

**The****SPEX**

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**Speaker**

## A RAPID SCAN OF TODAY'S SPECTROSCOPIES

**S**IR Isaac would be proud to learn that his spectroscopic descendants now number several dozen quite healthy—though decidedly individualistic—disciplines. His pretty colors have proliferated and one segment or other of the electromagnetic spectrum is exploited in thousands of laboratories to analyze substances and delineate their molecular, atomic and sub-atomic structures.

Even sorting out the numerous spectroscopies is a challenge. True, they can be divided into two camps, emission and absorption. But this is little more than a contrivance; optical emission is principally aimed at the determination of elements while the main thrust of fluorescence and Raman emission is the study of molecules. One commonality among emission methods is that they tend to be more responsive; they can detect what they are seeking at smaller concentrations or lower weights than absorption systems. "Emissionists" usually have little noise to contend with while "absorptionists" face background along with signal as an inverse function of concentration.

A better sorting parameter, might be volume or surface. In recent years a host of skills has been devised to study molecules, atoms and reactions between them that occur at surfaces. Various microprobes scrutinize catalysis reactions, intergranular corrosion of metals, semiconductor performance, etc. In fact, so much surface analysis has been done that it merits a sequel all its own. Accordingly, the present article will be devoted to spectrum examination of bulk samples, whether liquids, solids, gases or plasmas.

Before delving into the traits and claims to fame of the individual spectroscopies, a few words about detection, point by point or simultaneous. Inevitably, that method whereby the spectrum is queried by scanning over it is less expensive with respect to equipment and more wasteful of people who must examine one portion of the spectrum at a time. Felgett related time and the number of spectral features to signal-to-noise, concluding that for equal S/N the time involved could be reduced by the square root of  $n$  by recording  $n$  features simultaneously. Thus, in optical emission spectroscopy, if 36 photomultipliers monitor 36 elements simultaneously, equivalent detection can be accomplished in 1/6 the time required to scan the individual lines. Since most such measurements entail the analysis of alloys whose concentrations are sufficiently high so as not to be noise-limited, 36 PMTs improve analytical speed by 36 times.

A battery of photomultipliers actually ranks midway between a point-by-point analysis and a complete analysis of the spectrum at any given time. The photographic plate is the oldest and still the simplest example of a fully multiplexed detector. Its

electronic counterpart is a Vidicon, a television camera that views the entire spectrum essentially simultaneously. Multiplexing by computer involves the Fourier Transform, a mathematical treatment that resolves curves into their sinusoidal constituents. Over point-by-point measurements signal-to-noise improvements of 100 and above are easily attained with FT.

As applied to IR, FT spectroscopy begins with an interferometer instead of a diffraction grating. The interferometer can be thought of as the simplest type of diffraction grating, one with but two grooves. Where a diffraction grating consists of a large number of equally spaced lines to separate out the various orders ( $m$ ) in the famous Bragg equation,  $m\lambda = d \sin(\alpha + \beta)$ , an interferometer diffracts all spectral lines at all orders. The trick then is to separate a line, say, in the 429th order from another in the 651st order. In principle FT spectroscopy depends on the fact that the intensity of any particular wavelength, irrespective of its spectral order, is a function of displacement of the mirror in a Michelson interferometer. By translating the mirror and making intensity measurements as a function of the difference in distance between the two interfering beams, information can be sent to a computer for rapid Fourier transformation into a real spectrum.

### X-RAY SPECTROSCOPY ("Fluorescence")

**R**IGOROUSLY speaking, fluorescence is a popular misnomer for a type of analysis of widespread industrial significance. Many thousands of x-ray instruments are in operation in compositional control of alloys, Portland cements, ores and concentrates, and sulfur in fuel oils. As in true fluorescence in the visible region, the bombardment of a substance by radiation at one frequency generates radiation at a lower frequency. The origin of the effect is however, quite different.

In x-ray spectroscopy, a highly energetic beam of "white" x-rays is directed onto a sample, thereby knocking out one or more electrons from an inner level (shell) of its atoms. An electron from an outer level immediately jumps down into the hole, in the process releasing energy. This is equivalent to the difference in energy between the two shells and is thus characteristic of the particular atom. The energy can also be expressed as a frequency to which it is proportional by Planck's constant. The intensity of scattered x-rays at this frequency (or wavelength) is related to the concentration of the element present in a mixture, compound, or alloy.

An older way of measuring concentration of an element is to collimate the scattered beam and send it through a crystal. By knowing the lattice spacing of the crystal and plugging this value into Bragg's law, one can deduce from the angle of diffraction the particular element (actually, the energy transition

of that element) emitting that frequency. In practice, a large goniometer fitted with a detector (variants of Geiger counters) is moved around a circle to fixed angles corresponding to the frequencies of the elements sought. This frequency (or wavelength) dispersive technique involves point-by-point measurements and is thus inherently subject to the same limitations of poor analytical speed for a given signal-to-noise as are corresponding methods in other spectroscopies.

