

Chapter 2

FTIR Spectroscopy History, Theory, and Terminology

This chapter introduces the history, theory and terminology of modern Fourier transform infrared spectroscopy. At the same time, many of the basic design features of the Mattson Instruments Galaxy FTIR spectrometer are detailed.

Today, infrared spectroscopy is one of the most powerful techniques available to organic and analytical chemists. It serves both research applications and the more routine studies conducted in applications and process control laboratories. Furthermore, infrared analysis is applicable to both qualitative and quantitative analyses.

2.1 History

A. A. Michelson invented the interferometer in the 1890s to study the speed of light. As with many technological discoveries, the full range of commercial applications open to the interferometer was not readily apparent, and not surprisingly so. The Michelson interferometer was destined to revolutionize spectroscopy, but in the 1880s chemical infrared spectroscopy was just awakening as a science. Even by the 1940s, chemical infrared spectroscopy remained a young, immature scientific field. Only in the late 1940s, after commercial development of the optical null dispersive spectrophotometer, did chemical infrared spectroscopy come into widespread use. Dispersive instruments proved the value of chemical infrared analysis, and soon became the mainstay of the organic characterization laboratory.

In 1949 that Peter Fellgett, an astrophysicist, used an interferometer to measure light from celestial bodies, producing the first Fourier transform infrared spectrum. But for many years, Fourier transform infrared (FTIR) spectroscopy remained the domain of only a few advanced research groups, where large, expensive computers were available and personnel were able to tolerate the delays of up to 12 hours required to transform an interferogram into a spectrum. Not surprisingly, the use of these large, expensive and slow spectrometers was limited to the study of problems that could not be solved with dispersive spectroscopic techniques.

In the late 1960s, when microcomputers capable of performing the Fourier transform became available, the first commercial FTIR spectrometers began to appear. The 1966 development of the Cooley-Tukey algorithm, which could quickly perform a Fourier transform (the Fast Fourier Transform or FFT, also played an instrumental role in the commercialization of the FTIR spectrometer. Now, a computer sat in the laboratory beside the optical unit, controlling the data collection and immediately processing the interferograms into spectra. However, these first FTIR spectrometers were still large and quite expensive, and, thus, were found primarily in well-to-do research laboratories.

As often occurs with expensive but extremely useful equipment, advancing technology has reduced the cost, increased the availability, and enhanced the capabilities of FTIR spectroscopy systems. Indeed, the performance-to-price ratio demanded of FTIR spectrometers today was unthinkable only a decade ago.

2.2 Theory of Operation

An FTIR spectrometer's optical system is very simple: the interferometer requires two mirrors, a infrared light source, an infrared detector and a beamsplitter. See Figure 2-1 below.

The beamsplitter is the heart of the interferometer. Essentially a half-silvered mirror, the beamsplitter reflects about 50 percent of an incident light beam and at the same time transmits the remaining 50 percent. One part of this split light beam travels to a moving interferometer mirror while the other part travels to the interferometer's stationary mirror. The two mirrors reflect both beams back to the beamsplitter where the light rays recombine. At the beamsplitter, half of the recombined light is transmitted to the detector as the other half of the recombined light is reflected toward the infrared source.

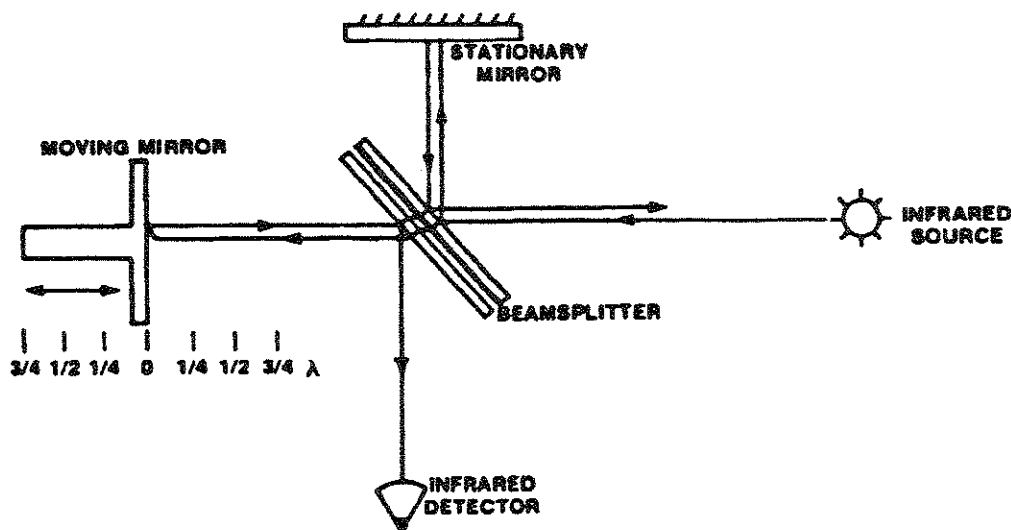


Figure 2-1: Michelson Interferometer Optical System. The beamsplitter reflects about 50 percent of an incident light beam and transmits the remaining 50 percent. One part of this split light beam travels to a moving interferometer mirror while the other part travels to the interferometer's stationary mirror. Both beams are reflected back to the beamsplitter where they recombine. Half of the recombined light is transmitted to the detector and half is reflected to the infrared source.

When the two light beams recombine at the beamsplitter, an interference pattern is generated. This interference pattern varies with the displacement of the moving

mirror along its axis and is detected by the infrared detector as variations in the infrared energy level.

2.2.1 An Example: Monochromatic Light

An example of how light is affected in an interferometer can further illustrate the interferometer's operation. Consider the interference pattern generated when monochromatic light, such as that produced by a helium-neon (HeNe) laser, serves as the light source.

Since an ideal beamsplitter neither generates nor absorbs radiation, the principle of conservation of energy applies. All of the light energy entering the interferometer from the source either returns back to the source or travels on to the infrared detector. As the moving mirror scans back and forth, on the average about half of the light energy returns to the source and about half goes to the detector.

However, depending on the position of the moving mirror at any moment, more or less than 50 percent of the total light energy goes to the detector at any given time. For example, if both interferometer mirrors are equidistant from the beamsplitter, the two light beams travel equal distances, return to the beamsplitter in phase with each other and, thus, recombine constructively. In this case, an ideal beamsplitter reflects all of the light back to the source and sends no light to the detector.

By contrast, if the moving mirror is displaced one-quarter of the wavelength of the HeNe laser radiation, light returning from the interferometer's moving mirror returns to the beamsplitter one-half wavelength out of phase with respect to the light returning from the fixed mirror. This results in complete destructive interference at the beamsplitter. In this idealized situation, no light is reflected back to the source and all light passes on to the detector. As the moving interferometer mirror scans back and forth, light and dark bands that correspond to constructive and destructive interference at the beamsplitter, are observed by the detector.

The signal received by the detector produces an interferogram that is a sine function. This sine wave, illustrated in Figure 2-2, goes from zero intensity, at the point where both mirrors are equidistant from the beamsplitter, to full signal intensity when the moving mirror has traveled one-quarter wavelength.

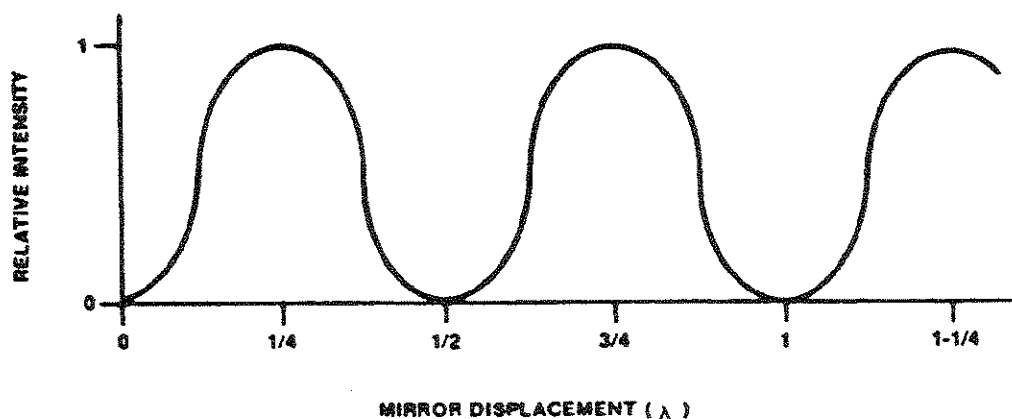


Figure 2-2: Modulated Monochromatic Light. The mirror displacement is measured in fractions of the wavelength of light (λ).

Thus, to go from constructive to destructive interference requires moving the scanning mirror one-quarter wavelength of the incident light. This distance depends on the light's wavelength and, therefore, its frequency.

Infrared sources emit light over a broad range of frequencies, each frequency producing a unique cosine signal. The resulting interferogram represents the sum of each cosine wave generated by each individual frequency component of the input light. The frequency and intensity of each cosine wave in the interferogram is resolved by the Fourier transformation. A computer uses this algorithm to convert the measured-intensity-versus-mirror-displacement signal (the interferogram) into a plot of intensity versus frequency (a spectrum).

2.2.2 Interferometer Advantages

An infrared spectrometer using an interferometer has several advantages over a dispersive spectrophotometer, as described below.

Multiplex Advantage (Fellgett's Advantage)

An interferometer does not separate light into individual frequencies before measurement. Thus, each point in the interferogram contains information from each wavelength present in the input light signal. In other words, if 8,000 data points along

the interferogram are collected, each wavelength in the input light is sampled 8,000 times. By contrast, when a dispersive spectrophotometer is used, measurement of 8,000 individual points across a spectrum samples each wavelength only once.

Throughput Advantage (Jacquinot's Advantage)

The simple optical path of the interferometer (no slits and fewer optical elements) permits more energy to get to the sample than is possible with dispersive spectrophotometers. This means more energy reaches the detector, increasing the potential signal-to-noise ratio of the spectrum. Together the multiplex and throughput advantages allow an FTIR spectrometer to obtain a high-quality infrared spectrum in a fraction of the time needed to get the same spectrum on a dispersive instrument.

Furthermore, to increase the resolution of dispersive instruments, the slits through which light must pass are narrowed, thereby decreasing the instrument's energy throughput. In an FTIR spectrometer, resolution is increased by lengthening the moving mirror stroke length with no resultant decrease in energy throughput. Therefore, as wavelength resolution is increased, the advantage of interferometric measurements over dispersive measurements increases.

Frequency Precision (Conne's Advantage)

With dispersive instruments, frequency precision and accuracy depend on calibration with external standards and on the ability of electromechanical mechanisms to uniformly move gratings and slits during and between scans. By contrast, the interferometer contains its own internal frequency standard, generally a helium-neon laser. Also, both mirror movement and detector sampling of the signal are clocked by the interferometer fringes from this monochromatic light. Furthermore, all frequencies in the output spectrum are calculated from the known frequency of the laser light.

An FTIR spectrometer easily achieves frequency precision and accuracy of better than 0.01 wavenumbers. This means that spectra collected using an FTIR spectrometer can be quantitatively compared whether they were collected five minutes or five years apart.

Constant Spectral Resolution

In an FTIR spectrometer the resolution of the measured spectrum is the same for all frequencies, not varied throughout the spectrum as may be true with dispersive instruments.

2.3 Additional Theory and Terminology

2.3.1 Data Collection

Before the computer can produce a spectrum, an interferogram must be collected. A monochromatic laser, which generates sinusoidal interferometer output, serves as the master clock signal for timing data collection. By counting fringes of the detected laser signal, the displacement (or retardation) of the scanning mirror may be accurately measured. Mattson Instruments uses a somewhat more sophisticated method of sensing the position and velocity of the moving mirror, a method we call laser quadrature. The HeNe laser is still used as described above, but a quarter-wave delay plate and polarizer is placed in the returning beam of the interferometer's fixed arm, as illustrated in Figure 2-3.

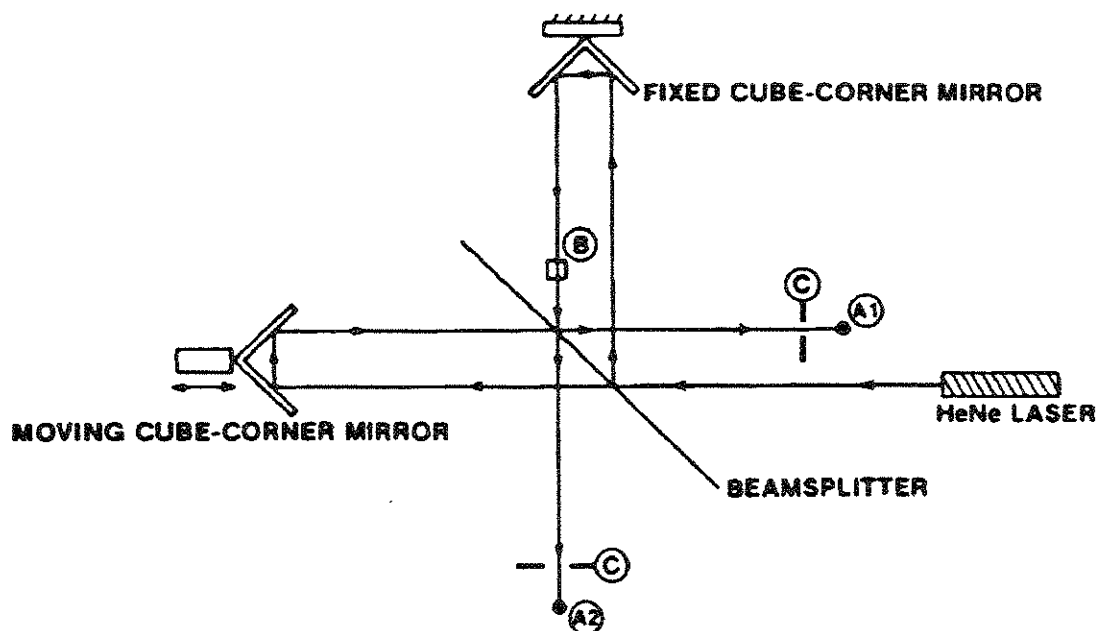


Figure 2-3: HeNe Laser Light Path In The Mattson Instruments Interferometer. A1 and A2 represent laser photodiodes, B represents the mica quarter-wave delay plate and polarizer, and C, in two locations, represents the two polarizing filters.

Together, the delay plate and polarizer generate a beam composed of two frequencies at right angles and 90 degrees out of phase with each other, as illustrated in Figure

2-4. This beam, which exhibits laser quadrature, recombines with the beam from the moving mirror at the beamsplitter. Half of the light is transmitted through the beamsplitter and half is reflected. This allows two separate photodiodes, also illustrated in Figure 2-4, to detect laser fringes. In front of each photodiode is a polarizing filter that allows each laser fringe detector to be tuned to one component of the laser quadrature beam. Figure 2-5 shows the output of the two photodiode detectors. Note that the waveform from one detector appears to lead the waveform from the other detector. These signals indicate how far the mirror has traveled and also in which direction the mirror is traveling.

