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VIBRATIONAL SPECTROSCOPIES AND NMR

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8.0 INTRODUCTION

In this chapter, three methods for measuring the frequencies of the vibrations of chemical bonds between atoms in solids are discussed. Two of them, Fourier Transform Infrared Spectroscopy, FTIR, and Raman Spectroscopy, use infrared (IR) radiation as the probe. The third, High-Resolution Electron Energy-Loss Spectroscopy, HREELS, uses electron impact. The fourth technique, Nuclear Magnetic Resonance, NMR, is physically unrelated to the other three, involving transitions between different spin states of the atomic nucleus instead of bond vibrational states, but is included here because it provides somewhat similar information on the local bonding arrangement around an atom.

The most commonly used of these methods, and the most inexpensive, is FTIR. In it a broad band source of IR radiation is reflected from the sample (or transmitted, for thin samples). The wavelengths at which absorption occurs are identified by measuring the change in intensity of the light after reflection (transmission) as a function of wavelength. These absorption wavelengths represent excitations of vibrations of the chemical bonds and are specific to the type of bond and the group of atoms involved in the vibration. IR spectroscopy as a method of quantitative chemical identification for species in solution, or liquids, has been commercially available for 50 years. The advent of fast Fourier transform methods in conjunction with interferometer wavelength detection schemes in the last 15 years has allowed

drastic improvement in resolution, sensitivity, and reliable quantification. During this time the method has become regularly used also for solids. The sensitivity toward different bonds (chemical groups) is extremely variable, going from zero (no coupling of the IR radiation to vibrational excitations because of dipole selection rules) to high enough to detect submonolayer quantities. Intensities and line shapes are also sensitive to local solid state effects, such as stress, strain, and defects (which can therefore be characterized), so quantification is difficult, but with suitable standards 5–10% accuracy in concentrations are achievable. The depth probed depends strongly on the material (whether it is transparent or opaque to IR radiation) and can be as little as 100 Å or as much as 1 mm. The chemical nature of opaque interfaces beneath transparent overlayers can therefore be studied. Grazing angle measurements greatly reduce the probing depth, restricting it to a monolayer for molecules absorbed on metal surfaces. Often there is no spatial resolution (mm), but microfocus systems down to 20 μm exist. In Raman spectroscopy IR radiation of a single wavelength from a laser strikes the sample and the energy losses (gains) due to the Raman scattering process, which lead to some light being reemitted at lower (higher) frequencies, are determined. These loss (or gain) processes are again due to the coupling of the vibrational processes in the sample with the incident IR radiation. So, though the physics of the Raman process is quite different from that of IR spectroscopy (scattering instead of absorption), the information content is very similar. The selection rules defining which vibrational modes can be excited are different from IR, however, so Raman essentially provides complementary information. Cross sections for Raman scattering are extremely weak, resulting in Raman sensitivity being about a factor of 10 lower than for FTIR. However, better spatial resolution can be achieved (down to a few μm) because the single wavelength nature of the laser source allows an easy coupling to optical microscope elements. For the “fingerprinting” identification of chemical composition not nearly so extensive a library of data is available as for IR spectroscopy. Because of this, and because instrumentation is generally more expensive, Raman spectroscopy is less widely used, except where the microfocus capabilities are important or where differences in selection rules are critical.

Both IR and Raman have the great practical advantage of working in ambient atmosphere, and one can even study interfaces through liquids. The third vibrational technique discussed here, HREELS, requires ultrahigh vacuum conditions. A monochromatic, low-energy electron beam (a few eV) is reflected from a sample surface, losing energy by exciting vibrations (cf., Raman scattering) as it does so. Since the reflected part of the beam does not penetrate the surface, the vibrational information obtained relates only to the outermost layers. Actually two separate scattering mechanisms occur. Scattering in the specular direction is a long-range dipole process that has the same selection rules as for IR. Impact scattering is short range and nonspecular. It is an order of magnitude weaker than dipole scattering and has relaxed selection rules. Taking data in both the specular and off-specular

directions therefore maximizes the amount of information obtainable. The wavelength range accessible is wider in HREELS than in IR spectroscopy, but the resolution is orders of magnitude poorer, leading to overlapped vibrational peaks and little detailed information on individual line shapes. The major uses of HREELS have been identifying chemical species, adsorption sites, and adsorption geometries (symmetry) for monolayer adsorption at single crystal surfaces. For non-single crystal surfaces the energy-loss intensities are drastically reduced, but the technique is still useful. It has been quite extensively used for characterizing polymer surfaces. For insulators charging can sometimes be a problem.

The last technique discussed here, NMR, involves immersing the sample in a strong magnetic field (1–12 Tesla), thereby splitting the degeneracy of the spin states of those nuclei that have either an odd mass or odd atomic number and hence possess a permanent magnetic moment. About half the elements in the periodic table have isotopes fulfilling these conditions. Excitation between these magnetic levels is then performed by absorption of radiofrequency (RF) radiation. By measuring the energy at which the absorptions occur (the “resonance” energies) the energy differences between the spin (magnetic) states are determined. For any given magnetic field the values are element specific, but the nuclear magnetic moments and electronic environment surrounding the target atoms also exert an influence, splitting the absorption resonances into multiple lines and shifting peak positions. From these effects the local environment of the atoms concerned—the coordination number, local symmetries, the nature of neighboring chemical groups, and bond distances—can be studied. H-atom NMR has been used as an analytical tool for molecules in liquids for about 40 years to identify chemical groupings, and the sequence of groupings containing H atoms. It is also, of course, the basis of Magnetic Resonance Imaging, MRI, which is used medically. In the solid state, crystalline phases can be identified, and quantitative analysis can be achieved directly in mixtures from the relative intensities of peaks and the use of well-defined model compound standards. In many cases the NMR spectra of solids are rather broad and unresolved due to strong anisotropic effects with respect to the applied magnetic field. There are a number of ways of removing these effects, the most popular being magic-angle spinning of the sample, which can collapse broad powder patterns into sharp resonances that can be easily assigned. NMR is intrinsically a bulk technique; the signal comes from the entire sample which is immersed in the magnetic field. At least 10 mg of material is required (powders, thin films, or crystals), and to get any information specific to surfaces or interfaces requires large surface areas (10–150 m²/gm). Costs vary a lot (\$200,000 to \$1,200,000), depending on how wide a range of elements needs to be accessed, since this determines the range and magnitude of the magnetic fields and RF capabilities required.

8.1 FTIR

Fourier Transform Infrared Spectroscopy

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- Introduction
- Basic Principles
- Methodologies and Accessories
- Interferences and Artifacts
- Conclusions

Introduction

The physical principles underlying infrared spectroscopy have been appreciated for more than a century. As one of the few techniques that can provide information about the chemical bonding in a material, it is particularly useful for the nondestructive analysis of solids and thin films, for which there are few alternative methods. Liquids and gases are also commonly studied, more often in conjunction with other techniques. Chemical bonds vary widely in their sensitivity to probing by infrared techniques. For example, carbon-sulfur bonds often give no infrared signal, and so cannot be detected at any concentration, while silicon-oxygen bonds can produce signals intense enough to be detected when probing submonolayer quantities, or on the order of 10^{13} bonds/cc. Thus, the potential utility of infrared spectrophotometry (IR) is a function of the chemical bond of interest, rather than being applicable as a generic probe. For quantitative analysis, modern instrumentation can provide a measurement repeatability of better than 0.1%. Accuracy and precision, however, are more commonly on the order of 5.0% (3σ), relative. The limitations arise from sample-to-sample variations that modify the optical quality of the material. This causes slight, complex distortions of the spectrum that are dif-

difficult to eliminate. Sensitivity of the sample to environmental influences that modify the chemical bonding and the need to calibrate the infrared spectral data to reference methods—such as neutron activation, gravimetry, and wet chemistry—also tend to degrade slightly the measurement for quantitative work.