As in other spectroscopies, too, this limitation is overcome by a multiplexing technique. In place of the frequency-dispersive technique, multiplexing of x-rays depends on energy dispersion. Since frequency and energy are proportional, a means of spreading the emitted x-ray energy is tantamount to a means for identifying its source. Multiplexing is achieved with a computer-assisted multichannel analyzer.

Energy-dispersive analysis hinges on a detector sensitive to energy differences. One such detector is a crystal of lithium-drifted silicon, often cooled with liquid nitrogen to improve resolution. The purpose of the lithium is to plug up any electron holes that may be present in an imperfect crystal of silicon. Treated in this fashion, the crystal responds by emitting electrons at a rate proportional to the x-ray energy impinging on it. This is so because each silicon atom requires exactly 3.8 electron volts of energy to ionize it and release an electron. The more energetic the x-ray beam, the greater the number of electrons emitted.

Elaborate multichannel analyzers have been devised to break the stream up into bundles of electrons of equal energy. When processed by a computer, the results can be portrayed on any kind of terminal, a popular type being a graphic display.

Assets and liabilities are trade-offs in the two systems of x-ray analysis. In terms of efficiency, the energy-dispersive method is favored not only because all elements may be measured simultaneously but because collimation of the emitting beam from the sample is unnecessary. Collimation, needed so all x-rays enter the analyzing crystal of a frequency-dispersive instrument at the same incidence angle, is inefficient, sopping up less than 15% of the total x-rays scattered by the sample. The detectivity of energy-dispersive instruments is so great that they successfully operate in conjunction with scanning electron microscopes. Hooked together, the system furnishes the analyst with not only a look at a micro particle but also with a map of its elemental composition. Energy-dispersive instruments can be miniaturized and made portable by substituting a radioactive source for the normal x-ray generator. Available are commercial devices which can be taken inside a home to examine wall paint for lead, and to a service station to make sure that gasoline is lead-free. On the other hand, present frequency-dispersive methods boast greater resolution and are thus subject to less elemental interference, especially important in the analysis of complex alloys and mixtures. Refinements of both methods have steadily improved the limits of detection to the point where it is quite common for heavier elements to be detected at concentration levels well below 1%. Modern evacuated instruments permit extension of the technique down to elements of atomic number 12 (magnesium) which emit soft x-rays absorbed by air.

## VACUUM ULTRAVIOLET

Despite the immense value of the x-ray and UV stretches of spectrum straddling it, the region 1-185 nm remains hemmed in, virtually unexplored by the analytical chemist. And it's not because of lack of information locked inside; potentially, the region

could be important for the determination of many non-metallic and gaseous elements including oxygen and nitrogen. The problem is purely instrumental. Applicable source and dispersing devices are complex and expensive. At the low wavelength end this is painfully apparent. A no-man's land, it is called the extreme ultraviolet (EUV) by one group of scientists, the soft x-ray region by another group, depending on the direction of approach. Here no material has been found to reflect or transmit radiation in a normal manner. The only way to get a signal dispersed by a diffraction grating is to resort to radiation at grazing incidence—an angle of incidence approaching 90°. But when light is dispersed at these high angles, it tends to exhibit extremely high astigmatism which, in turn, translates into a severe loss of signal strength. The alternate approach, from the x-ray side, depends on a crystal that is at once transparent to the radiation and is composed of a lattice with atoms spaced sufficiently far apart. Except for those effective only in a very narrow spectral region below about 1.5 nm, no such crystals are known.

Ideal sources for the region are stars, bodies so hot that electrons are stripped from most atoms, raising them to high-order ionization states. Not unnaturally, therefore, many EUV studies have been made from space vehicles. The main laboratory application of the vacuum UV is in hydrogen-fusion research for determination of electron temperatures, examination of reactions within the plasma and identification of contaminants dislodged from the walls of its container; all of which, hopefully, will lead one day to controlled release of energy.

At about the 50-185 nm region, familiarly referred to as VUV, the angle of incidence is reduced to 30° where astigmatism is no longer serious and the grazing incidence mount is replaced by one called "Seya-Namioka." Here the grating can be rotated about its own axis to scan wavelength. This is a formidable task with the grazing incidence mount, entailing moving the exit slit around the large Rowland circle, the diameter of which corresponds to the radius of the concave diffraction grating. Absorption in the VUV is plagued by yet another problem: no source is known that is capable of producing a long continuum; noble gases must be switched from one to the next in order to span the region.

## UV AND VISIBLE SPECTROPHOTOMETRY

If the space devoted to the types of spectroscopy were to be related to the marketplace, spectrophotometry would probably surpass the total of all others. The number of UV-visible spectrophotometers sold each year reaches into the tens of thousands. They range in price from a \$400 unit no larger than a hand-held calculator to ones replete with a dedicated computer at \$75,000 for automated clinical analysis. Provided the sample is large enough and the substance sought is present at sufficiently high concentrations, a recipe for its determination has probably been concocted. One has only to direct a chemical reaction so a "color" change results. Beer's Law relating the log of the intensity of the color (absorbance) to concentration generally applies, forming the basis for quantitation.

