INFRARED SPECTROSCOPY

1. Introduction

Infrared (ir) spectroscopy is a technique based on the vibrations of atoms of a molecule. An ir spectrum is commonly obtained by passing ir radiation through a sample and determining what fraction of the incident radiation is absorbed at a particular energy. The energy at which any peak in an absorption spectrum appears corresponds to the frequency of a vibration of a part of a sample molecule.

For a molecule to show ir absorptions, it must possess a specific feature: An electric dipole moment of the molecule must change during the movement. The interactions of ir radiation with matter may be understood in terms of changes in molecular dipoles associated with vibrations and rotations. The atoms in molecules can move relative to one another, ie, bond lengths can vary or one atom can move out of its present plane. This is a description of stretching and bending movements that are collectively referred to as vibrations. Vibrations can involve either a change in bond length (stretching) or bond angle (bending). Some bonds can stretch in-phase (symmetrical stretching) or out-of-phase (asymmetric stretching). If a molecule has different terminal atoms, then the two stretching modes are no longer symmetric and asymmetric vibrations of similar bonds, but will have varying proportions of the stretching motion of each group. In other words, the amount of coupling will vary.

There will be many different vibrations for even fairly simple molecules. The complexity of an ir spectrum arises from the coupling of vibrations over a large part of or over the complete molecule and are called skeletal vibrations. Bands associated with skeletal vibrations are likely to conform to a pattern or fingerprint of the molecule as a whole, rather than a specific group within the molecule.

2. Instrumentation

Infrared spectrometers have been commercially available since the 1940s. At that time, the instruments relied on prisms to act as dispersive elements, but by the mid-1950s, diffraction gratings had been introduced into dispersive machines. The most significant advances in ir spectroscopy, however, have come about as a result of the introduction of Fourier transform (ft) spectrometers. This type of instrument employs an interferometer and exploits the well-established mathematical process of Fourier transformation. Fourier transform infrared (ftir) spectroscopy has dramatically improved the quality of ir spectra and minimized the time required to obtain data. Also, with constant improvements to computers, ir spectroscopy has made great strides.

Fourier transform spectroscopy (1) is based on the idea of the interference of radiation between two beams to yield an interferogram. An interferogram is a signal produced as a function of the change of pathlength between the two beams. The two domains of distance and frequency are interconvertible by the mathematical method of Fourier transformation.

In an ftir spectrometer, the radiation emerging from a source is passed through an interferometer to the sample before reaching a detector. Upon amplification of the signal, in which high frequency contributions have been eliminated by a filter, the data are converted to a digital form by an analog-to-digital converter and transferred to the computer for Fourier transformation. The most common interferometer used in ftir spectrometry is a Michelson interferometer, which consists of two perpendicularly plane mirrors, one of which can travel in a direction perpendicular to the plane (Fig. 1). A semireflecting film, the beamsplitter, bisects the planes of these two mirrors. The beamsplitter material has to be chosen according to the region to be examined. Materials such as germanium or iron oxide are coated onto an ir transparent substrate such as potassium bromide or cesium iodide to produce beamsplitters for the mid- or near-ir regions. Thin organic films, such as polyethylene terephthalate, are used in the far-ir region.

If a collimated beam of monochromatic radiation of wavelength λ (cm) is passed into an ideal beamsplitter, 50% of the incident radiation will be reflected to one of the mirrors and 50% will be transmitted to the other mirror. The two beams are reflected from these mirrors, returning to the beamsplitter where they recombine and interfere. Fifty percent of the beam reflected from the fixed mirror is transmitted through the beamsplitter and 50% is reflected back in the direction of the source. The beam that emerges from the interferometer at 90° to the input beam is called the transmitted beam and this is the beam detected in ftir spectrometry. The moving mirror produces an optical path difference between the two arms of the interferometer. For path differences of $(n + ½)\lambda$, the two beams interfere destructively in the case of the transmitted beam and constructively in the case of the reflected beam.

The ftir spectrometers use a Globar or Nernst source for the mid-ir region. If the far-ir region is to be examined, then a high pressure mercury lamp can be used. For the near-ir, tungsten–halogen lamps are used as sources. There are two commonly used detectors used in the mid-ir region. The normal detector for routine use is a pyroelectric device incorporating deuterium tryglycine sulfate (DTGS) in a temperature resistant alkali halide window. For more sensitive work, mercury cadmium telluride (MCT) can be used, but has to be cooled to liquid nitrogen temperatures. In the far-ir germanium or indium–antimony detectors are employed, operating at liquid helium temperatures. For the near-ir, detectors are generally lead sulfide photoconductors.

The essential equations for a Fourier transformation relating the intensity falling on the detector, $I(\delta)$, to the spectral power density at a particular wavenumber, $\bar{v}$, given by $B(\bar{v})$ are as follows:

$$I\delta = \int_0^{+\infty} B(\bar{v}) \cos 2\pi\, \bar{v}\, \delta\, d\bar{v} \tag{1}$$

which is one-half of a cosine FT pair, the other being

$$B(\bar{v}) = \int_{-\infty}^{+\infty} I(\delta) \cos 2\pi\, \bar{v}\, \delta\, d\delta \tag{2}$$

These two equations are interconvertible and are known as a ft pair. The first shows the variation in power density as a function of the difference in path length, which is an interference pattern. The second shows the variation in intensity as a function of wavenumber. Each can be converted into the other by the mathematical method of Fourier transformation.

The essential experiment to obtain a ftir spectrum is to produce an interferogram with and without a sample in the beam and transforming the interferograms into spectra of (*1*) the source with sample absorptions and (*2*) the source without sample absorptions. The ratio of the former and the latter corresponds to a double-beam dispersive spectrum.

The interferogram is an analogue signal at the detector that has to be digitized in order to convert the Fourier transformation into a conventional spectrum. There are two particular sources of error in transforming the digitized information on the interferogram into a spectrum. First, the transformation carried out involves an integration stage over a finite displacement rather than over an infinite displacement. The mathematical process of Fourier transformation assumes infinite boundaries. The consequence of this approximation is that the apparent line shape of a spectral line may demonstrate a main band area with a series of negative and positive side lobes (or pods) with diminishing amplitudes.

The process of apodization is removal of the side lobes or pods by multiplying the interferogram by a suitable function before the Fourier transformation is carried out. A suitable function must cause the intensity of the interferogram to fall smoothly to zero at its ends. The ftir spectrometers offer a choice of apodization options. A good general purpose apodization function is the cosine function:

$$F(D) = [1 + \cos(\pi D)]/2 \tag{3}$$

where D is the optical path difference. The cosine function provides a good compromise between reduction in oscillations and deterioration in spectral resolution. When accurate band shapes are needed, more sophisticated mathematical functions may be utilized.