The goal of the basic infrared experiment is to determine changes in the intensity of a beam of infrared radiation as a function of wavelength or frequency (2.5–50 μm or 4000–200 cm^{-1} , respectively) after it interacts with the sample. The centerpiece of most equipment configurations is the infrared spectrophotometer. Its function is to disperse the light from a broadband infrared source and to measure its intensity at each frequency. The ratio of the intensity before and after the light interacts with the sample is determined. The plot of this ratio versus frequency is the *infrared spectrum*.

As technology has progressed over the last 50 years, the infrared spectrophotometer has passed through two major stages of development. These phases have significantly impacted how infrared spectroscopy has been used to study materials. Driven in part by the needs of the petroleum industry, the first commercial infrared spectrophotometers became available in the 1940s. The instruments developed at that time are referred to as *spatially dispersive* (sometimes shortened to *dispersive*) instruments because ruled gratings were used to disperse spatially the broadband light into its spectral components. Many such instruments are still being built today. While somewhat limited in their ability to provide quantitative data, these dispersive instruments are valued for providing qualitative chemical identification of materials at a low cost. The 1970s witnessed the second phase of development. A new (albeit much more expensive) type of spectrophotometer, which incorporated a Michelson interferometer as the dispersing element, gained increasing acceptance. All frequencies emitted by the interferometer follow the same optical path, but differ in the time at which they are emitted. Thus these systems are referred to as being *temporally dispersive*. Since the intensity-time output of the interferometer must be subjected to a Fourier transform to convert it to the familiar infrared spectrum (intensity-frequency), these new units were termed Fourier Transform Infrared spectrophotometers, (FTIR). Signal-to-noise ratios that are higher by orders of magnitude, much better resolution, superior wavelength accuracy, and significantly shorter data acquisition times are gained by switching to an interferometer. This had been recognized for several decades, but commercialization of the equipment had to await the arrival of local computer systems with significant amounts of cheap memory, advances in equipment interfacing technology, and developments in fast Fourier-transform algorithms and circuitry.

Beyond the complexities of the dispersive element, the equipment requirements of infrared instrumentation are quite simple. The optical path is normally under a purge of dry nitrogen at atmospheric pressure; thus, no complicated vacuum pumps, chambers, or seals are needed. The infrared light source can be cooled by water. No high-voltage connections are required. A variety of detectors are avail-

able, with deuterated tri-glycene sulfate (DTGS) detectors offering a good signal-to-noise ratio and linearity when operated at room temperature. For more demanding applications, the mercury cadmium telluride (HgCdTe, or mer-cad telluride) detector, cooled by liquid nitrogen, can be used for a factor-of-ten gain in sensitivity.

With the advent of FTIR instrumentation, IR has experienced a dramatic increase in applications since the 1970s, especially in the area of quantitative analysis. FTIR spectrophotometry has grown to dominate the field of infrared spectroscopy. Experiments in microanalysis, surface chemistry, and ultra-thin films are now much more routine. The same is true for interfaces, if the infrared characteristics of the exterior layers are suitable. While infrared methods still are rarely used to profile composition as a function of depth, microprobing techniques available with FTIR technology permit the examination of microparticles and *xy*-profiling with a spatial resolution down to 20 μm . Concurrent with opening the field to new areas of research, the high level of computer integration, coupled with robust and nondestructive equipment configurations, has accelerated the move of the instrument out of the laboratory. Examples are in VLSI, computer-disk, and chemicals manufacturing, where it is used as a tool for thin-film, surface coating, and bulk monitors.

Unambiguous chemical identification usually requires the use of other techniques in conjunction with IR. For gases and liquids, Mass Spectrometry (MS) and Nuclear Magnetic Resonance Spectrometry (NMR) are routinely employed. The former, requiring only trace quantities of material, determines the masses of the molecule and of characteristic fragments, which can be used to deduce the most likely structure. MS data is sometimes supplemented with infrared results to distinguish certain chemical configurations that might produce similar fragment patterns. NMR generally requires a few milliliters of sample, more than needed by either the FTIR or MS techniques, and can identify chemical bonds that are associated with certain elements, bonds that are adjacent to each other, and their relative concentrations. Solids can also be studied by these methods. For MS, the sensitivity remains high, but the method is destructive because the solid must somehow be vaporized. While nondestructive, the sensitivity of NMR spectrometry is typically much lower for direct measurements on solids; otherwise, the solid may be taken into solution and analyzed. For thin films, both the MS and NMR methods are destructive. Complementary data for surfaces, interfaces, and thin films can be obtained by techniques like X-ray photoelectron spectroscopy, static secondary ion mass spectrometry, and electron energy loss spectrometry. These methods probe only the top few nanometers of the material. Depending upon the sample and the experimental configuration, IR may be used as either a surface or a bulk probe for thin films. For surface analysis, FTIR is about a factor of 10 less sensitive than these alternative methods. Raman spectroscopy is an optical technique that is complementary to infrared methods and also detects the vibrational motion of chemical bonds. While able to achieve submicron spatial resolution, the sensitivity of the

Raman technique is usually more than an order of magnitude less than that of FTIR.

As a surface probe, FTIR works best when the goal is to study a thin layer of material on a dissimilar substrate. Lubricating oil on a metal surface and thin oxide layers on semiconductor surfaces are examples. FTIR techniques become more difficult to apply when the goal is to examine a surface or layer on a similar substrate. An example would be the study of thin skins or surface layers formed during the curing cycles used for photoresist or other organic thin films deposited from the liquid phase. If the curing causes major changes in the bulk and the surface, FTIR methods usually cannot discriminate between them, because the beam probes deeply into the bulk material. The limitations as a surface probe often are dictated by the type of substrate being used. A metal or high refractive-index substrate will reflect enough light to permit sensitive probing of the surface region. A low refractive index substrate, in contrast, will permit the beam to probe deeply into the bulk, degrading the sensitivity to the surface.

The discussions presented in this article pertain to applications of FTIR, because most of the recent developments in the field have been attendant to FTIR technology. In many respects, FTIR is a "science of accessories". A myriad of sample holders, designed to permit the infrared light to interact with a given type of sample in an appropriate manner, are interfaced to the spectrophotometer. A large variety of "hyphenated" techniques, such as GC-FTIR (gas chromatography-FTIR) and TGA-FTIR (thermo-gravimetric analysis-FTIR), also are used. In these cases, the effluent emitted by the GC, TGA, or other unit is directed into the FTIR system for time-dependent study. Hyphenated methods will not be discussed further here. Still, common to all of these methods is the goal of obtaining and analyzing an infrared spectrum.