Why do so many molecules absorb UV or visible radiation in broad chunks? A simple calculation tying together frequency and energy through Planck's constant reveals that absorption in the UV and visible region is correlated with electronic transitions. Analogous to the bands obtained in IR from vibrational transitions, UV spectra, arising from electronic transitions, should be similarly sharp. Instead, with the exception of gases, they tend to blur into broad waves. This is so because in liquids there is always a coupling between molecular transitions and the fundamental electronic rearrangements.

Specialized instruments begin with simple colorimeters offering plug-in narrow-band filters and selling for but a few dollars in quantity. At the sophisticated end, the research grade variety generally includes a double monochromator, to effectively screen out extraneous wavelengths, and fine-ruled gratings. These scanning instruments are capable of hundredths of a nanometer resolution, and lately they are digitized for computer compatibility. Suffice it here to note that intervening is an assortment of instruments produced by dozens of manufacturers.

### Correlation Spectroscopy

We have noted that the absorption spectrum of a gas in the UV, in contrast with that of liquids or solids, consists of sharp lines arising from pure electronic transitions. So sharp are the lines that it ordinarily takes a high-resolution, exceedingly stable and expensive instrument to record such spectra. Through an ingenious multiplexing scheme, correlation spectroscopy skirts this formidable problem. Its forte: surveys of pollutants in air, even from aircraft flying above the smog.

Suppose a spectral band of an air pollutant such as CO is photographed on a silica plate. If after development the plate is replaced in the spectrophotometer and CO is again encountered, the UV radiation passing through will be blocked to an extent related to the CO concentration. Unless the instrument is stabilized to a degree not feasible in any commercial spectrophotometers, however, the CO spectral lines are not likely to be aligned with the slots photographed.

In the correlation invention, the spectrum is swept from side to side by an oscillating grating. Despite any wavelength shifts in the spectrophotometer, at one point in the oscillating cycle, spectral lines and slots are certain to coincide. A lock-in amplifier slaved to the oscillation frequency completes the Correlation Spectroscopy package.

### Photoacoustic Spectroscopy

Appropriately enough, Bell Labs scientists have just refined an analytical method originally discovered by its founder, Alexander Graham Bell, in 1881. If a substance is placed in a closed container and exposed to UV-visible radiation, the substance emits a sound. Plotting the intensity of this sound against the electromagnetic frequency yields a spectrum remarkably similar to that derived from a normal spectrophotometer. Armed with modern tunable lasers, optical choppers, and lock in amplifiers, innovative investigators are rapidly turning Bell's curiosity into a highly valuable new tool. Although it is premature to evaluate definitively, PAS seems particularly applicable to examining opaque materials. Metals, semiconductors, and insulators—difficult, if not impossible to study by UV-visible reflection or absorption methods—lend themselves readily to PAS. Amorphous biological materials and coatings are other materials amenable to PAS but incompatible with ordinary spectrophotometry.

### OPTICAL EMISSION SPECTROSCOPY (OES)

Once the unchallenged monarch of its empire, emission spectroscopy has been forced aside from that exalted position by relative newcomers, some with a better threshold of detection, others with better accuracy, and still others more suitable for examining

surfaces or miniscule particles. Yet OES retains some pre-eminence: 1) providing semiquantitative values for as many as 60-odd metallic elements over a concentration range from parts per million to essentially 100%; 2) with appropriate standardization, yielding quantitative determinations on all of the elements—desirable and undesirable, except gases—present in alloys; 3) examining micro samples for major components; 4) analyzing materials with little or no sample preparation and without evacuation.

Although the 200 to 350 nm region is most fertile, OES spans the entire visible and ultraviolet spectrum. A controlled spark between two pins or between a pointed graphite rod and a smooth flat metal specimen is a typical source. Powders, made conductive by being mixed with high-purity graphite, are analyzed with either dc or ac arcs. And in recent years the hollow cathode (the sample being the cathode), glow discharges, and nebulized solution plasmas have made some impact.

Diffraction gratings have virtually replaced prisms as the spectrograph's dispersing element. Modern gratings have effectively eliminated the scattered light and non-linear-dispersion problems of their refracting forebears and not to be ignored is their relative economy compared to fused silica prisms.

The photographic plate was the first, and is still the preferred, detector for semiquantitative and qualitative analyses. Processed under carefully controlled conditions, modern photographic plates are strikingly similar from batch to batch, encouraging quantitative analyses. Once calibrated for density vs. exposure, plates require only occasional checks thereafter. Optical density, recorded on a microphotometer, however, is still a time-consuming process; electronic quantitation is faster and more accurate. Today's laboratory is often equipped with a photoelectric direct reader (its popular name) boasting as many as 60 PMTs, each permanently aligned with its own spectral partner. In the most sophisticated systems, a dedicated computer completes the package. Loaded with appropriate software and told which alloy it is to analyze, a computer can spew out quantitative figures, tag those elements that do not meet specifications, and dictate needed corrections for the heat in the melting furnace. All this while the alloy is still molten in the pot. Since emission spectroscopy has revolutionized the manufacture of ferrous and non-ferrous alloys, not only has the time to prepare a melt been slashed, but chemical tolerances have been tightened substantially. Accordingly, physical properties of modern alloys are held so closely that few changes are needed in fabricating techniques from one batch of an alloy to the next. Not too many years ago, the feed of a lathe tool often had to be adjusted for each batch of a rod made from the same alloy, whether the alloy was produced by the same or a different manufacturer.