Another source of error arises if the sample intervals are not exactly the same on each side of maxima corresponding to a zero path difference. Phase correction is required and this correction procedure ensures that the sample intervals are the same one each side of the first interval and correspond to a path difference of zero.

The resolution for an ftir instrument is limited by the maximum path difference between the two beams. The limiting resolution in wavenumber (cm^{-1}) is the reciprocal of the path length difference (cm). For example, a path length difference of 10 cm is required to achieve a limiting resolution of 0.1 cm^{-1}. This simple calculation appears to show that it is easy to achieve high resolution. Unfortunately, this is not the case since the precision of the optics and mirror movement mechanism become more difficult to achieve at longer displacements of path lengths.

The main advantages of rapid scanning instruments is the ability to increase the signal-to-noise ratio (SNR) by signal averaging, leading to an increase of SNR proportional to the square root of the time. There are diminishing returns for signal averaging in that it takes an increasingly longer time to achieve greater and greater improvement. The accumulation of a large number of repeat scans makes greater demands on the instrument if it is to exactly reproduce the conditions. It is normal to incorporate a laser monochromatic source in the beam of the continuous source. The laser beam produces standard fringes that can accurately line-up successive scans and can determine and control the displacement of the moving mirror at all times.

The ftir instruments have several significant advantages over older dispersive instruments. Two of these are the Fellgett (or multiplex) and the Jacquinot (or throughput) advantage. The Fellgett advantage is due to an improvement in the SNR per unit time proportional to the square root of the number of resolution elements being monitored. This results from the large number of resolution elements being monitored simultaneously. Also, because ftir spectrometry does not require the use of a slit or other restricting device, the total source output can be passed through the sample continuously. This results in a substantial gain in energy at the detector, translating to higher signals and improved SNRs. This is known as Jacquinot's advantage. Another strength of ftir spectrometry is its speed advantage. The mirror has the ability to move short distances quite rapidly, and this, together with the SNR improvements due to Fellgett's and Jacquinot's advantages, make it possible to obtain spectra on a millisecond timescale. In interferometry the factor that determines the precision of the position of an ir band is the precision with which the scanning mirror position is known. By using a helium–neon laser as a reference, the mirror position is known with high precision.

3. Sampling Methods

3.1. Transmission Methods. Transmission spectroscopy is the oldest and most straightforward ir method. The method is based upon the absorption of ir radiation at specific wavelengths as it passes through a sample. It is possible to analyze samples in liquid, solid, or gaseous form using this approach (2).

There are several different types of transmission liquid cells available. Fixed-path length sealed cells are useful for volatile liquids, but cannot be taken apart for cleaning. Semipermanent cells are demountable so that the windows can be cleaned. The spacer is usually made of polytetrafluoroethylene (PTFE, Teflon) and is available in a variety of thicknesses, allowing one cell to be used for various pathlengths. Variable path length cells incorporate a mechanism for continuously adjusting the pathlength and a vernier scale allows accurate adjustment. All these cell types are filled using a syringe and the syringe ports are sealed with PTFE plugs before sampling. If quantitative analysis of a sample is required, it is necessary to use a cell of known path length. An important consideration in the choice of ir cells is the type of window material. The material must be transparent to the incident ir radiation and normally alkali halides are used in transmission methods. The cheapest material is sodium chloride (NaCl), but other commonly used materials are potassium bromide (KBr), calcium fluoride (CaF_2), and cesium bromide (CsBr). Liquid films also provide a quick method of examining liquid samples. A drop of liquid may be sandwiched between two ir plates that are then mounted in a cell holder. Before producing an ir sample in solution, a suitable solvent must be chosen. In choosing a solvent for a sample, the following factors need to be considered: it has to dissolve the compound; it should be as nonpolar as possible to minimize solute–solvent interactions; and it should not strongly absorb ir radiation.

There are three general methods for examining solid samples in transmission ir spectroscopy: alkali halide disks, mulls, and films. The use of alkali halide disks involves mixing a solid sample with a dry alkali halide powder. The mixture is usually ground with an agate mortar and pestle and subjected to a pressure of ~10 ton/in.^{2} in an evacuated die. This sinters the mixture and produces a clear transparent disks. The most commonly used alkali halide is KBr, which is completely transparent in the mid-ir region. Certain factors need to be considered when preparing alkali halide disks. The ratio of the sample to alkali halide is important; suprisingly little sample is needed and ~2–3 mg of sample with ~200 mg of halide. The disk must not be too thick or too thin; thin disks are fragile and difficult to handle, while thick disks transmit too little radiation. A disk of ~1-cm diameter made from ~200 mg of material usually results in a good thickness of ~1 mm. If the crystal size of the sample is too large, excessive scattering of radiation results, especially at high wavenumbers (this is known as the Christiansen effect). The crystal size must be reduced, normally by further grinding of the solid using a mortar and pestle. If the alkali halide is not perfectly dry, bands due to water appear in the spectrum. Contributions due to water are difficult to avoid, but the alkali halide should be kept dessicated and warm prior to use to minimize the effect.

The mull method for solid samples involves grinding the sample then suspending (~50 mg) in 1–2 drops of a mulling agent. This is followed by further grinding until a smooth paste is obtained. The most commonly used mulling agent is Nujol (liquid paraffin). Although the mull method is quick and easy, there are some experimental factors to consider. The ratio of the sample to mulling agent must be correct; a rough guide to mull preparation is to use a microspatula tip of sample to 2–3 drops of mulling agent. If the crystal size of the sample is too large, this leads to the scattering of radiation that gets worse at the high wavenumber end of the spectrum. If the mull is not spread over the whole plate area, the beam of radiation passes part through the mull and part through only the plates, producing a distorted spectrum. The amount of sample placed between the ir plates is an important factor; too little leads to a very weak spectrum showing only the strongest absorption bands. Too much mull leads to poor transmission of radiation so that the baseline may be at 50% or less.

Films can be produced by either solvent or by melt casting. In solvent casting, the sample is dissolved in an appropriate solvent (the concentration depends on the required film thickness). A solvent needs to be chosen that not only dissolves the sample, but will also produce a uniform film. The solution is poured onto a leveled glass plate (such as a microscope slide) or a metal plate and spread to uniform thickness. The solvent may then be evaporated in an oven and, once dry, the film can be stripped from the plate. However, care must be taken as heating samples may cause degradation. Alternatively, it is possible to cast a film straight onto the ir window to be used. Solid samples that melt at relatively low temperatures without decomposition can be prepared by melt casting. A film is prepared by hot pressing the sample in a hydraulic press between heated metal plates.

