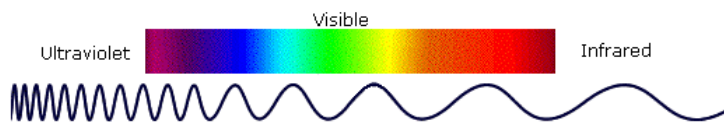


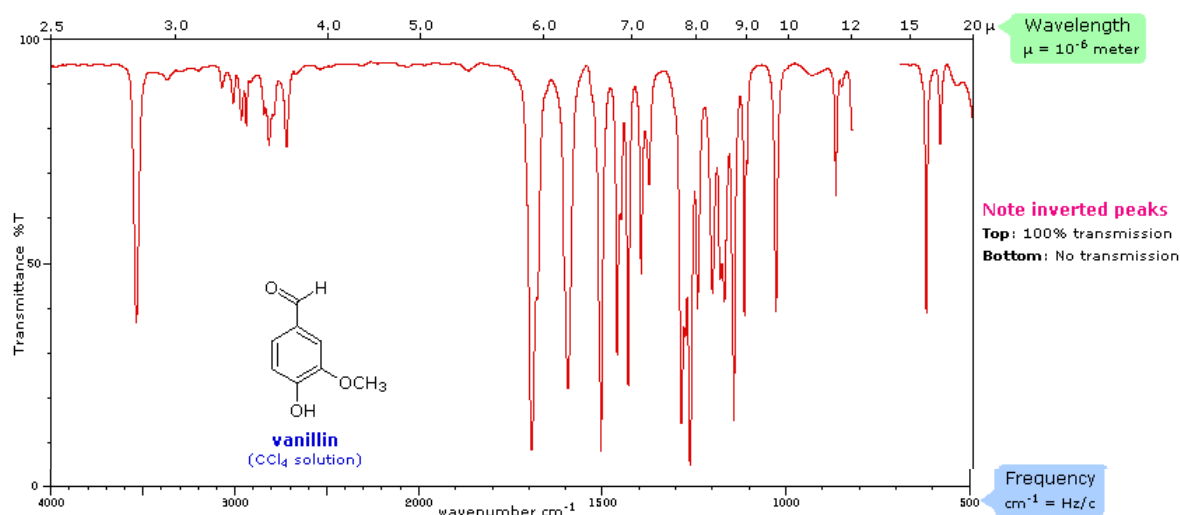
# Identification by infrared spectroscopy (IR). Comparison of transmission and reflectance techniques (KBr-tablet and Attenuated total

## 1. Introduction

As noted in a previous chapter, the light our eyes see is but a small part of a broad spectrum of electromagnetic radiation. On the immediate high energy side of the visible spectrum lies the ultraviolet, and on the low energy side is the infrared. The portion of the infrared region most useful for analysis of organic compounds is not immediately adjacent to the visible spectrum, but is that having a wavelength range from 2,500 to 16,000 nm, with a corresponding frequency range from  $1.9 \times 10^{13}$  to  $1.2 \times 10^{14}$  Hz.



Photon energies associated with this part of the infrared (from 1 to 15 kcal/mole) are not large enough to excite electrons, but may induce vibrational excitation of covalently bonded atoms and groups. The covalent bonds in molecules are not rigid sticks or rods, such as found in molecular model kits, but are more like stiff springs that can be stretched and bent. The mobile nature of organic molecules was noted in the chapter concerning [conformational isomers](#). We must now recognize that, in addition to the facile rotation of groups about single bonds, molecules experience a wide variety of vibrational motions, characteristic of their component atoms. Consequently, virtually all organic compounds will absorb infrared radiation that corresponds in energy to these vibrations. Infrared spectrometers, similar in principle to the UV-Visible spectrometer [described elsewhere](#), permit chemists to obtain absorption spectra of compounds that are a unique reflection of their molecular structure. An example of such a spectrum is that of the flavoring agent vanillin, shown below.



The complexity of this spectrum is typical of most infrared spectra, and illustrates their use in identifying substances. The gap in the spectrum between 700 & 800  $\text{cm}^{-1}$  is due to solvent (CCl<sub>4</sub>) absorption. Further analysis (below) will show that this spectrum also indicates the presence of an aldehyde function, a phenolic hydroxyl and a substituted benzene ring. The inverted display of absorption, compared with [UV-Visible spectra](#), is characteristic. Thus a sample that did not absorb at all would record a horizontal line at 100% transmittance (top of the chart).