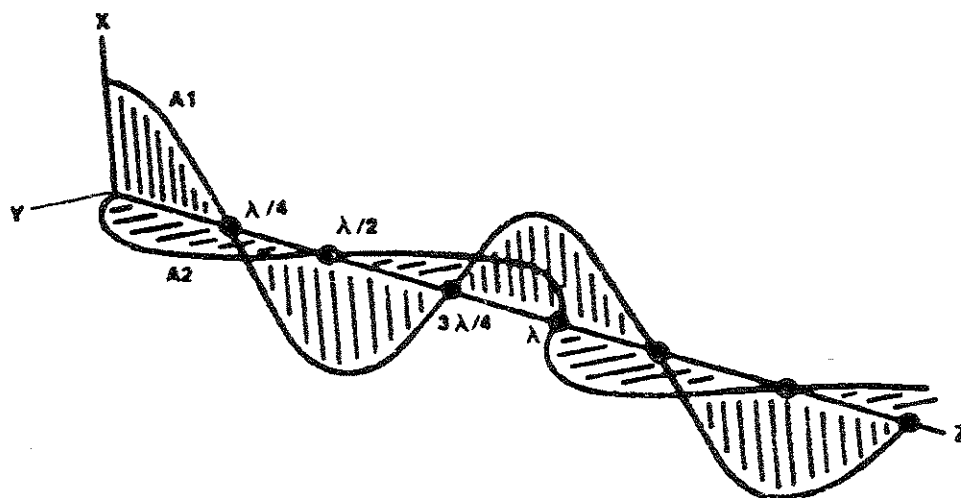


Figure 2-4: Three-Dimensional Laser Quadrature Representation.

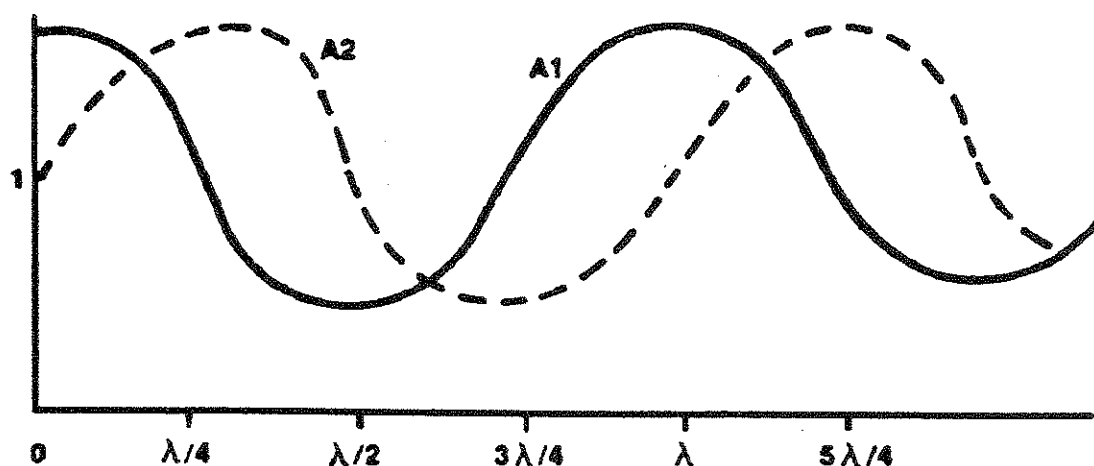


Figure 2-5: Two-Dimensional Laser Quadrature Representation.

The computer also uses these HeNe laser fringes to trigger the analog-to-digital converter at precisely spaced intervals. At selected zero crossings of the laser fringe, the computer triggers a sample-and-hold circuit which momentarily holds the analog signal level while a second circuit, the analog-to-digital converter, or ADC, measures the magnitude of the signal and produces a digital number that represents the precise intensity of the signal. This method converts the analog interferogram signal into a digital representation that the computer can process.

The Advantages of Laser Quadrature

The laser quadrature detector used by Mattson Instruments provides several advantages over the more conventional signal-channel laser system. First, because the direction of mirror motion is detected, the interferometer can collect data in both directions of mirror travel. The two resulting interferograms, one from each direction of mirror travel, must be processed separately due to phase shifts inherent in the signal paths. (See the discussion of phase correction provided below.) Also, bidirectional data collection substantially reduces data collection time when large numbers of scans are averaged. Another advantage is enhanced ability to measure transient phenomena with very rapid scanning, as with gas chromatography FTIR or kinetics measurements.

Collecting Double- and Single-Sided Interferograms

An FTIR spectrometer can collect either double-sided or single-sided interferograms. This means both low resolution measurements, with their improved signal-to-noise ratios, and high resolution measurements can readily be accommodated by the instrument.

Every point on an interferogram contains information about all frequencies present in the spectrum. Because this frequency information is dependent on the distance the mirror has moved away from the interferogram centerburst, or zero path difference point (ZPD), sampling on either side of the centerburst provides the same frequency information.

At lower resolutions, collecting equal amounts of data before and after the centerburst—a double-sided data collection—samples each frequency element twice and, thus, yields an superior signal-to-noise ratio. The signal-to-noise ratio of a double-sided data collection is equal to the square root of two over a single-sided data collection. Also, less time is required to collect one double-sided interferogram than is required to collect two single-sided interferograms.

High optical resolution measurements require large optical retardation, that is, greater mirror travel. But mechanical restrictions allow only a relatively small portion of the interferogram to be sampled before the interferogram centerburst. To circumvent this limitation, a single-sided interferogram can be collected to achieve the desired resolution. Figure 2-6a shows a double-sided interferogram. Figure 2-6b shows a single-sided, or *chirped* interferogram.

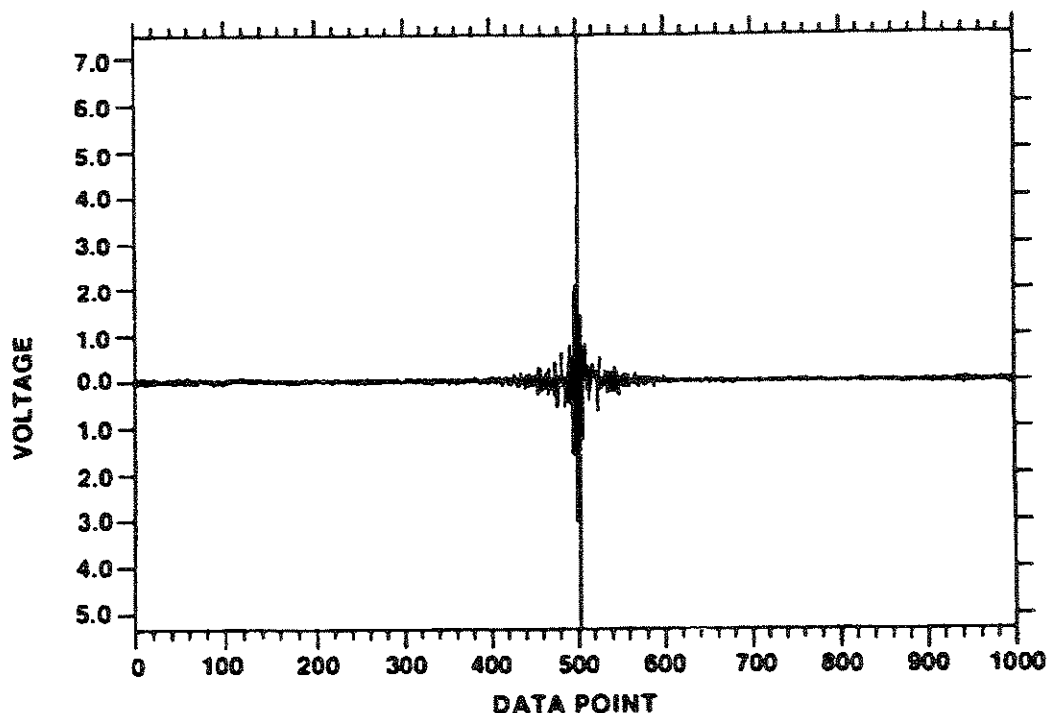


Figure 2-6a: Double-Sided Interferogram. The centerburst is located in the center of the interferogram, with equal numbers of data points before and after the zero path difference point. This type of data collection provides an improved signal-to-noise ratio.

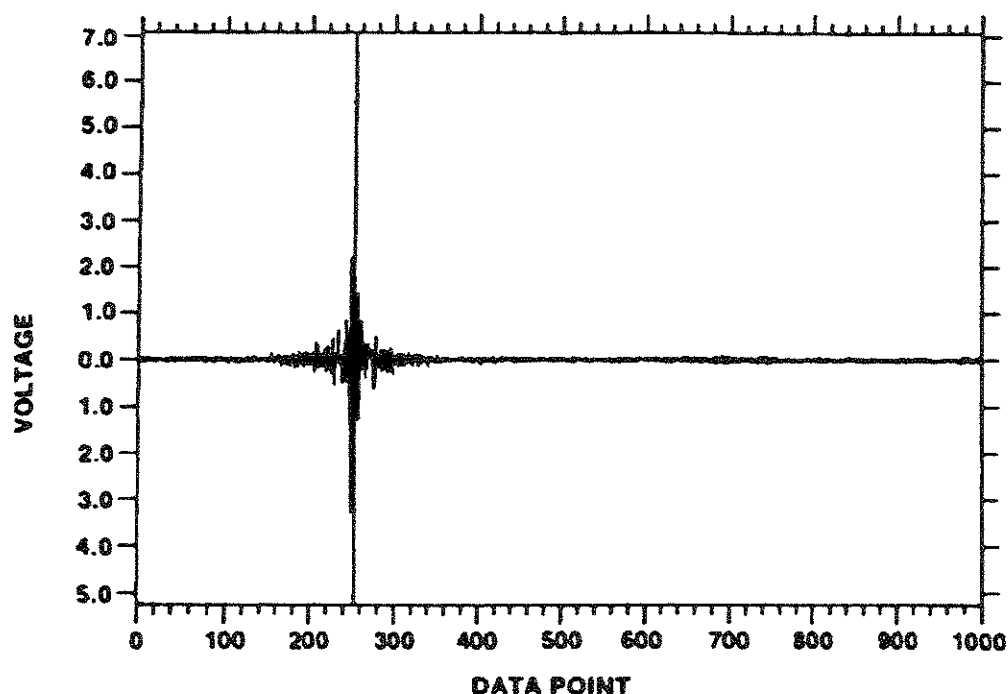


Figure 2-6b: Single-Sided Interferogram. The centerburst is located toward one end of the interferogram. This allows higher resolution spectra to be calculated even though the number of data points collected is the same as that for the double-sided interferogram illustrated in Figure 2-6a.

2.3.2 Resolution

In a dispersive spectrophotometer, frequency resolution is dependent on slit width and on the reciprocal of the linear displacement of the grating. As the slits are narrowed, the range of frequencies passed to the detector decreases, resulting in higher resolution. In an FTIR spectrometer, resolution is increased by increasing the spectrometer's optical retardation, that is, by moving the mirror further.

A relationship between resolution and optical retardation can be empirically derived by considering a spectrum made up of two sharp bands. Each band is at a distinct frequency and generates a sinusoidal signal. The total signal at the detector is the sum of these two sinusoidal signals. If the two frequencies are relatively far apart, the resulting signals are quite different in frequency and only a short movement of the mirror is needed to measure a complete cycle of the pattern made by the addition of the two waveforms. On the other hand, if the two frequencies in the spectrum are

closer together, the interferometer needs to scan a larger distance to measure a full cycle of the addition pattern.

The relationship between spectral line spacing and the interferogram is illustrated in Figure 2-7. We can see that

$$R = 1/d$$

where R is the resolution in wavenumbers and d is the optical retardation in centimeters. Thus, the length of mirror travel (retardation) must be doubled to reduce instrument resolution by half, or, in other words, to improve instrument resolution by a factor of two.

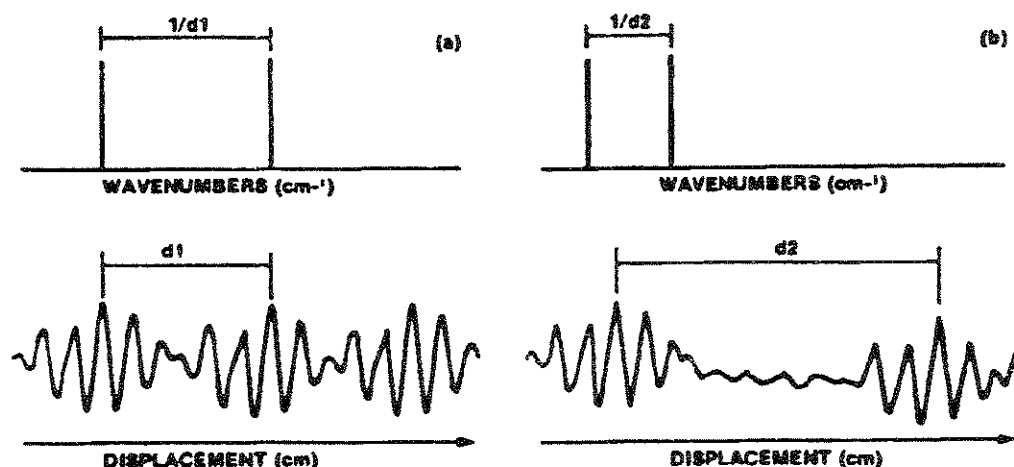


Figure 2-7: Frequency Resolution Versus Optical Retardation. Less mirror travel (retardation) is required to separate widely spaced spectral peaks, as illustrated in part (a), than is required to separate more closely spaced peaks, as illustrated in part (b).

Several different criteria are used to measure FTIR spectrometer resolution. These include the Rayleigh criteria and the full-width-at-half-height (FWHH) method. Measuring instrument resolution with the FWHH method involves collecting an absorption spectrum with very sharp peaks, such as that obtained from low-pressure CO at about 5 torr pressure.

Figure 2-8 illustrates a portion of a CO spectrum collected at a resolution of 0.5 cm⁻¹ and demonstrates how the instrument resolution is checked using the FWHH method.

One of the rotational fine structure lines in the vibration-rotation band is expanded and the width of this line at a point half-way between the baseline and the maximum absorbance value is measured. This value represents the instrument resolution using the FWHH method.