In flame photometry, an offshoot of OES, a few elements can be excited by a relatively cool flame. Notable among these are sodium, potassium, and calcium, the blood balance of which turns out to be essential to the well-being of every individual. Fortuitously, these elements are non-transitional and emit very few spectral lines, widely separated from one another, making it possible to construct an inexpensive flame spectrometer with an interference filter transmitting each of the lines. No self-respecting hospital or clinical laboratory is without at least one flame photometer. If you have had an operation in the past few years, you may have wondered why a nurse first jabbed you to extract a few ml of your blood. Take comfort from learning that the cytology department would thereby be able to restore your Na/K balance which, upset, could endanger your life.

## ATOMIC ABSORPTION SPECTROSCOPY

Virtually no analytical laboratory of any size is without at least one AA instrument. Despite the fact that for normal flame excitation samples must be dissolved prior to analysis and that a separate hollow cathode lamp is generally required for each element to be determined, the technique has proved so reliable, so rapid, applicable to so many elements, and capable of such excellent responsivity that it has become invaluable in chemical, industrial, university and governmental laboratories. For monitoring the amount of wear metals that build up in lubrication oils of engines, a routine preventive maintenance program has been set up by airlines, railroads, the Air Force and Navy around quantitative AA measurements, often incidentally, with Spex non-aqueous calibration standards. (Spex is also a major manufacturer of the garden variety of aqueous solutions.)

AA spectroscopy is based on the discovery by Fraunhofer early in the 19th century of dark lines in the otherwise continuum spectrum produced by the Sun. A hollow-cathode lamp containing a metallic element as its cathode emits the strongest lines of that element in the UV or visible region. When a flame is injected with an aspirated solution, the resonance lines of the elements it contains are absorbed in proportion to the concentration of their neutral atoms present in the flame. A spectrophotometer set to the appropriate wavelength, or an interference filter, isolates each line of interest and conventional photomultiplier detection completes the instrument.

Over OE, AA spectroscopy claims the advantage of much simplified, less expensive equipment. The emission spectrum of a transition element is so rich that a room-length spectrometer is needed to isolate the lines whose intensities are to be measured. By contrast, in AA the hollow cathode lamp is an essential part of the isolating device and the spectrometer is 1/10 the size of that for OE. Further, as in all absorption methods, the signal level is highest when the concentration sought is lowest. Detectors and attendant amplifiers are, accordingly, relatively inexpensive. Finally, ratioing is normally a frill in AA; on the other hand, spark and arc sources for OE usually give rise to intensity fluctuations of such magnitude that corrections by ratioing to an internal standard are the rule.

A notable recent advance in AA technology which is amenable to the determination of most elements is an ohmically heated rod of high-purity graphite rather than a flame to volatilize the sample. Evaporated in the space between the hollow cathode lamp and the spectrometer, exceedingly small samples can be analyzed without putting them into solution. As might be expected, however, this flameless technique is not without liabilities. Matrix effects, non-uniform volatilization, and loss of volatile elements during ashing (before analysis) are disadvantages not associated with aspiration of liquids into a flame.

Another recent improvement is the introduction of electrodeless discharge lamps. These are especially valuable for the determination of elements such as Cd, As, Se, Sb, whose resonance lines lie below 250 nm, where signal levels are poor. Compensating for the absorption of air and the reduced response of PMT's these new lamps are many times more intense than hollow-cathode lamps.

## SPECTROFLUOROMETRY

When radiation is absorbed by certain molecules, longer wavelength radiation is emitted. Analytically, this phenomenon of

fluorescence has become an essential quantitative tool to inorganic, organic and biological chemists. Even with the least expensive instrumentation, its excellent detectivity is rivaled by few other analytical methods. Further, fluorometry has been made highly specific through the introduction of new reagents and analytical methods which have been established for the determination of almost every element, commonly down to ppb levels. Fluorometry combined with liquid and thin-layer chromatography can boost their resolution and threshold of detection by orders of magnitude. With specific tagging chemicals primary amines, amino acids, and proteins can be identified down to levels of  $10^{-12}$  molar. With a short-wavelength Cd 229 nm lamp,  $\text{SO}_2$  has been found to fluoresce so strongly that it serves as the basis for a commercial device to monitor this corrosive but invisible gas as it stealthily seeps from many smokestacks. Oil slicks can be spotted on sea water from unmanned buoys. Residual morphine, codein and heroin can be found in urine after reacting it with cuprous halides. Toxic levels of lead can be found in a drop of blood, in seconds, with a simple filter fluorometer just developed by Bell Labs.

Not unimportant in evaluating fluorescence is the elegant simplicity of its apparatus for routine work. A high-pressure Hg-vapor lamp, an interference filter, and a photomultiplier module sets you up. More elaborate instruments are, of course, required for ongoing supportive research. Fluorescence it turns out, is not always that simple.

