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## EXPT. 7 CHARACTERISATION OF FUNCTIONAL GROUPS USING IR SPECTROSCOPY

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### Structure

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- Objectives
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### 7.1 INTRODUCTION

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In this laboratory course you have so far learnt about and carried out analytical determination using UV-visible spectrometry. In this experiment we move on to IR spectrometry. You have learnt about IR spectrometry in Unit 3 of the MCH-003 course. You would recall that IR spectrometry is a consequence of the interaction of the electromagnetic radiation in the infra red region with the molecules. The technique can be used for qualitative as well as quantitative applications. However, the qualitative aspect of the technique is the most powerful attribute of this diverse and versatile analytical technique. It is commonly used by organic and inorganic chemists for structure elucidation and compound identification.

In this experiment we would recapitulate the salient features of the IR spectrometric method and use a number of examples to demonstrate the potential of the technique in identifying the functional group present in an organic compound. You can interpret IR spectra by recognising characteristic shapes and patterns within the spectrum, and by applying the information obtained from extensive compilations of the group frequency data, along with other chemical and physical data of the sample. You would be required to identify the presence of functional groups in a few organic compounds on the basis of the provided IR spectra. Once equipped with the necessary interpretative skills, you can sharpen your skills by interpreting as many spectra as possible to attain a kind of mastery.

You would agree that it is not possible to make a person proficient interpretive spectroscopist by merely presenting the known relationships between structure and the observed spectra. The attempt in this experiment is to make you appreciate the visual aspects of the spectroscopy and how to interpret these relative to the structure and chemistry of a compound. In the next experiment we would take up the interpretation of NMR spectra in the same spirit.

### Objectives

After studying the contents and interpreting the sample IR spectra, you should be able to:

- state the principle and outline the salient features of the IR spectrometric method,
- describe the strategy used for the interpretation of IR spectrum of a molecule to identify the functional group present in it,
- list the characteristic frequencies of some common functional groups of organic compounds,
- identify the presence of different functional groups in an organic compound,

- predict the characteristic absorption bands in the IR spectra of a given organic compound on the basis of the functional groups present in the compound.

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## 7.2 PRINCIPLE

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You would recall from Unit 3 of Block 1 of MCH-003 course that,

- Infrared spectroscopy exploits the fact that molecules have specific frequencies at which they rotate or vibrate corresponding to discrete energy levels.
- The fundamental requirement for infrared activity, leading to absorption of infrared radiation, is that there must be a net change in dipole moment during the vibration for the molecule or the functional group under study.
- Infrared region of the electromagnetic spectrum spreads from the wavelengths of 0.8 to 1000  $\mu\text{m}$  or wave numbers roughly from 12,500 to 10  $\text{cm}^{-1}$ . It is bound by the red end of the visible region at lower wavelength end and the microwave region at higher wavelength end.
- It is further divided into three regions called near IR, mid IR and far IR regions. The far infrared region (200  $\text{cm}^{-1}$  to 10  $\text{cm}^{-1}$ ) is useful for molecules containing heavy atoms such as inorganic compounds and the near IR region (12000  $\text{cm}^{-1}$  to 4000  $\text{cm}^{-1}$ ) concerns routine quantitative determinations of the simple molecules like water,  $\text{CO}_2$  etc. of industrial and agricultural importance.
- It is the mid infrared region (4,000  $\text{cm}^{-1}$  to 200  $\text{cm}^{-1}$ ) that is of interest for general chemical analysis purposes.

The region of IR spectrum generally ranges from 4000-600  $\text{cm}^{-1}$  and the infrared spectrum can be broadly divided into three regions as given below.