The frequency scale at the bottom of the chart is given in units of **reciprocal centimeters ( $\text{cm}^{-1}$ )** rather than Hz, because the numbers are more manageable. The reciprocal centimeter is the number of wave cycles in one centimeter; whereas, frequency in cycles per second or Hz is equal to the number of wave cycles in  $3 \times 10^{10}$  cm (the distance covered by light in one second). Wavelength units are in micrometers, **microns ( $\mu$ )**, instead of nanometers for the same reason. Most infrared spectra are displayed on a linear frequency scale, as shown here, but in some older texts a linear wavelength scale is used. A calculator for interconverting these frequency and wavelength values is provided on the right. Simply enter the value to be converted in the appropriate box, press "Calculate" and the equivalent number will appear in the empty box. Infrared spectra may be obtained from samples in all phases (liquid, solid and gaseous). Liquids are usually examined as a thin film sandwiched between two polished salt plates (note that glass absorbs infrared radiation, whereas NaCl is transparent). If solvents are used to dissolve solids, care must be taken to avoid obscuring important spectral regions by solvent absorption. Perchlorinated solvents such as carbon tetrachloride, chloroform and tetrachloroethene are commonly used. Alternatively, solids may either be incorporated in a thin KBr disk, prepared under high pressure, or mixed with a little non-volatile liquid and ground to a paste (or mull) that is smeared between salt plates.

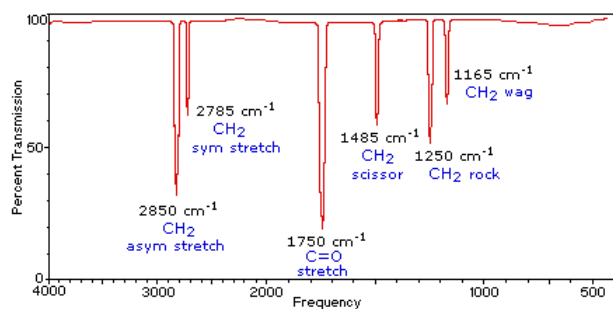
### Frequency - Wavelength Converter

<input type="text" value="2000"/>	Frequency in $\text{cm}^{-1}$	<input type="button" value="Calculate"/>
<input type="text" value="5"/>	Wavelength in $\mu$	<input type="button" value="Clear Input"/>

## 2. Vibrational Spectroscopy

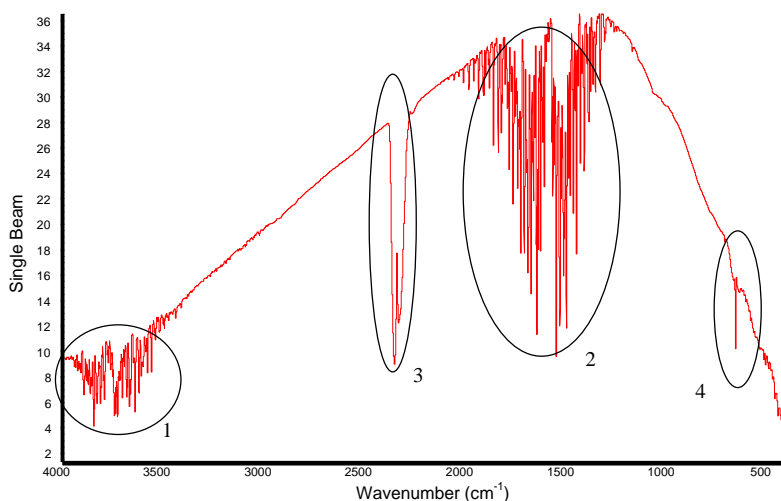
A molecule composed of  $n$ -atoms has  $3n$  degrees of freedom, six of which are translations and rotations of the molecule itself. This leaves  $3n-6$  degrees of vibrational freedom ( $3n-5$  if the molecule is linear). Vibrational modes are often given descriptive names, such as stretching, bending, scissoring, rocking and twisting. The four-atom molecule of formaldehyde, the gas phase spectrum of which is shown below, provides an example of these terms. If a ball & stick model of formaldehyde is not displayed to the right of the spectrum, press the **view ball&stick model** button on the right. We expect six fundamental vibrations (12 minus 6), and these have been assigned to the spectrum absorptions. To see the formaldehyde molecule display a vibration, click one of the buttons under the spectrum, or click on one of the absorption peaks in the spectrum.