Actually, fluorescence combines two spectroscopies, excitation and emission. An excitation spectrum is obtained when the sample is flooded with light of changing frequency while the emission frequency observed is kept constant. Conversely, an emission spectrum is obtained when the sample is flooded with light of a fixed frequency while the emission frequency is scanned. The strongest emission bands occur when the excitation frequency corresponds with an absorption peak. As ramifications of identical transitions, absorption and excitation spectra are theoretically identical when the substance has a constant quantum efficiency over the wavelength scanned. Over UV absorption, however, fluorescence excitation is orders of magnitude more responsive.

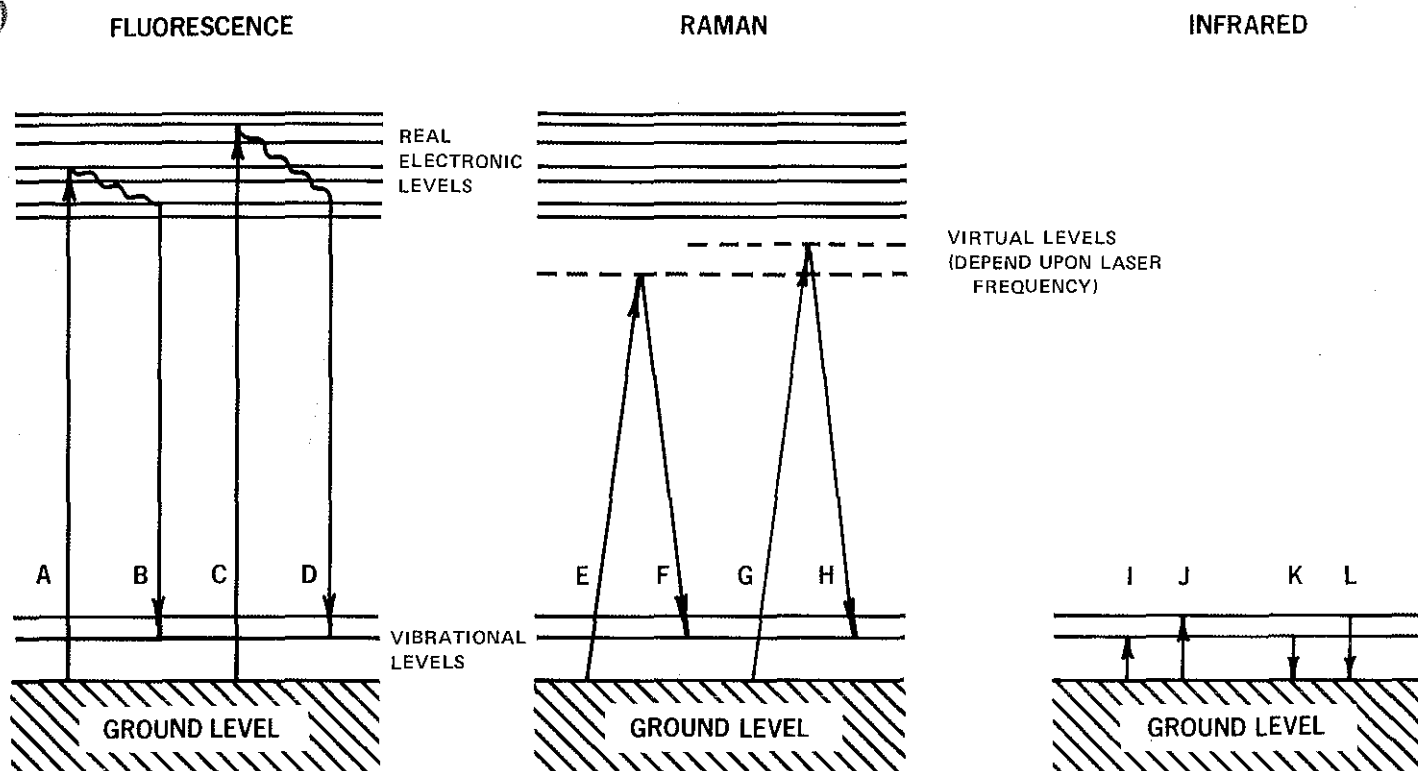
Detection limits as well as spectral purity are hampered by instrumental defects, notably scattered light. Neither gratings nor prisms are perfect dispersers of radiation. Set any spectrometer to one wavelength and a fraction of the intensity measured will emanate from other, spurious wavelengths scattered by the monochromator. To overcome this, monochromators are doubled. If the ratio of scattered light to light from the set wavelength is  $10^{-5}$  with a single grating, it will be reduced to  $10^{-10}$  with two gratings in tandem. Holographic gratings, an order of magnitude below ruled gratings in their scattering imperfections, have brought still further improvement.

An advanced spectrofluorometer recently introduced by Spex in two versions, the FLUOROLOG and its computerized companion, the FLUOROCOMP, is designed to measure absorption simultaneously with emission and excitation, include facilities to take many types of spectral ratios, and is optimized throughout to afford highest levels of detectivity.

Molecules can be characterized by lifetime of fluorescence as well as spectral features. A good deal of fundamental research is currently under way with gating circuitry to home in on a particular fluorescing species. Considering that fluorescence lifetimes can be shorter than  $10^{-9}$  seconds and that light travels only about one-third of a meter in that time, the fragile and delicate nature of such investigations can be appreciated.