Gases have densities that are several orders of magnitude less than liquids, hence path lengths must be correspondingly greater, usually 10 cm or longer (3). The walls are of glass or brass with the usual choice of windows. The cells can be filled by flushing or from a gas line. To analyze complex mixtures and trace impurities, longer path lengths are necessary. As the sample compartment size in the instrument is limited, a multireflection gas cell is necessary to produce higher path lengths. In such a cell, the ir beam is deflected by a series of mirrors that reflect the beam back and forth many times until it exits the cell after having traveled the required equivalent path length. This type of cell allows a path length of up to 40 m to be attained.

3.2. Reflectance Methods. Reflectance techniques may be used for samples that are difficult to analyze by the conventional transmittance methods. Attenuated total reflectance spectroscopy (atr) utilizes the phenomenon of total internal reflection (Fig. 2). A beam of radiation entering a crystal will undergo total internal reflection when the angle of incidence at the interface between the sample and crystal is greater than the critical angle. The critical angle is a function of the refractive indexes of the two surfaces. The beam penetrates a fraction of a wavelength beyond the reflecting surface and when a material that selectively absorbs radiation is in close contact with the reflecting surface, the beam loses energy at the wavelength where the material absorbs. The resultant attenuated radiation is measured and plotted as a function of wavelength by the spectrometer and gives rise to the absorption spectral characteristics of the sample. The depth of penetration in atr is a function of wavelength, λ, the refractive index of the crystal, n_2, and the angle of incident radiation, θ. The depth of penetration, d_p, for a nonabsorbing medium is given by the following formula:

$$d_\mathrm{p} = (\lambda/n_1)/\ (2\pi[\sin\,\theta - (n_1/n_2)^2]^{1/2}) \tag{4}$$

where n_1 is the refractive index of the sample. The crystals used in atr cells are made from materials that have low solubility in water and are of a very high refractive index. Such materials include zinc selenide (ZnSe), germanium (Ge), and thallium/iodide (KRS-5).

Different designs of atr cells allow both liquid and solid samples to be examined. It is also possible to set up a flow-through atr cell by including an inlet and outlet into the apparatus. This allows for continuous flow of solutions through the cell and permits spectral changes to be monitored with time. Multiple internal reflectance (mir) and atr are similar techniques, but mir produces more intense spectra from multiple reflections. While a prism is usually used in atr work, mir uses specially shaped crystals that cause many internal reflections, typically 25 or more.

Specular reflectance occurs when the reflected angle of radiation equals the angle of incidence. The amount of light reflected depends on the angle of incidence, the refractive index, surface roughness, and absorption properties of the sample. For most materials, the reflected energy is only 5–10%, but in regions of strong absorptions, the reflected intensity is greater. The resultant data appears different from normal transmission spectra, as derivative-like bands result from the superposition of the normal extinction coefficient spectrum with the refractive index dispersion (based upon Fresnel's relationships). However, the reflectance spectrum can be corrected using a Kramers–Kronig transformation (or K–K transformation). The corrected spectrum appears like the familiar transmission spectrum.

Increased path lengths through thin coatings can be achieved using grazing angles of incidence (up to 85°). Grazing angle sampling accessories allow measurements to be made on samples over a wide range of angles of incidence. Solid samples, particularly coatings on reflective surfaces, are simply placed on a flat surface. The technique is also commonly used for liquid samples that can be poured into a Teflon trough. Oriented films on the liquid surface can be investigated using this method.

In external reflectance, the energy that penetrates one or more particles is reflected in all directions and this component is called diffuse reflectance. In the diffuse reflectance technique, commonly called drift, a powdered sample is usually mixed with KBr powder. The drift cell reflects radiation to the powder and collects the energy reflected back over a large angle. Diffusely scattered light can be collected directly from material in the sampling cup or, alternatively, from material collected using an abrasive sampling pad. The drift is particularly useful for sampling powders or fibers. Kubelka and Munk developed a theory describing the diffuse reflectance process for powdered samples that relates the sample concentration to the scattered radiation intensity. The Kubelka–Munk equation is

$$(1-R)^2/2R = c/k \tag{5}$$

where R is the absolute reflectance of the layer, c is the concentration, and k is the molar absorption coefficient. An alternative relationship between the concentration and the reflected intensity is now widely used in near-ir diffuse reflectance spectroscopy:

$$\log\,(1/R) = k'c \tag{6}$$

where k' is a constant.

Photoacoustic spectroscopy (pas) is a noninvasive reflectance technique with penetration depths in the range from micrometres down to several molecular monolayers. Gaseous, liquid, or solid samples can be measured using pas and the technique is particularly useful for highly absorbing samples. The photoacoustic effect occurs when intensity modulated light is absorbed by the surface of a sample located in an acoustically isolated chamber filled with an inert gas. A spectrum is obtained by measuring the heat generated from the sample due to a reabsorption process. The sample absorbs photons of the modulated radiation, which have the energy corresponding to the vibrational states of the molecules. The absorbed energy is released in the form of heat generated by the sample, which causes temperature fluctuations and, subsequently, periodic acoustic waves. A microphone detects the resulting pressure changes that are then converted to an electrical signal. Fourier transformation of the resulting signal produces a characteristic ir spectrum.

3.3. Microsampling Methods. It is possible to combine an ir spectrometer with a microscope facility in order to study very small samples (4–7). In recent years, there have been considerable advances in ftir microscopy with samples of the order of microns being characterized. In ftir microscopy, the microscope sits above the ftir sampling compartment. Infrared radiation from the spectrometer is focused onto a sample placed on a standard microscope x–y stage. After passing through the sample, the ir beam is collected by a Cassegrain objective that produces an image of the sample within the barrel of the microscope. A variable aperture is placed in this image plane. The radiation is then focused on a small area MCT detector by another Cassegrain condenser. The microscope also contains glass objectives to allow visual inspection of the sample. In addition, by switching mirrors in the optical train, the microscope can be converted from transmission mode to reflectance mode.

If a microscope facility is not available, there are other special sampling accessories available to allow examination of microgram or microliter amounts. This is accomplished using a beam condenser so that as much as possible of the beam passes through the sample. Microcells are available with volumes of ∼4 μl and path lengths up to 1 mm. A diamond anvil cell (DAC) uses two diamonds to compress a sample to a thickness suitable for measurement and increase the surface area. This technique can be used at normal atmospheric pressures, but it may also be applied to study samples under high pressures and improve the quality of the spectrum of trace samples. Alternatively, a multiple internal reflectance cell may also be used as this technique can produce stronger spectra.

