Instrumental Chemical Analysis

Infrared Spectroscopy

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- Energy of **Infrared** photon is insufficient to cause electronic excitation. It only could make transitions between vibrational levels.
- **IR spectroscopy** (also called **Vibrational Spectroscopy)** is a tool for examining vibrations in molecules.
- Although the IR region of the electromagnetic spectrum ranges in wavelength from 2 -15 μm, but IR spectra are usually taken in the range λ ~ 2.5 to 40.0μm, which corresponds to 4000 to 250 cm⁻¹ wavenumber.





Conventionally the IR region is subdivided into three regions, near IR, mid IR and far IR. Most of the IR used originates from the mid IR region.

Number of vibrational modes

• A molecule can vibrate in many ways, and each way is called a **vibrational mode**. Molecules with **N** atoms, have 3N–5 degrees of vibrational modes if linear, whereas nonlinear molecules have 3N–6 degrees of vibrational modes (also called vibrational degrees of freedom). For example H_2O , a non-linear molecule, will have $3\times3-6 = 3$ vibrational degrees of freedom.



- In order for a vibrational mode in a molecule to be "IR active," it must be associated with changes in the dipole moment ($\Delta\mu \neq 0$).
- $\circ \mu = q \times r$, r is the bond length and q is the partial charge on opposite atoms which is related to the deference in their electronegativities.
- Simple diatomic molecules have only one bond and only one vibrational band. If the molecule is symmetrical, e.g. N₂, then this bond vibration will not observed in the IR spectrum (called transparent bonds in IR), while asymmetrical diatomic molecules, e.g. CO, absorbs in the IR spectrum.
- The atoms in a —CH₂ group, commonly found in organic compounds. It could be vibrate in deferent modes, among these we could counter: symmetric and asymmetric stretching, scissoring, rocking, wagging and twisting.

The IR Spectroscopic Process

There are two types of bond vibration:

• Stretch – Vibration or oscillation along the line of the bond



H C H





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symmetric

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asymmetric

• **Bend** – Vibration or oscillation not along the line of the bond





out of plane



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The IR Spectroscopic Process

As a covalent bond oscillates – due to the oscillation of the dipole of the molecule – a varying electromagnetic (EM) fields are produced. These fields were differed by energies and frequencies (v₀, v₁, v₂, v₃,... etc.)



 The greater the dipole moment change through the vibration, the more intense the EM field that is generated.

The IR Spectroscopic Process

• When an electromagnetic wave of infrared light encounters this oscillating EM field generated by the oscillating dipole of the same frequency, the two waves couple, and IR light is absorbed, and the amplitude of the vibration is increased. The frequencies causing this effect are called **Fundamental frequencies**. They are associated with the transition having $\Delta v=1$ (difference between vibration energy levels).



- If a transition occurs with $\Delta v=2$, then these frequencies are called **Overtones**. An overtone is a multiple of a given frequency, as 2v (first overtone), 3v (second overtone), etc.
- **Overtones** are usually have lower intensities than fundamentals.

The IR Spectroscopic Process

 Fundamental frequency of absorption of radiation can be predicted with a modified Hooke's Law for simple Harmonic oscillator.





Where: v = wavenumber of the abs. peak (cm⁻¹) c = speed of light (3 x 10¹⁰ cm/s) k = force constant (N/m) $\mu =$ reduced mass of the atoms, $\mu = \frac{M_x \bullet M_y}{M_x + M_y}$ $M_x =$ mass of **atom** x in kg $M_y =$ mass of **atom** y in kg