### Gas Phase Infrared Spectrum of Formaldehyde, $\text{H}_2\text{C}=\text{O}$



ArtTextJml/Sj

Jmol



**Fig 3.** MIR spectrum of air (background). Signals 1 and 2 correspond to water vapours (wavenumber  $1559\text{ cm}^{-1}$  is suitable for humidity determination); bands 3 and 4 belong to carbon dioxide.

## 3. Cuvette material

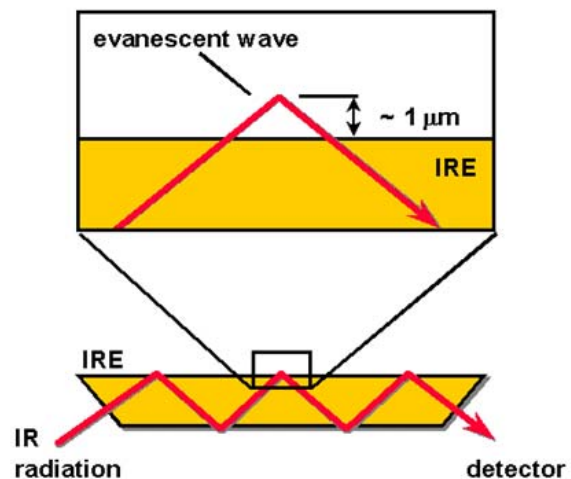
The material must be transparent for IR radiation. Neither glass nor quartz are suitable.

KBr	40,000-400	1.53		Very soft, water soluble crystal; low cost and good transmission range; fogs.
ZnSe	17,000-720	2.2		A hard and brittle crystal; inert; ideal material for ATR. Also known as Irtran-1.
<del>SiO<sub>2</sub> (Quartz)</del>	<del>65,000-2,700</del>	<del>1.4</del>	<del></del>	<del>A hard crystal, clear in the visible</del>

## Another technique of measurement

# Instrumental Setup: Attenuated Total Reflectance (ATR) Technique

- IR radiation passes through (IRE-internal reflection element) crystal and hits sample at a 45 degree angle
  - IRE made of high refractive index material (zinc selenide, diamond, germanium)
- Incident radiation penetrates into sample (~1 micrometer) where it can be absorbed
- Attenuated radiation is reflected



## Spectra Comparison

- Resulting peaks from ATR are very similar in intensity and wavelength to transmittance technique

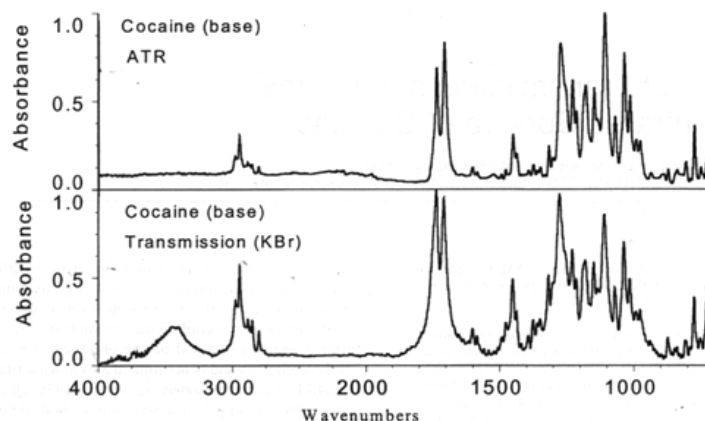


FIG. 1—The ATR and absorption spectra of cocaine (base) are presented to illustrate the correspondence and differences between internal reflection and transmission measurements.

Koulis, Cynthia, et. al. Comparison of Transmission and Internal Reflection Infrared Spectra of Cocaine. Journal of Forensic Sciences, 2001.