Basic Principles

Infrared Spectrum

Define I_0 to be the intensity of the light incident upon the sample and I to be the intensity of the beam after it has interacted with the sample. The goal of the basic infrared experiment is to determine the intensity ratio I/I_0 as a function of the frequency of the light (ω). A plot of this ratio versus the frequency is the infrared spectrum. The infrared spectrum is commonly plotted in one of three formats: as transmittance, reflectance, or absorbance. If one is measuring the fraction of light transmitted through the sample, this ratio is defined as

$$T_{\omega} = \left(\frac{I_t}{I_0} \right)_{\omega} \quad (1)$$

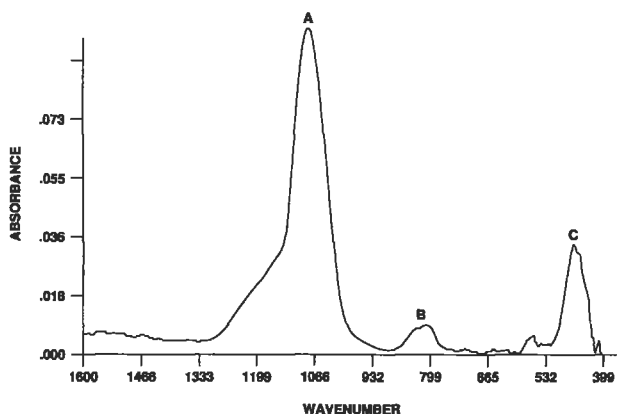


Figure 1 The FTIR spectrum of the oxide of silicon (thin film deposited by CVD). Primary features: (a), asymmetric stretching mode of vibration; (b), bending mode of vibration; (c), rocking mode of vibration.

where T_w is the transmittance of the sample at frequency w , and I_t is the intensity of the transmitted light. Similarly, if one is measuring the light reflected from the surface of the sample, then the ratio is equated to R_w , or the reflectance of the spectrum, with I_t being replaced with the intensity of the reflected light I_r . The third format, absorbance, is related to transmittance by the Beer-Lambert Law:

$$A_w = -\log T_w = (\epsilon_w) (bc) \quad (2)$$

where c is the concentration of chemical bonds responsible for the absorption of infrared radiation, b is the sample thickness, and ϵ_w is the frequency-dependent absorptivity, a proportionality constant that must be experimentally determined at each w by measuring the absorbance of samples with known values of bc . As a first-order approximation the Beer-Lambert Law provides a simple foundation for quantitating FTIR spectra. For this reason, it is easier to obtain quantitative results if one collects an absorbance spectrum, as opposed to a reflectance spectrum. Prior to the introduction of FTIR spectrophotometers, infrared spectra were usually published in the transmittance format, because the goal of the experiment was to obtain qualitative information. With the growing use of FTIR technology, a quantitative result is more often the goal. Today the absorbance format dominates, because to first order it is a linear function of concentration.

Qualitative and Quantitative Analysis

Figure 1 shows a segment of the FTIR absorbance spectrum of a thin film of the oxide of silicon deposited by chemical vapor deposition techniques. In this film, sil-

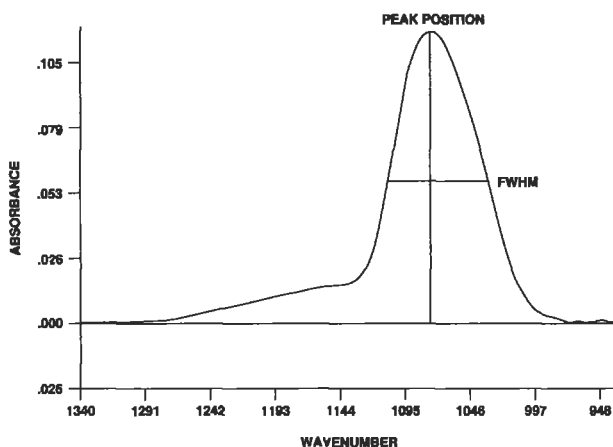


Figure 2 Spectral parameters typically used in band shape analysis of an FTIR spectrum: peak position, integrated peak area, and FWHM.

icon is tetrahedrally coordinated with four bridging oxygen atoms. Even though the bond angles are distorted slightly to produce the random glassy structure, this spectrum is quite similar to that obtained from crystalline quartz, because most features in the FTIR spectrum are the result of nearest neighbor interactions. In crystalline materials the many vibrational modes can be classified by the symmetry of their motions and, while not rigorous, these assignments can be applied to the glassy material, as well. Thus the peak near 1065 cm^{-1} arises from the asymmetric stretching motions of the Si and O atoms relative to each other. The band near 815 cm^{-1} arises from bending motions, while the one near 420 cm^{-1} comes from a collective rocking motion. These are not the only vibrational modes for the glass, but they are the only ones that generate electric dipoles that are effective in coupling with the electromagnetic field. For example, the glass also has a symmetric stretching mode, but since it generates no net dipole, no absorption band appears in the FTIR spectrum. For more quantitative work, the fundamental theory of infrared spectroscopy delineates a band shape analysis illustrated in Figure 2. Three characteristics are commonly examined: peak position, integrated peak intensity, and peak width.

Peak position is most commonly exploited for qualitative identification, because each chemical functional group displays peaks at a unique set of characteristic frequencies. The starting point for such a functional-group analysis is a table or computer database of peak positions and some relative intensity information. This provides a fingerprint that can be used to identify chemical groups. Thus the three peaks just described for the oxide of silicon can be used to identify that material. Typical of organic materials, C–H bonds have stretching modes around 3200 cm^{-1} ; C=O, around 1700 cm^{-1} . Thus, the composition of oils may be qualitatively identified by classifying these and other peak positions observed in the spectrum. In

addition, some bands have positions that are sensitive to physicochemical properties. As a result, applied and internal pressures, stresses, and bond strain due to swelling can be studied.

The Beer-Lambert Law of Equation (2) is a simplification of the analysis of the second-band shape characteristic, the integrated peak intensity. If a band arises from a particular vibrational mode, then to the first order the integrated intensity is proportional to the concentration of absorbing bonds. When one assumes that the area is proportional to the peak intensity, Equation (2) applies.

In solids and liquids, peak width—the third characteristic—is a function of the homogeneity of the chemical bonding. For the most part, factors like defects and bond strain are the major sources of band width, usually expressed as the full width at half maximum (FWHM). This is due to the small changes these factors cause in the strengths of the chemical bonds. Small shifts in bond strengths cause small shifts in peak positions. The net result is a broadening of the absorption band. The effect of curing a material can be observed by peak-width analysis. As one anneals defects the bands become narrower and more intense (to conserve area, if no bonds are created or destroyed). Beyond the standard analysis, higher order band shape properties may also be examined, such as peak asymmetry. For example, the apparent shoulder on the high-frequency side of the band in Figure 2 may be due to a second band that overlaps the more prominent feature.

For many applications, quantitative band shape analysis is difficult to apply. Bands may be numerous or may overlap, the optical transmission properties of the film or host matrix may distort features, and features may be indistinct. If one can prepare samples of known properties and collect the FTIR spectra, then it is possible to produce a calibration matrix that can be used to assist in predicting these properties in unknown samples. Statistical, chemometric techniques, such as PLS (partial least-squares) and PCR (principle components of regression), may be applied to this matrix. Chemometric methods permit much larger segments of the spectra to be comprehended in developing an analysis model than is usually the case for simple band shape analyses.

Methodologies and Accessories

A large number of methods and accessories have been developed to permit the infrared source to interact with the sample in appropriate ways. Some of the more common approaches are listed below.