Infrared imaging using ftir microspectroscopic techniques has emerged as an effective approach to studying complex or heterogeneous specimens (8). The technique can be used to produce a two- or three-dimensional (2D or 3D) picture of the properties of a sample. This is possible because, instead of reading the signal of only one detector as in conventional ftir spectroscopy, a large number of detector elements are read during the acquisition of spectra. This is possible due to the development of focal plane array (FPA) detectors. Currently, a step-scanning approach is commonly used, which means that the moving mirror does not move continuously during data acquisition, but waits for each detector readout to be completed before moving onto the next position. This allows thousands of interferograms to be collected simultaneously and then transformed into ir spectra. The ir beam from a Michelson interferometer is focused onto a sample with a reflective Cassegrain condenser. The light transmitted is collected by a Cassegrain objective and focused onto a FPA detector. The data are collected as interferograms with each pixel on the array having a response determined by its corresponding location on the sample. Each point of the interferogram represents a particular moving mirror position and the spectral data is obtained by performing an ft for each pixel on the array. Thus, each pixel (or spatial location) is represented by an ir spectrum.

3.4. Chromatography–Infrared Spectroscopy. Infrared spectroscopy may be combined with each of a number of possible chromatographic techniques, with gas chromatography–infrared (gcir) spectroscopy the most widely used (9,10). Gas Chromatography–infrared allows for the identification of the components eluting from a gas chromatograph. In gc, the sample in a gaseous mobile phase is passed through a column containing a liquid or solid stationary phase. The retention of the sample depends on the degree of interaction with the stationary phase and its volatility: The higher the affinity of the sample for the stationary phase, the more the sample partitions into that phase and the longer it takes before it passes through the chromatograph. The sample is introduced into the column housed in an oven via injection at one end and a detector monitors the effluent at the other end. A common method for coupling a gas chromatograph to an ftir spectrometer is to use a light pipe: a heated flow cell that allows the continuous scanning of the effluent emerging for the gc column.

The nature of this technique requires that interferograms are collected in short time intervals. Data can be displayed in real time and is commonly monitored as the changing spectrum of the gc effluent and the changing ir absorption as a function of time. The latter is called a Gram–Schmidt chromatogram.

Liquid chromatography (lc) may also be used in conjunction with ir spectroscopy (11). The effluent from a liquid chromatograph may be passed through a liquid flow-through cell. Supercritical fluid chromatography (sfc), where supercritical CO_2 is commonly used as a mobile phase, is used with ftir to improve detection limits.

3.5. Thermal Analysis-Infrared Spectroscopy.

Infrared spectrometers may also be combined with thermal analysis instrumentation. Thermal analysis methods provide information about the temperature-dependent physical properties of materials. However, it is not always possible to gain information about the chemical changes associated with changes in temperature using standard thermal analysis equipment. It is possible to combine thermal analysis apparatus with an ir spectrometer in order to obtain a complete picture of the chemical and physical changes occurring in thermal processes (12,13).

The most common approach is to combine a ftir spectrometer with a thermal method such as thermogravimetric analysis (tga) to obtain an evolved gas analysis (ega). An evolved gas analyses involves the measurement and characterization of the gaseous products that evolve from a sample when it is heated. A sample is placed in a furnace while being suspended from a sensitive balance. The change in sample mass is recorded while the sample is maintained either at a required temperature or while being subjected to a programmed heating sequence. A tga curve may be plotted as sample mass loss as a function of temperature or in a differential form where the change in sample mass with time is plotted as a function of temperature. The evolved gases can be carried from the furnace to the spectrometer where that can be examined in a long path length gas cell. Data may be illustrated as a function of time using a Gram–Schmidt plot.

3.6. Emission Spectroscopy.

In emission spectrometry, the sample is the ir source. Materials emit ir radiation by virtue of their temperature. Kirchhoff's law states that the amount of ir radiation emitted and absorbed by a body in thermal equilibrium must be equal at each wavelength. A blackbody must therefore produce a smooth emission spectrum that has the maximum possible emission intensity of any body at the same temperature. The emissivity, ε, of a sample is the ratio of its emission to that of a blackbody at the same temperature. Any sample dilute or thin enough for transmission spectroscopy produces a structured emission spectrum that is analogous to its transmission spectrum because the emissivity is proportional to the absorptivity at each wavelength. Emission spectroscopy is principally used for remote samples, thin coatings on metal substrates, or hot gases (1).

3.7. Other Techniques. Variable temperature cells, which are controlled to 0.1°C in the range −180 to 250°C, may be used in ir spectrometers. An electrical heating system is used for temperatures above ambient, and liquid nitrogen with a heater for low temperatures. These cells can be used to study phase transitions and the kinetics of reactions. As well as transmission temperature cells, variable temperature atr cells and temperature cells for microsampling are available.

Optical fibers may be used in conjunction with ir spectrometers to carry out remote measurements. The fibers transfer the signal to and from a sensing probe and are made of materials that are flexible and ir transparent.

For some samples, dipole moment changes may be in a fixed direction during a molecular vibration and, as such, can only be induced when the ir radiation is polarized in that direction. Polarized ir radiation can be produced by using a polarizer consisting of a fine grating of parallel metal wires. This approach is known a linear ir dichroism (14).

4. Spectral Analysis

4.1. Group Frequencies. The ir spectrum can be divided into three main regions: the far-ir (<400 cm^{-1}), the mid-ir (4000–400 cm^{-1}), and the near-ir (13,000–4,000 cm^{-1}). Many ir applications employ the mid-ir region, but the near- and far-ir also provide important information about certain materials. The mid-ir spectrum (4000–400 cm^{-1}) can be approximately divided into four regions and the nature of a group frequency may generally be determined by the region in which it is located. The regions are generalized as: the X−H stretching region (4000–2500 cm^{-1}), the triple-bond region (2500–2000 cm^{-1}), the double-bond region (2000–1500 cm^{-1}), and the fingerprint region (1500–600 cm^{-1}).

The fundamental vibrations in the region 4000–2500 cm^{-1} are generally due to O−H, C−H, and N−H stretching. The O−H stretching produces a broad band that occurs in the range 3700–3600 cm^{-1}. By comparison, N−H stretching is usually observed between 3400 and 3300 cm^{-1}. This absorption is generally much sharper than O−H stretching and may, therefore, be differentiated. The C−H stretching bands from aliphatic compounds occur in the range 3000–2850 cm^{-1}. If the C−H bond is adjacent to a double bond or aromatic ring, the C−H stretching wavenumber increases and absorbs between 3100 and 3000 cm^{-1}.

Triple-bond stretching absorptions fall in the 2500–2000-cm^{-1} region because of the high force constants of the bonds. The C≡C bonds absorb between 2300 and 2050 cm^{-1}, while the nitrile group (C≡N) occurs between 2300 and 2200 cm^{-1}. These groups may be distinguished since C≡C stretching is normally very weak, while C≡N stretching is of medium intensity. These are the most common absorptions in this region, but it is possible to come across some X−H stretching absorptions, where X is a more massive atom like phosphorus or silicon. These absorptions usually occur near 2400 and 2200 cm^{-1}, respectively.