- The region spanning the high frequency range from 3600 to 1200  $\text{cm}^{-1}$  is called the **functional group region** and includes the stretching vibrations or group frequencies of common functional groups. The absorptions in this region provide information about the presence of characteristic functional groups, such as  $-\text{OH}$ ,  $-\text{NH}$ ,  $\text{C}=\text{O}$ ,  $-\text{SH}$  and  $-\text{C}=\text{C}-$  etc. The absence of absorption in the assigned ranges for different functional groups can usually be used as an evidence for the absence of such groups in the molecule. However, this feature should be used with care as sometimes the signals may be too broad to be noticed and may mislead.
- The region that includes all frequencies in the range of 1300  $\text{cm}^{-1}$  to 900  $\text{cm}^{-1}$  is called the **fingerprint region** and includes molecular vibrations, characteristic of the entire molecule or large fragments of the molecule. The absorption pattern in this region is frequently quite complex. However, this region is useful for confirming the identity of a particular molecule by comparing with the spectral absorptions of its authentic sample.
- The region below 900  $\text{cm}^{-1}$  is referred to as the low frequency region. This region is particularly significant in ascertaining the substitution pattern in aromatic moieties.
- In addition to the presence (or even the absence) of a particular functional group, the analysis of IR spectrum gives the following information:
  - Presence of hydrogen bonding in the molecule (3200-3600  $\text{cm}^{-1}$ )
  - Geometry (cis or trans) in case of alkenes

The vibrational spectrum of a molecule is considered to be a unique physical property and is characteristic of the molecule.

Over the years, a lot of data on the fundamental absorption frequencies of different molecules and the possible structure-spectrum correlations has been published. These spectral compilations are the key to unlocking the structures-spectral relationships of

the associated molecular vibrations in wide range of molecules. This information can be obtained from a large number of texts available on spectroscopy or from the open source material available on the internet.

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## 7.3 REQUIREMENTS

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As mentioned in the introduction, the main objective of this experiment is to highlight the structure-spectrum relationships of organic molecules and formulate a strategy to interpret the IR spectrum of some simple organic molecules. We intend to inculcate elementary skills in you so that you can take up the interpretation of the IR spectrum of some simple molecules to determine the functional group present in them. Accordingly, we need some typical IR spectra to be used as examples and some to be used as study problems.

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## 7.4 STRATEGY FOR THE INTERPRETATION OF IR SPECTRA

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You would have realised from your study of the MCH-003 course on Spectroscopic Methods of Analysis that there is no unique methodology to decipher the structural aspects of the molecule on the basis of their spectra. However, there are some suggestive guidelines based on empirical relationships between structure and spectra. What follows is one such approach. Let us reiterate that this is not a unique approach, you may follow any other strategy available elsewhere with an objective of being able to decipher the functional group of the molecule from its IR spectrum. No wonder that with some practice you may devise your own strategy.

### A. Nature of carbon skeleton (aliphatic / aromatic)

- i) **C–H stretching :** The =C–H stretch in aromatics is observed at 3100-3000  $\text{cm}^{-1}$  whereas the –C–H stretching frequencies for saturated aliphatic hydrocarbons is below 3000  $\text{cm}^{-1}$ .
- ii) **C–C ring stretching vibrations:** The aromatic hydrocarbons show C-C ring stretching vibrations in the regions 1600-1585  $\text{cm}^{-1}$  and 1500-1400  $\text{cm}^{-1}$ .
- iii) **Out of plane C–H bending vibrations:** These are observed in the region 900-675  $\text{cm}^{-1}$  and provide information about the substitution pattern of aromatic compounds.

**Important**  
*sp*<sup>3</sup> C-H stretching :  
2850 to 3000  $\text{cm}^{-1}$   
*sp*<sup>2</sup> C-H stretching :  
above 3000  $\text{cm}^{-1}$   
*sp* C-H stretching :  
~ 3300  $\text{cm}^{-1}$ .

Thus, a weak absorption in the region 3080-3030  $\text{cm}^{-1}$  accompanied by medium absorption in the ring vibrations region indicates the presence of an aromatic ring. A signal around 1605  $\text{cm}^{-1}$  is quite a good indicator of an aromatic molecule; occasionally it splits into a doublet. The out of plane bending vibrations are also very significant. A lack of strong absorption band in the 900-650  $\text{cm}^{-1}$  region generally indicates a non aromatic structure.

Having established the aliphatic/ aromatic nature of the molecule the next step is to look for the characteristic frequencies of different functional groups. As the possible functional group in a molecule depends on its elemental constitution, the suggested guidelines are categorized according to the elemental composition.

### B. Molecules containing only C and H i.e., hydrocarbons

For hydrocarbon the first step would be to look for the carbon skeleton as described above.