The IR Spectroscopic Process

Example: Calculate the approximate wavenumber (cm⁻¹) of the fundamental absorption due to the stretching vibration of a carbonyl group C=O. (The force constant for the typical double bond is about 1x10³ N/m)

$$M_{c} = \frac{12x10^{-3} kg / mol}{6.02x10^{23} atoms / mol} x 1 atom = 2.0x10^{-26} kg$$
$$M_{o} = \frac{(16x10^{-3})}{(6.02x10^{23})} = 2.7x10^{-26} kg$$
$$\mu = \frac{M_{c}M_{o}}{M_{c} + M_{o}} = \frac{2.0x10^{-26} kg x 2.7x10^{-26} kg}{(2.0 + 2.7)x10^{-26} kg} = 1.1x10^{-26} kg$$
$$\overline{v} = 5.3x10^{-12} \sqrt{\frac{k}{\mu}}$$
$$\overline{v} = 5.3 \times 10^{-12} s/cm \sqrt{\frac{1 \times 10^{3} N/m}{1.1 \times 10^{-26} kg}} = 1.6 \times 10^{3} cm^{-1}$$



The carbonyl stretching band is found experimentally to be in the region of 1600 to 1800 cm^{-1} (6.3 to 5.6 µm)

IR Spectrum

- Transmittance% vs Wavenumber .
- Stretching bands have higher wavenumbers than those of bending.



- Finger print region is complicated but unique for every compound
- A nonpolar bond in a symmetrical molecule will absorb weakly or not at all
- The high bond strength (short bond), the high IR wavenumber



• **Hybridization affect** the force constant. As (s) character in the hybridized orbital increases, the bond becomes more shorter and stronger and absorbs at higher wavenumber.



IR Spectrum

• Conjugation effect— by resonance, conjugation lowers the energy of a double or triple bond. The effect of this is readily observed in the IR spectrum:



 Conjugation will lower the observed IR band for a carbonyl from 20-40 cm⁻¹ provided conjugation gives a strong resonance contributor



 Inductive effects are usually small, unless coupled with a resonance contributor (note –CH₃ and –Cl above).

IR Spectrum

 Steric effects – usually not important in IR spectroscopy, unless they reduce the strength of a bond (usually π) by interfering with proper orbital overlap:



Here the methyl group in the structure at the right causes the carbonyl group to be slightly out of plane, interfering with resonance

• Strain effects – changes in bond angle forced by the constraints of a ring will cause a slight change in hybridization, and therefore, bond strength



IR Spectrum

- Hydrogen bonding
 - Hydrogen bonding causes a broadening in the band due to the creation of a continuum of bond energies associated with it.
 - In the solution phase these effects are readily apparent; in the <u>gas phase</u> where these effects disappear or in presence of <u>steric effects</u>, the band appears as sharp as all other IR bands:



IR Spectrum

 Main stretching bands are distributed from 400 to 4000 cm⁻¹ according to the reduced mass and bond strength.

4000	25	FRE 00 20	QUENCY (cr 00 18	n ⁻¹) 00 16	50 15	50 650
О-H N-H	C-H	C≡C C≡N X=C=Y (C,O,N,S)	VERY FEW BANDS	C=0	C=N C=C N=C	C-CI C-O C-N C-C

IR Peak properties

- Position (cm⁻¹) in the spectrum
- Shape (broad or sharp)
- Intensity (weak, medium or strong).
 The intensity of an IR band is affected by two primary factors:
 - Whether the vibration is one of stretching or bending. Stretching is more intense.
 - Electronegativity difference of the atoms involved in the bond.

Designation	%Transmission	Absorbance	
vvs	<5	>1.3	
VS	25~	0.6~	
S	50~	0.3~	
м	60~	0.2~	
MW	75~	0.1~	
w	85~	0.07~	
vw	95~	0.02~	
vvw	>98	0.01~	



IR Spectrum "Examples"



IR Spectrum "Examples"



IR Spectrum "Examples"



IR instrumentation

- Two types of instruments for IR absorption measurements are commonly available:
 - (1) <u>Dispersive spectrophotometers</u> with a grating <u>monochromator</u>. It function in a sequential mode.
 - (2) <u>Fourier transform spectrometers employing an interferometer</u>. It is capable of simultaneous analysis of the full spectral range.
- The first category uses a monochromator with a motorized grating that can scan the range of frequencies studied.
- The second is based on the use of a <u>Michelson interferometer</u> or similar device coupled to a specialized computer that can calculate the spectrum from the interferogram obtained from the optical bench.
- However, the light sources and optical materials are identical for all instruments.