The principal bands in the 2000–1500-cm^{-1} region are due to C=C and C=O stretching. Carbonyl stretching is one of the easiest absorptions to recognize in an ir spectrum. It is usually the most intense band in the spectrum, and depending on the type of C=O bond, occurs in the region 1830–1650 cm^{-1}. Note also that metal carbonyls may absorb above 2000 cm^{-1}. Carbon–carbon double-bond stretching is much weaker and occurs at ~1650- cm^{-1}, but this band is often absent for symmetry or dipole moment reasons. The C=N stretching also occurs in this region and is usually stronger.

So far, it has been assumed that each band in an ir spectrum can be assigned to a particular deformation of the molecule, the movement of a group of atoms or the bending or stretching of a particular bond. This is possible for many bands, particularly stretching vibrations of multiple bonds that are well behaved. However, many vibrations are not so well behaved and may vary by hundreds of wavenumbers even for similar molecules. This applies to most bending and skeletal vibrations, which absorb in the 1500–650-cm^{-1} region, for which small steric or electronic effects in the molecule lead to large shifts. A spectrum of a molecule may have a hundred or more absorption bands present, but there is no need to assign the vast majority. The spectrum can be regarded as a "fingerprint" of the molecule and so this region is referred to as the fingerprint region.

The absorptions observed in the near-ir region (13,000–4,000 cm^{-1}) are overtones or combinations of the fundamental stretching bands that occur in the region 3000–1700 cm^{-1} (15). The bands involved are usually due to C–H, N–H, or O–H stretching. The resulting bands in the near-ir are usually weak in intensity and the intensity generally decreases by a factor of 10 from one overtone to the next. The bands in the near-ir are often overlapped, making them less useful than the mid-ir region for qualitative analysis. However, there are important differences between the near-ir positions of different functional groups and these differences can often be exploited for quantitative analysis.

The far-ir region is defined as the region 400–100 cm^{-1} (16). This region is more limited than the mid-ir for spectra–structure correlations, but does provide information regarding the vibrations of molecules containing heavy atoms, molecular skeleton vibrations, molecular torsions, and crystal lattice vibrations. Intramolecular stretching modes involving heavy atoms can be helpful for characterizing compounds containing halogen atoms, organometallic compounds, and inorganic compounds. Skeletal bending modes involving an entire molecule occur in the far-ir for molecules containing heavier atoms because bending modes are usually no more than one-half the wavenumber of the corresponding stretching mode. Torsional modes arise because the rotation about single bonds is not free. As a result, when certain small groups are bonded to a large group, they undergo a motion with respect to the heavier "anchor" group. Crystal lattice vibrations are associated with the movement of whole molecular chains with respect to each other in crystalline solids.

4.2. Spectrum Manipulation. There are a number of techniques available to users of ir spectrometers that help with both the qualitative and the quantitative interpretation of spectra. It is usual in quantitative ir spectroscopy to use a baseline joining the points of lowest absorbance on a peak, preferably in reproducibly flat parts of the absorption line. The absorbance difference between the baseline and the top of the band is then used.

Noise in a spectrum can be diminished by a smoothing process. After a spectrum is smoothed, it becomes similar to the result of an experiment at a lower resolution. The features are blended into each other and the noise level decreases. A smoothing function is basically a convolution between the spectrum and a vector whose points are determined by the degree of smoothing applied. Generally, a degradation factor is required, which will be some positive integer. A low value, say 1, will produce only subtle changes, while a high value has a more pronounced effect on the spectrum.

The most straightforward method of analysis for complex spectra is difference spectroscopy. Difference spectroscopy may be carried out simply by subtracting the ir spectrum of one component of the system from the combined spectrum to leave the spectrum of the other component. If the interaction between components results in a change in the spectral properties of either one or both of the components, the changes will be observed in the difference spectra. The changes may manifest themselves via the appearance of positive or negative peaks in the spectrum.

Spectra may also be differentiated. The benefits of derivative techniques are twofold. Resolution is enhanced in the first derivative since changes in the gradient are examined. The second derivative gives a negative peak for each band and shoulder in the absorption spectrum. With ftir spectrometers it is possible to apply what is known as Fourier derivation. During this process the spectrum is first transformed into an interferogram. It is then multiplied by an appropriate weighting function and finally it is retransformed to give the derivative. This technique provides more sensitivity than conventional derivatization.

Deconvolution is the process of compensating for the intrinsic linewidths of bands in order to resolve overlapping bands (17). The technique yields spectra that have much narrower bands and is able to distinguish closely spaced features. The instrumental resolution is not increased, but the ability to differentiate spectral features can be significantly improved. The deconvolution technique generally involves several steps: computation of an interferogram of the sample by computing the inverse ft of the spectrum; multiplication of the interferogram by a smoothing function, and by a function consisting of a Gaussian–Lorentzian bandshape; and Fourier transformation of the modified interferogram. The deconvolution procedure is typically repeated iteratively for best results. At iteration, the lineshape is adjusted in an attempt to provide narrower bands without excessive distortion.

Quantitative values for band areas of heavily overlapped bands can be achieved by using curve-fitting procedures. Many curve-fitting procedures are based on a least-squares minimization procedure. Least-squares curve fitting covers the general class of techniques whereby one attempts to minimize the sum of the squares of the difference between an experimental spectrum and a computed spectrum generated by summing the component curves. Generally, the procedure involves entering the values of the wavenumbers of the component bands (determined using derivatives and/or deconvolution) and then the programme determines the best estimate of the parameters of the component curves. Apart from the obvious variables of peak height and width, the type of band shape needs to be considered. The class of band shape of an ir spectrum depends on the type of sample. A choice of Gaussian, Lorentzian, or a combination of these band shapes is usually applied.

4.3. Quantitative Analysis. The Beer–Lambert law is used to relate the amount of light transmitted by a sample to the thickness of the sample. The absorbance of a solution is directly proportional to the thickness and the concentration of the sample:

$$A = \epsilon cl \tag{7}$$

where A is the absorbance of the solution, c is the concentration, and l the path length of the sample. The constant of proportionality is usually given the symbol epsilon, ε, and is referred to as molar absorptivity. The absorbance is equal to the difference between the logarithms of the intensity of the light entering the sample (I_0) and the intensity of the light transmitted (I) by the sample:

$$A = \log_{10}\ (I_0/I) \tag{8}$$

Absorbance is therefore dimensionless. Transmittance is defined as

$$T = I/I_0 \tag{9}$$

The Beer–Lambert law tells us that a plot of absorbance against concentration should be linear with a gradient of εl and pass through the origin. In theory, to analyze a solution of unknown concentration, solutions of known concentration need to be prepared, a suitable band chosen, the absorbance at this wavenumber measured, and a calibration graph plotted. The concentration of the compound in solution can be read from the calibration graph, given its absorbance is known.