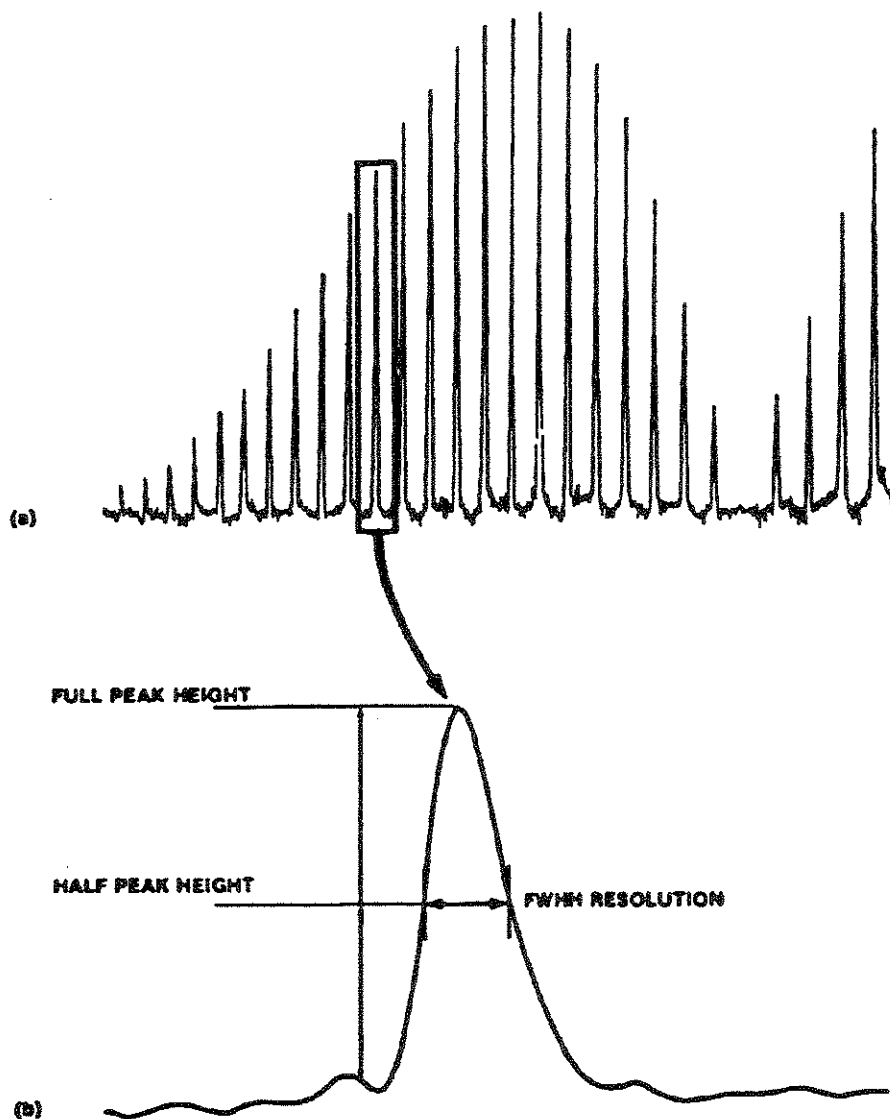


Figure 2-8: FWHH Instrument Resolution. The two parts of this figure illustrate how instrument resolution is measured using the full-width-at-half-height method on the rotational lines of CO. The pressure in the gas cell was nine torr to avoid pressure broadening of the peak in this spectrum.

2.3.3 Undersampling

The interferogram is digitized according to the fringe pattern of the HeNe laser. The frequency reference for the spectral computation is the frequency of this HeNe laser line. If a data point is collected at each zero crossing of the of the HeNe signal channel, the mathematics of the Fourier transformation provide a spectrum from 0 to 15,798 wavenumbers, that is, from 0 wavenumbers to the frequency of the reference light, which for the He Ne laser is 15,798 wavenumbers. Again, interferometer resolution is dependent only on the mirror displacement.

It is also possible to sample the interferogram less often. For example, sampling on every other crossing is typical in normal operation. In this case, the number of data points collected is halved but the resolution remains the same. Also, the frequency range of the Fourier transformation is halved to about 7,900 wavenumbers. Since this is still above the mid-infrared region of 4000 to 400 wavenumbers, no penalty is incurred. The advantage is that the data set processed through the Fourier transform is half the size, therefore, the computation is completed faster. It also means that smaller data arrays store the interferograms and spectra, allowing more spectra to be stored on the computer system.

2.3.4 Apodization

To be of any practical use to the spectroscopist, data collected from the interferometer must first be processed through the Fourier transform to produce a spectrum. For those interested in the mathematics involved in the classical Fourier transform and in the faster version derived by Cooley and Tukey, "Introductory Fourier Transform Spectroscopy" by R. J. Bell presents a thorough and rigorous treatment.

The formula used to calculate the Fourier transform integrates from positive infinity to negative infinity. However, as was pointed out in the preceding discussion of resolution, there are specific limits on how far the moving mirror can scan. Since we have a finite data set, the transform of that data set contains the effects of the start and end of the data collection. The data set start and end correspond to what is known as a boxcar function.

This boxcar function is part of the collected data and is, therefore, transformed along with the spectral information in the interferogram. The transform of the boxcar

function is a sinc(x) function. When the sinc(x) function is convolved with the spectral data by the fast Fourier transform (FFT) program, the result is ringing at the edges of spectral absorption bands. By assigning less weight to the data set start and end, as with a triangular function, the ringing about the baseline can be reduced. The tradeoff for the removal of the ringing in the baseline is a reduction in the resolution of the spectrum when triangle apodization is used.

The Fourier transform of the triangular function is a sinc function, which, when convolved with the spectral data, yields practically no ringing and yields a spectral band contour very similar to that obtained with a grating spectrometer. The effects of apodization during the Fourier transformation require that all spectra be processed by the same function when quantitative measurements, such as spectral subtraction, are performed.

2.3.5 Phase Correction

Theoretically, the interferogram should be perfectly symmetrical around the ZPD, or centerburst. If we look at an interferogram collected on an FTIR spectrometer we will see that the interferogram is somewhat asymmetrical. The asymmetry is primarily due to beamsplitter characteristics and to the electronics required to process the signal before it is digitized.

These elements introduce frequency-dependent phase delays which give the interferogram this asymmetrical appearance. Such an interferogram is said to have a *chirped* centerburst. Each frequency of the light entering the interferometer produces a cosinusoidal output. The effect of the frequency-dependent phase shifts is to introduce sinusoidal components into the interferogram. Phase correction is the process by which these phase shifts are removed from the spectrum.

When a single-sided interferogram is collected, a small portion of the signal before the centerburst must still be included. This accomplished two things. First, it identifies the actual ZPD which is needed for the transform. Second, it allows a small area around the centerburst to be transformed and used to determine the phase correction function which is applied to the entire spectrum as it is transformed.

2.3.6 Cube-Corner Interferometers

In his original interferometer, Michelson used two flat mirrors. Flat mirrors can work satisfactorily, but only as long as each remains exactly perpendicular to the incident light beam. One of the predominant difficulties involved in using flat-mirror Michelson interferometers is keeping the moving mirror from tilting during an experiment. When the mirror tilts, the beam diverges and loses coherence (the ability to form a proper interference signal) at the beamsplitter.

A common solution to this problem is to use air bearings, whereby the mirror travels virtually friction free on a cushion of pressurized gas. While this method is quite effective, air bearings are not without their own drawbacks; they are relatively costly, susceptible to damage and require a supply of compressed gas.

When Peter Fellgett advocated the development of Fourier transform spectrometers, he proposed using cube-corner reflectors constructed of three flat mirrors, each oriented precisely 90 degrees to the others. The advantage of cube-corner reflectors is that any light ray entering the reflector always exits parallel to the incoming ray. (See Figure 2-9.) Small amounts of tilt during the scan is automatically compensated for by the reflector, and coherence is maintained. Only shear motion (vertical or side-to-side movement) can affect the operation of interferometers that use cube-corner mirrors. But, this sensitivity to shear is orders of magnitude less than the tilt sensitivity of flat-mirror interferometers.

Thus, an interferometer employing cube-corner reflectors can be built with more rugged and reliable mechanical bearings, and can still provide the performance required to achieve high resolution and exceptional stability. Mechanical bearings also eliminate the cost and inconvenience of having to supply pressurized gas to the spectrometer system. The instrument may still be purged if desired, but in most cases it is not necessary.

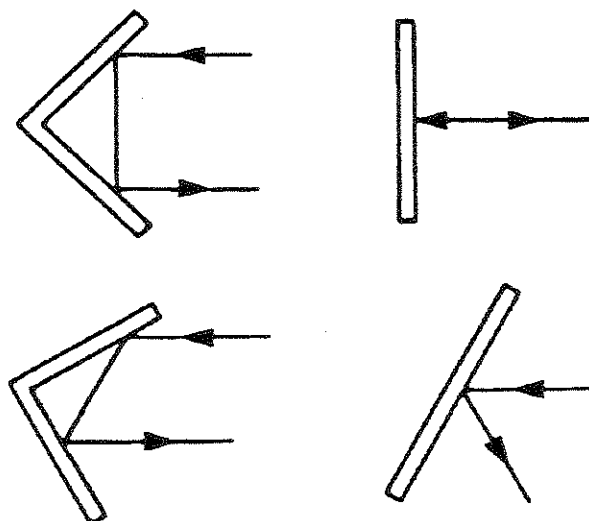


Figure 2-9: Mirror Tilt Effects. Cube-corner reflectors are insensitive to deleterious mirror tilt because the returning rays are always parallel to the incident light rays. Flat mirrors are very sensitive to tilt, which can introduce spectral artifacts and reduce spectral resolution.

2.4 For Additional Information

This chapter is intended to serve only as a brief introduction to modern FTIR spectroscopy for chemical analysis. Appendix B at the back of this manual lists a number of articles and books that provide further information regarding FTIR spectroscopy.

Chapter I

THEORY

A. ELECTROMAGNETIC RADIATION

Infrared waves like X-rays, light and radio waves are classified as electromagnetic radiation since they consist of both alternating electric and magnetic fields. Each of these types of radiation has a different amount of energy. The classification of radiation according to its energy gives rise to the electromagnetic spectrum. This is illustrated in Figure 1.

The classical description of electromagnetic radiation is that it is continuous and has a sinusoidal wave motion. The wave motion of electromagnetic radiation can be described in terms of wavelength and frequency. The wavelength, λ , of radiation is the distance between two successive maxima or minima of the wave motion, as illustrated in Figure 2. The frequency, ν , is defined as the number of cycles which pass a given point per second.

Wavelength and frequency are interrelated according to the following equation:

$$\lambda = \frac{c}{\nu} \quad (1)$$

where: λ = wavelength (cm)
 c = velocity of light (3.0×10^{10} cm/sec)
 ν = frequency (Hz). ...

Frequency and energy are interrelated according to the following equation:

$$E = h \nu \quad (2)$$

where: E = energy of a quantum in ergs
 h = Planck's constant (6.62×10^{-27} erg sec).

This classical description of electromagnetic radiation satisfactorily explained the properties of visible radiation but failed to explain the properties of radiation in the ultraviolet region. According to equations derived for the behavior of electromagnetic

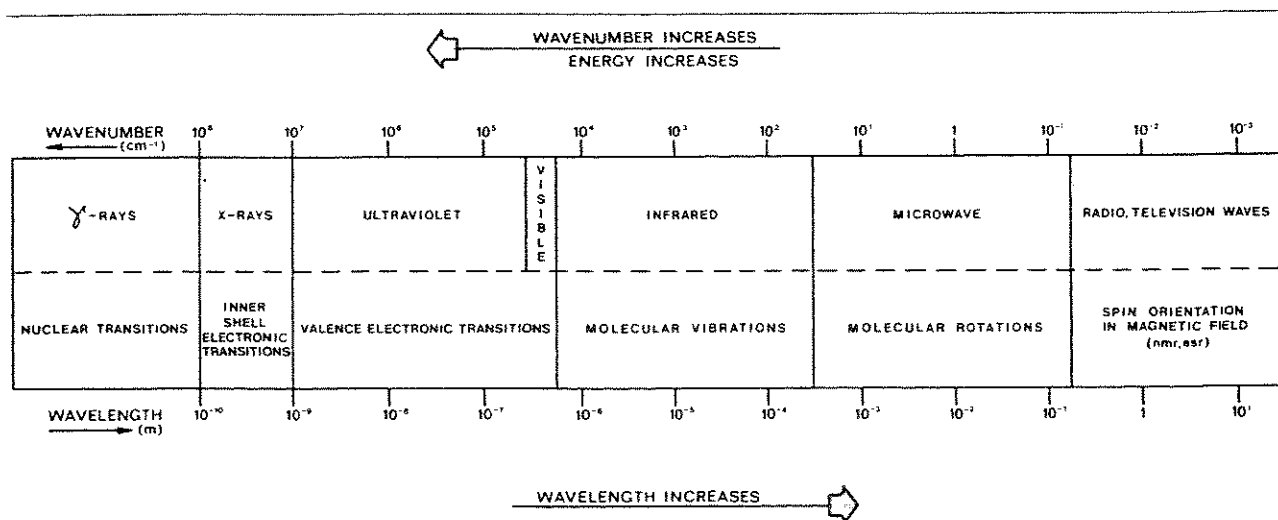


Figure 1—Electromagnetic Spectrum

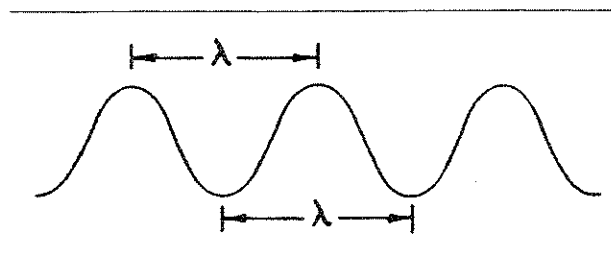


Figure 2—Sinusoidal Wave

radiation based upon the concept of continuous wave motion, the energy emitted by a black body source at finite temperature increases without limit as the wavelength of the radiation approaches zero. This behavior is not experimentally observed. However, if one assumes, as did Planck, that radiation is emitted by a source in discrete units called quanta or photons, and not continuously, then the behavior of radiation in the ultraviolet region can be satisfactorily explained. This concept of discrete units for electromagnetic radiation is the basis of quantum theory which is necessary for a fundamental understanding of infrared spectroscopy.

B. MOLECULAR ENERGY

When a molecule absorbs electromagnetic radiation there is an increase in its total energy. According to quantum theory, only a quantum of radiation of a specific energy can be absorbed by a molecule, thereby raising its energy from the ground state to an excited state. *Figure 3* shows this process schematically where E_1 and E_2 represent the energy of the molecule in the ground state and excited state, respectively, and E_p is the energy of the photon. It is important to note that the energy of transition, ΔE , is equal to the energy of the interacting photon and, thus, equal to $h\nu$. This is stated mathematically according to equation (3).

$$\Delta E = E_2 - E_1 = E_p = h\nu \quad (3)$$

The total energy, E_T , of a gas-phase molecule is comprised of electronic, vibrational, rotational, and translational energies:

$$E_T = E_e + E_v + E_r + E_t \quad (4)$$

where: E_T = total energy of a gas-phase molecule
 E_e = electronic energy
 E_v = vibrational energy
 E_r = rotational energy
 E_t = translational energy.

The energy involved in the transition from the electronic ground state to the first excited electronic state of a molecule usually requires radiation of

greater energy than that available in the infrared region of the electromagnetic spectrum. Therefore, electronic energies and transitions usually do not have to be considered in discussing the theory of infrared spectroscopy.

C. DEGREES OF FREEDOM AND MOLECULAR MOTIONS

The remaining energies of a molecule are due to vibrational, rotational, and translational motions associated with the molecule. These molecular motions are commonly referred to as degrees of freedom. For every atom in a molecule there are three degrees of freedom corresponding to motions along the three mutually perpendicular x, y, and z coordinates in space. For a nonlinear molecule containing N atoms, there will be $3N$ degrees of freedom: three translational, three rotational, and the remainder, $3N-6$, will be vibrational. These degrees of freedom are illustrated in *Figure 4*.

For a linear molecule there are $3N-5$ vibrational degrees of freedom since a linear molecule has only two degrees of rotational freedom. No change occurs in a linear molecule because of rotation about its bond axis. Of these vibrational degrees of freedom, $N-1$ modes will be due to stretching vibrations and $2N-4$ modes will be due to deformation. For a nonlinear molecule, $2N-5$ modes will be due to deformation.

Infrared radiation is of sufficient energy to cause transitions within the translational, rotational, and vibrational energy levels of a molecule. Infrared spectroscopy is the study of transitions within these various energy levels due to the absorption of infrared radiation. Due to instrumental and sampling considerations, translational and rotational transitions are not normally considered in diagnostic studies of coatings materials. Therefore, this book is concerned primarily with transitions between vibrational energy levels of a molecule and the various types of molecular vibrations.