IR instrumentation

Dispersive spectrophotometers



IR instrumentation

Dispersive spectrophotometers

Dispersive Double beam IR Spectrophotometer

- The radiation coming from the light source is split in two by a set of mirrors.
- For small intervals in wavelength defined by the monochromator, light that has alternately travelled both paths (reference and sample) arrives at the detector.
- A mirror (chopper) rotating at a frequency of approximately 10 Hz orients the beam towards each of the optical paths.
- The comparison of both signals, obtained in a very short time period, can be directly converted into transmittance.
- Depending on the spectral range and on various constraints (rotation of the monochromator grating, response time of the detector) the spectrum can be recorded <u>within minutes</u>.
- The detector in this type of instrument is only exposed to a <u>weak amount of</u> <u>energy</u> in a given period of time because the monochromator only transmits a narrow band of wavelengths.

IR instrumentation

Dispersive spectrophotometers



IR instrumentation

Fourier transform spectrophotometers



IR instrumentation

Fourier transform spectrophotometers

- In a FTIR spectrometer, the single beam instrument works on the same principles such as the dispersive instruments except that an interferometer of the Michelson type is placed between the source and the sample, replacing the monochromator.
- Irradiation from the source impacts on the <u>beam splitter</u> which is made of a germanium film on an alkali halide support (KBr).
- This device allows the generation of two beams, one of which falls on a fixed mirror and the other on a mobile mirror whose distance from the beam splitter varies.
- An interferometer uses a moving mirror to displace part of the radiation produced by a source, thus producing an <u>interfere ram</u>, which can be transformed using an equation called the 'Fourier transform' in order to extract the spectrum from a series of overlapping frequencies.

Interferometer

Michelson interferometer: a certain configuration of mirrors, one of which is moved by a motor. As this mirror moves, each wavelength of light in the beam is exits the interferometer is the result of two beams "interfering" with each other. The resulting signal is called an interferogram which has the unique property that every data point (a function of the moving mirror position) which makes up the signal has information about every infrared frequency which comes from the source.



IR instrumentation

Fourier transform spectrophotometers

- Fourier transform spectrometers have the advantages of speed, reliability, signal to noise (S/N).
 - In this technique, a full spectral scan can be acquired in about 1s, compared with the 2-3 min required for a dispersive instrument to acquire a spectrum.
 - Also, because the instrument is attached to a computer, <u>several spectral</u> <u>scans can be taken</u> and averaged in order to improve the signal to noise ratio for the spectrum.
 - In FTIR method there <u>is no stray light</u>, and replacement of the entrance slit by an iris yields a brighter signal so that the detector receives more energy
 - Wavelengths are calculated with a high precision which facilitates the comparison of spectra
 - The <u>resolution is constant</u> throughout the domain studied.



IR instrumentation

FT-IR components: (2) The Interferometer

Interferometric system consists of a He-Ne laser, mirrors, beamsplilter. Laser signal is used to control the speed of the mirror-drive system at a constant level.





IR instrumentation

FT-IR components: (3) The Sample

- Sample types: Gas, liquid (Solution or neat liquids) or solid.
- KBr or NaCl discs (or windows) where used to support the analysed materials. KBr and NaCl (and most of inorganic salts) does not contains covalent bonds that may absorb IR radiation.
- Gas : filled in glass tube that has KBr windows in the two sides.

• Neat liquids : pressed as a thin film sandwiched between two KBr discs and placed in the sample holder inside the instrument.



https://orgchemboulder.com/Technique/Procedures/IR/IRliquid.shtml

IR instrumentation

FT-IR components: (3) The Sample

 Solution : sample dissolve in a solvent (non polar solvent) and injected between two KBr windows with specific thickness. Solvent reading should be subtracted out by taking background/reference spectrum.