## Lambert – Beer’s law is still valid though not applicable for identification

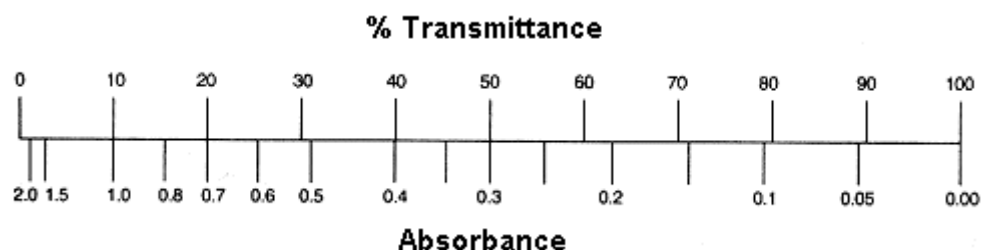
The law states that there is a logarithmic dependence between the transmission (or transmissivity),  $T$ , of light through a substance and the product of the **absorption coefficient** of the substance,  $\alpha$ , and the distance the light travels through the material (i.e. the path length),  $l$ . The **absorption coefficient** can, in turn, be written as a product of either a **molar absorptivity** of the absorber,  $\epsilon$ , and the **concentration**  $c$  of absorbing species in the material, or an **absorption cross section**,  $\sigma$ , and the (number) density  $N$  of absorbers.

For liquids, these relations are usually written as:

$$T = \frac{I}{I_0} = 10^{-\alpha l} = 10^{-\epsilon l c}$$

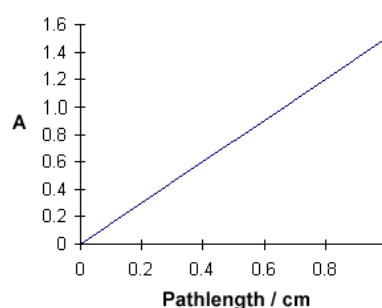
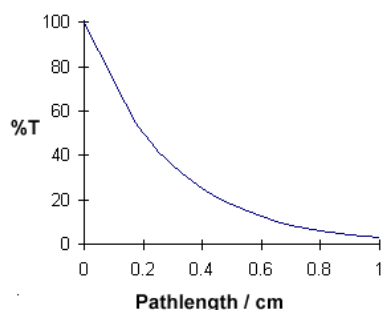
whereas for gases, and in particular among physicists and for spectroscopy and spectrophotometry, they are normally written

$$T = \frac{I}{I_0} = e^{-\alpha' l} = e^{-\sigma l N}$$



Examples:

Path length / cm	0	0.2	0.4	0.6	0.8	1.0
%T	100	50	25	12.5	6.25	3.125
Absorbance	0	0.3	0.6	0.9	1.2	1.5



# Identification of organic compounds by IR

## *Chemicals and Instruments*

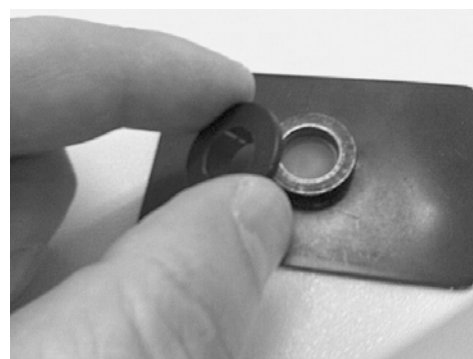
- Potassium bromide, ethanol, PS-foil for calibration, standards + samples
- FT-IR spectrometr Nicolet Impact 410, KBr tablet press, homogenizator, spatula, balances

## *KBr tablet preparation*

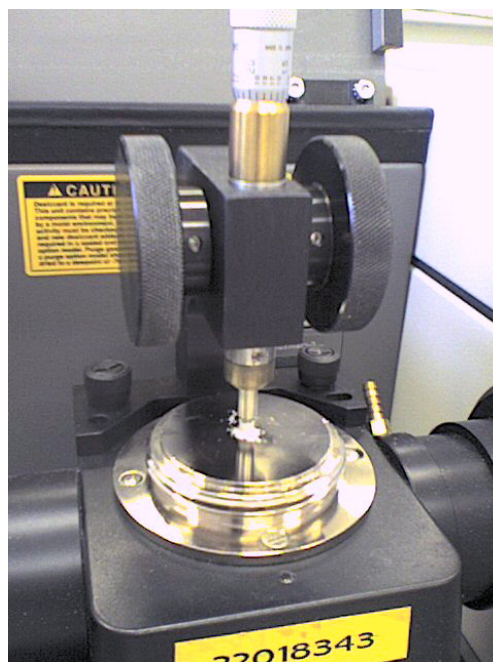
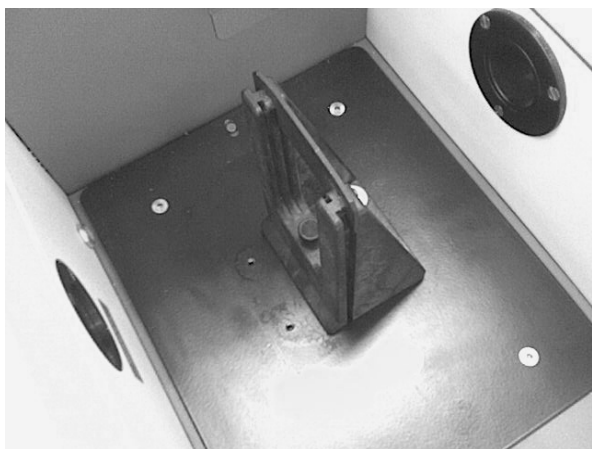
- KBr dried in oven at 120-130°C.
- cca **0,1-0,5 mg** of a sample is mixed with dry KBr (400-500 mg). The mixture must be homogenized.