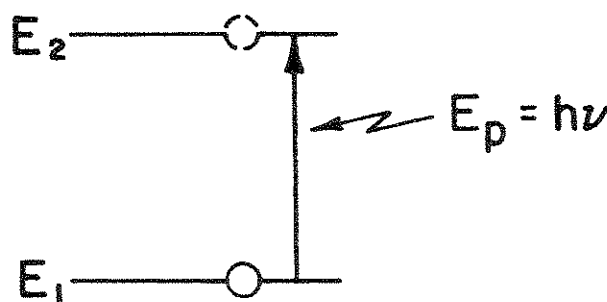


Figure 3—Absorption of Electromagnetic Radiation

D. FUNDAMENTAL VIBRATIONS

Vibrational transitions or fundamental modes of vibration are classified as stretching modes and deformation modes. Stretching modes are described as changes in bond lengths and deformation modes as giving rise primarily to changes in bond angles. The fundamental modes of vibration of the methylene group are shown in Figure 5. The approximate spectral positions where these vibrations will absorb infrared radiation are also given.

To a first approximation, a two-atom pair may be thought of as a simple harmonic oscillator, such as two balls attached together with a spring. It is then possible to calculate the spectral position due to the stretching vibration of this pair using the following relationship:

$$\bar{\nu}(\text{cm}^{-1}) = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad (5)$$

where: $\bar{\nu}(\text{cm}^{-1})$ = spectral position in wavenumbers

$$\left(\frac{1}{\lambda}\right)$$

k = force constant in dynes/cm

μ = reduced mass of the atom pair in grams

c = speed of light in cm/sec.

The force constant is a measure of the bond energy of the two-atom bond and can be calculated empirically or obtained from the literature. Force constants are usually on the order of 10^5 dynes/cm. The reduced mass of the atom pair is calculated from the expression:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \cdot \frac{1}{N} \quad (6)$$

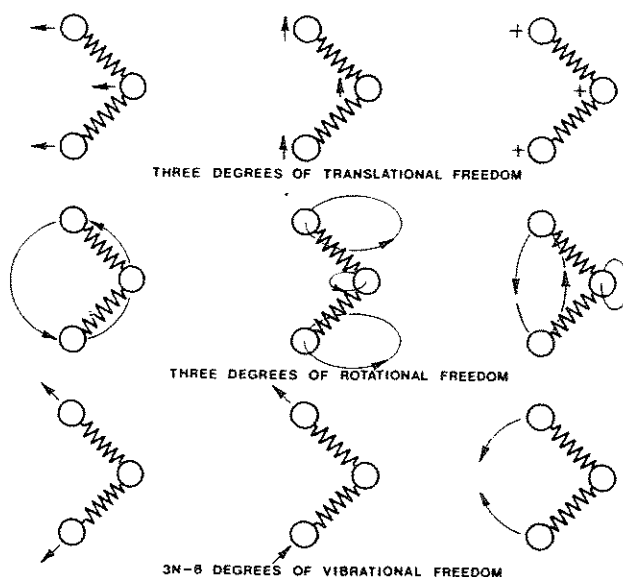
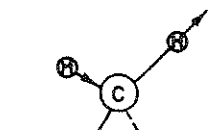


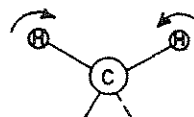
Figure 4—Degrees of Freedom of a Molecule



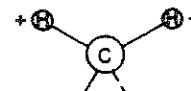
Asymmetric stretching
2926 cm^{-1} (3.42 nm)



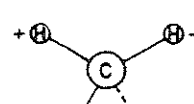
Symmetric stretching
2853 cm^{-1} (3.51 nm)



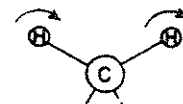
Scissoring deformation
1468 cm^{-1} (6.81 nm)



Wagging deformation
1305 cm^{-1} (7.66 nm)



Twisting deformation
1305 cm^{-1} (7.66 nm)



Rocking deformation
720 cm^{-1} (13.89 nm)

Figure 5—Fundamental Stretching and Deformation Vibrations for the Methylene Group

where: m_1 and m_2 = the atomic masses of the two atoms involved in the vibration

N = Avogadro's Number (6.023×10^{23} atoms/mole).

The reduced mass is always less than the mass of either of the atoms involved in the vibration. The carbonyl group can be used as an example of the calculation of the spectral position due to a stretching vibration. The reduced mass of this atom pair is:

$$\mu_{\text{C=O}} = \frac{m_{\text{C}} m_{\text{O}}}{m_{\text{C}} + m_{\text{O}}} \cdot \frac{1}{N}$$

$$\mu_{\text{C=O}} = \frac{\left(\frac{12.00 \text{ g atom}}{\text{mole}}\right) \left(\frac{15.99 \text{ g atom}}{\text{mole}}\right)}{\left(\frac{12.00 \text{ g atom}}{\text{mole}} + \frac{15.99 \text{ g atom}}{\text{mole}}\right)} \cdot \frac{1}{\left(\frac{6.023 \times 10^{23} \text{ atoms}}{\text{mole}}\right)}$$

$$\mu_{\text{C=O}} = \frac{191.9 \text{ g}^2 \text{ atom}^2 / \text{mole}^2}{27.99 \text{ g atom/mole}} \cdot \frac{1}{6.023 \times 10^{23} \text{ atom/mole}}$$

$$\mu_{\text{C=O}} = 1.14 \times 10^{-23} \text{ g}$$

The force constant for the carbonyl stretching vibration is approximately 12×10^5 dynes/cm. From this value and the reduced mass for the carbonyl atom pair, the spectral position for this stretching vibration can be calculated using equation (5).

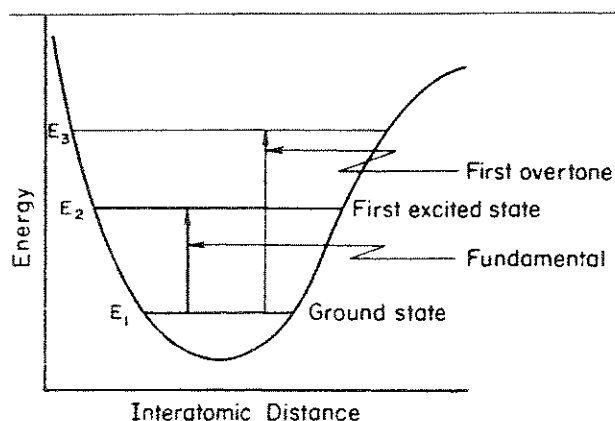


Figure 6—Potential Energy Diagram for Vibrational Transitions

$$\bar{\nu}_{c=0} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$\bar{\nu}_{c=0} = \frac{1}{2(3.14)(3.0 \times 10^{10} \text{ cm/sec})} \sqrt{\frac{12 \times 10^5 \text{ dynes/cm}}{1.14 \times 10^{-23} \text{ g}}}$$

$$\bar{\nu}_{c=0} = 1.7 \times 10^3 \text{ cm}^{-1}$$

The actual position for the stretching vibration of most carbonyl groups is in the spectral region between 1850 and 1650 cm^{-1} .

Having obtained the spectral position of this vibration, it is possible to calculate the vibrational frequency from the expression:

$$\nu = c \bar{\nu} \quad (7)$$

where: ν = the frequency of the vibration in sec^{-1} .
Therefore, $\nu_{c=0} = 3.0 \times 10^{10} \text{ cm/sec} \times 1.7 \times 10^3 \text{ cm}^{-1}$
 $= 5.2 \times 10^{13} \text{ sec}^{-1}$

With equation (2) it is possible to calculate the energy required for the transition between the ground state and the first excited state for the carbonyl stretching vibration.

$$\Delta\epsilon = \epsilon_2 - \epsilon_1 = \epsilon_\nu$$

$$\Delta\epsilon_\nu = h\nu$$

where: ϵ = transitional energy in ergs/atom
 $\Delta\epsilon_{c=0} = (6.625 \times 10^{-27} \text{ erg sec/atom})(5.2 \times 10^{13} \text{ sec}^{-1})$
 $\Delta\epsilon_{c=0} = 3.5 \times 10^{-13} \text{ ergs/atom}$.

In terms of kilocalories per mole, this is equal to:

$$\Delta\epsilon_{c=0} = (3.5 \times 10^{-13} \text{ ergs/atom})(2.39 \times 10^{-8} \text{ cal/erg}) \cdot (6.023 \times 10^{23} \text{ atom/mole})$$

$$\Delta\epsilon_{c=0} = 5.0 \times 10^3 \text{ cal/mole} = 5.0 \text{ Kcal/mole}$$

This type of transition is depicted schematically in Figure 6.

E. THEORETICAL CONSIDERATIONS

As a heteronuclear molecule vibrates, the interatomic distance between atoms changes as does its dipole moment. The vibrating molecule produces

an alternating dipolar electric field. The magnitude of this alternating dipolar electric field changes periodically with time at a frequency equal to the vibrational frequency. It is this dipolar electric field which interacts with the electrical component of the electromagnetic radiation giving rise to the absorption of energy. This absorption of electromagnetic radiation is what is observed when recording an infrared spectrum.

If a diatomic molecule is homonuclear, there is no change in dipole moment with the vibration and no alternating dipolar electric field is produced. Thus, the molecule does not interact with or absorb infrared radiation.

Whenever a change in dipole moment occurs, the fundamental vibration is said to be infrared active. When a vibrating molecule produces no change in its dipole moment because of symmetry, the fundamental vibration is said to be infrared inactive.

In molecules with a high degree of symmetry, many of the vibrations may occur between groups of atoms with the same reduced mass and same force constant. These vibrations will have the same frequency and will be superimposed on the spectrum. When this occurs, the vibrations are said to be degenerate. In symmetrical molecules several modes of vibration may occur at identical frequencies, such as the three asymmetric C-H stretching vibrations in CH_3Cl . Also, many normal modes of vibration can have nearly identical frequencies, such as the CH_2 vibrations in linear polyethylene. In cases like these, symmetry does not require the frequencies to coincide; however, due to chemical considerations, the absorption bands overlap. Thus, a highly symmetrical molecule of many atoms, such as benzene, will give a simple infrared spectrum because many of its modes of vibration are degenerate. Also, the spectra of polymers can appear simpler than expected due to the accidental degeneracy of the chemically similar groups.

It is also possible to obtain a more complex infrared spectrum than that predicted from the 3N-6 equation. This will usually be due to overtones of a fundamental vibration or the combination of two or more fundamental vibrations, or both. Overtone vibrations are due to transitions between the vibrational ground state and the second or third vibrational quantum energy states (see Figure 6). The intensity of the first overtone of a fundamental is usually at least an order of magnitude less than that of the fundamental vibration. The position of an overtone frequently occurs at slightly less than whole number multiples of very intense fundamental vibrations. If infrared radiation of energy equal to the sum (or difference) of energies of two fundamental transitions is absorbed, an absorption band will appear in the spectrum at a frequency equal to this sum (or difference). The absorption band resulting from the sum of two or more fundamentals is

called a combination band, and that resulting from the difference of two fundamentals is known as a difference band.*

F. GROUP FREQUENCIES

Vibrational motions, both stretching and deformation of any particular atom pair, occur even when other atoms or functional groups are involved in the vibrational transitions. However, depending on the types of atoms involved and their environments in the molecule, each transition will have a specific energy. Each of these vibrational modes will give rise to the absorption of infrared radiation in a specific region of the infrared spectrum.

In many cases, the vibrational frequency of a functional group is unaffected by surrounding groups. Thus, carbon-hydrogen stretchings all occur near 3000 cm^{-1} , aromatic rings absorb at frequencies between 690 and 900 cm^{-1} (depending upon the ring substitution), sulfonates always have strong absorption in the 1130 - 1230 cm^{-1} region, and most carbonyl stretchings occur between 1650 and 1790 cm^{-1} . These, and many others, are characteristic group frequencies, and this forms the basis for qualitative analysis and structural determinations by infrared spectroscopy. Many group frequency absorptions are shown in *Tables 5 and 6*.

G. ADDITIONAL CONSIDERATIONS

If vibrations within a molecule were independent of the rest of the molecule, each mode of vibration would be limited to a definite frequency. As an example, all carbon-carbon stretching vibrations, regardless of the molecule, would have the same frequency. However, for real molecules, vibrational modes can occur over a range of frequencies. The frequency depends upon the mass of the adjacent atoms, resonance and inductive effects, and coupling of this vibration to other vibrations. Other factors such as physical state and matrix may also influence the frequency.

It is possible to closely estimate the positions and types of the fundamental vibrations for molecules. This derivation, however, involves the use of quantum mechanics and group theory, and is beyond the scope of this book.

The effect of mass on the fundamental stretching vibration can be computed from equation (5). Thus, if the force constants for two diatomic molecules are the same, the molecule having the heavier atoms will have its stretching vibrational mode at a lower frequency. However, the change in position of a

vibrational mode when one of the atoms is changed cannot be totally attributed to mass effects. The change in position is partially due to the change in the electron distribution brought about by a substituted atom or group of atoms. As an example, these inductive and resonance effects account for most of the shift in the carbonyl stretching frequency as one changes the atom adjacent to the carbon atom of the carbonyl group. The carbonyl stretching frequency for an acid chloride is higher than that for an ester, which is in turn higher than that for a ketone or amide. The high frequency associated with an acid chloride is due primarily to the inductive effects of the highly electronegative chlorine atom. The low frequency of the carbonyl for an amide is due predominantly to the resonance within the molecule. The position of the carbonyl stretching frequency for an ester depends upon both inductive and resonance effects. The inductive effect tends to raise the frequency of a vibrational mode while resonance tends to lower the frequency.

The interaction or coupling of vibrational modes can also give rise to a shift in the frequency for a given type of vibration. Thus, two carbon-carbon bonds having a carbon atom in common will give rise to two frequencies—one above and one below the frequency of a single carbon-carbon bond. The vibration at the higher frequency is due to the asymmetrical stretch, while the vibration at the lower frequency is due to the symmetrical C-C-C stretch. Anhydrides are another class of compounds which exhibit coupling. The two carbonyl stretching frequencies are coupled, giving rise to asymmetrical and symmetrical stretching frequencies. However, the coupling effect is not very strong since the frequencies are only separated by 70 cm^{-1} .

The intensities and shapes of vibrational bands are of considerable importance in spectral interpretation and infrared quantitative analysis. The intensity of an infrared band is directly proportional to the probability for the transition between the ground state and a vibrational excited state. This probability, in turn, depends primarily upon the square of the rate of change in the dipole moment for a particular vibration. An intense band indicates a large change in the dipole moment of the atoms involved during a vibration, or that many atoms or functional groups within the molecule have the same vibrational energy.

Band shapes may be sharp or broad depending upon the chemical environment that the molecule experiences. Intermolecular hydrogen bonding will increase the intensity and broaden the O-H stretching frequency in compounds such as alcohols and phenols, whereas the unassociated hydroxyl group has a sharp band of medium intensity. Band broadening may also occur when the spectrophotometer slit width is greater than the width of the absorption band being measured.

* Difference bands arise from vibrationally excited states and are often weak and temperature dependent.

