Infrared spectroscopy, an analytical technique that takes advantage of the vibrational transitions of a molecule, has been of great significance to scientific researchers in many fields such as protein characterization, nanoscale semiconductor analysis and space exploration.

**Introduction**

Infrared spectroscopy is the study of interaction of infrared light with matter, which can be used to identify unknown materials, examine the quality of a sample or determine the amount of components in a mixture. Infrared light refers to electromagnetic radiation with wavenumber ranging from 13000 – 10 cm\(^{-1}\) (corresponding wavelength from 0.78 – 1000 \(\mu\)m). Infrared region is further divided into three subregions: near-infrared (13000 – 4000 cm\(^{-1}\) or 0.78 – 2.5 \(\mu\)m), mid-infrared (4000 – 400 cm\(^{-1}\) or 2.5 – 25 \(\mu\)m) and far-infrared (400 – 10 cm\(^{-1}\) or 25 – 1000 \(\mu\)m). The most commonly used is the middle infrared region, since molecules can absorb radiations in this region to induce the vibrational excitation of functional groups. Recently, applications of near infrared spectroscopy have also been developed.

By passing infrared light through a sample and measuring the absorption or transmittance of light at each frequency, an infrared spectrum is obtained, with peaks corresponding to the frequency of absorbed radiation. Since all groups have their characteristic vibrational frequencies, information regarding molecular structure can be gained from the spectrum. Infrared spectroscopy is capable of analyzing samples in almost any phase (liquid, solid, or gas), and can be used alone or in combination with other instruments following different sampling procedures. Besides fundamental vibrational modes, other factors such as overtone and combination bands, Fermi resonance, coupling and vibration-rotation bands also appear in the spectrum. Due to the high information content of its spectrum, infrared spectroscopy has been a very common and useful tool for structure elucidation and substance identification.

**Instrumentation**

Most commonly used instruments in infrared spectroscopy are dispersive infrared spectrometer and Fourier transform infrared spectrometer.

**Dispersive infrared spectrometer**

Dispersive infrared spectrometer is mainly composed of radiation source, monochromator and detector. For mid-infrared region, Globar (silicon carbide), Nernst glower (oxides of zirconium, yttrium and erbium) and metallic helices (chromium-nickel alloy or tungsten) are frequently used as radiation sources. Tungsten-halogen lamps and metallic conductors coated with ceramic are utilized as sources for near-infrared region. A mercury high-pressure lamp is suitable for far-infrared region.

Monochromator in conjunction with slits, mirrors and filters separates the wavelengths of light emitted. The dispersive elements within monochromator are prisms or gratings. Gratings have gradually replaced prisms due to their comparatively low cost and good quality. As shown in Figure 1, radiation passes through both a sample and a reference path. Then the beams are directed to a diffraction grating (splitter), which disperses the light into component frequencies and directs each wavelength through a slit to the detector. The detector produces an electrical signal and results in a
Two types of detectors are employed in dispersive infrared spectrometer, namely, thermal detectors and photon detectors. Thermal detectors include thermocouples, thermistors, and pneumatic devices, which measure the heating effect generated by infrared radiation. Photon detectors are semiconductor-based. Radiation is able to promote electrons in photon detectors from valence band to conduction band, generating a small current. Photon detectors have faster response and higher sensitivity than do thermal detectors but are more susceptible to thermal noise.

### Fourier transform infrared spectrometer

Dispersive infrared spectrometer has many limitations because it examines component frequencies individually, resulting in slow speed and low sensitivity. Fourier transform infrared (FTIR) spectrometer is preferred over dispersive spectrometer, since it is capable of handling all frequencies simultaneously with high throughput, reducing the time required for analysis. The radiation sources used in dispersive infrared spectrometer can also be used in FTIR spectrometer.

In contrast with the monochromator in dispersive spectrometer, FTIR spectrometer as shown in Figure 2 employs an interferometer. The beamsplitter within the interferometer splits the incoming infrared beam into two beams, one of which is reflected by a fixed mirror, while the other one reflected by a moving mirror perpendicular to the fixed one. The length of path one beam travels is fixed and that of the other one is changing as the mirror moves, generating an optical path difference between the two beams. After meeting back at the beamsplitter, the two beams recombine, interfere with each other, and yield an interferogram. The interferogram produces inference signal as a function of optical path difference. It is converted to a spectrum of absorbance or transmittance versus wavenumber or frequency by Fourier transform.