- Solids can be :
 - 1- Deposited as thin film on KBr disc by solvent evaporation
 - CCl₄ is best, but now expensive/hard to find
 - CHCl₃ & CH₂Cl₂ next best, do not obscure much of spectrum

IR instrumentation

FT-IR components: (3) The Sample

- 2- Mixed with Nujol (petroleum oil, high boiling)
 - mixtures typically applied to polished NaCl or KBr plate (IR inactive)
 - obscure aliphatic region



- 3- Pressed into KBr pellet
 - The common method, but it is difficult to get right



Note: adventitious water can be a problem (false ID of ROH and RCO₂H) in all preperation methods

IR instrumentation

FT-IR components: (3) The Sample

Attenuated Total Reflectance (ATR)

- For samples that are difficult to deal with, such as solids of limited solubility, films, threads, pastes, adhesives, and powders.
- The materials used as <u>ATR crystals include</u> ZnSe, AgCI, Ge, and Si materials.





IR instrumentation

FT-IR components: (3) The Sample

Attenuated Total Reflectance (ATR)

- One of the major advantages of ATR spectroscopy is that absorption spectra are readily obtainable on a wide variety of sample types with a minimum of preparation. Threads, yarns, fabrics, and fibers can be studied by pressing the samples against the dense crystal. Pastes, powders, or suspensions can be handled in a similar way. Aqueous solutions can also be accommodated provided the crystal is not water soluble.
- The spectra obtained with ATR methods can <u>differ</u> from IR absorption spectra.

Spectrum of L-Arginine (Comparison of KBr pellet method and single-reflection ATR method)



IR instrumentation

FT-IR components: (4) The Detectors (Transducers)

1. Thermal transducer

- Constructed of a bimetal junction, which has a temperature dependant potential (V). (similar to a thermocouple)
- Have a slow response time, so they are not well suited to FT-IR.

2. <u>Pyroelectric transducer</u>

- Constructed of crystalline wafers of triglycine sulfate (TGS) that have a strong temperature dependent polarization.
- Have a fast response time and are well suited for FT-IR.





IR instrumentation

FT-IR components: (4) The Detectors (Transducers)

3. <u>Photoconducting transducer</u>

- Constructed of a semiconducting material (lead sulfide, mercury/cadmium telluride, or indium antimonide) deposited on a glass surface and sealed in an evacuated envelope to protect the semiconducting material from the environment.
- Absorption of radiation promotes nonconducting valence electrons to a conducting state, thus decreasing the resistance (Ω) of the semiconductor.
- Fast response time, but require cooling by liquid N₂.



Application

- IR is very useful in providing information about the <u>presence or absence</u> of specific **functional groups**.
- IR provide molecular fingerprint that could be used in <u>comparing samples</u>. If two pure samples display the same IR spectrum it could be said that they are for the same compound.
- IR <u>don't provide detailed information</u> or proof about molecular formula or structure. It provides information on molecular fragments, specifically functional groups.
- Therefore its scope is very limited, and must be used in conjunction with other techniques to lead for a comprehensive perception about the molecular structure.
- Infrared spectroscopy is not widely used for quantitative analysis as UV/Vis, even though absorption should obey the Beer-Lambert law. <u>Calibration problems</u> arise because of the high sensitivity of band intensities to small changes in slit width of the radiation source. Another problem with IR spectroscopy is that <u>peaks are often not well resolved</u>. Most cells used in IR spectrometry have KBr window and the <u>path length is likely to vary</u> with use due to corrosion.

Interpretation

	О-Н С-Н N-Н	C≡N C≡C X=C=Y (C,O,N,S)	Very few bands	C=0	C=N C=C N=O	C-CI C-O C-N C-C N=O*
4000 2500 2000 1800 1650 1550 650 FREQUENCY (cm ⁻¹)						

Bond	Functional group	Characteristic range of wavenumber / cm ⁻¹
C-Cl	chloroalkane	600-800
C-0	alcohol, ether, ester, carboxylic acid	1000-1300
C=C	alkene	1610-1680
C=0	aldehyde, ketone, carboxylic acids, ester	1700-1750
C≡C	alkyne	2100-2260
0-H	hydrogen bonded in carboxylic acids	2400-3400
C-H	alkane, alkene, arene	2840-3100
0-H	hydrogen bonded in alcohols, phenols	3200-3600
N-H	primary amine	3300-3500
Interpretation