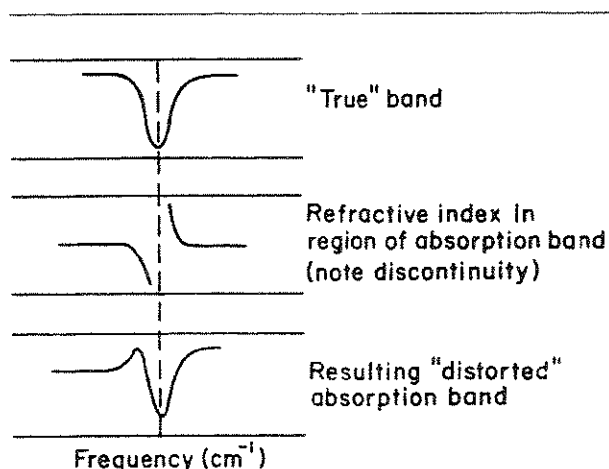


Figure 7—Christiansen Effect

Bands whose shapes are not symmetrical often appear in the infrared spectrum of a material in a solid matrix. This effect is known as the "Christiansen effect" and is due to the particle size and refractive index differences between the material and matrix. The radiation loss by scattering is a function of this refractive index difference. At frequencies slightly higher than the absorption maximum of a band, the refractive index of the sample decreases rapidly and approaches the refractive index of the matrix. This results in less scattering and a rapid increase in transmission. At frequencies slightly lower than the absorption maximum, the refractive index of the sample is markedly different than that of the matrix and the transmission is much lower than would be caused by the absorption band alone. The resulting phenomenon is represented in Figure 7.

Another phenomenon which adds to the complexity of an infrared spectrum is known as Fermi resonance. Fermi resonance is the result of an interaction of a fundamental vibration with an overtone or combination band which has nearly the same frequency and the same symmetry group. The result is the appearance of two bands equally displaced on both sides of the predicted interacting frequencies. The intensities of the two bands resulting from this interaction are not ordinarily the same. An example of Fermi resonance is the doublet centered at 1765 cm^{-1} for benzoyl chloride.

H. NOMENCLATURE

The following list of terms, their definitions and abbreviations, are most frequently used in papers on infrared spectroscopy.

Absorbance, A—The logarithm to the base 10 of the reciprocal of the transmittance.

$$A = \log_{10} (1/T) = abc$$

Absorption Band—A region of the absorption spectrum in which the absorbance passes through a maximum.

Absorption Spectrum—A plot of absorbance or any function of absorbance against wavelength or any function of wavelength.

Absorptivity, a—Absorbance divided by the product of the sample pathlength (b) and the concentration of the absorbing substance (c).

$$a = A/bc$$

(Not used: absorbance index, extinction coefficient, or specific extinction.)

Background—Apparent absorption caused by anything other than the substance for which the analysis is being made.

Baseline—Any line drawn on an absorption spectrum to establish a reference point representing a function of radiant power incident on a sample at a given wavelength or frequency.

Beer-Lambert Law— $A = abc$

Concentration, c—Quantity of the substance contained in a unit quantity of sample (e.g., g/l or moles/l).

Sample Pathlength, b—Internal cell or sample length, usually given in centimeters.

Spectrometry—Branch of physical science treating the measurement of spectra.

Spectrophotometer—Spectrometer with associated equipment, so that it furnishes the ratio, or a function of the ratio, of the radiant power of two beams as a function of spectral wavelength. These two beams may be separated in time, space, or both.

Spectroscopy—Study of the interaction of electromagnetic radiation with matter.

Transmittance, T—The ratio of radiant power transmitted by a sample (I) to the radiant power incident on the sample (I_0)

$$T = \frac{I}{I_0}$$

Wavenumber, $\bar{\nu}$ —The number of waves per unit length in a vacuum, usually given in reciprocal centimeters, cm^{-1} .

Chapter II

INSTRUMENTATION

A. INTRODUCTION

This chapter is concerned with the instrumentation used to record infrared absorption spectra. A knowledge of infrared instrumentation and an understanding of the instrumental parameters involved in obtaining spectra will enable the analyst to obtain higher quality spectra. The quality of an infrared spectrum is dependent upon the quality of the instrumentation, i.e., the characteristics of the source, monochromator, and detector. A brief discussion of each of these components will be given in ensuing sections.

It is convenient to divide the infrared region into three sections, shown in *Figure 8*. Different radiation sources, optical systems (monochromators), and detectors are needed in each of the spectral regions.

Many infrared spectrophotometers cover the range from 4000 to 200 cm^{-1} . Although many instruments employing prism monochromators are still in use, current instruments employ grating monochromators. Grating instruments give higher resolution than their prism counterparts. This higher resolution permits separation of closely spaced absorption bands and more accurate measurement of band positions and intensities. Recently,

infrared spectrophotometers based on Fourier-Transform interferometry have gained acceptance. These instruments offer even more favorable resolution and signal-to-noise characteristics than dispersion instruments.

B. DISPERSION SPECTROPHOTOMETERS

A typical dispersion infrared spectrophotometer operates as follows (*Figure 9*). Energy from a source emitting infrared radiation is chopped at a low frequency, normally 10-26 Hz, and is alternately divided into *sample* and *reference* beams. The energy is recombined and passed into the monochromator where dispersion of the energy into its component frequencies occurs. The dispersed energy is then focused on the *detector*. Spectral recording is performed using optical null, ratio recording, or computer techniques.

1. Infrared Sources

Basically, the source is an object which is heated to a high temperature so that it emits infrared radiation. Ideally, an infrared source should emit continuous and intense radiant energy throughout the entire infrared spectral region. However, commer-

Figure 8—Infrared Spectral Regions

Region	Near-Infrared	Mid-Infrared	Far-Infrared
Wavenumber (cm^{-1})	12,000 to 4000	4000 to 200	200 to 10
Radiation Source	Tungsten Filament	Nernst glower, globar, or nichrome wire	High-pressure mercury-arc, globar
Optical System	Prism-grating double monochromator	Monochromator, interferometer	Monochromator, interferometer
Detector	Lead sulfide photocell	Thermocouple, bolometer or Golay cell	Golay cell, pyroelectric detector

cially available infrared sources exhibit energy distribution curves similar to those shown in Figure 10. The radiation intensity of a source is a function of its temperature, and this fact is critical in the design of infrared sources.

Many different infrared sources have been used; however, the most common sources are the Nernst glower, the nichrome wire, and the Globar.

The Nernst glower is composed of a mixture of rare earth oxides which are fabricated into the shape of a small rod. Since the oxides are not electrical conductors at room temperature, the rod must be preheated to raise it to a conducting state. Once it is in a conducting state, an electric current is passed through it to raise its temperature to as high as 1900°C. This source offers advantages for applications at short wavelengths but has the disadvantage of introducing stray radiation at longer wavelengths. The latter problem has been overcome by employing efficient monochromators and filters in modern infrared instruments.

The nichrome wire source is simply a spiral wound nichrome wire which emits infrared radiation upon being heated by passage of a current. Stability and a positive temperature coefficient of resistance are its main advantages. Nonuniformity of the spiral wire is its greatest disadvantage; however, this deficiency can be overcome by coating the wire with a ceramic material. This source is usually operated at a temperature of 1100°C.

The Globar consists of a silicon carbide rod and has approximately the same radiation characteristics as the Nernst glower. It is operated at approximately 1100°C and is a fairly rugged and highly efficient source. Because of its larger size and power dissipation, the Globar is operated in either a water-cooled or air-cooled housing. A variable transformer is used to maintain a constant voltage

since the resistance of the source increases with the length of operating time. These limitations eventually cause hot spots (chemical changes within the source) and nonuniform emission of radiation.

2. Infrared Monochromators

The function of a monochromator is to disperse radiant energy into its individual wavelengths. While performing this function, the monochromator should also display convenient operating characteristics. Some of these are: optimization of the output/input radiant energy ratio as a function of spectral slit width; high efficiency throughout its spectral range; freedom from stray radiation; and ease of wavenumber selection. In order to meet these demanding requirements, the monochromators of commercial infrared spectrophotometers usually contain dispersing elements, entrance and exit slits, a collimating mirror, and filters. A schematic diagram of an infrared monochromator showing the radiation path is given in Figure 9.

The dispersing elements employed in monochromators are either prisms made of alkali halides or diffraction gratings. The dispersing element is probably the most critical component in the monochromator.

Initially, prisms were exclusively utilized as a means of dispersing infrared radiation. However, their transmission limits and narrow spectral dispersion ranges were serious disadvantages.

More recently, plane diffraction gratings have been replacing prisms as a means of dispersing infrared radiation. The diffraction grating is an aluminum-coated plate usually containing a few to several hundred equally spaced grooves per millimeter. Gratings of this type are used throughout the infrared spectral region. The major advantage of

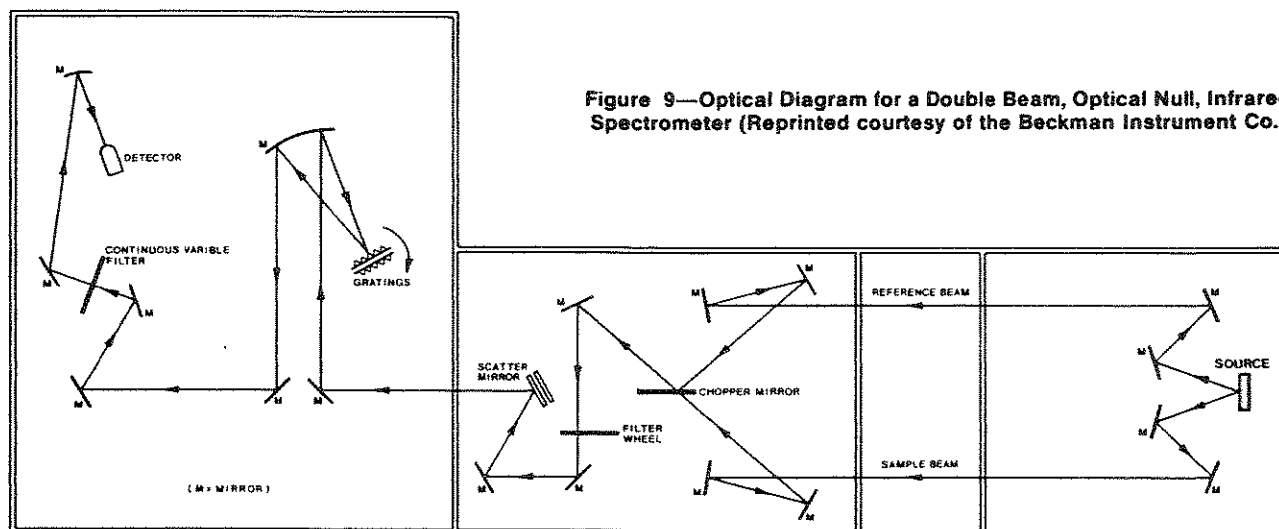


Figure 9—Optical Diagram for a Double Beam, Optical Null, Infrared Spectrometer (Reprinted courtesy of the Beckman Instrument Co.)

a grating over a prism is its greater resolution. The main limitations of diffraction gratings are the relatively narrow spectral range over which they are useful and their creation of higher orders of diffracted radiation. To overcome the first limitation, two or more gratings are usually employed when scanning a large spectral region. The higher orders of radiation are eliminated primarily by using filters or a small prism in series with the grating. The highest resolution will be accomplished by using large gratings. The number of lines per millimeter also dictates the usable spectral region over which the grating may be employed.

Monochromator entrance and exit slits are present in instruments to define sharply and limit the width of the radiation. Slits consist of two moveable metal pieces containing precisely machined parallel edges which face each other to form a narrow aperture. The main purpose of the slits is to increase the ability of the dispersing element to resolve radiation into its various wavelengths. In most instruments, the slits are programmed to open or close as the spectral region is traversed. This is necessary to maintain a nearly constant energy since the source energy is varying, as shown in Figure 10.

As previously stated, the purpose of the filters is to eliminate stray radiation and unwanted grating orders. Four different classes of filters are available for use in infrared instrumentation. These are scattering filters, transmission filters, reflectance filters, and interference filters (a type of transmission filter). Transmission filters are the most commonly employed type. These filters absorb radiation over a specific wavelength region but possess good transmission characteristics on either side of this region.

3. Infrared Detectors

The thermocouple is the most commonly used, reliable, and convenient detector for measuring infrared radiation. The thermocouple is an efficient detector since its response is nearly independent of wavelength and is directly proportional to the intensity of incident radiation. A thermocouple consists of conducting alloys having excellent thermal efficiencies. Gold is evaporated onto the surface of one junction to produce a highly efficient reflector of infrared radiation. The second junction is darkened to increase its infrared absorption characteristics. A potential difference will exist at each junction since there are two different materials present. This thermocouple is placed in an evacuated housing containing a KBr or CsI window. When infrared radiation falls on the coated junction, its temperature will rise above that of the uncoated junction. This will give rise to a potential difference between the two junctions. This potential difference is directly proportional to the number of photons of any

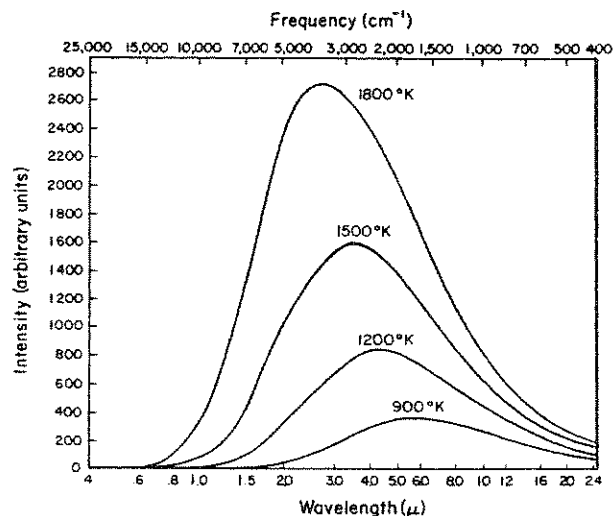


Figure 10—Energy Distribution from a Blackbody Radiator as a Function of Temperature

particular wavelength impinging upon the coated surface.

The bolometer is a small conducting element that is blackened to absorb infrared energy, and its resistance is a linear function of temperature. If a constant direct current is passed through the bolometer, the voltage drop across it will vary with temperature which, in turn, depends upon the amount of infrared energy falling on the conductive element.

The Golay cell is a pneumatic detector consisting of a gas chamber, one wall of which is an infrared absorbing film that serves as the detector. The opposite wall is a flexible mirror. Absorption of radiation by the film heats the gas in the chamber. This causes the flexible mirror to deform. The mirror's deformation is translated by an auxiliary electro-optical system to an electrical voltage. The Golay cell is more efficient at longer infrared wavelengths than either the bolometer or the thermocouple detectors.

Photoconductive detectors, such as lead sulfide, lead telluride, and lead selenide are primarily used in the near-infrared region and need not concern us further.

4. Spectrum Recording

Most commercial double-beam infrared spectrophotometers use the optical-null method for recording spectra. Another common method is ratio recording. In addition, computer processing of infrared spectral data is becoming more commonplace. These techniques will be discussed briefly.

(a) **OPTICAL-NULL METHOD:** In double-beam infrared spectrophotometers, two beams of infrared radiation are employed; these are the reference and sample beams. The reference beam not only serves as a reference of the source energy but also compensates for atmospheric water vapor and carbon dioxide absorption occurring in the sample beam. The two equivalent beams originating from the source pass through the monochromator and alternately impinge upon the detector. The optical diagram shown in *Figure 9* indicates the two radiation paths. The radiation falling upon the detector produces a voltage output for both the sample and reference beams. If the intensity of the two beams is the same, the voltage output remains constant. However, if the intensity of the two beams is different, there will be a voltage output from the amplifier that is proportional to the difference in the energy of the two beams. This voltage is used to drive a motor which moves an attenuator comb or optical wedge in and out of the reference beam. This movement of the attenuator changes the reference beam energy at the detector, producing a change in its voltage output. When the intensity of the two beams reaching the detector is again the same, the voltage output of the detector will again be constant. There will then be no further output from the amplifier, and the attenuator comb will stop its movement. Since the recorder pen is linked to the attenuator, the resulting curve is directly related to the radiation transmitted by the sample.