# SPECTRA AND ENERGY LEVELS

These energy-level diagrams reveal several significant differences between fluorescence and Raman, and relate the latter to infrared. In every case, the same molecule is being referenced.



The fluorescence reaction of the molecule to two impinging ultraviolet frequencies, A and C indicates each is absorbed, raising the molecule from the ground level to a vibronic (electronic plus vibrational) high-level excited configuration or "state." Of course, the energy of the excited state will be higher with C, the shorter wavelength of ultraviolet. Energy is then lost from the excited states by internal, radiationless transitions, until the molecule reaches a lower state that is favored by quantum selection rules for decay to near ground level. Here the molecule emits radiation, as in B or D. Since the internal transitions are not instantaneous, emission is delayed (even if only by nanoseconds) from the excitation, thus giving the molecule enough time to rotate and lose most or all of its polarization alignment. Note two significant features: all the energy levels are real states of the molecule; and the emitted frequency is not changed by a change in excitation frequency, that is,  $B=D$ .

By contrast with fluorescence, in Raman spectroscopy the molecule is not converted to a high-energy state. Although it is a mathematical convenience to show "virtual" levels, the two impinging excitation frequencies depend only on the laser capability, not on the molecule. Emissions F and H occur when the electrons drop to lower vibrational levels. Since the virtual levels are not real, the process takes place essentially instantaneously. Further, the molecule having no time to move, the emitted light retains its polarization. The most salient point, however, is that although the emitted frequency of Raman radiation varies, the frequency difference between excitation and emission remains constant ( $E-F=C-H$ ).

When the molecule is exposed to relatively low-frequency, long-wavelength infrared light, not enough energy is available to excite it to upper levels. It can be raised only to the lower-lying vibrational levels by absorbing the amount of energy corresponding to I or J. This removes energy from the infrared illumination yielding the familiar infrared absorption spectrum. Once the molecule has been excited to these vibrational levels, by radiation, chemical reactions or heat, it will return to the ground level as in K or L, and display an infrared emission spectrum at the corresponding wavelengths. Obviously,  $I=K$  and  $J=L$ , so that infrared absorption and emission spectra correspond.

In some molecules, quantum selection rules allow both infrared and Raman transitions for a given level. As expected for these cases, the Raman difference is the same as the infrared energy, or  $E-F=K$ . In more symmetrical molecules certain transitions (such as K and G-H) may be forbidden. When that occurs, the two techniques complement each other, for while L might be seen only in infrared K (which equals E-F) might be seen only in Raman.

If the energy levels in the illustration were greatly expanded, we would find that they actually consist of the fine structure of many extremely closely spaced levels. These represent different modes of molecular rotation, or the hyperfine splitting due to nuclear magnetic fields. These levels are so close together that they cannot be resolved except in dilute gases, where they will not be smeared together by collision broadening. Transitions between these levels involve much less energy than infrared transitions; they correspond to the microwave spectrum.

## INFRARED ABSORPTION

The spectrum from around 4000 to 200 wavenumbers is considered the "fingerprint" region where vibrational frequencies occur for most organic compounds. As in emission spectroscopy, the grating has evolved as today's dispersing element. Outmoded except for cells and windows are the various alkali halides needed not long ago in the series of prisms for spanning the spectrum. The source here is usually a silicon carbide rod (Globar) which emits black-body radiation throughout the IR when heated below 1700C. The most responsive detector, once the thermopile, is a HgCdTe semiconductor, becoming popular despite its expense. A very recent model requiring only LN<sub>2</sub> rather than LHe cooling is especially valuable for instruments designed to analyze gas chromatographic effluents "on the fly."

Procedures for IR analysis have been devised for almost any imaginable kind of sample. Liquids are routinely handled in macro or micro cells that hold a few microliters of sample. Solids are either milled with mineral oil or ground with KBr and pressed into 13-mm discs. For air pollutants or other gases multi-reflection cells provide path lengths up to 120 meters. Coatings on opaque substances may be analyzed by an optical configuration known as attenuated total reflection (ATR). Carbon monoxide detectors, based on nondispersive IR, are spaced out in tunnels to warn authorities when the air might be dangerous to breathe.

Rigorously a non-dispersive spectrometer is not a spectrometer at all since it does not attain its discriminating ability through frequency dispersal. A single constituent monitor consists of two compartments. In the simplest version, one is fixed, containing a "no-go" amount of the gas being determined; the other is a flow-through cell for the gas being analyzed. An interference filter is selected for an IR band of heavy absorption and electronic circuitry keeps tabs on the ratio of intensities between the two cells.

At the opposite extreme are computer assisted Fourier Transform IR instruments. As we described earlier, by virtue of multiplexing all of the energy, FT techniques are 10 to 100 times faster than conventional scanning over a frequency-dispersed spectrum. Moreover, compactness and the ability to telemeter the spectral information have made FT instruments standard for space vehicles. But the greatest laboratory application of FT-IR spectroscopy has been in the Far IR.