C-H bond

Bonds with more **s** character in hypredization absorb at a higher frequency.



increasing s character in bond

increasing CH Bond Strength

increasing force constant K

C-C bond

Increasing bond order leads to higher frequencies:

C-C	1200 cm ⁻¹ (fingerprint region)
C=C	1600 -1680 cm ⁻¹
C≡C	2200 cm ⁻¹ (weak or absent if internal)

Conjugation lowers the frequency:

isolated C=C	1640-1680 cm ⁻¹
conjugated C=C	1620-1640 cm ⁻¹
aromatic C=C	approx. 1600 cm ⁻¹

Interpretation

O-H and N-H bonds

• Both O-H and N-H stretches appear around 3300 cm⁻¹, but they look different.

Alcohol O-H

Broad with rounded tip when hydrogen bonding is present (sharp in the absence of hydrogen bonding).

Carboxylic O-H

Broad band from 2400-3500 cm⁻¹

Secondary amine (R₂NH)

- Broad (usually) with one sharp spike **Primary amine (RNH₂)**
- Broad (usually) with two sharp spikes.
 No signal for a tertiary amine (R₃N)







Benzene ring

Carbonyl bonds C=O



How to approach analysis of IR spectra

- Guideline
 - Calculate Degrees of Unsaturation (DoU) (molecular formula)

$$DoU = \frac{2C+2+N-X-H}{2}$$

- ${\boldsymbol{C}}$ is the number of carbons
- N is the number of nitrogens
- X is the number of halogens (F, Cl, Br, I)
- H is the number of hydrogens
- Note any band at 1715 cm⁻¹ (carbonyl)
- Check for O-H and N-H
- Check for triple bonds
- Check for C=C and benzene ring
- Check for C-O and nitro group below 1550 cm⁻¹
- Lock at C-H region (C=C-H, C-C-H)



● If a carbonyl group is present: Strong absorption between 1820-1660 cm⁻¹

- **2** Check for OH : Broad absorption near 3600-3300 cm⁻¹
- Check for NH : Medium absorption near 3500 cm⁻¹
- Output Check for Triple Bonds
- CEC Weak absorption near 2150 cm⁻¹
- C Medium absorption near 2250 cm⁻¹
- Check for Double Bonds and / or Aromatic Rings
- C==C Weak absorption near 1650 cm⁻¹
- **C** Medium to strong absorption near 1650-1450 cm⁻¹ due to aromatic ring

• Check for NO₂: Two strong absorption near 1550 and 1350 cm⁻¹

Check for C-O : Strong absorption near 1300-1000 cm⁻¹

Output Check for the position of substitution on the aromatic ring :



Example



Example



Example





Q.





Which one of the following structures most likely produced the IR spectrum shown below?

Interpretation

How could you use IR spectroscopy to distinguish between the following pairs of isomers?



Tables

Alkanes

Functional group	Vibrational mode and strength	Wavenumber (cm ⁻¹)
Methyl (-CH ₃)	C-H stretching, s	2870 (sym); 2960 (asym)
Methylene (-CH2-)	C-H stretching, s	2860 (sym); 2930 (asym)
Methyl (-CH ₃)	Bending, m	1375 (sym); 1450 (asym)
Methylene (-CH ₂ -)	Bending, m (scissoring, rocking)	1465; 720 (if four or more CH ₂ groups in an open chain); weak bands in the 1100–1350 region
gem-Dimethyl ^a	Bending, m	Doublet (two peaks); 1380–1390 and 1365–1370
Aldehyde (-CHO) ^b	Aldehydic C—H stretching, m	2690-2830 (two peaks often seen)
Aldehyde (-CHO) ^b	Aldehydic C—H bending, m	1390

^aThe term *gem*-dimethyl refers to two methyl groups attached to the same carbon atom, such as in an isopropyl group.

