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Author's Review

A New Era for Applications of Vibrational Spectroscopy in Industry

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Relatively recent developments in vibrational spectroscopy are impacting all areas of typical industrial R&D. These include Fourier transform infrared spectroscopy, computerized Raman spectroscopy, micro techniques, combined techniques (including separation and thermal methods with spectroscopy), and a plethora of novel and effective sampling handling devices. Of greatest importance among these developments, however, is the dramatic increase in *in-situ* methods for examining materials or following reactions. Whether in catalysis, polymer chemistry, corrosion or petroleum research, the use of vibrational spectroscopy for real-time experiments is opening a new era of impressive applications.

Examples of analytical problem solving in this new era of applications will be given to illustrate the above points.

INTRODUCTION

Relatively recent developments in vibrational spectroscopy are impacting all areas of typical industrial R & D. These include Fourier transform infrared spectroscopy, computerized Raman spectroscopy, micro techniques, combined techniques (including separation and thermal methods with spectroscopy), and a plethora of novel and effective sampling handling devices. Of greatest importance among these developments, however, is the dramatic increase in *in situ* methods for examining materials or following reactions. Whether in catalysis, polymer chemistry, corrosion or petroleum research, the use of vibrational spectroscopy for real-time experiments is opening a new era of impressive applications.

In quite a different arena, the evolution of small, lower-cost, benchtop instruments has occurred, which are robust, portable and easy to use. These will encourage the use of FT-IR as an integral part of equipment and process control applications, as well as for robotics and expert systems. And in the analytical laboratory, the totally networked system, designed to maximize cost-effective use of sophisticated equipment, is becoming a reality.

FOURIER TRANSFORM INFRARED SPECTROSCOPY

Infrared spectroscopy is a widely used industrial tool for the structural and compositional analysis of organic, inorganic, or polymeric samples and for quality control of raw materials and commercial products.[1-3] It is a relatively simple technique, non-destructive, and versatile enough to handle solids, liquids and gases with a minimum of sample preparation, and accurate enough for both the qualitative identification of the structure of unknown materials and the quantitative measurement of the components in a complex mixture. An extensive body of literature on group frequency correlations exists as well as excellent reference spectral collections. Instrumentation has been reliable and low cost.

But in spite of all these benefits, infrared spectroscopy has certain drawbacks which become more critical as the difficulty of the analytical problem increases. These drawbacks stem from the fact that infrared is an energy-limited technique. The energy distribution of the blackbody radiation of the IR source reaches a peak in the low wavelength region of the spectrum (2—5 μm), and falls off sharply and drastically at longer wavelengths. For routine operation there is generally more than sufficient spectral energy to obtain IR spectra useful for qualitative structural characterization and for the development of quantitative methods. However, situations frequently occur where there is not enough energy to accurately measure very weak or very strong bands necessary for an analysis. The bands could be weak because they are due to low concentrations of the component(s) of interest in an absorbing matrix, such as additives or impurities, or to extremely small amounts of sample, such as trapped chromatographic fractions. Or they could be bands which are naturally very weak but which must be optimized for some analysis. In addition, many IR spectrometers are not able to reliably record spectra of very thick materials, or highly absorbing, intractable materials such as polymers.

But the applications of infrared spectroscopy today have experienced an explosive »transformation« with the introduction of interferometric methods of obtaining infrared spectra and the subsequent mathematical processing of the interferogram via fast Fourier transform algorithms to recover the frequency spectrum. The »transformation« has given us impressive time and signal-to-noise advantages, as well as a whole new generation of instrumentation.

Some of the special advantages of Fourier transform infrared spectroscopy are given in Table I. These include energy limited, time limited, or signal-to-noise limited situations. For the spectroscopist who in the past has dealt with an analog instrument, there are aspects of the data processing in Fourier

TABLE I

Special Advantages of Fourier Transform IR

- Energy Limited Situations
    - Opaque samples $< 1\%$ transmission
    - IR emission studies
    - Very high resolution requirements
- Time Limited Situations
    - Kinetic studies
    - Unstable compounds
    - Reaction or catalytic intermediates
- Signal/Noise Limited Situations
    - Trace analysis
    - Interfering absorption
    - Atmospheric sampling

transform infrared applications which must be appreciated in order to not only take full advantage of the technique, but also to understand the measurement sufficiently for proper data manipulation and meaningful results.[2]

FT-IR has found particularly wide application in the field of polymer analysis for compositional, structural and quantitative analyses.[4,5] It is possible to look at intractable, thick, intensely absorbing materials, and also to observe chemical and physical changes in the polymer structure as they are occuring.