There are a few factors that need to be considered first when taking this approach. First, the preparation of solutions of known concentration: the concentrations have to give sensible absorbance values—not too weak and not too intense. There is also the choice of a suitable absorption peak: This technique needs to be as sensitive as possible so an intense peak should be chosen. However, often ir spectra have many, sometimes overlapping peaks. A peak isolated from others, with a high molar absorptivity should be found if possible. A further problem that sometimes arises, especially in the spectra of solid samples, is the presence of asymmetric bands. In these cases, peak height cannot be used because the baseline will vary from sample to sample and peak area measurements must be used instead. The ftir spectrometers have accompanying software that can carry out these calculations. Quantitative measurements need to be carried out on absorbance spectra. Thus, transmittance spectra need to be converted to absorbance spectra.

The determination of the concentration of a gas needs to be considered separately from solids and liquids (18). The ideal gas law relates the physical properties of a gas to its concentration. The ideal gas law states that:

$$PV = nRT \tag{10}$$

where P is the pressure, V is the volume, n is the number of moles, R is the universal gas constant, and T is the temperature. Given that the concentration of a gas in an ir cell is given by $c = n/V$, equation 10 may be rewritten as

$$A = P\epsilon l/RT \tag{11}$$

Thus, for gases the absorbance also depends on the pressure and the temperature of the gas.

Infrared spectroscopy can be used to measure the number of functional groups in a molecule, eg, the number of $-OH$ or $-NH_2$ groups. It has been found that the molar absorptivity of the bands corresponding to the group is proportional to the number of groups that are present, ie, each group has its own intensity that does not vary drastically from molecule to molecule. This approach has been used to measure chain length in hydrocarbons by using the C−H deformation, the methylene group at 1467 and 1305 cm^{-1}, and the number of methyl groups in polyethylene.

Simple solid mixtures may also be quantitatively analyzed. They are more susceptible to errors because of scattering of radiation. These analyses are usually carried out with KBr disks or in mulls. The problem here is the difficulty in measuring the path length. However, this measurement becomes unnecessary when an internal standard is used. Addition of a constant known amount of an internal standard is made to all samples and calibration standards. The calibration curve is obtained by plotting the ratio of the absorbance of the analyte to that of the internal standard against the concentration of the analyte. The absorbance of the internal standard varies linearly with the sample thickness and thus compensates for this parameter. The disks or mulls must be made under exactly the same conditions to avoid intensity changes or shifts in band positions. The standard must be carefully chosen and it should ideally: have a simple spectrum with very few bands; be stable to heat and not absorb moisture; be easily reduced to a particle size less than the incident radiation without lattice deformation; nontoxic, giving clear disks in a short time; and be readily available in the pure state. Some common standards used include calcium carbonate, sodium azide, naphthalene, and lead thiocyanate.

The improvement in computer technology associated with spectroscopy has led to the expansion of quantitative ir spectroscopy (18–22). The most commonly used statistical methods in ir spectroscopy are classical least squares (cls); inverse least squares (ils); partial least squares (pls); and principal component regression (pcr). The cls (also known as K-matrix methods) and pls (also known as P-matrix methods) are least-squares methods involving matrix operations. These methods can be limited when very complex mixtures are investigated and factor analysis methods such as pls and pcr can be more useful. The factor analysis methods use functions to model the variance in a data set.

If it is not necessary to know the specific concentration of the species of interest, but to simply know whether the species is present or not in a complex sample, then a multivariate pattern recognition method, such as linear discriminant analysis (lda) or artificial neural networks (anns), may be used to identify the spectral characteristics of the species of interest (23). Such methods are capable of comparing of large number of variables within a data set, such as intensity, frequency, and bandwidth. Both lda and anns are known as supervised methods because a priori information is available about the data set. There are also unsupervised methods, such as hierarchical clustering, which may be used to determine the components in a data set without any prior information about the data.

5. Applications

One of the most common applications of ir spectroscopy is to the identification of organic compounds. There are a number of useful collections of spectral information regarding organic molecules that may be used for reference (2,3,24–29). Generally, the ir bands for inorganic materials are broader, fewer in number, and appear at lower wavenumbers than those for organic materials. The bands in the spectra of ionic or coordination compounds will depend on the structure and orientation of the ion or complex. The ir spectra of metal complexes and minerals have also been widely reported. There is a number of specialist books on the subject (30–36).

Infrared spectroscopy is a popular method for characterizing polymers (2,37–42). This spectroscopy may be used to identify the composition of polymers, to monitor polymerization processes, to characterize polymer structure, to examine polymer surfaces, and to investigate polymer degradation processes.

Infrared spectroscopy has proved to be a powerful tool for the study of biological molecules and the application of this technique to biological problems is continually expanding, particularly with the advent of increasingly sophisticated sampling techniques such as ir imaging. Biological systems, including lipids, proteins, peptides, biomembranes, nucleic acids, animal tissue, microbial cells, plants, and clinical samples, have all been successfully studied using ir spectroscopy (2,43–53). Infrared spectroscopy has been employed for a number of decades for the characterization of isolated biological molecules, particularly proteins and lipids. However, the last decade has seen a rapid rise in the number of studies of more complex systems, such as diseased tissues. Microscopic techniques combined with sophisticated analytical methods allow for complex samples of micron size to be investigated.

This technique also finds use in a wide range of industrial applications. Infrared spectroscopy has been extensively used in both qualitative and quantitative pharmaceutical analysis (2,54–56). The technique is important for the evaluation of the raw materials used in production, the active ingredients, and the excipients. Both mid- and near-ir techniques may be used to obtain qualitative and quantitative information about food samples (57–62). Commercial grains are commonly analyzed using nir spectroscopy (61,63). Infrared spectroscopy also plays an important role in quality control in the pulp and paper industry (64,65) and is used in the paint industry for quality control, product improvement and failure analysis, and for forensic identification purposes (66–70). In addition, the technique has been applied to a broad range of environmental sampling problems, including air, water, and soil analysis (71). The development of remote sensing ir techniques has been particularly useful in this field and simple practical ir techniques have been developed for measuring trace gases and atmospheric composition (71–75).

BIBLIOGRAPHY

"Infrared Technology" in *ECT* 3rd ed., Vol. 13, pp. 337–355, by C. Warren, AGA Infrared Systems AB; in *ECT* 4th ed., Vol. 14, pp. 379–416, by Roger W. Jones, Ames Laboratory, USDOE; "Infrared Technology" in *ECT* (online), posting date: December 4, 2000, by Roger W. Jones, Ames Laboratory, USDOE.