Single-pass transmission

The direct transmission experiment is the most elegant and yields the most quantifiable results. The beam makes a single pass through the sample before reaching the detector. The bands of interest in the absorbance spectrum should have peak absorbances in the range of 0.1–2.0 for routine work, although much weaker or stronger bands can be studied. Various holders, pellet presses, and liquid cells have been

developed to permit samples to be prepared with the appropriate path length. *Diamond anvil cells* permit pliable samples to be squeezed to extremely thin path lengths or to be studied under applied pressures. Long path-length cells are used for samples in the gas phase. Thin films and prepared surfaces can be studied by transmission if the supporting substrate is transparent to the infrared. The highest sensitivity is obtained with double-beam or pseudo-double-beam experimental configurations. An example of the latter is the *interleaf* experiment, where a single beam is used, but a sample and reference are alternately shuttled into and out of the beam path.

Reflection

If the sample is inappropriate for a transmission experiment, for instance if the supporting substrate is opaque, a reflectance configuration will often be employed. Accessories to permit specular, diffuse, variable-angle, and grazing-incidence experiments are available. The angle of incidence can be adjusted to minimize multiple-reflection interferences by working at the Bragg angle for thin films, or to enhance the sensitivity of the probe to surface layers. A subset of this technique, Reflection Absorption (RA) spectroscopy, is capable of detecting submonolayer quantities of materials on metal surfaces. These grazing and RA techniques can enhance surface sensitivities by using geometries that optimize the coupling of the electromagnetic field at the metal surface. In some instances it has been possible to deduce preferred molecular orientations of ordered monolayers.

Attenuated Total Reflection

In this configuration an Attenuated Total Reflection (ATR) crystal is used, illustrated in Figure 3. The infrared beam is directed into the crystal. Exploiting the principles of a waveguide, the change in refractive index at the crystal surface causes the beam to be back-reflected several times as it propagates down the length of the crystal before it finally exits to the detector. If the sample is put into contact with the crystal surface, the beam will interact weakly with the sample at several points. For extremely thin samples, this is a means of increasing the effective path length. Since the propagating beam in the crystal barely penetrates through the surface of the sample adjacent to the crystal, signals at a sample surface can be enhanced, as well. This also helps in the study of opaque samples. Approximately fivefold amplifications in signals are typical over a direct transmission experiment. The quality of the crystal-sample interface is critical, and variability in that interface can make ATR results very difficult to quantify.

Emission

When samples are heated, they emit infrared radiation with a characteristic spectrum. The IR emission of ceramics, coals, and other complicated solids and thin films can be studied. Also, if conditions make it difficult to use an infrared source

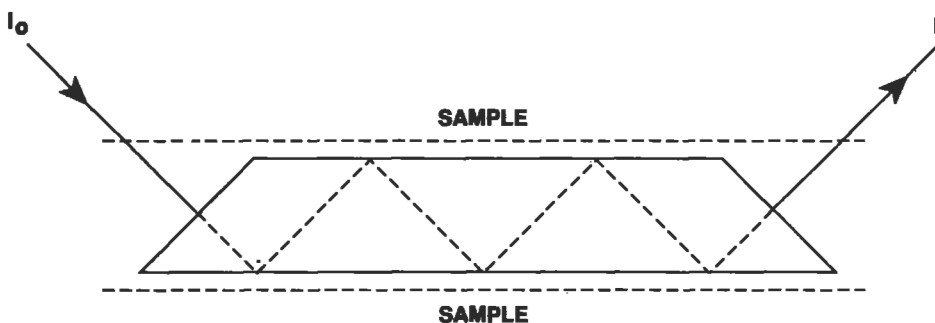


Figure 3 Typical beam path configuration for collecting an FTIR spectrum using an attenuated total reflectance element: I_0 is the incident infrared beam, I is the exiting beam.

(such as an *in situ* measurement of a thin film in the deposition chamber) but permit the controlled heating of a sample, then emission methods provide a means of examining these materials.

Microscopy

Infrared microscopes can focus the beam down to a 20- μm spot size for microprobing in either the transmission or reflection mode. Trace analysis, microparticle analysis, and spatial profiling can be performed routinely.

Interferences and Artifacts

Equipment

Equipment technology and processing software for FTIR are very robust and provide a high degree of reliability. Concerns arise for only the most demanding applications. For quantitative work on an isolated feature in the spectrum, the rule of thumb is that the spectrometer resolution be one-tenth the width of the band. FTIR instruments routinely meet that requirement for solids.

Short- and long-term drift in the spectral output can be caused by several factors: drift in the output of the infrared light source or of the electronics, aging of the beam splitter, and changes in the levels of contaminants (water, CO_2 , etc.) in the optical path. These problems are normally eliminated by rapid, routine calibration procedures.

The two complicating factors that are encountered most frequently are the linearity of detector response and stray light scattering at low signal levels. DTGS

detectors are quite linear and reliable, while MCT detectors can saturate at relatively low light levels. Stray light can make its way to the detector and be erroneously detected as signal, or it can be backscattered into the interferometer and degrade its output. A problem only at very low signal levels or with very reflective surfaces, proper procedures can minimize these effects.

Intrinsic or Matrix

Few cross sections for infrared absorption transitions have been published and typically they are not broadly applicable. The strength of the absorption depends upon changes in the dipole moment of the material during the vibrational motion of the constituent atoms. However, these moments are also very sensitive to environmental factors, such as nearest neighbor effects, that can cause marked changes in the infrared spectrum. For example, carbon–halogen bonds have a stretching mode that may be driven from a being very prominent feature to being an undetectable feature in the spectrum by adding electron-donating or -withdrawing substituents as nearest neighbors. For careful quantitative work, then, model compounds that are closely representative of the material in question are often needed for calibration.

Interface Optical Effects

For thin-film samples, abrupt changes in refractive indices at interfaces give rise to several complicated *multiple reflection* effects. Baselines become distorted into complex, sinusoidal, fringing patterns, and the intensities of absorption bands can be distorted by multiple reflections of the probe beam. These artifacts are difficult to model realistically and at present are probably the greatest limiters for quantitative work in thin films. Note, however, that these interferences are functions of the complex refractive index, thickness, and morphology of the layers. Thus, properly analyzed, useful information beyond that of chemical bonding potentially may be extracted from the FTIR spectra.

Many materials have grain boundaries or other microstructural features on the order of a micrometer or greater. This is on the same scale as the wavelength of the infrared radiation, and so artifacts due to the wavelength-dependent scattering of light at these boundaries can be introduced into the spectra. Thin films, powders, and solids with rough surfaces are the most affected. Again these artifacts are difficult to realistically model, but properly analyzed can provide additional information about the sample.

Conclusions

The principles of infrared spectroscopy can be exploited to extract information on the chemical bonding of an extremely wide variety of materials. The greatest strength of the technique is as a nondestructive, bulk probe of glassy and amor-

phous materials, where few alternate methods exist for obtaining chemical information. For other materials, FTIR is a valuable member in the arsenal of characterization tools. Other methods that are most likely to provide similar information include raman spectroscopy, X-ray photoelectron spectroscopy, NMR, MS, SIMS, and high-resolution electron energy-loss spectroscopy. The nondestructive, noninvasive potential of the infrared technique, and its ease of use, continues to distinguish it from these other methods, with the exception of Raman spectroscopy.

The trends begun with the general introduction of FTIR technology will undoubtedly continue. It is safe to say that the quality of the data being produced far exceeds our ability to analyze it. In fact, for many current applications, the principle limitations are not with the equipment, but rather with the quality of the samples. Thus, the shift from qualitative to quantitative work will proceed, reaching high levels of sophistication to address the optical and matrix interference problems discussed above.