(b) **RATIO-RECORDING METHOD:** In this type of recording, energy from the sample and reference beams alternately impinge upon the detector. This optical energy is converted, by the detector, to an electrical signal which is proportional to the intensity. The ratio of the electrical intensities of the sample and reference beam is found in order to obtain the required spectral information.

An electrical-null system is normally used in the actual recording process. The resistance network (Wheatstone Bridge) used to obtain the sample/voltage ratio is a slidewire. The slidewire and recorder pen are simultaneously actuated by a servomotor. When the sample and reference beam intensities are in balance, no movement of the recorder pen occurs. During absorption, the intensity of the sample beam changes relative to the reference beam, causing a voltage to be produced in the resistance network which drives the servomotor. The servomotor changes the slidewire resistance and recorder pen position until the driving voltage is balanced (nulled). The recorder pen registers this process as an infrared absorption band.

A ratio recording instrument has several advantages over an optical-null type: A signal proportional to the reference beam energy is always available as a measure of instrument performance and extraneous absorption due to atmospheric effects.

The recording servo mechanism tends to be simpler in ratio recording instruments. Difficulties caused by using a light attenuator in the reference beam are avoided. Ordinate scale expansion is simpler to perform. On the other hand, ratio recording spectrophotometers are more expensive than optical-null instruments.

(c) **COMPUTER-ASSISTED INFRARED SPECTROPHOTOMETRY:** Microprocessors and computers are now being utilized for controlling infrared spectrophotometers and for manipulating acquired data. Microprocessors control instrumental parameters to provide optimized spectral information from each analysis. Computer processing of infrared spectra enables simple and rapid acquisition of background subtracted spectra, multiple scan capability, and difference spectra, as well as providing data for automatic library searching of reference spectra.

C. FOURIER TRANSFORM SPECTROPHOTOMETERS

The Fourier transformation is a perfectly general mathematical operation. By the use of this operation, one can transform results obtained as a function of time (interferogram) and express them as a function of frequency (absorbance spectra). The discussion in previous sections was concerned with infrared spectrophotometers utilizing dispersion monochromators. However, dispersion instruments do have certain limitations. For example: measurements are relatively slow, requiring from 5 to 30 minutes to obtain spectra with acceptable resolution and signal-to-noise for the common spectral region from 4000 to 200 cm^{-1} ; the detectability of low level components is not good; and useful spectra cannot be routinely obtained for extremely small samples.

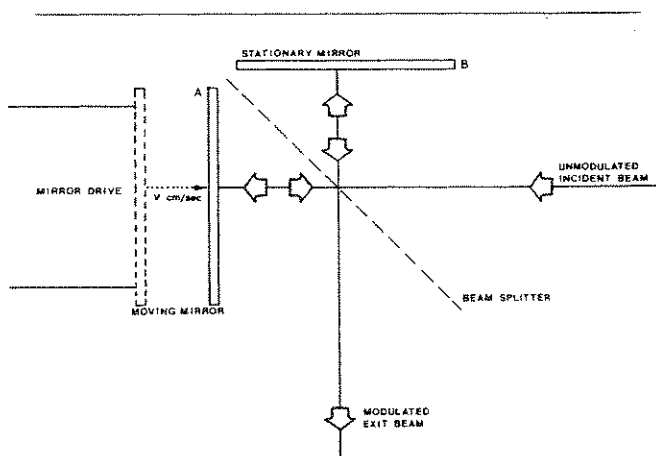


Figure 11—Diagram of a Michelson Interferometer

Development of Fourier transform infrared spectrophotometers greatly alleviated these problems.

The basis of Fourier transform infrared spectroscopy is the Michelson Interferometer shown in *Figure 11*. Collimate energy from an infrared source passes to a beam splitter. The two equal beams are then directed to mirrors A and B. If the mirrors are positioned such that the optical paths of the beams are equal, the beams are in phase when they return to the beam splitter. Consequently, the beams interfere constructively, giving an energy maximum. Displacing the movable mirror by one-quarter wavelength of the incident light will bring the two beams 180 degrees out of phase when they return to the beam splitter. This results in destructive interference (an energy minimum). Movement of mirror A gives an alternating energy maximum and minimum for each quarter wavelength movement of the mirror. This corresponds to a wavelength

change of $\lambda/2$ since the beam travels this distance twice.

If monochromatic energy of wavelength λ is passed through the interferometer (*Figure 11*) and mirror A is moved with velocity, V , the signal detected will have a frequency, f , given by equation (8).

$$f = \frac{2V}{\lambda} \quad (8)$$

The result of plotting detector response versus mirror travel is a pure cosine function. When polychromatic radiation is used as the source, the detector output signal becomes a complex cosine function. The resulting output is called an interferogram and must undergo a Fourier transformation to yield the familiar absorption spectrum. This transformation requires the use of a digital computer. A typical Fourier transform infrared spectrophotometer is shown in *Figure 12*.

LEGEND

S1	- Source
M1	- Spherical Mirror
A1	- Aperture and Chopper
M2	- Spherical Mirror
M3	- Flat Mirror
BS1	- Beamsplitter and Compensator
BS2	- White Light Beamsplitter
M4	- Fixed Mirror
M5	- White Light Mirror
P1	- Centerline Laser Prism
M6	- 4-Position, Computer-Controlled Flat Mirror
M7	- Flat Mirror
M16, M17	- 2-Position, Computer-Controlled Flat Mirrors
M12, M13, M14, M15	- Off-Axis Parabolic Mirror
M18	- Flat Mirror
M19	- Off-Axis Parabolic Mirror
D2	- IR Detector
L2	- Centerline Laser
L1	- Alignment Laser
BE1	- Beam Expander
M20	- Flat Mirror

White Light Beam - - - - -
 Infrared Beam = = = = =
 Laser Beam - - - - -

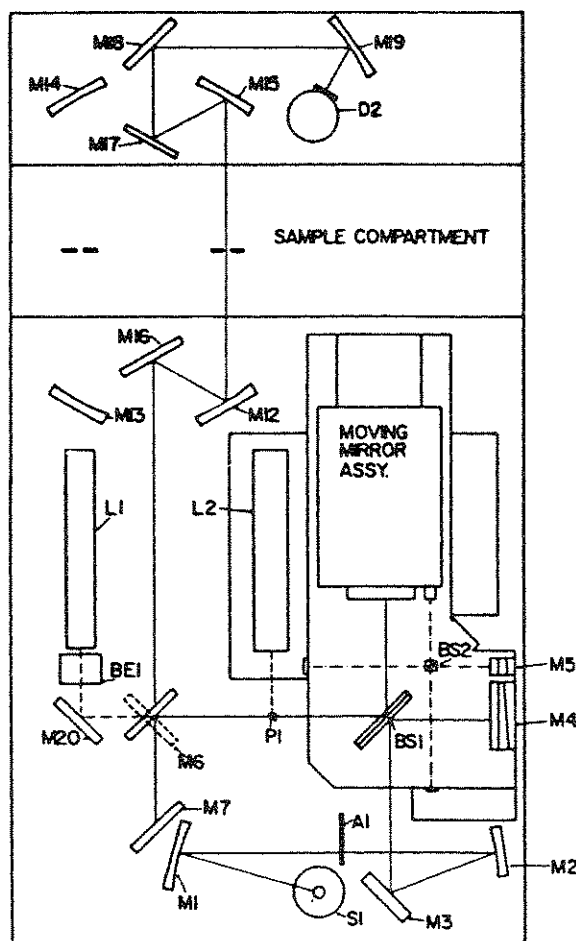


Figure 12—Diagram of a Typical Fourier Transform Infrared Spectrophotometer (Reprinted courtesy of Nicolet Instrument Corp.)

The Fourier transform infrared technique offers certain advantages over dispersive infrared techniques. These include:

1. *Fellgett's Advantage*—The Fourier transform spectrophotometer measures all wavelengths of the infrared spectrum simultaneously. Dispersive spectrophotometers measure only one wavelength at a time. Therefore, a Fourier transform system is capable of measuring a complete spectrum in the same time it takes a dispersive spectrophotometer to measure one resolution element. It can be shown that for equivalent experiments, the Fourier transform system is N times faster than dispersive spectrophotometers (where N is the number of resolution elements in the spectrum). Alternately, for the same measurement time, the Fourier transform system has better signal-to-noise characteristics than a dispersive spectrophotometer.
2. *Jacquinot's Advantage*—This advantage concerns comparison of the light through-put of the interferometer versus a dispersive instrument at a given resolution. The interferometer has a circular aperture of, for example, 50 mm diameter, and has no slits. A dispersive instrument operating at 1 cm^{-1} resolution has a slit area of approximately 1 mm^2 . Comparison of these figures suggests a through-put advantage of nearly 2000 for the interferometer. However, the solid angle of view for a dispersive instrument is about 50 times that of an interferometer, hence the actual through-put advantage for the interferometer is more nearly a factor of 40.
3. *Connes' Advantage*—Fourier transform infrared spectrophotometers use a laser to calibrate the wavelength of each scan. This insures wavelength precision.
4. *Stray Light Advantage*—In Fourier transform systems, each infrared frequency is "chopped" by the interferometer [see equation (8)] at a different frequency, resulting in essentially zero stray light reaching the detector.

D. SPECIAL PURPOSE INFRARED SPECTROPHOTOMETERS

This class of infrared spectrophotometers include nondispersive and dispersive process control instruments and portable air and gas sampling instruments. Further discussion of this class of spectrophotometers is not warranted in a book of this nature. However, further information can be obtained from the appropriate manufacturers' literature.

Chapter III

ACCESSORIES FOR INFRARED INSTRUMENTATION

A. INFRARED ABSORPTION CELLS AND CRYSTALS

Two types of materials are generally used as support media in infrared spectroscopy. They are: (1) water-soluble alkali halides such as NaCl, KBr, and CsI and (2) water-insoluble materials such as AgCl, Ge, CaF₂, KRS-5, Irtran, and polyethylene. The type of sample and the frequency range one wishes to study dictate which material should be used as an infrared cell or crystal. *Table 1* lists the common types of materials used and their useful frequency ranges. It is only necessary to decide on the frequency range desired and choose a cell material which will be compatible with the physical state and the chemical properties of the sample. Obviously a NaCl cell would not be selected to run samples containing water or a AgCl cell to obtain the spectrum of ammonia.

Several types of cells are commercially available. These are: sealed cells, demountable cells, variable thickness cells, microcells, gas cells, multiple pass cells, high and low temperature cells, elevated pressure cells, and flow through cells.

1. Sealed Cells

As the name implies, this cell is permanently sealed. It consists normally of alkali halide plates separated by a very thin gasket. These gaskets are usually made of lead or silver of various thicknesses. The cell is sealed through mercury amalgamation of the gasket. The thickness of a cell used for the study of pure liquids varies with the type of sample. A cell thickness of 0.05 mm can be used satisfactorily for aliphatic materials while a cell thickness of 0.015 mm may be required for aromatics, esters, and ketones. For solution spectra, a cell thickness of 0.1 mm is most commonly used. For studies in the mid or far infrared regions, cells of even greater thickness may be required.

2. Demountable Cells

These are similar to the above mentioned cells except that they can be taken apart to be cleaned and to enable the use of different size spacers. This cell is most useful with viscous liquids and mulls. Demountable cells have two inherent disadvantages: (1) liquids with low surface tension and/or high volatility are easily lost through leakage, and (2) reproducible thicknesses are very difficult to obtain. Spacers for these cells are commonly made from Teflon or lead.

3. Variable Thickness Cells

These are sealed cells in which the pathlength can be continuously varied. The pathlength of these cells can be varied from approximately 0.005 to 5 mm and, therefore, they are very useful for a wide

Table 1—Transmission Limits for Optical Materials

Material	Cutoff Wavenumber (cm ⁻¹)	Cutoff Wavelength (μM)
Glass	3000	3.3
Quartz	2500	4.0
Lithium fluoride	1500	6.6
Calcium fluoride	1200	8.3
Barium fluoride	850	11.7
Irtran-2	750	13.4
Sodium chloride	600	16.5
Potassium bromide	350	28.6
Silver chloride	350	28.6
KRS-5 (TlI ₂ • TlBr ₂ Eutectic)	250	40.0
Cesium bromide	250	40.0
Cesium iodide	200	50.0
Polyethylene*	100	100.0

* Cannot be used above 650 cm⁻¹ (15.4 μ)

variety of samples. Another use of these cells is for solvent compensation in solution studies. However, they are expensive, difficult to repair, and require a large volume of sample.

4. Microcells

These cells can be constructed from any suitable material and are designed to minimize the "dead" volume within the cell. The volume of the cells is about 50 μl . Smaller cells are available, but usually require a beam condensing system. Cells used with a beam condensing system are referred to as cavity cells or ultra-micro cells and are used to obtain infrared spectra of samples on the order of 0.5 μl or less.

5. Gas Cells

These cells consist of a glass or metal tube fitted at both ends with "salt" windows which will transmit infrared radiation over the desired spectral region and which will not react with the sample. The cell must also have stopcocks attached for evacuation and filling. A convenient cell length is 10 cm, but cells of different pathlengths are available.

6. Multiple Pass Cells

The effective pathlength of a gas cell can be increased dramatically through the use of several concave mirrors. Designs, such as shown in *Figure 13*, permit the infrared beam to traverse the cell several times while still allowing the cell to fit into most spectrophotometers. Effective pathlengths of up to 120 meters are commercially available. However, transmission losses of up to 80 % are observed at this pathlength.

7. High and Low Temperature Cells

High temperatures can be achieved by placing within a cell a thin resistance wire which forms one arm of a Wheatstone bridge circuit. After calibration, the temperature can easily be controlled to $\pm 0.2^\circ\text{C}$.

Low temperature infrared spectra can be obtained by attaching the sample cell to the bottom of

a "cold finger" Dewar or constructing it as an integral part of the "cold finger." The whole assembly is then placed into another chamber and evacuated to prevent the condensation of moisture on the salt plates of the cell. The "cold finger" can be filled with a coolant such as an acetone-dry ice mixture or liquid nitrogen to obtain the desired temperature.

No special cells are needed if the temperature of the sample is to be varied slightly below or above room temperature. This small variation in temperature can be performed by blowing hot or cold dry nitrogen over the sample cell.

8. Elevated Pressure Cells

The choice of optical crystal for elevated pressure cells is primarily dependent on the pressure at which the sample is to be studied. While diamond crystal is capable of withstanding pressures up to 3000 atm, it is the most expensive and absorbs very strongly between 1800 and 2600 cm^{-1} , leaving a blank portion in the resulting spectrum. CaF_2 windows can be used at pressures up to 1200 atm. NaCl and KBr crystals can be used at pressures of less than 300 atm.^{E203} Beam condensers are often needed with elevated pressure cells.

9. Flow-Through Cells

As the name implies, these cells are essentially liquid cells which have been modified to allow solutions to flow continuously through them. These cells have been used in kinetic studies, in process control, and to monitor chromatographic effluents.