### Far Infrared

Spilling over into the normal IR at one extreme and microwave technology at the other, the 700 to 10 wavenumber range is known as the far infrared. Until dedicated computers made Fourier Transform spectroscopy practical in 1962, the region had been almost ignored by instrument makers. Sources of radiation are so pitifully weak, dispersing materials so rare, and detectors so poor (and expensive) as to discourage commercialization. FT instrumentation, by virtue of the tremendous improvement in signal level it affords, has revitalized the FIR and several manufacturers offer systems today.

For the most part FIR is a research tool, suitable more for structural than chemical analysis. Rotational frequencies of most molecules and vibrational frequencies of heavy fragments appear in this region providing the IR segment to fully complement the Raman spectrum, as we shall soon note. In a recent report of a single crystal of AgBr doped with 200 ppm of RhBr<sub>3</sub>, six fundamental vibrational modes were predicted to occur in the region below 260 cm<sup>-1</sup>. Two modes appear in the FIR spectrum and three in the Raman spectrum; the sixth, being neither IR nor Raman active, does not appear in either. It should be pointed out that, fortuitously, the excitation wavelength of the Kr<sup>+</sup> laser (5682A)

corresponds to an absorption peak in AgBr and the spectrum obtained actually involved Resonance Raman, thus permitting detection of so low a concentration.

## RAMAN SPECTROSCOPY

To Raman spectroscopy, the invention of the laser became an immediate solution to a long-persistent problem, that of concentrating enough light on a sample to excite its exceedingly weak Raman or frequency-shifted spectrum. When monochromatic light impinges on a sample, it is scattered, mostly at the same frequency, the molecule returning to the ground state after having been raised to some higher energy level. Referred to as Rayleigh scatter, this excitation does not include the handful of electrons that return not to the ground state but to a higher transitional state. The energy difference between the two produces the Raman spectrum corresponding to the frequency shift. Although modern lasers emit many different wavelengths with which to excite Raman spectra, the shift from the Rayleigh to the Raman line is invariant for a particular molecular transition. Corrected for intensity, Raman spectra are identical irrespective of whether a blue, green, or red laser is the excitation source—an important consideration in analyzing colored materials which often burn up when hit with light they absorb.

Had the laser been invented 30 years earlier, it is speculated, the roles of Raman and IR spectroscopy would be reversed today. Because of this historical quirk, tens of thousands of IR instruments grind out routine quals and quants daily while Raman stars as a research tool, a powerful probe of molecular structure and subatomic interactions to chemist and physicist alike.

Together, the two spectroscopies share the ability to reveal all vibrational and rotational movements of molecules. Complex organic molecules consist largely of functional groups bonded together in discrete ways and in discrete positions relative to one another. During an analysis, neither IR nor Raman disturbs these units so that their spectra appear as "group frequencies" at designated spectral positions. Just a glance at its IR or Raman spectrum will tell an experienced spectroscopist whether the molecule contains a C-H or a C-O component.

It turns out that such compositional clues are symbiotically complementary in Raman and IR spectroscopy. A symmetrical molecule like CCl<sub>4</sub> emits a strong Raman spectrum but is so poorly absorbing in the IR that it is suitable instead as a solvent. An asymmetrical molecule like water (its oxygen atoms wag up and down and breathe in and out, out of phase) gives rise to such intense IR spectra that aqueous solutions are ordinarily avoided. The Raman spectrum of water is, by contrast, unobtrusively weak.

The rule for IR absorption is that a molecular fragment must contain a permanent dipole moment which is changed by absorption of IR energy. Since a dipole is by definition different at either end, IR normally deals with asymmetrical molecules, or asymmetrical fragments of molecules.

Quite the opposite is true in Raman: a substance gives rise to a Raman spectrum only if one of its molecular vibrations causes a change in its polarizability. Exposed to electromagnetic radiation (visible laser light) protons and electrons, charged oppositely, are attracted and repelled oppositely, inducing a dipole, the value of which divided by the strength of the radiation field is a measure of the polarizability of the substance.

For a particular vibration, the absolute frequency as determined by IR is identical with the Raman or shifted frequency, which is the difference between the laser frequency and the emitted Raman band. Since the transitions forbidden by the one are allowed (and strongest) in the other, often, running a sample by

both techniques results in a complete characterization of its molecular structure.

Applications of laser-Raman spectroscopy are still growing rapidly. For the chemist, polymers can be characterized as to chain length and their degree of crystallization, while copolymers can be quantitatively assayed for major constituents. Samples as small as 1 ng have been identified, their spectra scanned in less than 3 minutes. Reactions in situ have been successfully monitored. Body fluids can be analyzed, a difficult IR task because water absorbs so heavily in the infrared. The physicist is mainly concerned with crystals. Investigations of interactions between photons and electrons, phonons, magnions, and other subatomic particles have helped elucidate the structure of semiconductors, piezo electric crystals, optical elements, capacitors, electrostatic materials, etc.