With extensive computerization, the ease of use, and the robustness of equipment, movement of the instrumentation from the research laboratory to the manufacturing environment, for application as *in situ* and at-line monitors, will continue. *In situ* work in the research laboratory will also grow. New environments for application appear every day and improved computer-based data processing techniques make the rapid analysis of large sets of data more commonplace. These developments, coupled with rapid data acquisition times, are making possible the timely evaluation of the results of large-scale experiments. Most likely, much of the new physicochemical information developed by applying FTIR technology will come from trends observed in detailed studies of these large sample data sets.

Related Articles in the Encyclopedia

Raman Spectroscopy and HREELS

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8.2 Raman Spectroscopy

WILLIAM B. WHITE

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Introduction

To a surprisingly accurate approximation, molecules and crystals can be thought of as systems of balls (atoms) connected by springs (chemical bonds). These systems can be set into vibration, and vibrate with frequencies determined by the mass of the balls (atomic weights) and by the stiffness of the springs (bond force constants). Diatomic molecules (O_2 , CO , HCl , etc.) having two balls connected by a single spring have only one fundamental vibrational frequency. The same is true for diatomic crystals, which have a single diatomic formula unit in the primitive unit cell (NaCl , ZnS , diamond, etc.), although the details are more complicated. The number of possible vibrational motions is $3n-6$ for nonlinear molecules and $3n-3$ for crystals, where n is the number of atoms in the molecule or in the primitive unit cell of the crystal. The mechanical molecular and crystal vibrations are at very high frequencies, in the range 10^{12} – 10^{14} Hz (3–300 μm wavelength), which places them in the infrared (IR) region of the electromagnetic spectrum. Coupling between incident infrared radiation and the electronic structure of the chemical bond produces the infrared absorption spectrum as a direct means of observing molecular

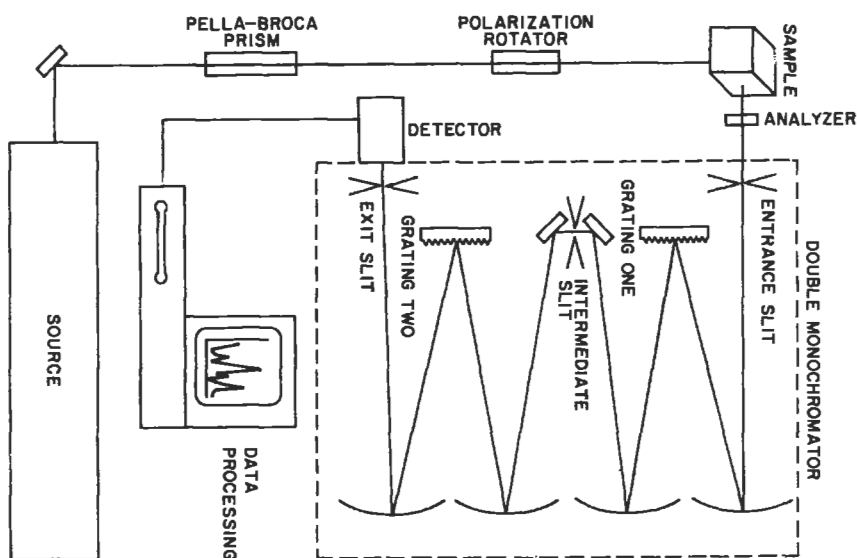


Figure 1 Drawing of single-channel Raman spectrometer showing Czerny–Turner type double monochromator. Collecting optics for scattered beam are not shown.

and crystal vibrations (see the article on FTIR). The Raman spectrum arises from an indirect coupling of high-frequency radiation (usually visible light, but also ultraviolet and near infrared) with the electron clouds that make up the chemical bonds. Thus, although both IR absorption and Raman spectroscopy measure the vibrational spectra of materials, the physical processes are different, the selection rules that determine which of the vibrational modes are excited are different, and the two spectroscopies must be considered to be complementary. Both, however, are characterization probes that are sensitive to the details of atomic arrangement and chemical bonding.

Raman spectroscopy is primarily a structural characterization tool. The spectrum is more sensitive to the lengths, strengths, and arrangement of bonds in a material than it is to the chemical composition. The Raman spectrum of crystals likewise responds more to details of defects and disorder than to trace impurities and related chemical imperfections.

Basic Principles

The essentials of the Raman scattering experiment are shown in Figure 1. An intense monochromatic light beam impinges on the sample. The electric field of the incident radiation distorts the electron clouds that make up the chemical bonds in the sample, storing some energy. When the field reverses as the wave passes, the

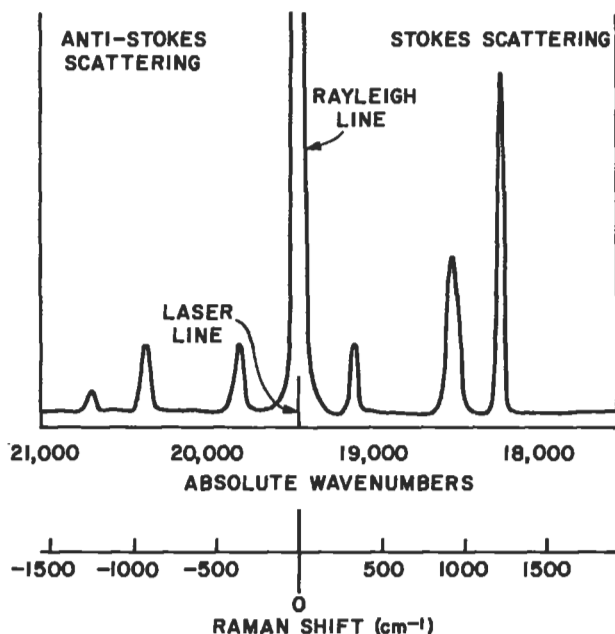


Figure 2 Schematic Raman scattering spectrum showing Rayleigh line, Stokes Raman scattering and anti-Stokes Raman scattering. Note arrangements of wavenumber scales with Rayleigh line defining the zero on the Raman wavenumber scale.

distorted electron clouds relax and the stored energy is reradiated. Although the incident beam may be polarized so that the electric field is oriented in a specific direction with respect to the sample, the scattered beam is reradiated in all directions, making possible a variety of scattering geometries. Most of the stored energy is reradiated at the same frequency as that of the incident exciting light. This component is known as the Rayleigh scattering and gives a strong central line in the scattering spectrum (Figure 2). However, a small portion of the stored energy is transferred to the sample itself, exciting the vibrational modes. The vibrational energies are deducted from the energy of the incident beam and weak side bands appear in the spectrum at frequencies less than that of the incident beam. These are the Raman lines. Their separation from the Rayleigh line is a direct measure of the vibrational frequencies of the sample.¹