10. Maintenance of Crystals and Cells

Considerable care should be given to absorption cells and crystals. However, through normal use of a cell or crystal, the surface(s) will become fogged and scratched. When this happens, it is necessary to recondition the surface(s) of a crystal in order to restore the original optical properties.

If the crystal has been freshly cleaved or if the surface is badly scratched or has an adhering film, a grinding process must be performed before beginning the polishing process. Emery paper of various grades, such as #200, #400, and #600, is used to grind the surface of the crystal. The coarseness of the paper used depends upon the extent of the surface imperfections. The grinding process of a crystal is performed in a figure eight motion on the emery paper wetted with an alcohol. The figure eight motion is necessary to prevent generating a lens from the flat crystal. Successively finer grades of paper are used during the grinding process. It is only necessary to carry out one or two strokes on each grade of paper.

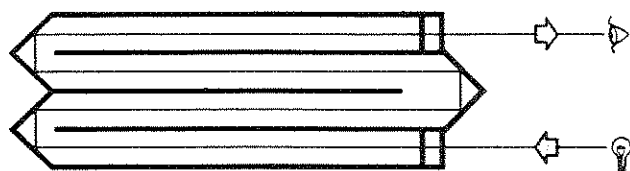


Figure 13—Schematic Diagram of Multiple Pass Gas Cell

Once grinding is completed, it is necessary to polish the crystal. The technique most widely used is the "clothlap" method. This method may be used for a variety of materials with the only modifications being that of the solvent and abrasive used for the different types of crystals. An alcohol is normally used for alkali halide crystals and water can be used for KRS-5* windows. Concentrated HCl has been used as a solvent for crystals made of CaF_2 , BaF_2 , and LiF . The technique is as follows: a piece of cloth (soft and lint-free) is stretched tightly over a thick piece of flat glass and fastened by any suitable means, such as rubber bands or o-rings. Any material having a very fine particle size ($5\ \mu\text{m}$) with good hardness can be used as a polishing agent. Alumina, magnesia, and titania have all been used successfully. A small amount of the polishing material is spread over the cloth and wetted with the solvent. The crystal to be polished is held with the fingers and lapped across the cloth in a figure eight motion. When it appears that the crystal is no longer fogged or scratched, it is slid off the pad onto another piece of cloth tightly stretched over a flat surface. Generally, good results are obtained if the crystal is slid across the second piece of cloth in one straight sweeping motion. The pressure must be sufficient to dry the surface and remove excess polishing agent but not great enough to fog or scratch the surface. By noting the number of interference fringes when the crystal is placed on an optically flat piece of glass and illuminated with monochromatic light, one can obtain an idea of the flatness of the crystal. The fewer the number of fringes, the greater the degree of flatness.

After a crystal has been properly polished, it should be stored in a dry atmosphere to protect it from moisture. Desiccators have been widely used to store crystals. However, crystals of the alkali halides can also be stored in a 1:1 mixture of toluene and acetone for any length of time. This solvent mixture provides the added advantage of cleaning the crystal while it is being stored. Therefore, it is only necessary to perform a brief polishing of the surface to assure that the previous sample material is totally removed.

B. ACCESSORIES FOR SURFACE STUDIES

Several accessories are available to study the composition of almost any type of surface. Obviously, these accessories are of utmost importance to the coatings industry. These accessories are attenuated total reflectance (ATR), multiple internal

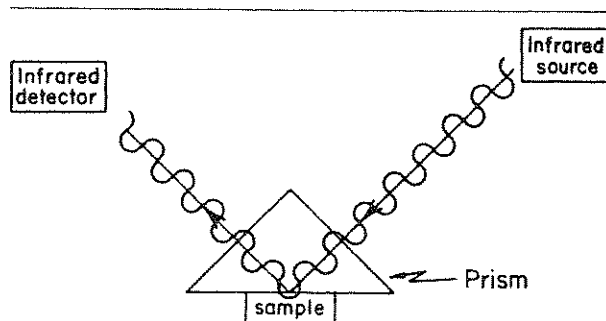


Figure 14—Schematic Arrangement Employed in Attenuated Total Reflectance

reflectance (MIR), specular reflectance, and micro attenuated total reflectance. Each of these accessories will be discussed in more detail due to their great applicability in the coatings industry.

1. Attenuated Total Reflectance (ATR) And Multiple Internal Reflectance (MIR)

Figure 14 shows schematically the experimental arrangement employed in attenuated total reflectance. The infrared source and detector are those of any readily available infrared spectrophotometer. The prism and sample are arranged in the path of infrared radiation.

To observe ATR, the angle of incidence of the infrared radiation at the prism and sample interface must be greater than the critical angle. The intensity of the radiation reflected from the surface of the sample is dependent upon the angle of incidence and the refractive index of the prism. Silver chloride, germanium, and KRS-5 are generally used as prism materials since they all are transparent to infrared radiation and have a high refractive index.

The infrared radiation impinging on the sample penetrates to a depth of a few micrometers. Any material in intimate contact with the prism can absorb the incident radiation, thus attenuating its intensity, and give rise to an infrared spectrum. Since the depth of penetration is only a few micrometers, only the surface composition can be studied, and the spectrum obtained is independent of the sample thickness. However, the depth of penetration is proportional to wavelength and, therefore, a steadily increasing depth of sample is "observed" as the spectrum is scanned from short to long wavelength.

The energy absorbed for a single reflection is normally small, and the resultant absorption bands are usually weak. To overcome this limitation of ATR, optical plates have been designed which give multiple internal reflectance (MIR). A schematic arrangement for MIR is depicted in Figure 15. The optical plate must be transparent to infrared radiation and have a high refractive index as is required

* It should be noted that KRS-5 is highly toxic and proper caution should be exercised.

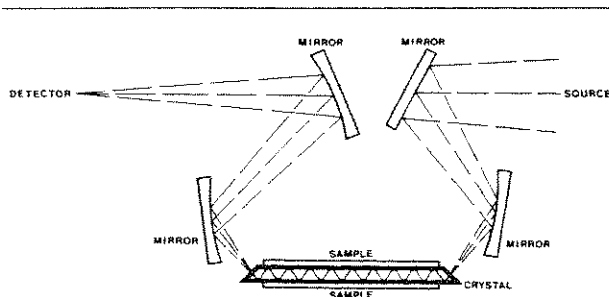


Figure 15—Schematic Arrangement Employed in Multiple Internal Reflection Spectroscopy.

of the prism in ATR. The major difference between ATR and MIR is that in MIR the infrared radiation encounters the sample-prism interface several times. Therefore, the intensity of absorbed radiation is dependent upon the amount of sample in contact with the surface of the prism. Varying the contact area or the angle of incidence (number of reflections) in MIR has the same effect as varying the thickness in transmission infrared spectroscopy.

Since the depth of penetration of the infrared radiation is very small for both ATR and MIR, these techniques are ideally suited to the study of coatings surfaces, surface contaminants, and laminates. ATR and MIR can be used to study the effects of weathering and radiation on a surface, drying rates, chemical aging, absorption of contaminants on a surface, diffusion to the surface of solvents and plasticizers, and the nature of the chemical bonding forces at the surface. Many other types of materials have been studied using ATR and MIR. These include adhesives, residues, powders, fibers and fabrics, foams, coated wires, minerals, glass, skin, and plastic films. The internal reflection spectra of plastic films are free from troublesome interference fringes which are common to transmission spectra.

Sample preparation for ATR and MIR is relatively simple for many samples that are difficult to prepare for transmission measurements. The material to be identified is placed in contact with the internal reflectance plate and sufficient pressure is applied to hold the sample in intimate contact with

the plate. If increasing the pressure increases the amount of sample in contact with the plate, the intensity of the spectrum will be increased. Coatings can be applied to a plate directly with a brush and allowed to dry, or a film can be dried on a plastic backing and placed in contact with the plate. In the case where the coating is applied directly to the plate, the surface being observed may or may not be the same as the surface of the same coating on another substrate.

Cells are also commercially available for studying liquids. ATR and MIR techniques are suitable for the study of samples which contain water since the crystals used are usually water insoluble.

Qualitatively, the spectra obtained by ATR and MIR are similar to those obtained by transmission. However, proper selection of internal reflection elements, reflection angle, and number of reflections is critical in order to obtain high quality reflection spectra. There are always band ratio differences between internal reflection spectra and transmission spectra. Therefore, since qualitative analysis requires attention to band ratios, reference spectra should be run using the same techniques as for the unknown. Direct quantitative analysis by either ATR or MIR is difficult since it is extremely difficult to obtain reproducible contact between the sample and plate. However, a band ratio technique can be used to obtain good data.

2. Micro Multiple Internal Reflectance (MMIR)

When the spectrum of a micro quantity of intrac-table material or of a limited sample area is needed, micro multiple internal reflectance (MMIR) may be used. MMIR is basically a miniature version of the multiple internal reflectance apparatus previously described. Due to the small optical crystals employed, correct optical alignment is critical to provide sufficient infrared energy for accurate spectra. Integral to most MMIR accessories is a beam condensing system to focus the infrared energy into a fine beam and onto the micro crystal.

3. Specular Reflectance (Double Transmission)

This technique is used to obtain the infrared absorption spectra of materials on highly reflective substrates. Figure 16 shows the schematic arrangement for specular reflectance. Varying the distance of the mirror directly in front of the sample varies the number of reflections possible and, thus, the intensity of the absorption spectrum. This accessory has been used to study surface phenomena of highly reflective coatings and transparent plastic films which have been cast onto a reflecting metal substrate.

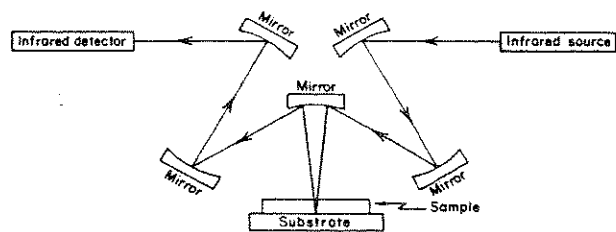


Figure 16—Schematic Arrangement Employed in Specular Reflectance

provides information pertaining to the amount and identity of a specific functional group present in a molecule. Adjacent atoms, such as halogens, increase the intensity of weakly absorbing vibrations such as CH wagging, twisting, or bending, and these increased intensities provide an indication for the presence of these atoms. Functional groups that give rise to a large change in the dipole moment of a molecule, upon undergoing a vibration, will give rise to very intense absorption bands. Excellent examples are the carbonyl and ether groups.

C. TECHNIQUES OF INTERPRETATION

1. Sight Recognition And Direct Comparison

Probably the simplest method of interpretation is to consider the entire spectrum as though it were a picture and compare this picture with the spectrum of known materials which have been either physically or mentally cataloged. If the spectra are the same, or very similar, it is a reasonable assumption that the materials are nearly identical. As experience is gained and more spectra are committed to memory, a great many materials can be recognized by inspection. Reference spectra prove invaluable in this type of interpretation, especially when a definite identification must be made.

2. Negative Interpretation

Once it is known which bands are characteristic, the absence of these bands from a spectrum can be used to establish which functional groups are not present in detectable amounts. Table 2 shows the position of several common group frequencies. If no absorption appears in a region specified on the chart, little or none of this particular functionality is present in the unknown sample. Therefore, for practical purposes, any suspect compound with that functionality can be eliminated. For example, if an ester is suspected and there is no band at approximately 1735 cm^{-1} then, obviously, no ester is present. This method of analysis is important since the spectroscopist is frequently requested to establish the presence or absence of a particular functionality. As an example, if the request is to determine the presence of $-\text{NH}_2$ or $-\text{OH}$ and there is no absorption in the region between 4000 and 3100 cm^{-1} , there is no $-\text{NH}_2$ or $-\text{OH}$ present in the sample.

If there is absorption present in a particular region, no information can be obtained from that region by negative interpretation. Positive interpretation or other techniques must then be relied upon.

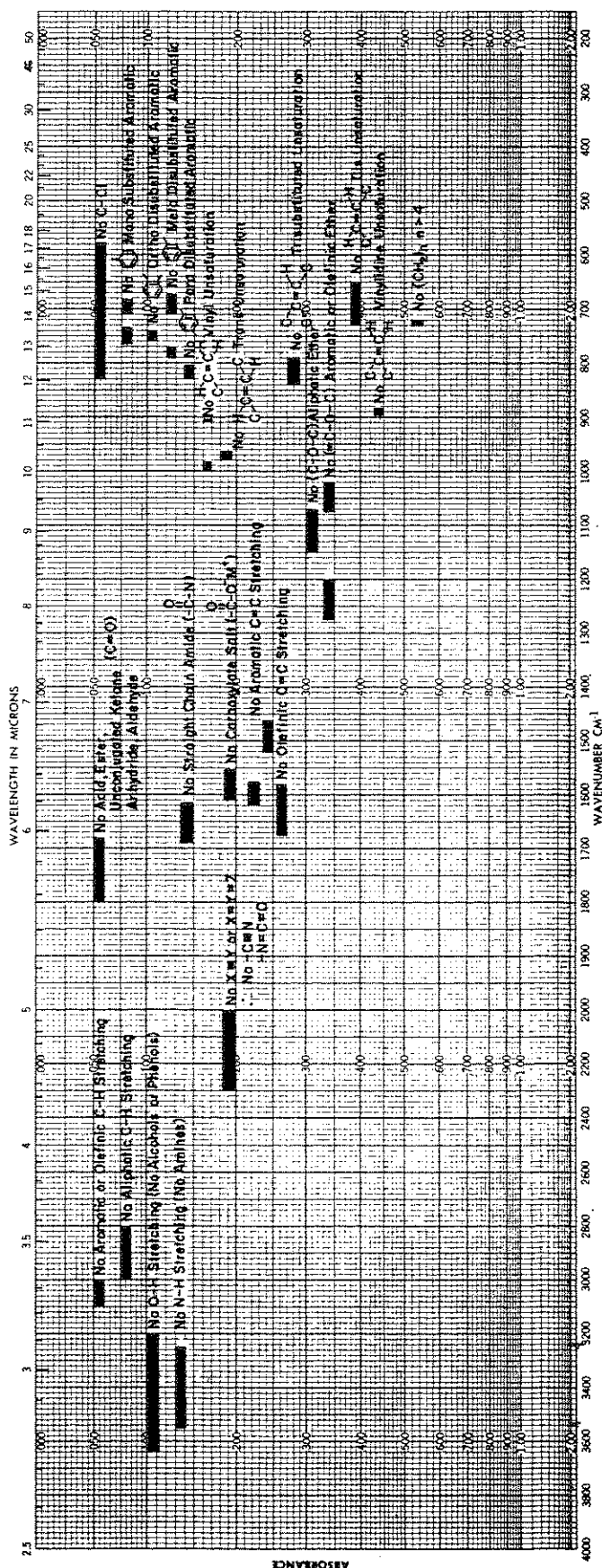


Table 2—Characteristic Group Frequencies for Negative Interpretation

true with the spectra of large molecules with minor differences, such as paraffin and polyethylene waxes and bisphenol-A epoxies above 1000 number average molecular weight. This can also be the case with mixtures where only the minor components vary in quantity or type. With experience, the spectroscopist will learn when either complete identifications or only chemical class type identifications can be made.

E. SPECTRAL INTERPRETATION

Since it is beyond the scope of this publication to interpret all the spectra included, only a representative number will be interpreted to illustrate the various approaches and techniques and to indicate what information can be obtained.