Look for **C–H stretching** whether it is in the region 3000–2850  $\text{cm}^{-1}$  or above 3000  $\text{cm}^{-1}$ ? The absorption above 3000  $\text{cm}^{-1}$  indicates a double or a triple bond.

The following are other important signals to look for in a hydrocarbon to ascertain its nature.

- i) The C=C bond usually gives rise to a moderate band in the region 1680-1640  $\text{cm}^{-1}$ .
- ii) The  $\text{C}\equiv\text{C}$  stretch appears as a weak band from 2260-2100  $\text{cm}^{-1}$ .
- iii) The bending vibrations of the =C-H group are observed in the 1000-650  $\text{cm}^{-1}$  region
- iv) The terminal  $\text{C}\equiv\text{C}$ -H stretch is observed as a strong, narrow band in the range 3330-3270  $\text{cm}^{-1}$ .
- v) The  $\text{C}\equiv\text{C}$ -H bending vibration is observed in 700-600  $\text{cm}^{-1}$  range.
- vi) If a band observed at 1380  $\text{cm}^{-1}$  happens to be a doublet, it may be due to the presence of more than one methyl group on the same carbon atom.

### C. Molecules containing C, H and O or N

Look for a strong absorption in the region, 1820-1660  $\text{cm}^{-1}$  for a C=O group.

If carbonyl group is present, then we have a number of possibilities; look for the following

- i) Two weak absorptions near 2850 and 2750  $\text{cm}^{-1}$  on the lower wave number side of the CH absorptions.  
These are due to O=C-H stretching vibrations. The band near 2830  $\text{cm}^{-1}$  usually overlaps with other C-H stretching vibration bands however, the presence of a moderate band near 2720  $\text{cm}^{-1}$  is very likely to be helpful in determining whether or not a compound is an **aldehyde**. It often appears as a shoulder-type peak.
- ii) Broad band in the region 3300-2500  $\text{cm}^{-1}$ , centred at about 3000  $\text{cm}^{-1}$ .  
This arises due to the stretching vibration of O-H group of **carboxylic acids**. The broad nature of the band is due to the fact that carboxylic acids usually exist as hydrogen-bonded dimers.
- iii) Two or more strong absorption bands in the region 1300-1000  $\text{cm}^{-1}$   
These are due to the C-O stretching vibrations in **esters**.
- iv) If the above three are absent then the molecule could be a **ketone**

Similarly, if C=O absorption is absent, look for the following

- i) The N-H stretching vibrations of **amines** in the region 3300-3000  $\text{cm}^{-1}$   
These are observed to be weaker and sharper than those observed for the O-H stretching vibrations of alcohols which appearing in the same region. The presence of two bands is suggestive of a primary amine whereas a single band is indicative of a secondary amine.
- ii) The corresponding C-N stretching vibrations of aliphatic amines are observed as medium or weak bands in the region 1250-1020  $\text{cm}^{-1}$ . The same for aromatic amines are usually observed as strong band in the 1335-1250  $\text{cm}^{-1}$ .
- iii) Nitrile ( $\text{C}\equiv\text{N}$ ) shows a medium, sharp absorption band in the range 2260-2220  $\text{cm}^{-1}$ . The isomeric isocyanate's strong bands are observed in the range 2275-2240  $\text{cm}^{-1}$ .

#### D. Molecules containing C, H, O and N

For the molecules having this elemental composition, two most common functional groups are amide and nitro. Their absorptions can be looked for in the following regions.

- i) **Amide:** The amides show a characteristic absorption band for the carbonyl group in the region,  $1700\text{--}1640\text{ cm}^{-1}$ . It is also referred to as the **Amide I band**.

In addition, the N–H stretching vibrations are observed in the  $3500\text{--}3100\text{ cm}^{-1}$ . The primary amides show two N–H stretching bands whereas the secondary amides give rise to only one such band.

- ii) **Nitro:** In nitroalkanes the N–O stretching vibrations occur in the range of  $1550\text{--}1365\text{ cm}^{-1}$ ; the band at higher value being the stronger of the two. On the other hand for the nitro group attached to an aromatic ring, the N–O stretching bands are observed in the ranges of  $1550\text{--}1475\text{ cm}^{-1}$  and  $1360\text{--}1290\text{ cm}^{-1}$ .