CITED PUBLICATIONS

1. P. R. Griffiths and J. A. de Haseth, *Fourier Transform Infrared Spectrometry*, John Wiley & Sons, Inc., New York, 1986.
2. B. Stuart, *Infrared Spectroscopy: Fundamentals and Applications*, John Wiley & Sons, Inc., Chichester, 2004.
3. H. Günzler and H. U. Gremlick, *IR Spectroscopy: An Introduction*, Wiley-VCH, Weinheim, 2002.
4. A. J. Sommer, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons Inc., New York, 2002, p. 1369.
5. J. E. Katon, *Micron* **27**, 303 (1996).
6. H. J. Humecki, eds., *Practical Guide to Infrared Microspectroscopy*, Marcel-Dekker, New York, 1999.
7. R. G. Messerschmidt and M. A. Harthcock, eds., *Infrared Microspectroscopy: Theory and Applications*, Marcel-Dekker, New York, 1998.
8. L. H. Kidder, A. S. Haka, and E. N. Lewis, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons Inc., New York, Vol. 2, 2002, p. 1386.
9. T. Visser, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons Inc., New York, Vol. 2, 2002, p. 1605.
10. N. Ragunathan, K. A. Krock, C. Klawun, T. A. Sasaki, and C. L. Wilkins, *J. Chromatogr. A* **856**, 349 (1999).
11. G. W. Somsen, C. Gooijer, N. H. Velthorst, and U. A. T. Brinkman, *J. Chromatogr. A* **811**, 1 (1998).
12. J. W. Hellgeth, in J. M. Chalmers, and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons Inc., New York, Vol. 2, 2002, p. 1699.
13. P. J. Haines, *Thermal Methods of Analysis: Principles, Applications and Problems*, Chapman and Hall, London, 1995.
14. T. Buffeteau and M. Pezolet, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Inc., New York, Vol. 1, 2002, p. 693.
15. L. G. Weyer and S. C. Lo, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Inc., New York Vol. 3, 2002, p. 1817.
16. P. R. Griffiths, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Inc., New York, Vol. 1, 2002, p. 229.
17. J. K. Kauppinen, D. J. Moffatt, H. H. Mantsch, and D. G. Cameron, *Appl. Spectrosc.* **35**, 271 (1981).

18. B. C. Smith, *Quantitative Spectroscopy: Theory and Practice*, Elsevier, Amsterdam, The Netherlands, 2002.
19. H. Mark, *Principles and Practice of Spectroscopic Calibration*, John Wiley & Sons, Inc., New York, 1996.
20. T. Hasegawa, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons Inc., New York, Vol. 3, 2002, p. 2293.
21. S. D. Brown and R. A. Meyers, eds., *Encyclopedia of Analytical Chemistry*, John Wiley & Sons, Inc., Chichester, Vol. 11, 2000, p. 9669.
22. J. E. Franke, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Inc., New York, Vol. 3, 2002, p. 2276.
23. H. Yang, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Inc., New York, Vol. 3, 2002, p. 2094.
24. R. M. Silverstein and F. X. Webster, *Spectrometric Identification of Organic Compounds*, 6th ed., John Wiley & Sons, Inc., New York, 1997.
25. D. Linvien, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, Boston, 1991.
26. H. F. Shurvell, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Inc., New York, Vol. 3, 2002, p. 1783.
27. J. Coates and R. A. Meyers, eds., *Encyclopedia of Analytical Chemistry*, John Wiley & Sons, Inc., Chichester, Vol. 12, 2000, p. 10815.
28. L. G. Weyer and S. C. Lo, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Inc., New York, Vol. 3, 2002, p. 1817.
29. C. E. Miller, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Inc., New York, Vol. 1, 2002, p. 196.
30. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part A, Theory and Applications in Inorganic Chemistry*, John Wiley & Sons, Inc., New York, 1997.
31. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B, Applications in Coordination, Organometallic and Bioinorganic Chemistry*, John Wiley & Sons, Inc., New York, 1997.
32. R. A. Nyquist, C. L. Putzig, and M. A. Leugers, *Handbook of Infrared and Raman Spectra of Inorganic Compounds and Organic Salts*, Academic Press, San Diego, 1997.
33. R. J. H. Clark and R. E. Hester, eds., *Spectroscopy of Inorganic Based Materials*, John Wiley & Sons, Inc., New York, 1987.
34. S. D. Ross, *Inorganic Vibrational Spectroscopy*, Marcel-Dekker, New York, 1971.
35. N. N. Greenwood, *Index of Vibrational Spectra of Inorganic and Organometallic Compounds*, Butterworths, London, 1972.
36. A. K. Brisdon, *Inorganic Spectroscopic Methods*, Oxford University Press, Oxford, 1998.
37. D. I. Bower and W. F. Maddams, *The Vibrational Spectroscopy of Polymers*, Cambridge University Press, Cambridge, 1989.
38. H. W. Siesler and K. Holland-Moritz, *Infrared and Raman Spectroscopy of Polymers*, Marcel-Dekker, New York, 1980.
39. J. M. Chalmers and R. A. Meyers, eds., *Encyclopedia of Analytical Chemistry*, John Wiley & Sons, Inc., Chichester, Vol. 9, 2000, p. 7702.
40. J. M. Chalmers, R. W. Hannah, and D. W. Mayo, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Inc., New York, Vol. 3, 2002, 1893.
41. F. J. Boerio, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Inc., New York, Vol. 4, 2002, p. 2419.