1. Application of Negative Interpretation

The infrared spectrum shown in *Figure 19* will be analyzed using negative interpretation.

The first region of the spectrum to be examined is that due to the stretching vibration of hydrogen attached to other elements. This region is from 4000 to 2100 cm^{-1} . The region from 4000 to 3200 cm^{-1} is associated with O-H and N-H stretching vibrations. Since the spectrum does not contain a band in this region, primary and secondary amines and amides, and all alcohols and organic acids are absent. The region between 3100 and 3000 cm^{-1} is associated with aromatic and olefinic C-H stretching. Again, since no bands are present, all compounds which have unsaturation may be eliminated. In the region from 3000 to 2800 cm^{-1} strong bands are noted; therefore, positive interpretation is used. Positive interpretation indicates that these bands arise from the asymmetric and symmetric stretching frequencies of methyl, methylene, and/or methine groups within the molecules.

The region from 2500 to 2000 cm^{-1} is very specific to stretching vibrations associated with adjacent double bonds and triple bonds. Since no absorption occurs in this region, compounds containing isocyanate or nitrile functionalities are not present.

The region from 1870 to 1550 cm^{-1} is associated with carbonyl stretching vibrations and is one of the most important regions of an infrared spectrum. Subdivision of this region into narrow ranges allows the differentiation between anhydrides, esters, ketones, carboxylic acids, amides, and carboxylic acid salts. All of these functionalities may be eliminated in this example.

The C=C stretching modes of olefinic compounds absorb in the region between 1690 and 1630 cm^{-1} . This functionality is not indicated in the spectrum.

The stretching modes of aromatic ring systems absorb between 1600 and 1450 cm^{-1} . Normally, four

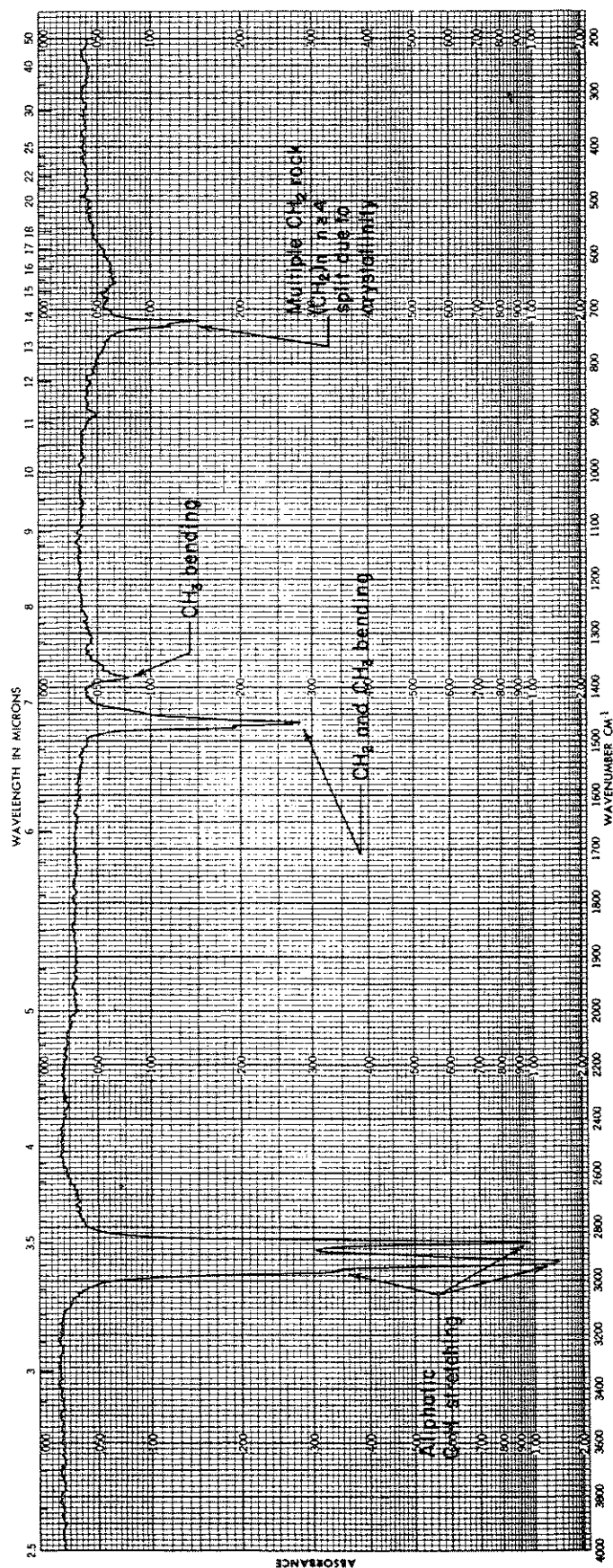


Figure 19—Infrared Spectrum for Negative Interpretation

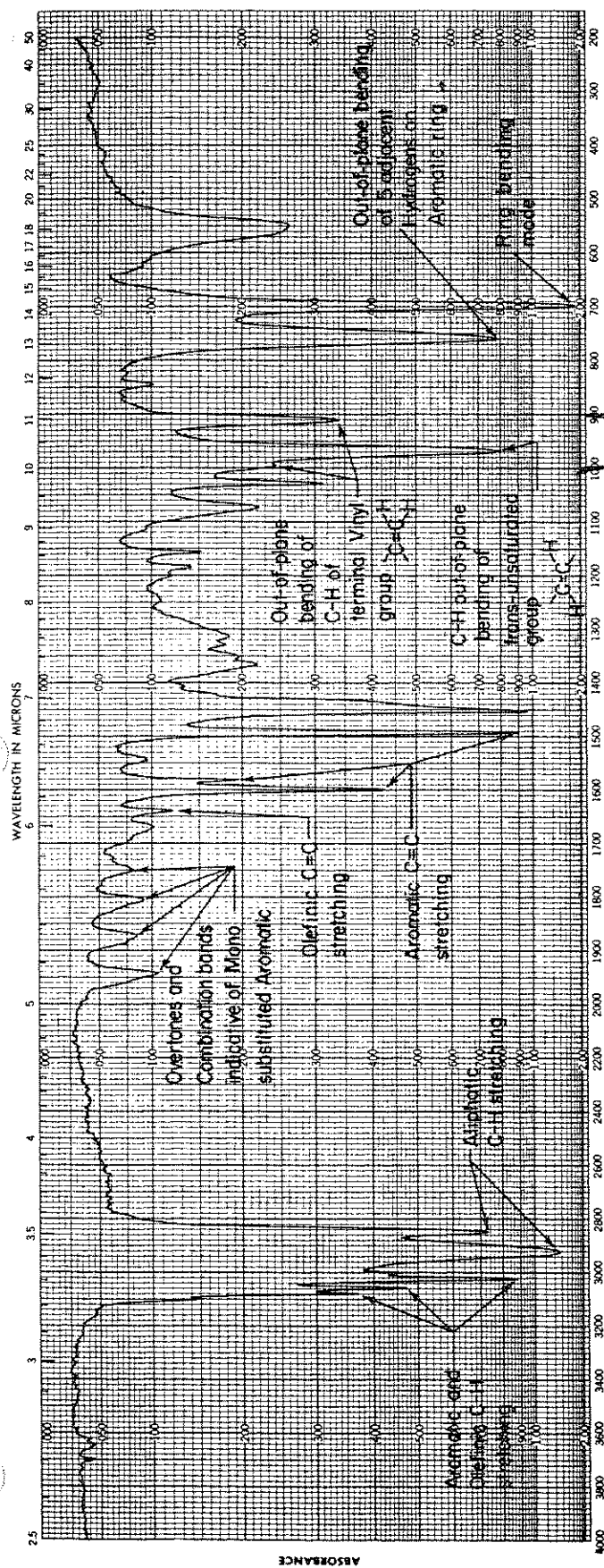
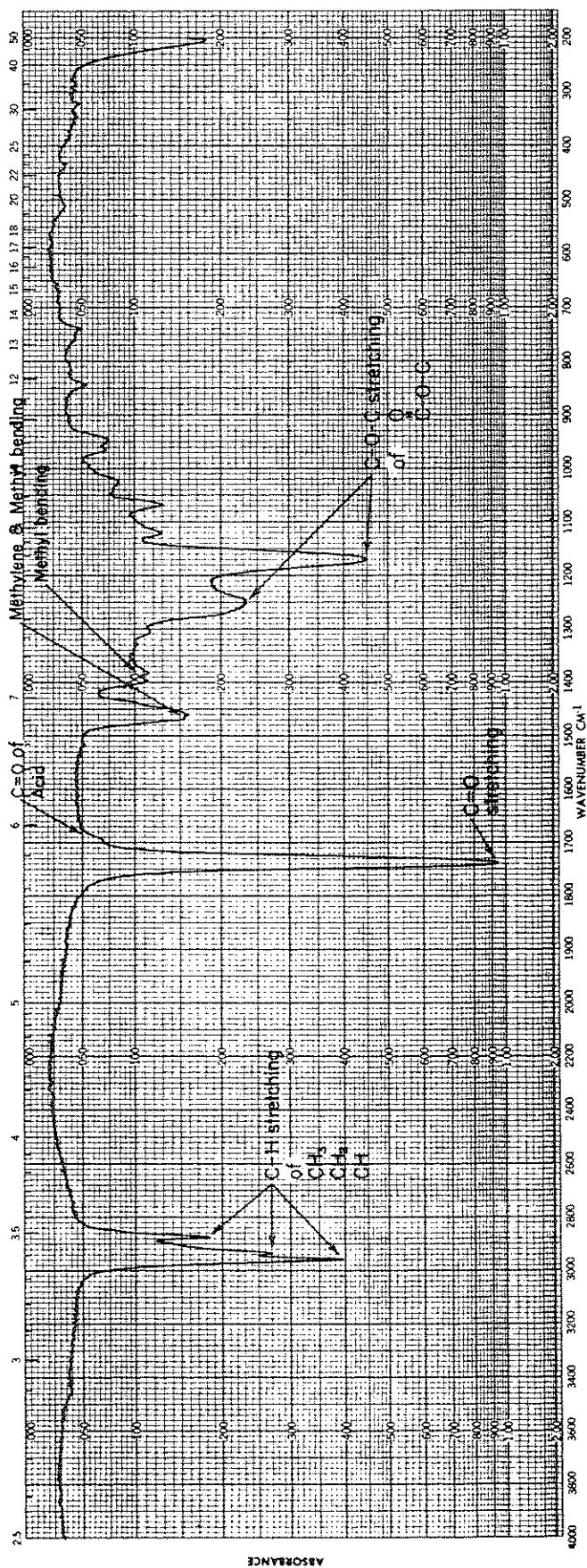


Figure 20—Infrared Spectrum for Positive Interpretation



due to methyl bending, but it should be noted that it is more intense than most methyl bendings and more intense than the methylene bending at 1470 cm^{-1} . This band is intensified since the methyl

group is attached directly to the carbonyl ($\text{CH}_3\text{-}\overset{\text{O}}{\parallel}\text{C-}$) and indicates the presence of an acetate ester. The bands from 700 to 600 cm^{-1} are also characteristic of an acetate ester; the band at 605 cm^{-1} is due to a bending vibration of the acetate group.

When comparing the spectra of poly(vinyl acetate) with an acrylic, several differences can be observed. Since acrylics do not have methyl groups adjacent to the carbonyl, the methyl bending at 1370 cm^{-1} is less intense than the methylene bending at 1465 cm^{-1} . This is not the case with poly(vinyl ace-

tate). Also, the $\overset{\text{O}}{\parallel}\text{C-O-CH-}$ stretching is shifted to 1170 cm^{-1} from 1020 cm^{-1} and its intensity is increased. With copolymers of poly(vinyl acetate) containing small modifications of acrylic, the only indication of acrylic is the 1170 cm^{-1} band which appears as a shoulder on the 1240 cm^{-1} band of the poly(vinyl acetate).

(b) O-PHTHALIC ALKYDS AND POLYESTERS: While it is normally very easy to recognize alkyds and polyesters from their infrared spectra, the identification of all of the monomers used in their preparation is usually impossible.

In the spectrum of a simple o-phthalic alkyd (Figure 23), the strong carbonyl absorption at 1735 cm^{-1} indicates an ester. This is confirmed by the $\overset{\text{O}}{\parallel}\text{C-O-C-}$ stretching vibration at 1275 cm^{-1} . This is not an acetate ester since the intensity of the methyl bending at 1380 cm^{-1} is not enhanced. The intense C-H stretching between 3000 and 2800 cm^{-1} , relative to the carbonyl, indicates that there is a fair amount of hydrocarbon in this molecule. This ratio gives a good indication of the amount of oil modification. This spectrum should be compared with the spectrum of a simple polyester where there is no oil modification (Figure 24). The bands between 3100 and 3000 cm^{-1} are due to unsaturated $=\text{C-H}$ stretching. The band at 1640 cm^{-1} confirms olefinic unsaturation due to the oil. There is also aromatic unsaturation which can be confirmed by the 1600 , 1500 , and 1490 cm^{-1} bands due to the $\text{C}=\text{C}$ vibrations of the aromatic nucleus. The

Table 3—Information Obtained from an Analysis of the Spectrum Shown in Figure 21

Region of Spectrum Being Examined	Positive Information	Negative Information
4000 cm^{-1} to 3100 cm^{-1}	None (The band at 3460 cm^{-1} is an overtone)	No absorption indicates no NH or OH
3100 cm^{-1} to 3000 cm^{-1}	None	No aromatic $\text{C}=\text{C-H}$ or olefinic $\text{C}=\text{C-H}$ structure
3000 cm^{-1} to 2800 cm^{-1}	Methyl, methylene and/or methine C-H stretching	None
2300 cm^{-1} to 1900 cm^{-1}	None	No $\text{x}=\text{y}$ or $\text{x}=\text{y}=\text{z}$ No $\text{C}\equiv\text{N}$ or $\text{N}=\text{C}=\text{O}$
1900 cm^{-1} to 1750 cm^{-1}	None	No anhydride, cyclic imide, or lactone
1750 cm^{-1} to 1690 cm^{-1}	Band at 1740 cm^{-1} due to $\text{C}=\text{O}$ stretching; possibly ester. Small shoulder $\text{C}=\text{O}$ stretching possibly carboxylic acid	None
1680 cm^{-1} to 1620 cm^{-1}	None	No amide $\text{C}=\text{O}$ or olefinic $\text{C}=\text{C}$ stretching
1620 cm^{-1} to 1580 cm^{-1}	None	No aromatic $\text{C}=\text{C}$ stretching
1520 cm^{-1} to 1470 cm^{-1}	None	Same as above
1470 cm^{-1} to 1400 cm^{-1}	Methyl or methylene bending	None
1400 cm^{-1} to 1300 cm^{-1}	Methyl bending	No 1360 and 1380 cm^{-1} band, therefore, gem-dimethyl, isopropyl or tertiary butyl are absent.
1270 cm^{-1} to 1150 cm^{-1}	$\overset{\text{O}}{\parallel}\text{C-O-C}$ stretching of aliphatic esters like acrylic	None
1140 cm^{-1} to 1080 cm^{-1}	None	No strong band, therefore, little indication of any aliphatic ether (C-O-C).
1080 cm^{-1} to 650 cm^{-1}	Many small bands, but since aromatic and olefinic absorption have been eliminated, these are most likely other less intense absorptions of the ester. These bands can be used as a fingerprint when compared with spectra of known esters.	None