With the strategy outlined above, you may now venture into looking at the IR spectra of some organic compounds for characterising the possible functional groups present in them. For your convenience, a table from the Unit 3 of MCH-003 course compiling the characteristic absorption frequencies of different functional groups is being reproduced at the end of this experiment. In the next section you are provided with some representative IR spectra of known organic compounds so that you can look into the structure-spectral correlations.

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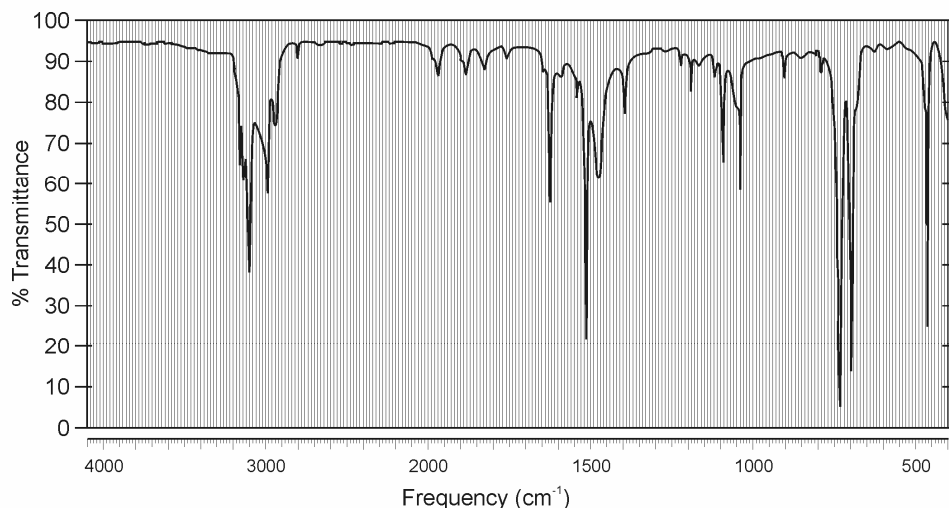
### 7.5 PRACTICE PROBLEMS

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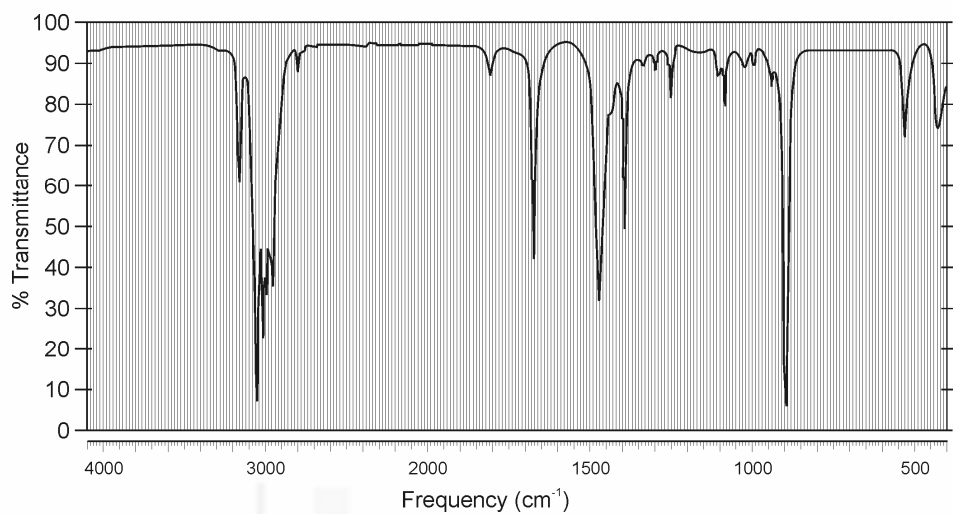
The IR spectra of some simple molecules are given below as practice problems. You are expected to arrive at the possible structure of these molecules by using the correlation table and the strategy outlined above. The assignment of the characteristic peaks in these spectra is given at the end of the experiment. You may compare your interpretation with the one given there. Please do solve the problem before venturing into looking into the answers.