42. J. L. Koenig, *Spectroscopy of Polymers*, 2nd ed., Elsevier, Amsterdam, The Netherlands, 1999.
43. R. J. H. Clark and R. E. Hester, *Biomedical Applications of Spectroscopy*, John Wiley & Sons, Inc., Chichester, 1996.
44. H. U. Gremlich and B. Yan, *Infrared and Raman Spectroscopy of Biological Materials*, Marcel-Dekker, New York, 2000.
45. M. Jackson, D. J. Moore, H. H. Mantsch, and R. Mendelsohn, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Inc., New York, Vol. 5, 2002, p. 3508.
46. V. F. Kalasinsky, *Appl. Spectrosc. Rev.* **31**, 193 (1996).
47. H. H. Mantsch and D. Chapman, eds., *Infrared Spectroscopy of Biomolecules*, John Wiley & Sons, Inc., New York, 1996.
48. D. Naumann, *Appl. Spectrosc. Rev.* **36**, 239 (2001).
49. W. Petrich, *Appl. Spectrosc. Rev.* **36**, 181 (2001).
50. R. A. Shaw and H. H. Mantsch, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Inc., New York, Vol. 1, 2002, p. 3295.
51. R. A. Shaw and H. H. Mantsch, in R. A. Meyers, eds., *Encyclopedia of Analytical Chemistry*, John Wiley & Sons, Inc., Chichester, Vol. 1, 2000, p. 83.
52. B. H. Stuart, *Biological Applications of Infrared Spectroscopy*, John Wiley & Sons, Inc., Chichester, 1997.
53. B. H. Stuart and R. A. Meyers, eds., *Encyclopedia of Analytical Chemistry*, John Wiley & Sons, Inc., Chichester, Vol. 1, 2000, p. 529.
54. D. Clark, in J. M. Chalmers and P. R. Griffiths, eds., in *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Inc., New York, Vol. 5, 2002, p. 3574.
55. D. E. Bugay, *Adv. Drug Deliv. Rev.* **48**, 43 (2001).
56. D. S. Aldrich and M. A. Smith, *Appl. Spectrosc. Rev.* **34**, 275 (1999).
57. E. C. Y. Li-Chen, A. A. Ismail, J. Sedman, and F. R. van de Voort, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Inc., New York, Vol. 5, 2002, p. 3629.
58. S. K. Anderson, P. W. Hansen, and H. V. Anderson, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Inc., New York, Vol. 5, 2002, p. 3672.
59. M. Meurens and S. H. Yan, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Inc., New York, Vol. 5, 2002, p. 3663.
60. W. F. McClure and D. L. Stanfield, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Inc., New York, Vol. 1, 2002, p. 212.
61. B. G. Osborne and T. Fearn, *Near-infrared Spectroscopy in Food Analysis*, John Wiley & Sons, Inc., New York, 1988.
62. G. T. Reedy and M. M. Mossaka, in M. M. Mossaka, eds., *Spectral Methods in Food Analysis*, Marcel-Dekker, New York, 325, 199.
63. P. Williams, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Inc., New York, Vol. 5, 2002, p. 3693.
64. D. F. Leclerc and T. P. Trung, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Inc., New York, Vol. 4, 2002, p. 2952.
65. D. F. Leclerc, and R. A. Meyers, eds., *Encyclopedia of Analytical Chemistry*, John Wiley & Sons, Inc., Chichester, Vol. 10, 2000, p. 8361.
66. E. G. Bartick, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Inc., New York, Vol. 4, 2002, p. 2993.
67. C. Carr, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Inc., New York, Vol. 4, 2002, p. 2935.

68. K. Adamsons, *Prog. in Polymer Sci.* **25**, 1363 (2000).
69. M. W. Urban and R. A. Meyers, eds., *Encyclopedia of Analytical Chemistry*, John Wiley & Sons, Inc., Chichester, Vol. 3, 1756 (2000).
70. S. G. Ryland, in H. J. Humecki, eds., *Practical Guide to Infrared Microspectroscopy*, Marcel-Dekker, New York, 1995, p. 163.
71. T. Visser, R. A. Meyers, eds., *Encyclopedia of Analytical Chemistry*, John Wiley & Sons, Inc., Chichester, Vol. 1, 2000, 1.
72. D. W. T. Griffith, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Inc., New York, Vol. 4, 2002, p. 2823.
73. D. W. T. Griffith and I. M. Jamie, in R. A. Meyers, eds., *Encyclopedia of Analytical Chemistry*, John Wiley & Sons, Inc., Chichester, Vol. 3, 2000, p. 1979.
74. R. J. Yokelson and I. T. Bertschi, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Inc., New York, Vol. 4, 2002, p. 2879.
75. K. Kawaguchi, in J. M. Chalmers and P. R. Griffiths, eds., *Handbook of Vibrational Spectroscopy*, John Wiley & Sons, Inc., New York, Vol. 4, 2002, p. 2803.

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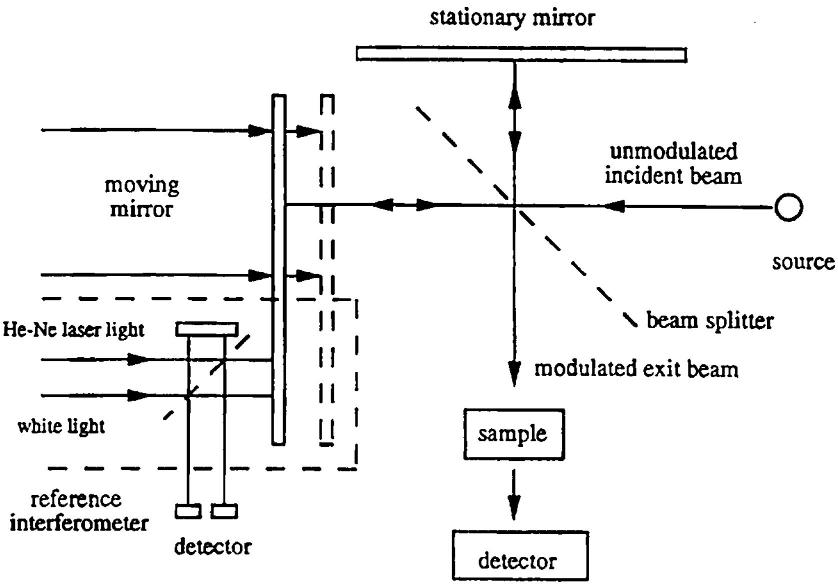

Fig. 1. Michelson interferometer.

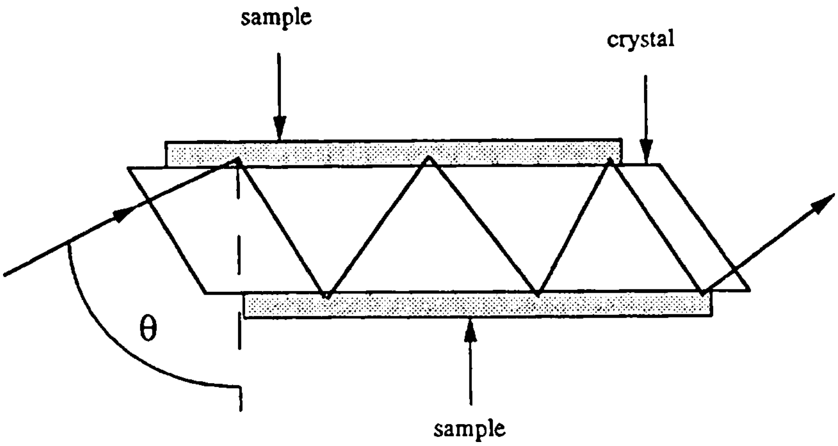

Fig. 2. Attenuated total reflectance cell.