The reverse process also occurs. Existing vibrations that have been excited by thermal processes, can be annihilated by coupling with the incident beam and can add their energies to that of the source. These appear as side bands at higher wavenumbers. The Raman process that excites molecular and crystal vibrations is called Stokes scattering; the process that annihilates existing vibrations is called anti-Stokes scattering. The two spectra are mirror images on opposite sides of the Ray-

leigh line (Figure 2). However, because anti-Stokes scattering depends on the existence of thermally activated vibrations, the anti-Stokes intensities are strongly temperature dependent, whereas the Stokes intensities are only weakly temperature dependent. For this reason, anti-Stokes scattering is rarely measured, except for the specialized technique known as *coherent anti-Stokes Raman spectroscopy*.² Because the vibrational frequencies are measured by differences between the frequency of the Raman line and the Rayleigh line, most spectrometers are set up to display the difference frequency (wavenumber) directly, defining the exciting frequency as 0. The result sometimes causes confusion: as the displayed Raman wavenumber increases, the true wavenumber decreases. The Raman effect is extremely weak. Rayleigh scattering from optically transparent samples is on the order of 10^{-3} – 10^{-5} of the intensity of the exciting line. Raman scattering is from 10^{-3} to 10^{-6} of the intensity of the Rayleigh line. For this reason Raman spectroscopy prior to the 1960s was a highly specialized measurement carried out in a few laboratories mainly with mercury discharge lamp sources, fast prism spectrographs, and photographic plate detectors. In such equipment, the most intense Raman lines are at the threshold of visibility to the darkness-adapted human eye. The invention of continuous gas lasers, which provided the needed intense monochromatic source, and the invention in 1965 of the double monochromator system for stray light discrimination combined to make the modern Raman spectrometer possible.

Instrumentation

Single-Channel Dispersive Instruments

The most widely used equipment for Raman spectroscopy follows the scheme shown in Figure 1. The source is usually a continuous gas laser. The 488-nm and 514.5-nm lines of the argon ion laser are commonly used, although argon has other, somewhat weaker lasing lines that can be used for special purposes. He–Ne lasers (632.8 nm) and the red line of the krypton laser (647.1 nm) also are used. The Raman scattering intensity decreases as the fourth power of the wavelength so that there is an advantage to using the shorter wavelength argon ion lines unless other circumstances, such as sample fluorescence, sample photodecomposition, or the location of the optical absorption edge in semiconductor materials, require a less energetic excitation source. The output from gas lasers is intrinsically polarized so that a polarization rotator is needed to control the polarization orientation with respect to the sample, especially with oriented single-crystal specimens.

The sample holder is indicated by a cube in Figure 1 to show the 90° scattering arrangement. The part of the sample actually measured is a volume, typically 200–500 μm on a side, where the laser beam and the scattered beam intersect. Omitted from the sketch are the focusing optics that collect the scattered light and bring it to a focus on the entrance slit. Many sample mounting arrangements are possible,

depending on the physical state of the sample. An analyzer in front of the entrance slit permits the determination of the polarization of the scattered beam.

The commonly used monochromator is a Czerny–Turner grating type, usually of 1-m focal length, as sketched in Figure 1. This design features two collimating mirrors and a planar grating that is rotated to sweep the spectrum across the exit slit. Because Raman spectra are extremely weak, stray light within the monochromator must be effectively suppressed. The second monochromator, used as a stray light filter, reduces the stray light to the 10^{-12} range, providing a clean background for the Raman spectra.

Photomultipliers are used as detectors in the single-channel instruments. GaAs cathode tubes give a flat frequency response over the visible spectrum to 800 nm in the near IR. Contemporary Raman spectrometers use computers for instrument control, and data collection and storage, and permit versatile displays.

Diode Array and Charge-Coupled Detector Systems

A disadvantage of the single-channel scanning monochromator is that substantial times are needed to collect a spectrum, which is unsatisfactory for transient species, kinetic studies, and observation of unstable compounds. Linear diode array detectors allow the entire spectrum to be captured at one time, although resolution is limited by the number of pixels. Charge-coupled device detector arrays are now used on some commercial spectrometers. These are two-dimensional arrays of detector elements, 578×385 pixels being a common choice. Both diode array and charge-coupled detectors permit the use of pulsed laser sources and provide infrared sensitivity. Nd–YAG lasers operating at a wavelength of $1.06 \mu\text{m}$ can then be used to eliminate many problems of fluorescence and sample photodecomposition.

Fourier Transform Raman Spectrometers

A relatively recent development is the adaptation of Fourier transform spectrometers commonly used for infrared absorption spectroscopy to Raman spectroscopy. Fourier transform Raman spectroscopy has the same advantages as other applications of interferometric techniques. Elimination of the slits greatly increases energy throughput, an important advantage for weak Raman signals. The multiplex advantage permits more rapid accumulation of spectral data, although the alternative of diode array or charge-coupled detectors makes this advantage less important for Raman spectroscopy than for IR spectroscopy.

Sample Requirements

Liquids

Liquids and solutions can be measured in special cells that have optical windows at right angles, or they can be contained in capillary tubes or small vials. The latter are

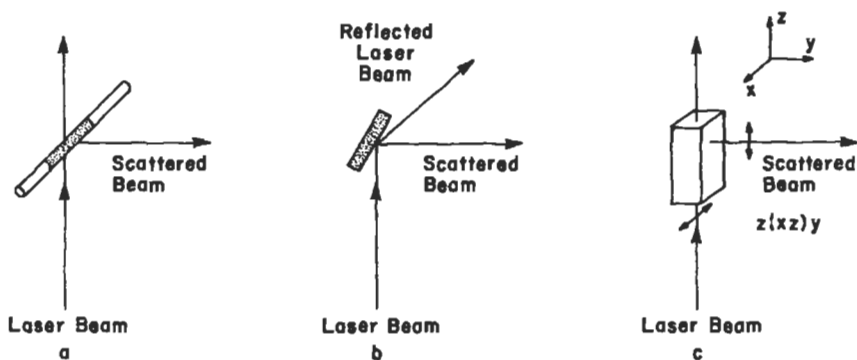


Figure 3 Scattering geometries appropriate to (a) liquids in capillaries or glass fibers; (b) powder pellets, solid slabs of ceramic or rock, or films on substrates; and (c) oriented single crystals.

mounted so that the laser passes along one diameter of the capillary while the scattered beam is along a perpendicular diameter (Figure 3).

Powders and Polycrystalline Solids

Usually, particle size has relatively little effect on Raman line shapes unless the particles are extremely small, less than 100 nm. For this reason, high-quality Raman spectra can be obtained from powders and from polycrystalline bulk specimens like ceramics and rocks by simply reflecting the laser beam from the specimen surface. Solid samples can be measured in the 90° scattering geometry by mounting a slab of the solid sample, or a pressed pellet of a powder sample so that the beam reflects from the surface but not into the entrance slit (Figure 3).

Single-Crystal Measurements

Maximum information is obtained by making Raman measurements on oriented, transparent single crystals. The essentials of the experiment are sketched in Figure 3. The crystal is aligned with the crystallographic axes parallel to a laboratory coordinate system defined by the directions of the laser beam and the scattered beam. A useful shorthand for describing the orientational relations (the Porto notation) is illustrated in Figure 3 as $z(xz)y$. The first symbol is the direction of the laser beam; the second symbol is the polarization direction of the laser beam; the third symbol is the polarization direction of the scattered beam; and the fourth symbol is the direction of the scattered beam, all with respect to the laboratory coordinate system.

Spectra From Thick and Thin Films

Raman spectroscopy is especially suited for structural characterization of films and coatings. Both oblique (Figure 3b) and backscattering geometries can be used. The effective penetration depth of the laser depends on film transparency and on the scattering geometry but in most cases the spectrum of the substrate will be superimposed on the spectrum of the film and must be accounted for. The minimum observable film thickness varies with the intrinsic scattering power of the material but is in the range of a few μm for most materials. Resonance enhancement may decrease the minimum thickness. Useful data usually can be obtained from both crystalline and noncrystalline films.