You may proceed to the next section only after solving the practice problems and when you feel confident about taking up newer problems.

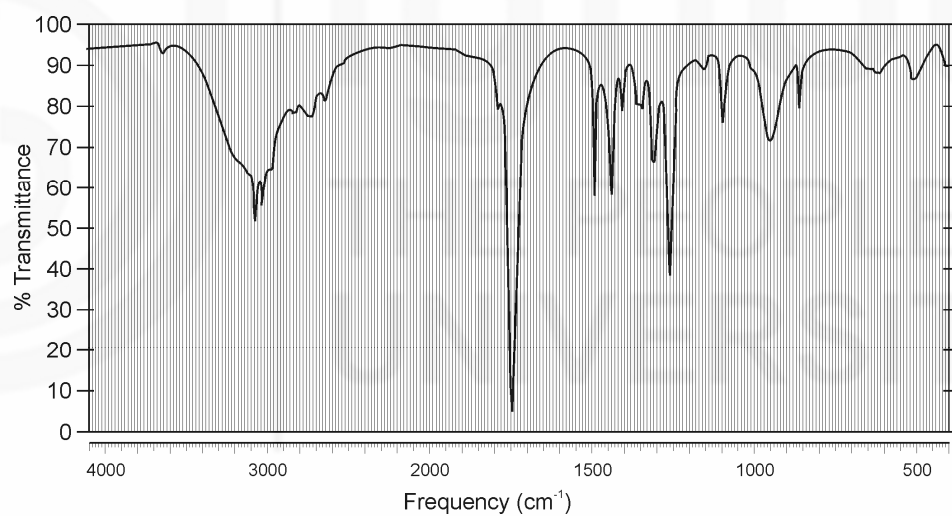
#### Sample spectrum 1: Toluene



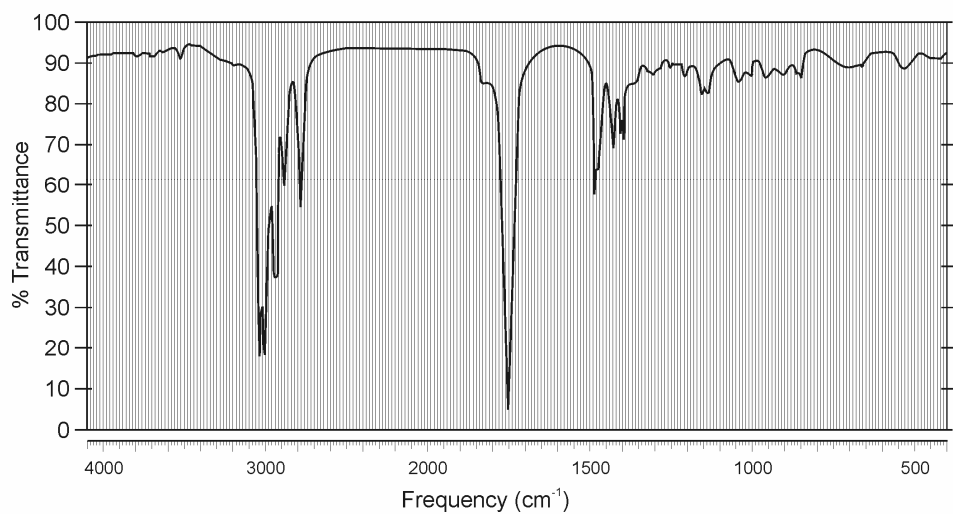
**Sample spectrum 2: 2-methyl butene**



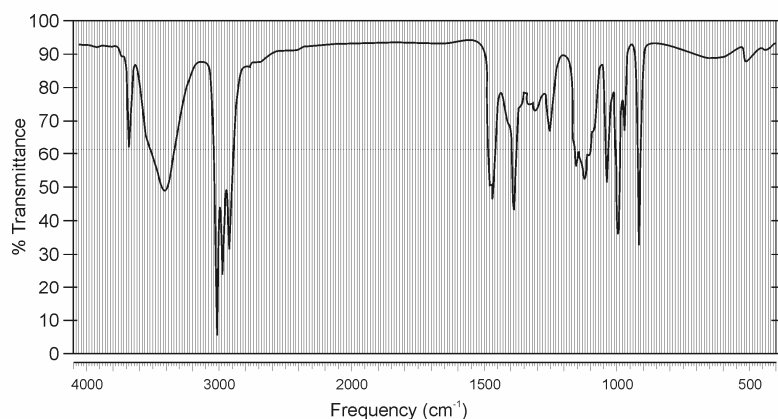
**Sample spectrum 3: Propanoic acid**



**Sample spectrum 4: Hexanal**



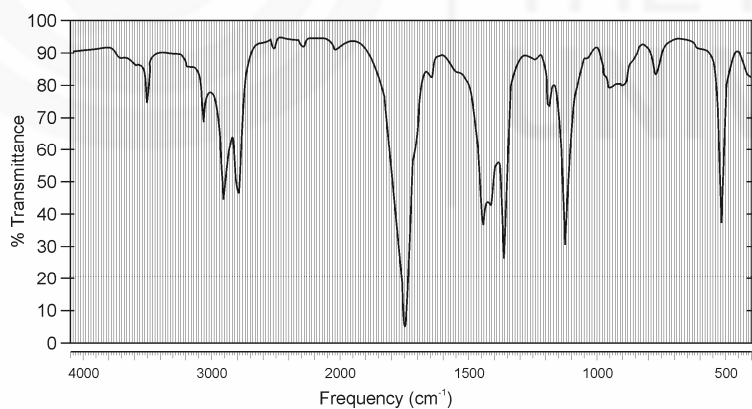
### Sample spectrum 5: 2-Butanol



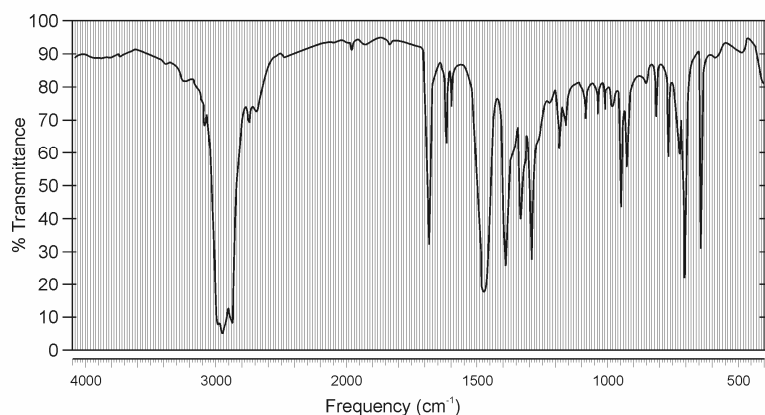
## 7.6 PROBLEMS FOR THE SESSION

Having solved the problems raised in the previous section we hope you are somewhat equipped to interpret the given IR spectra of some simple organic molecule and determine the functional group present in them. You are provided with five spectra for interpretation. You may take the spectra in any sequence and try to interpret on the basis of the knowledge gained and the Table and other hints provided in section 7.3. (Your counselor may provide you other IR spectra of simple organic molecules to assess your understanding.) You must pin up the spectra in the record book and submit your observations and results to your counsellor for evaluation.