*homogenisator*







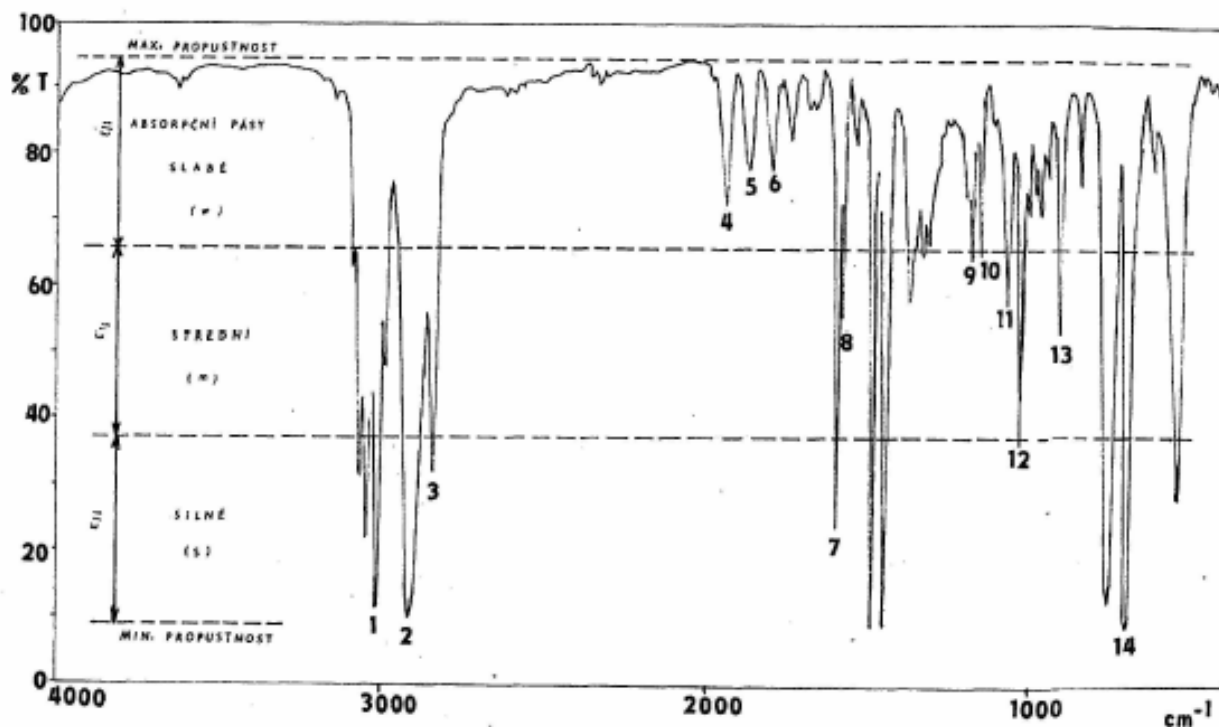
### **Tasks:**

1. Measure IR spectra of given standards and samples, both by KBr-tablet technique and by ATR.
2. Interpret the spectra by matching the bands characteristic wavenumbers to typical functional groups

