

CH 424 Instrumental Analysis Lab

Qualitative Analysis by IR spectroscopy

Introduction

IR spectroscopy, one of the vibrational spectroscopic techniques, is a valuable tool for qualitative analysis. IR radiation is generally considered to be from about 10,000-100 cm^{-1} , however, most instruments are limited to the range where most application occur between 4000-400 cm^{-1} . In this technique, the IR radiation is absorbed and converted by a sample molecule into energy of molecular vibration. The masses of the atoms in the molecule, the force constants of the bonds, and the geometric structure of the molecule determine the frequency of absorption. IR spectra can be used to provide information on the functional groups as well as the structure of a molecule as a whole.

IR spectra are commonly divided into three main regions. The high-frequency region, between 4000-1300 (2-7.7 μm), is called *functional group region* because the characteristics stretching frequencies for important functional groups such as C=O, OH, and NH occur in this region. The middle-frequency region, between 1300-900 cm^{-1} (7-11 μm) is known as the *fingerprint region*, in which the absorptions occur are complex and normally due to combinations of interacting vibrational modes, providing a unique fingerprint for every molecule. The spectrum in this region is especially valuable if examined in reference to other regions. The region between 900-650 cm^{-1} (11-15 μm) provides general classification of molecules from the pattern of absorptions, such as substitution patterns on a benzene ring. The absence of absorptions in the low-frequency region can provide a good evidence for the absence of an aromatic compound. Obtaining a broad, moderately intense absorption in the low-frequency region indicates the presence of carboxylic dimers, amines, or amides. Evaluation of the spectra is normally begun with assigning the bands of high and medium intensities, especially in the functional group region and low-frequency region.

You will use the Fourier transform (FT) IR spectrometer to collect the data in this experiment. The FT-IR instruments do not require a dispersing unit; the radiation containing all wavelengths from the light source is monitored simultaneously. Most of FT-IR instruments are based on scanning Michelson interferometer that consists of a moving mirror, a fixed mirror, and a beamsplitter. Radiation from the IR source is divided at the beamsplitter in which half the beam passes to a fixed mirror, the another half is reflected off the moving mirror. The two beams will recombine at the beamsplitter, and a constructive or destructive interference will occur depending on the difference of the distance between the beamsplitter to the fixed and moving mirror. The result of a variation of intensities is an oscillatory series of destructive and constructive combinations, called an interferogram. Fourier transformation converts this interferogram from the time domain into normal IR spectra, which is in the frequency domain. FT-IR provides several advantages such as high sensitivity, resolution, and speed.

In this experiment, you will familiar with the operation FT-IR spectrometer and sample handling in IR technique for both liquid and solid samples, learn how to interpret IR spectra, and identify unknown compounds.

Procedure

1. Using a single scan, record a full-range (4000 cm^{-1} to 600 cm^{-1}) spectrum of polystyrene. Plot the interferogram, transform the data, and then plot the full-range spectrum over the interferogram. Note on how long all this took.
2. Now perform a 4 scans run, noting how long this takes, transform the data and plot the spectrum. Repeat for 16 scans. Comment on the improvement in the signal-to-noise obtained.
3. Obtain unknown compounds and a list of possible unknown compounds from your instructor and make a note for the unknown numbers. You will receive one unknown liquid compound and one unknown solid compound.
4. Record a full-range (4000 cm^{-1} to 600 cm^{-1}) spectrum of a liquid unknown as thin films between sodium chloride plates. Clean sodium chloride plates with chloroform and tissues; handling them with care, by the edges only.
5. Record a full-range (4000 cm^{-1} to 600 cm^{-1}) spectrum of a solid unknown. How do you prepare the sample?

Your compounds will be in the list of possible IR unknown compounds. From appropriate tables or IR correlation charts, identify possible functional groups in your compound from characteristic bands in your spectrum, and write them next to the assigned bands. Once you have narrow the number of possible compounds down to a few compounds from the list of the possible unknown compounds, consult some standard source of IR spectra. Then tabulate to make a comparison between the spectra of most probable compounds from a reference IR spectra with your unknown spectra. The suggested comparison table contains headings such as wave number of absorption peaks (cm^{-1}), supposed groups, group present and their types of vibration.

Questions

- (1) What are the main analytical applications of IR spectroscopy?
- (2) Explain why absorption of IR radiation by a molecule is actually quantized but the vibrational spectra appear as bands rather than as lines.

References

- (1) R.M Silverstein, G. Claton Bassler and Terence C. Morrill, "Spectrometric Identification of organic Compounds, 5th Ed., John Wiley & Sons, New York, 1991.

- (2) Ernő Pungor, "A practical Guide to Instrumental Analysis", CRC Press, London, 1995.
- (3) Donald T. Sawyer, William R. Heinman and Janice M. Beebe, "Chemistry Experiments for Instrumental Methods", John Wiley & Sons, New York, 1984.
- (4) Hobart H. Willard, Lynne L. Merritt, John A. Dean and Frank A. Settle, "Instrumental Methods of Analysis", Wadsworth Publishing Company, Belmont, 1988.

List of Possible IR Unknown Compounds

Acetanilide
Acetylsalicylic acid
Benzoic acid
Benzylmethanamine
3-bromo-1-propanol
caffeine
2-chlorobenzoic acid
dibutylmaleate
ethyl acetate

ethyl caproate
ethyl cinnamate
p-nitroaniline
2-nitrotoluene
5-nitrosalicylaldehyde
3-pentanol
acetonylacetone
p-bromoanisole
sec-butyl amine
1-chloro-2-propanol
o-Xylene
m-Xylene
p-Xylene
Toluene
Ethylbenzene