Surface-Enhanced Raman Spectroscopy

Intensity enhancement takes place on rough silver surfaces. Under such conditions, Raman scattering can be measured from monolayers of molecular substances adsorbed on the silver (pyridine was the original test case), a technique known as surface-enhanced Raman spectroscopy.³ More recently it has been found that surface enhancement also occurs when a thin layer of silver is sputtered onto a solid sample and the Raman scattering is observed through the silver.

High-Temperature and High-Pressure Raman Spectroscopy

Because Raman spectroscopy requires one only to guide a laser beam to the sample and extract a scattered beam, the technique is easily adaptable to measurements as a function of temperature and pressure. High temperatures can be achieved by using a small furnace built into the sample compartment. Low temperatures, easily to 78 K (liquid nitrogen) and with some difficulty to 4.2 K (liquid helium), can be achieved with various commercially available cryostats. Chambers suitable for Raman spectroscopy to pressures of a few hundred MPa can be constructed using sapphire windows for the laser and scattered beams. However, Raman spectroscopy is the characterization tool of choice in diamond-anvil high-pressure cells, which produce pressures well in excess of 100 GPa.⁴

Fluorescence, Sample Heating and Sample Photodecomposition

Although Raman spectroscopy is very versatile with regard to sample form, particle size, and composition, certain interferences occur. Many transparent solid samples contain impurities that fluoresce under excitation by the laser beam. Fluorescence bands are usually extremely broad and are often of sufficient intensity to completely mask the weaker Raman scattering. Fluorescence can sometimes be avoided by using lower energy excitation, such as the red lines of He–Ne or Krypton lasers, or by using a Nd–YAG laser with a diode array detector. If solid samples of interest are being synthesized for measurement, one can sometimes eliminate fluorescence by deliberately doping the sample with luminescence poisons like ferrous iron. Nar-

row-band fluorescence can be distinguished from Raman scattering by measuring the spectra using two different wavelength exciting lines (the 488-nm and 514.5-nm lines of argon, for example). Because the instrument wavenumber scale is set to 0 at the laser line, Raman lines will appear at the same wavenumber position under both excitations whereas fluorescence lines will appear to shift by the wavenumber difference between the two exciting lines.

Because the laser beam is focused on the sample surface the laser power is dissipated in a very small area which may cause sample heating if the sample is absorbing and may cause break-down if the sample is susceptible to photodecomposition. This problem sometimes may be avoided simply by using the minimum laser power needed to observe the spectrum. If that fails, the sample can be mounted on a motor shaft and spun so that the power is dissipated over a larger area. Spinners must be adjusted carefully to avoid defocusing the laser or shifting the focal spot off the optic axis of the monochromator system.

Bulk Raman Spectroscopic Analysis

Fingerprinting

Raman spectra of molecules and crystals are composed of a pattern of relatively sharp lines. The wavenumber scale for most vibrations extends from 50 cm^{-1} to about 1800 cm^{-1} with some molecular vibrations extending to 3500 cm^{-1} . Line widths are on the order of $1\text{--}5\text{ cm}^{-1}$. The Raman spectrum thus has a fairly high density of information and can be used as a fingerprint for the identification of unknown materials by direct comparison of the spectrum of the unknown with spectra in a reference catalog. An example for a series of strontium titanates is shown in Figure 4. This approach is widely used for NMR spectra, X-ray diffraction powder patterns, and infrared spectra as well. As with these other techniques, the success of fingerprinting depends on the availability of a complete, high-quality catalog of reference spectra. Catalogs of reference Raman spectra are much less complete than the corresponding catalogs for IR, ultraviolet, and nuclear magnetic resonance spectra. Users of Raman spectroscopy should compile their own reference spectra.

Crystal Spectra

From a knowledge of the crystal structure it is possible to calculate selection rules for each orientation position and thus gain considerable insight into the vibrational motions of the crystal. The interpretation of such spectra, which show a lot of detail, goes well beyond characterization applications.⁵

Ordered Structures and Phase Transitions

Raman spectroscopy is sensitive to ordering arrangements of crystal structures, the effect depending on the type of order. Ordering atoms onto specific lattice sites in

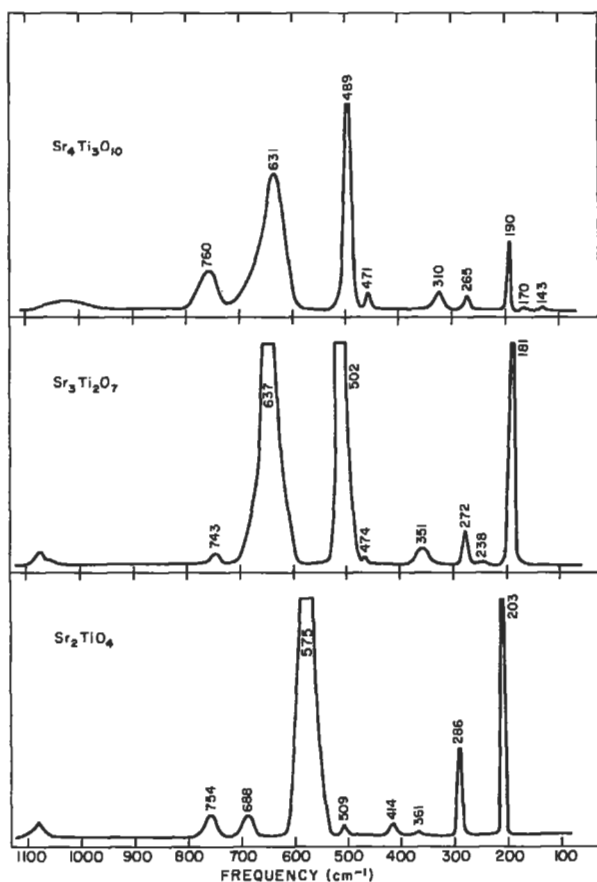


Figure 4 Raman spectra of a series of strontium titanates showing typical line shapes and information available for fingerprinting. The broadening of the high-wavenumber lines is related to the polar character of the TiO_6 octahedra that occur in all of these structures.

the parent structure often forms derivative structures having different space groups. The new symmetry leads to relaxed selection rules, which in turn lead to new Raman lines or to the splitting of the lines of the parent structure. Group theoretical calculations allow a good prediction of expected spectral behavior for possible ordering schemes, and Raman (IR) spectra can be used select the correct model.

Some materials undergo transitions from one crystal structure to another as a function of temperature and pressure. Sets of Raman spectra, collected at various temperatures or pressures through the transition often provide useful information on the mechanism of the phase change: first or second order, order/disorder, soft mode, etc.