vlnočty charakteristických vibrací v IČ oblasti

skupina (vazba)	typ sloučeniny	Oblast vlnočtů (cm <sup>-1</sup> )	intenzita pásu
C-H	alkany (-CH <sub>3</sub> , -CH <sub>2</sub> -)	2965-2840	silná
	-CH <sub>3</sub>	1450, 1380	střední
	-CH <sub>2</sub> -	1465	střední
	alkeny (=CH <sub>2</sub> )	3095-3010 1000-700	střední silná
	aldehydy	2850-2700	slabá
	na benzenovém kruhu	900-650	silná
C-C	alkany	1200-700	slabá
C=C	alkeny	1680-1620	variab.
C≡C	alkiny	2260-2100	variab.
C=C	aromáty	1670-1450	střední
C=O	amidy	~1650	silná
	karboxylové kyseliny	~1710	silná
	ketony	~1715	silná
	aldehydy	~1725	silná
	estery	~1735	silná
C-OH	alkoholy	1150-1040	silná
O=C-O-	estery karbox. kyselin	1300-1100	silná
	ethery	1150-1070	silná
O-H	alkohol volný	3650-3590	var. (ostrý pás)
	alkohol s vodíkovým můstkem	3400-3200	silná (široký pás)
N-H	prim. amin, amid	3500-3300	střední
	sekundární amin, amid	3500	střední
	terciární amin, amid	-	
C-N	aminy	1350-1000	střední
C≡N	nitrily	2280-2200	silná
NO <sub>2</sub>	nitro skupina	1550, 1370	silná

## POLYSTYRENE FOR WAVENUMBER CALIBRATION



Čísla jsou označeny pásy vhodné pro vlnočtovou kalibraci:

1 - 3027, 2 - 2924, 3 - 2851, 4 - 1944, 5 - 1871, 6 - 1802, 7 - 1601, 8 - 1583, 9 - 1181, 10 - 1154, 11 - 1069, 12 - 1028, 13 - 907, 14 - 699  $\text{cm}^{-1}$

V levé části obrázku je znázorněno určení relativní intenzity absorpčních pásů

**Tab. 2.2.24-1** *Minima propustnosti a přijatelné tolerance polystyrenového filmu*

Minima propustnosti ( $\text{cm}^{-1}$ )	Přijatelná tolerance ( $\text{cm}^{-1}$ )	
	přístroje s monochromátorem	přístroje s Fourierovou transformací
3060,0	$\pm 1,5$	$\pm 1,0$
2849,5	$\pm 2,0$	$\pm 1,0$
1942,9	$\pm 1,5$	$\pm 1,0$
1601,2	$\pm 1,0$	$\pm 1,0$
1583,0	$\pm 1,0$	$\pm 1,0$
1154,5	$\pm 1,0$	$\pm 1,0$
1028,3	$\pm 1,0$	$\pm 1,0$



## Characteristic IR Band Positions

Group	Frequency Range (cm <sup>-1</sup> )
OH stretching vibrations	
Free OH	3610-3645 (sharp)
Intramolecular H bonds	3450-3600 (sharp)
Intermolecular H Bonds	3200-3550 (broad)
Chelate Compounds	2500-3200 (very broad)
NH Stretching vibrations	
Free NH	3300-3500
H bonded NH	3070-3350
CH Stretching vibrations	
=C-H	3280-3340
=C-H	3000-3100
C-CH <sub>3</sub>	2862-2882, 2652-2972
O-CH <sub>3</sub>	2815-2832
N-CH <sub>3</sub> (aromatic)	2810-2820
N-CH <sub>3</sub> (aliphatic)	2780-2805
CH <sub>2</sub>	2843-2863, 2916-2936
CH	2880-2900
SH Stretching Vibrations	
Free SH	2550-2600
C=N Stretching Vibrations	
Nonconjugated	2240-2260
Conjugated	2215-2240
C=C Stretching Vibrations	
C=CH (terminal)	2100-2140
C-C=C-C	2190-2260
C-C=C-C=CH	2040-2200
C=O Stretching Vibrations	
Nonconjugated	1700-1900
Conjugated	1590-1750
Amides	~1650

C=C Stretching Vibrations	
Nonconjugated	1620-1680
Conjugated	1585-1625
CH Bending Vibrations	
CH <sub>2</sub>	1405-1465
CH <sub>3</sub>	1355-1395, 1430-1470
C-O-C Vibrations in Esters	
Formates	~1175
Acetates	~1240, 1010-1040
Benzoates	~1275
C-OH Stretching Vibrations	
Secondary Cyclic Alcohols	990-1060
CH out-of-plane bending vibrations in substituted ethylenic systems	
-CH=CH <sub>2</sub>	905-915, 985-995
-CH=CH-(cis)	650-750
-CH=CH-(trans)	960-970
C=CH <sub>2</sub>	885-895