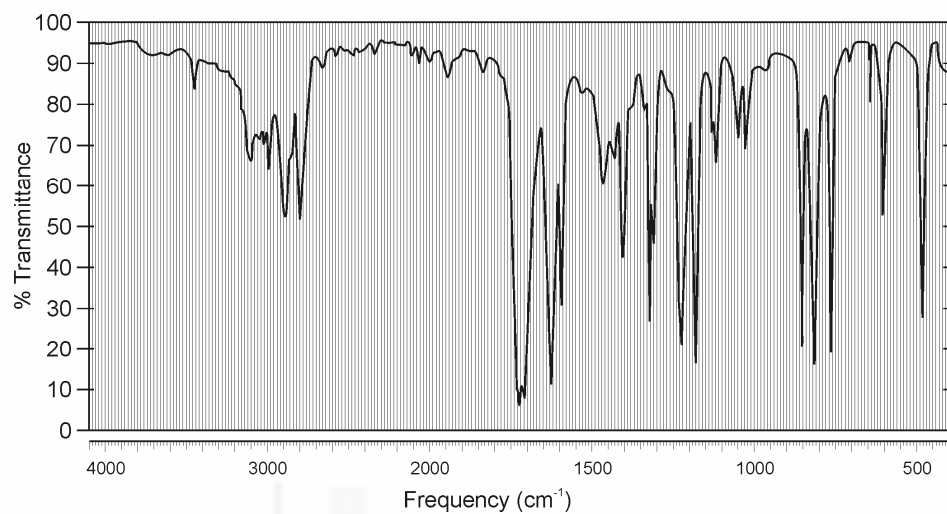
### Problem spectrum 1



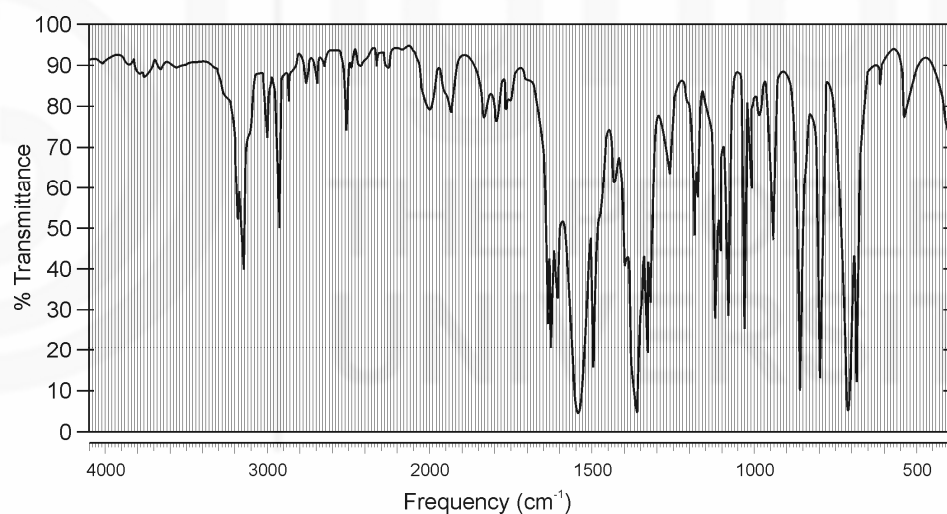
### Problem spectrum 2



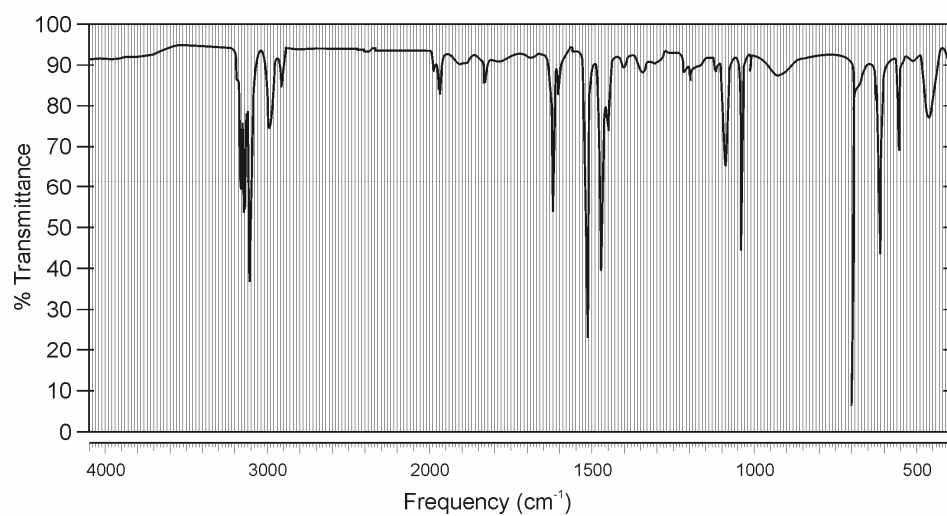
**Problem spectrum 3**



**Problem spectrum 4**



**Problem spectrum 5**





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## 7.7 SOLUTIONS TO THE PRACTICE PROBLEMS