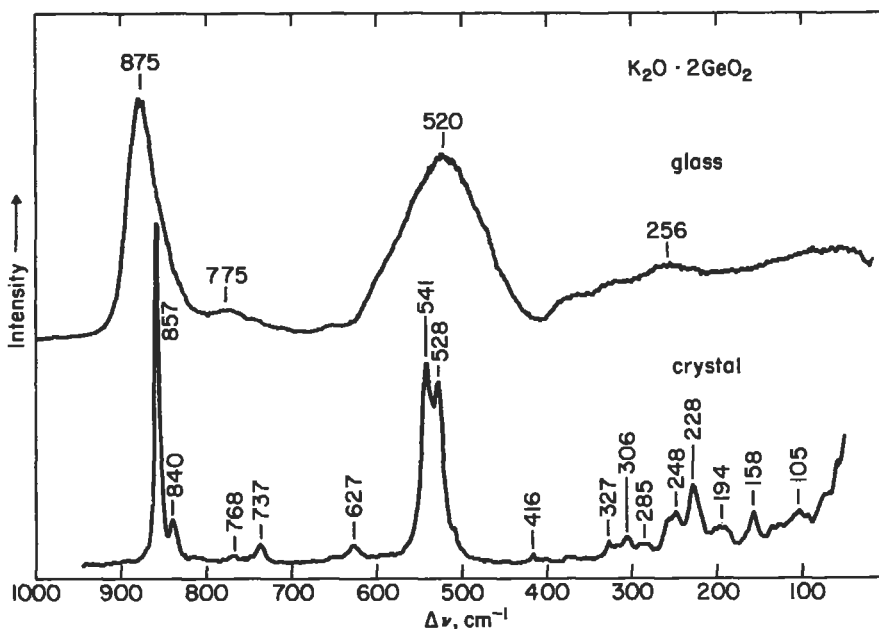


Figure 5 Raman spectra of crystalline and glassy potassium digermanate showing comparison between crystal spectra and glass spectra.

Defects and Structural Disorder

Raman spectra of solid solutions, crystals with lattice defects, and systems having other types of structural disorder usually exhibit a pronounced line broadening in comparison with ordered structures. Structural defects, such as lattice vacancies, produce line broadening with little temperature dependence. Orientational disorder, arising from alternative possible orientations of molecules in crystals, dipoles in highly polar crystals, and nonbonding lone pair electrons in ions like Pb^{2+} and As^{3+} , produce Raman lines that are broad at room temperature but become narrow as temperatures are lowered into the liquid nitrogen or liquid helium range. At high defect concentrations, greater than 10–20% mole, the broadened Raman lines give way to a scattering continuum having little structure.

Glasses and Gels

Raman spectroscopy is particularly useful for investigating the structure of noncrystalline solids. The vibrational spectra of noncrystalline solids exhibit broad bands centered at wavenumbers corresponding to the vibrational modes of the corresponding crystals (Figure 5). In silicate glasses shifts in the high-wavenumber bands

is a measure of the degree of polymerization of the silicate network.⁶ The processes of nucleation and crystallization in glasses can be readily followed by the Raman spectrum because the sharp crystal bands are easily detected against the much weaker and broader glass bands.

Gels are more disorganized than glasses and often have weaker Raman spectra. The processing steps from solution to sol, to gel, to glass in the sol-gel process of glass making can be followed in the Raman spectra. The loss of organic constituents of the gel can be followed as can the development of the bulk glass structure.

Microfocus Raman Spectroscopic Analysis

By successfully marrying a Raman spectrometer to an optical microscope it is possible to obtain spectra having the resolution of optical microscopy—a few μm . The essential feature is a beam splitter through which the laser beam passes on its way to the microscope objective. The beam emerges from the objective to strike a sample held on a standard microscope stage. Raman scattering is observed in the backscattering geometry. The scattered beam also passes through the beam splitter and reaches the entrance slit of the monochromator.

Grain-by-Grain Analysis and Crystal Zoning

The obvious application of microfocus Raman spectroscopy is the measurement of individual grains, inclusions, and grain boundary regions in polycrystalline materials. No special surface preparation is needed. Data can be obtained from fresh fracture surfaces, cut and polished surfaces, or natural surfaces. It is also possible to investigate growth zones and phase separated regions if these occur at a scale larger than the 1–2 μm optical focus limitation.

With a special optical system at the sample chamber, combined with an imaging system at the detector end, it is possible to construct two-dimensional images of the sample displayed in the emission of a selected Raman line.⁷ By imaging from their characteristic Raman lines, it is possible to map individual phases in the multiphase sample; however, Raman images, unlike SEM and electron microprobe images, have not proved sufficiently useful to justify the substantial cost of imaging optical systems.

Precipitates and the Liquid/ Solid Interface

With the microfocus instrument it is possible to combine the weak Raman scattering of liquid water with a water-immersion lens on the microscope and to determine spectra on precipitates in equilibrium with the mother liquor. Unique among characterization tools, Raman spectroscopy will give structural information on solids that are otherwise unstable when removed from their solutions.

Fluid Inclusions

Natural crystals, synthetic crystals, and glasses often contain small bubbles that preserve samples of the fluid from which the crystals grew or of the atmosphere over the glass melt. Using a long focal length lens, the laser beam can be focused into inclusions at some depth below the crystal or glass surface. The Raman spectra then permit the identification of molecular species dissolved in the aqueous solutions or of components in the gas bubbles.⁸

Grain Boundaries, Cracks, and Stressed Materials

Stress in crystalline solids produces small shifts, typically a few wavenumbers, in the Raman lines that sometimes are accompanied by a small amount of line broadening. Measurement of a series of Raman spectra in high-pressure equipment under static or uniaxial pressure allows the line shifts to be calibrated in terms of stress level. This information can be used to characterize built-in stress in thin films, along grain boundaries, and in thermally stressed materials. Microfocus spectra can be obtained from crack tips in ceramic material; and by a careful spatial mapping along and across the crack estimates can be obtained of the stress fields around the crack.⁹

Thick and Thin Films

Because it is nondestructive, can be fine focused, and can be used in a backscattering geometry, Raman spectroscopy is a useful tool for characterizing films and layers either free standing or on various substrates. Semiconductors such as silicon, germanium and GaAs produce Raman spectra that give information on film crystallinity, the presence of impurity layers, and the presence of amorphous material. Films are ideal samples on the microscope stage of the microfocus instrument, and comparisons can easily be made between centers and margins of deposition zones. Raman spectroscopy has been applied to the characterization of chemical vapor deposition-grown diamond films, proving the formation of diamond and characterizing the presence of graphite and various amorphous carbons.¹⁰

The depth of film penetrated and sampled depends on the transparency of the sample to the laser radiation used. This is strongly dependent on the sample material and on the laser wavelength, and can vary from as little as a few μm to significant fractions of a mm. If a film or coating is transparent, the film/substrate interface and any other material deposited there is also accessible and may provide a detectable Raman signal. The absolute sensitivity of the Raman technique is routinely such that a film thickness of at least $0.1 \mu\text{m}$ is required to provide a workable signal. Special instrumentation, particularly high-sensitivity detectors, can reduce this to a few tens of nm and, as mentioned already, for surface-enhanced Raman scattering of molecules adsorbed on rough silver (and a few other) surfaces, sub-monolayer amounts are detectable.

Conclusions

Raman spectroscopy is a very convenient technique for the identification of crystalline or molecular phases, for obtaining structural information on noncrystalline solids, for identifying molecular species in aqueous solutions, and for characterizing solid–liquid interfaces. Backscattering geometries, especially with microfocus instruments, allow films, coatings, and surfaces to be easily measured. Ambient atmospheres can be used and no special sample preparation is needed.

In-situ Raman measurements will become more important in the future. In many types of vapor and liquid deposition systems, it is important to monitor the progress of reactions and changes in structure as films or crystals are grown. Fiber optic cables, sapphire light pipes and other optical systems are available for bringing the laser beam into the reaction chamber and for collecting the scattered light. Spectra can be collected without disturbing the deposition process.

Related Articles in the Encyclopædia

FTIR and HREELS

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