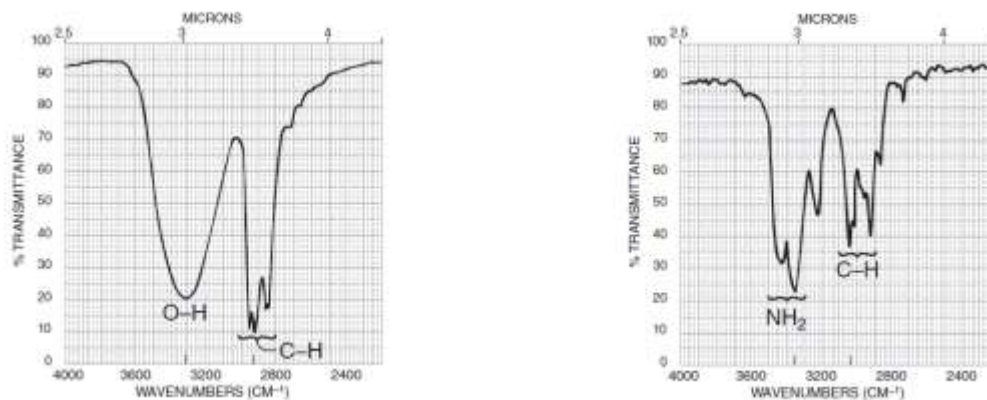


FIG. 4 A comparison of the shapes of the absorption bands for the O-H and N-H groups.

Table 1. A Simplified Correlation Chart

Type of Vibration		Frequency (cm ⁻¹)	Intensity	Page Reference
C-H	Alkanes (stretch)	3000-2850	s	31
	-CH ₃ (bend)	1450 and 1375	m	
	-CH ₂ - (bend)	1465	m	
	Alkenes (stretch)	3100-3000	m	33
	(out-of-plane bend)	1000-650	s	
	Aromatics (stretch)	3150-3050	s	43
	(out-of-plane bend)	900-690	s	
Alkyne (stretch)	ca. 3300	s	35	
Aldehyde		2900-2800	w	56
		2800-2700	w	
C-C	Alkane	Not interpretatively useful		
C=C	Alkene	1680-1600	m-w	33
	Aromatic	1600 and 1475	m-w	43
C≡C	Alkyne	2250-2100	m-w	35
C=O	Aldehyde	1740-1720	s	56
	Ketone	1725-1705	s	58
	Carboxylic acid	1725-1700	s	62
	Ester	1750-1730	s	64
	Amide	1700-1640	s	70
	Anhydride	1810 and 1760	s	73
	Acid chloride	1800	s	72
C-O	Alcohols, ethers, esters, carboxylic acids, anhydrides	1300-1000	s	47, 50, 62, 64, and 73
O-H	Alcohols, phenols			
	Free	3650-3600	m	47
	H-bonded	3400-3200	m	47
	Carboxylic acids	3400-2400	m	62
N-H	Primary and secondary amines and amides			
	(stretch)	3500-3100	m	74
	(bend)	1640-1550	m-s	74
C-N	Amines	1350-1000	m-s	74
C-N	Imines and oximes	1690-1640	w-s	77
C≡N	Nitriles	2260-2240	m	77
X-C-Y	Allenes, ketenes, isocyanates, isothiocyanates	2270-1940	m-s	77
N-O	Nitro (R-NO ₂)	1550 and 1350	s	79
S-H	Mercaptans	2550	w	81
S-O	Sulfoxides	1050	s	81
	Sulfones, sulfonyl chlorides, sulfates, sulfonamides	1375-1300 and 1350-1140	s	82
C-X	Fluoride	1400-1000	s	85
	Chloride	785-540	s	85
	Bromide, iodide	< 667	s	85

Table 2. Base Values for Absorptions of Bonds

O-H	3400 cm ⁻¹	C≡C	2150 cm ⁻¹
N-H	3400	C=O	1715
C-H	3000	C=C	1650
C≡N	2250	C-O	1100

References:

1. *Introduction to Spectroscopy* by **Donald L. Pavia**