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### Sample spectrum 1

The given molecule is an aromatic hydrocarbon; we can note the presence of

- i) The signals at 3099, 3068, 3032  $\text{cm}^{-1}$  due to the  $=\text{C}-\text{H}$  stretches of aromatics.
- ii) The signals at 2925  $\text{cm}^{-1}$  due to the  $-\text{C}-\text{H}$  stretching vibration of the alkyl (methyl) group.
- iii) The signals at 1614, 1506, 1465  $\text{cm}^{-1}$  are due to the breathing vibrations of the aromatic ring.
- iv) The signals below 900  $\text{cm}^{-1}$  due to the out of plane vibrations of the aromatic ring and are indicative of the substitution pattern.

You may also note that the carbonyls etc are absent here.

### Sample spectrum 2

The given molecule is an aliphatic alkene; we can note the presence of

The signal at 3100  $\text{cm}^{-1}$  due to the  $=\text{C}-\text{H}$  vibration

The signal at 2980  $\text{cm}^{-1}$  due to the  $-\text{C}-\text{H}$  vibration

The signal at 1620  $\text{cm}^{-1}$  due to the  $-\text{C}=\text{C}-$  vibration

You may note that the aromatic ring and carbonyls are absent here.

### Sample spectrum 3

As the molecule is a carboxylic acid we can clearly note the presence of

The signal at 1700  $\text{cm}^{-1}$  due to the  $\text{C}=\text{O}$  vibration

The signal at 3000  $\text{cm}^{-1}$  due to the  $\text{O}-\text{H}$  stretching

You may note that the absence of the signals due to aromatic ring

### Sample spectrum 4

As the molecule is an aliphatic aldehyde we can clearly note the presence of

The signal at  $\sim 1730 \text{ cm}^{-1}$  due to the  $\text{C}=\text{O}$  vibration

The characteristic signal at  $\sim 2720 \text{ cm}^{-1}$  due to the aldehydic  $\text{C}-\text{H}$  vibration

Here again you may note that the absence of the signals due to aromatic ring

### Sample spectrum 5

As the molecule is an aliphatic alcohol we can clearly note the presence of

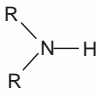
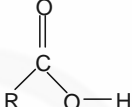

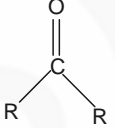
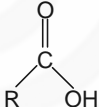
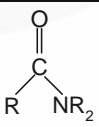
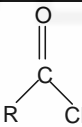
The signal at  $\sim 3300 \text{ cm}^{-1}$  due to the  $\text{O}-\text{H}$  stretching vibration

The signal at 2900  $\text{cm}^{-1}$  due to the  $\text{C}-\text{H}$  stretching

### For counsellors

However, if the study centre has a working IR spectrometer it will be highly appreciated that if the learners are demonstrated how to take an IR spectra and then interpret the same for the functional groups.

**Spectroscopic Methods  
Lab**

Functional group	Structure	IR frequency range (cm <sup>-1</sup> )	Functional group	Structure	IR frequency range (cm <sup>-1</sup> )
Alkane (C-H)	R <sub>3</sub> C-H (R= H or C)	3000-2800	Alkyne (C≡C)	RC≡CR (R=H or C)	2260-2100
Alcohol (O-H)	RO-Hs	3600-3200 (broad band)	Nitrile (C≡N)	RC≡N	2260-2200
Amines, Amide (N-H)	 -----	3500-3300 (One band)  3500-3300 (two bands), 1650-1560 (bending)	Alkene (C=C)	R <sub>2</sub> C=CR <sub>2</sub> (R=H or C)	1600-1680
Carboxylic acid (O-H)		3200-2500 (broad band)	Benzene ring (C=C)	 (C=C ring "breathing")	1450-1600 2 to 3 bands
Aldehydes or Ketones (C=O)		1750-1705	Alcohol or Ether (C-O)	--- (R=H or C)	1300-1000
Carboxylic acid (C=O)	 (R=H or C)	1790-1680	Alkyne (C-H)	RC≡C-H (R=C)	3300
Amide (C=O)	 (R-H or C)	1850-1800 and 1790-1730	Acid chloride (C=O)	 (R=H or C)	1815-1790