### Application

Since different molecules with different combination of atoms produce their unique spectra, infrared spectroscopy can be used to qualitatively identify substances. In addition, the intensity of the peaks in the spectrum is proportional to the amount of substance present, enabling its application for quantitative analysis.

### Qualitative analysis

For qualitative identification purposes, the spectrum is commonly presented as transmittance versus wavenumber.
Functional groups have their characteristic fundamental vibrations which give rise to absorption at certain frequency range in the spectrum (Figure 3).

Figure 3. Infrared spectrum of 1-hexanol.

Each band in a spectrum can be attributed to stretching or bending mode of a bond. Almost all the fundamental vibrations appear in the mid-infrared region. For instance, 4000 – 2500 cm\(^{-1}\) region usually can be assigned to stretching modes of O-H, N-H or C-H. Triple-bond stretching modes appear in the region of 2500 – 2000 cm\(^{-1}\). C=C and C=O stretching bands fall in the 2000 – 1500 cm\(^{-1}\) region. Hence, characterization of functional groups in substances according to the frequencies and intensities of absorption peaks is feasible, and also structures of molecules can be proposed. This method is applicable to organic molecules, inorganic molecules, polymers, etc. A detailed frequency list of functional groups is shown in Figure 4. Note that several functional groups may absorb at the same frequency range, and a functional group may have multiple-characteristic absorption peaks, especially for 1500 – 650 cm\(^{-1}\), which is called the fingerprint region.

Figure 4. Characteristic infrared absorption frequencies.

Bands in the near-infrared region are overtones or combination bands. They are weak in intensity and overlapped, making them not as useful for qualitative analysis as those in mid-infrared region. However, absorptions in this region are helpful in exploiting information related to vibrations of molecules containing heavy atoms, molecular skeleton vibrations, molecular torsions and crystal lattice vibrations.

Besides structural elucidation, another qualitative application of infrared spectroscopy is the identification of a compound with a reference infrared spectrum. If all the peaks of the unknown match those of the reference, the compound can be identified. Additional reference spectra are available online at databases such as NIST Chemistry WebBook.

### Quantitative analysis

Absorbance is used for quantitative analysis due to its linear dependence on concentration. Given by Beer-Lambert law, absorbance is directly proportional to the concentration and pathlength of sample:

\[
A = \varepsilon c l
\]

where \(A\) is absorbance, \(\varepsilon\) the molar extinction coefficient or molar absorptivity which is characteristic for a specific substance, \(c\) the concentration and \(l\) the pathlength (or the thickness) of sample. The conversion from transmittance to absorbance is given by

\[
A = -\log T
\]

where \(T\) is transmittance.

For quantitative analysis of liquid samples, usually an isolated peak with high molar absorptivity that appears in the spectrum of the compound is chosen. A calibration curve of absorbance at the chosen frequency against concentration of the compound is acquired by measuring the absorbance of a series of standard compound solution with known concentrations. These data are then graphed to get a linear plot, from which the concentration of the unknown can be
calculated after measuring its absorbance at the same frequency. The number of functional groups can also be calculated in this way, since the molar absorptivity of the band is proportional to the number of functional groups that are present in the compound.

For solid samples, an internal standard with a constant known amount is added to the unknown sample and the standards. Then similar procedures as those with liquid samples are carried out except that the calibration curve is a graph of the ratio of absorbance of analyte to that of the internal standard versus concentration of the analyte.

A multi-component analysis of the mixture is also feasible since different components have different values of molar absorptivity at the same frequency.

However, infrared spectroscopy may be more susceptible to deviation from Beer's law than is UV-Vis spectroscopy because of its narrow bands, complex spectra, weak incident beam, low transducer sensitivity and solvent absorption.

Reference


Outside Links


Contributor

- Xixuan Li (UC Davis)