^bAn aldehyde group has a hydrogen bonded to a carbon atom that also has double bond to the oxygen atom.

Alkenes and Alkynes

Functional group	Vibrational mode and strength	Wavenumber (cm ⁻¹)
$C=C \rightarrow H$	Stretching, w	3000-3040
$C=C \downarrow H$	Bending, s (oop)	650-1000
$C = CH_2$	Vinyl stretching, m	2990 (sym), 3085 (asym)
$C = CH_2$	Vinyl bending, s	910, 990
$C \equiv C \rightarrow H$	Stretching, s	3285-3320
C≡C↓H	Bending, s	610-680
C=►C	C=C stretching, s ^a	1600-1680
C≡►C	C≡C stretching, m-w ^a	2120 (terminal); 2200 (nonterminal)

^aThe C=C and C=C stretch is weak or absent in symmetric molecules.

Substitution positions	Wavenumber (cm^{-1})	Band strength
Monosubstitution	730-770	S
	680-720	S
1,2 Disubstitution (ortho)	740-770	S
1,3 Disubstitution (meta)	860-890	m
	760-810	S
	680-710	S
1,4 Disubstitution (para)	800-855	S
1,2,3 Trisubstitution	740-790	S
	680-720	m
1,2,4 Trisubstitution	860-900	m
	790-830	S
1,3,5 Trisubstitution	820-910	S
	670-700	m

Aromatic C-H Ring Deformation Modes and Benzene Ring Substitution



Functional group	Vibrational mode and strength	Wavenumber (cm ⁻¹)
Aliphatic alcohols		
$\hat{CO} \rightarrow H$	OH stretch (free), s	3600-3640
	OH stretch (hydrogen-bonded), s	3200-3400
С—О↓Н	C-O-H bend, w	1200 - 1400
$C - C \rightarrow O$	C-C-O stretch (out-of-phase, asym), s	1000 - 1260
Phenols		
$CO \rightarrow H$	OH stretch (free), s	3600
	OH stretch (hydrogen-bonded), s	3100-3300
С—О↓Н	C-O-H bend, s	1300-1400
$C - C \rightarrow O$	C-C-O stretch (oop, asym), s	1160-1300
Carboxylic acids		
$CO \rightarrow H$	OH stretch (free)	Not usually observed
	OH stretch (hydrogen-bonded), s	2500-3200
С—О↓Н	C-O-H bend (in-plane), m	1400 - 1440
	C-O-H bend (dimer, oop), m	900-950
$C - C \rightarrow O$	CCO stretch (dimer), m	1200-1320

OH and Related C-O Group Frequencies for Alcohols and Carboxylic Acids

Functional group	Vibrational mode and strength	Wavenumber (cm^{-1}) $(\pm 10 cm^{-1})$
Aldehydes		
Aliphatic $C \Rightarrow O$	C=O stretch, s	1730
Aromatic $C \Rightarrow O$	C=O stretch, s	1690
Amides		
$C \Rightarrow O$	C=O stretch, s	1690
Carboxylic acids		
Aliphatic $C \Rightarrow O$	C=O stretch (dimer), s	1710
Aromatic $C \Rightarrow O$	C=O stretch, s	1690
Esters		
Aliphatic $C \Rightarrow O$	C=O stretch, s	1745
Aromatic $C \Rightarrow O$	C=O stretch, s	1725
Ketones		
Aliphatic $C \Rightarrow O$	C=O stretch, s	1710
Aromatic $C \Rightarrow O$	C=O stretch, s	1690
Aromatic C \Rightarrow O Esters Aliphatic C \Rightarrow O Aromatic C \Rightarrow O Ketones Aliphatic C \Rightarrow O Aromatic C \Rightarrow O	C==O stretch, s C==O stretch, s C==O stretch, s C==O stretch, s C==O stretch, s	1690 1745 1725 1710 1690