Equipment for Raman spectroscopy is generally clustered around a double (or even triple) spectrometer, in which the light is dispersed by two (or three) gratings. This arrangement, especially of late with holographic gratings, squelches instrumental scatter by many orders of magnitude so that Rayleigh light does not swamp out the Raman spectra. High-powered (2-15 watt) Ar<sup>+</sup> lasers are the most popular excitation sources. Photomultipliers selected for high responsivity and low noise are the best detectors. Overall instrumental improvements made in the past few years permit scans of rotational-vibrational spectral wings of gases at atmospheric pressure in a few minutes, a task which in pre-laser days, took exposures of several days on the fastest photographic plates.

### Resonance Raman

When an excitation frequency falls within an absorption band of a molecule, its response is to emit a spectrum identical as to frequency shift but up to one million times stronger than an ordinary Raman spectrum. Intriguing in its implications to the analytical chemist, the effect is known as resonance Raman spectroscopy. Equally intriguing is its implications with respect to selectivity. Provided a laser could be tuned to any wavelength, it should be possible to single out a substance at one of its spectral absorption edges to the exclusion of other substances in the same solution.

Until the dye laser came along, practice lagged behind theory. With ordinary lasers, relatively few excitation frequencies were applicable for Raman work. Considering the other restraints imposed on the laser—high intensity, stability, continuous rather than pulsed mode, price—only four wavelengths were really practical: 488 and 514 nm from an Ar<sup>+</sup> laser, 647 nm from a Kr<sup>+</sup> laser and 633 nm from a He-Ne laser.

Current development of dye lasers is rapidly changing this picture. Through an interspersed diffraction grating, a powerful Kr<sup>+</sup> laser, itself emitting at many wavelengths from UV through visible, interacts with a series of fluorescing dyes. By choosing a number of dyes the fluorescence of which overlaps and spans the full visible spectrum, a continuously variable laser is achieved, one that can emit with sufficient intensity for much Raman work from 450 to 750 nm, with few spectral gaps. But versatility and convenience are often forces that counteract one another and so it remains to be seen how well such elaborate laser systems fare.

### Coherent Anti-Stokes Raman Scattering

Too new for a thorough appraisal, CARS is a type of resonance Raman spectroscopy which relies on heterodyning two laser

frequencies. Typically, 940 cm<sup>-1</sup> (1064 nm) from a YAG laser is doubled to 532 nm and passed through a fluorescing dye, the frequency of which is varied with a diffraction grating. Differing from ordinary Raman, both 532 nm and the varying frequency excite the sample. The spectrum generated for gases is almost 10<sup>6</sup> more intense than that of normal Raman, and on the high side of the excitation frequency instead of the Stokes side so fluorescence from the sample is avoided. For remotely monitoring specific air or smoke pollutants the technique holds promise. Disadvantages include the need for two or more dyes to span  $\Delta 4000$  cm<sup>-1</sup> and inapplicability to opaque materials.

### MICROWAVE SPECTROSCOPY

When gases are sufficiently dilute, energy levels lying close (yet not too close) together are no longer smeared and can be resolved with the highest-resolution instruments to reveal fine and hyperfine structure. In the region of visible and IR spectroscopy, the finest resolution has been attained with tunable diode lasers. But far better resolution is achieved with microwave spectroscopy, which examines the differences between these closely spaced levels.

What transitions give rise to these close spacings? While the rotational lines of a diatomic molecule are spaced regularly, tens of wavenumbers apart, an asymmetrical top molecule (such as water) will exhibit a profusion of lines with random spacings. Transitions between some of these may correspond to energies of fractions of a wavenumber; that is to say, their wavelengths may be many centimeters. Another source is hyperfine splitting due to the nuclear magnetic field. The degree of splitting then gives information on nuclear spin, as well as uniquely identifying the molecule. Finally, a few molecular motions carry low enough force constants so that they represent low-frequency vibrations. The best known is the ammonia inversion, where its "umbrella" flips back and forth  $2 \times 10^{10}$  times per second (wavelength 1.5 cm). Others are torsional oscillations or hindered internal rotations in complex molecules.

As an analytical tool, microwave spectroscopy has lagged behind other spectroscopies. Spectra of many materials are now being compiled, however, and information on bond angles and strengths, nuclear spins, moments of inertia and relativistic effects is being derived for energies unresolvable optically. In radio-astronomy, microwave emission from molecules many light-years away has been precise enough to identify dozens of organic and inorganic species and determine their temperature, speed with respect to the earth, and even identify isotopic mixtures!

Antennas hundreds of meters across—both fixed and movable—located in Puerto Rico, West Virginia, England, and elsewhere are aimed at stellar bodies. Through the vast microwave "window" they are amassing data that are turning astronomers into chemical analysts. Indeed a microwave pollution detector might become a most valuable application should development engineering mitigate the liability involved in having to pump down to such low densities.

**H**AVING scanned the gamut of spectroscopies from x-ray to microwave, limiting ourselves from the start to bulk rather than surface phenomena, we now come upon another limit switch. We shall not include the disciplines unassociated with the electromagnetic spectrum. Mossbauer, Gamma Ray and Mass Spectroscopy, Nuclear Magnetic Resonance, Electron Spin Resonance, Neutron Activation and doubtless unknown technologies are being left for another time or place.



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