Carbonyl Stretching Frequencies for Selected Compound Classes

Functional group	Vibrational mode and strength	Wavenumber (cm ⁻¹)
Aliphatic amines		
Primary R-NH ₂	$N \rightarrow H$ stretch (sym and asym), m	3300-3500 Doublet
Secondary R ₂ NH	$N \rightarrow H$ stretch, w	3300 Singlet
Tertiary R ₃ N	No NH	
Primary R-NH ₂	$N \downarrow H$ bend, s	1550-1650; 800
Secondary R ₂ NH	$N \downarrow H$ bend, s	700
Tertiary R ₃ N	No NH	
Aromatic amines		
Primary Ar-NH ₂	$N \rightarrow H$ stretch, m	3500
Secondary Ar ₂ NH	$N \rightarrow H$ stretch, m	3400
Tertiary Ar ₃ N	No NH	
Primary Ar-NH ₂	$N \downarrow H$ bend, s-m	1620, 650
Nitriles, isonitriles		
C-C≡N	C≡N stretch, w-m	2220-2260
C-N≡C	N≡C stretch, w-m	2110-2180
Nitro compounds		
Aliphatic RNO ₂	NO ₂ stretch, asym, s	1530-1580
	NO_2 stretch, sym, s	1350-1390
Aromatic ArNO ₂	NO_2 stretch, asym, s	1500-1550
	NO_2 stretch, sym, s	1285-1350
Nitrates RONO ₂	NO_2 stretch, asym, s	1620-1650
-	NO ₂ stretch, sym, s	1280
Azides	N≡N stretch, m	2140

Frequencies of Selected Nitrogen-Containing Functional Groups

Amino Acid Absorptions

Functional group	Vibrational mode and strength	Wavenumber (cm ⁻¹)
Amine cation, RNH ₃ ⁺ Amine cation, RNH ₃ ⁺	$N \rightarrow H, s$ $N \downarrow H, s$ CO^{-} ion stratch s	2700–3100 1600 (asym); 1500 (sym) 1600 (asym); 1400 (sym)

Functional group	Vibrational mode and strength	Wavenumber (cm ⁻¹)
Aliphatic halide	$C \rightarrow F, s$	720-1400
	$C \rightarrow Cl, s$	530-800
	$C \rightarrow Br, s$	510-690
	$C \rightarrow I, s$	>600
Aromatic halide ^a	$C \rightarrow F, s$	1100 - 1250
	$C \rightarrow Cl, s$	1000 - 1100
	$C \rightarrow Br, s$	1000 - 1090

Halogen-Containing Functional Groups

^aThe halide atom is substituted directly on a carbon atom in an aromatic ring.

Exercises





















TASK 1


TASK 1



TASK 2



TASK 3 1) Propene reacts with HBr to form **H**. **H** reacts with sodium hydroxide to form **I**, and **I** reacts with warm acidified potassium dichromate (VI) to form **J**. The infra-red spectra of **H**, **I** and **J** are given below, but it does indicate which is which. Identify the three compounds **H**, **I** and **J**, using the infra-red spectra below, and decide which spectrum belongs to which compound.



TASK 3

- 2) Compound E, which is a branched chain haloalkane, was found to have the composition by mass of 39.8% C, 7.3% H, and 52.9% Br. There were two peaks for the molecular ions in the spectrum at 150 and 152, of approximately equal intensity. E reacts with sodium hydroxide to form F, whose infra-red spectrum is shown. F does not undergo dehydration with concentrated sulphuric acid.
 - **F** reacts further with acidified potassium dichromate (VI) to form **G**, whose infra red spectrum is also shown. Draw the structures and name **E**, **F** and **G**. Identify the species responsible for the peaks at 150 and 152 in the mass spectrum of **E**.



Explain

IR spectra for 5-hydroxy-2-pentanone and 4-hydroxy-2-pentanone were generated and table below illustrate some information:

5-hydroxy-2-pentanone	4-hydroxy-2-pentanone
3432 cm ⁻¹	3409 cm ⁻¹
1714 cm ⁻¹	1705 cm ⁻¹

Explain the shift observed for these bands?