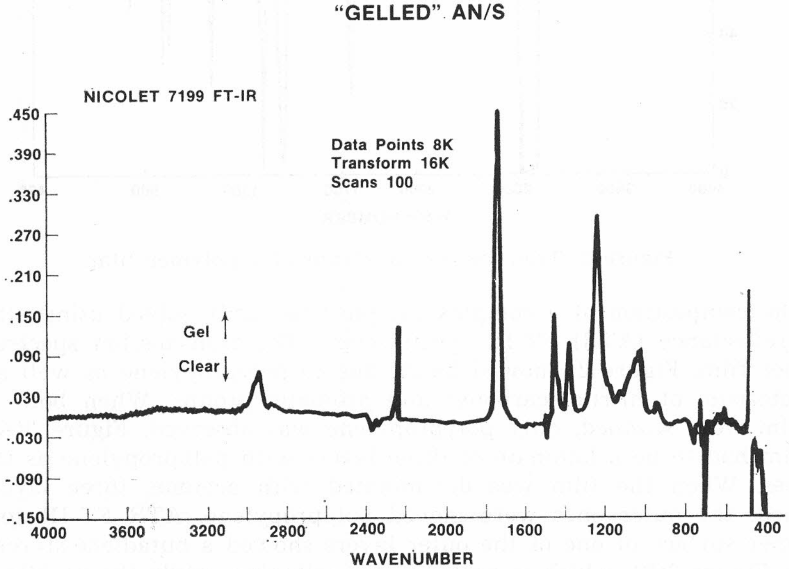

Figure 1. Gelled AN/S copolymer difference spectrum. Gelled section minus clear section.

A typical industrial application of FT-IR in troubleshooting a polymer problem is shown in Figure 1.[6] Orientation of an acrylonitrile/styrene copolymer film resulted in development of very small spots throughout the film. The spots appeared to be chunks of gelled resin, but it was also possible that they might be due to a contaminant, a small amount of homopolymer, or even a trapped liquid or gas. FT-IR subtraction spectra of a pinhole aperture section of the oriented film, subtracting the clear area from the spots, gave a spectrum that was easy to identify as polyvinyl acetate, an obvious contaminant in the polymer.

Over the years we have seen the development of many useful sampling techniques and accessories for infrared spectroscopy. Today there is a seemingly endless choice. Because of the innovative sampling tools and sophisticated data processing methods, we can selectively examine portions of samples, get information on very energy-limited samples, and tackle problems of qualitative or quantitative analysis on extremely complex materials. Today we get more specific information on more difficult samples quickly and cheaply — and we take advantage of the reliable high information content inherent in the infrared spectra of materials.

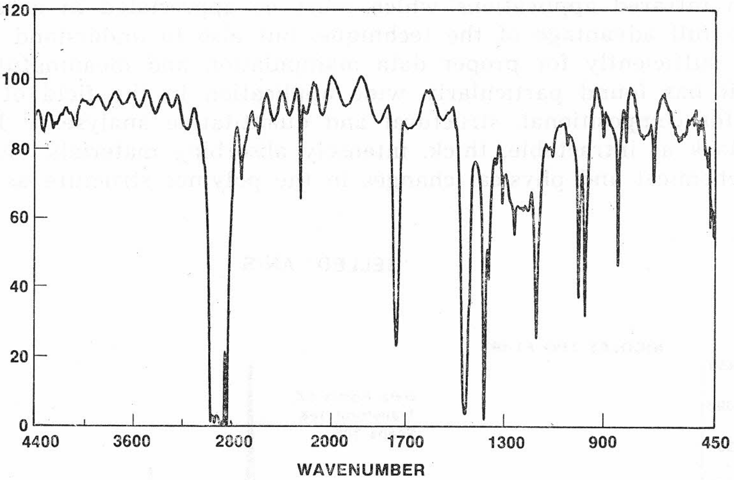

Figure 2. Transmission spectrum of a polymer film.

The composition of a complex sample was easily solved using attenuated total reflectance (ATR) FT-IR spectroscopy. The transmission spectrum of a polymer film, Figure 2, showed bands due to polypropylene as well as bands characteristic of nitrile, carbonyl and aromatic groups. When both sides of the film were scanned, only polypropylene was observed, Figure 3(A). Thus, the film had to be a laminate of three layers with polypropylene as the outer surfaces. When the film was delaminated with acetone, three layers were obtained: the outer ones were indeed polypropylene. ATR FT-IR spectra of the inner surface of one of the outer layers showed a butadiene/styrene copolymer, Figure 3(B), which is probably the adhesive, while the middle layer is an acrylonitrile/methyl acrylate copolymer, Figure 3(C).

ATR FT-IR spectroscopy is a widely used technique for surface analysis. A less common FT-IR method is CIRCLE ATR, which was originally designed to study aqueous systems that are difficult to analyze due to strong water absorbance in transmission measurements. Recent studies of styrene/acrylic acid copolymer dissolved in aqueous solvent show that with the use of this technique it is possible to detect very low concentrations of solute (0.001 w/w). The use of the CIRCLE ATR technique for the study of films and fibers was recently reported.[7]

COMBINED TECHNIQUES

There is no question that one of the most exciting areas of application of FT-IR spectroscopy has come about because of the time advantage that is gained in the interferometric method for obtaining an IR spectrum *i. e.*, the real time coupling of an infrared spectrometer to a gas chromatograph was finally realized. Not only the packed column GC separation, but now also capillary GC separations have benefited from the identification power of the FT-IR spectrometer. For all these applications, special attention must be paid to the configuration and dimensions of the lightpipe and the transfer

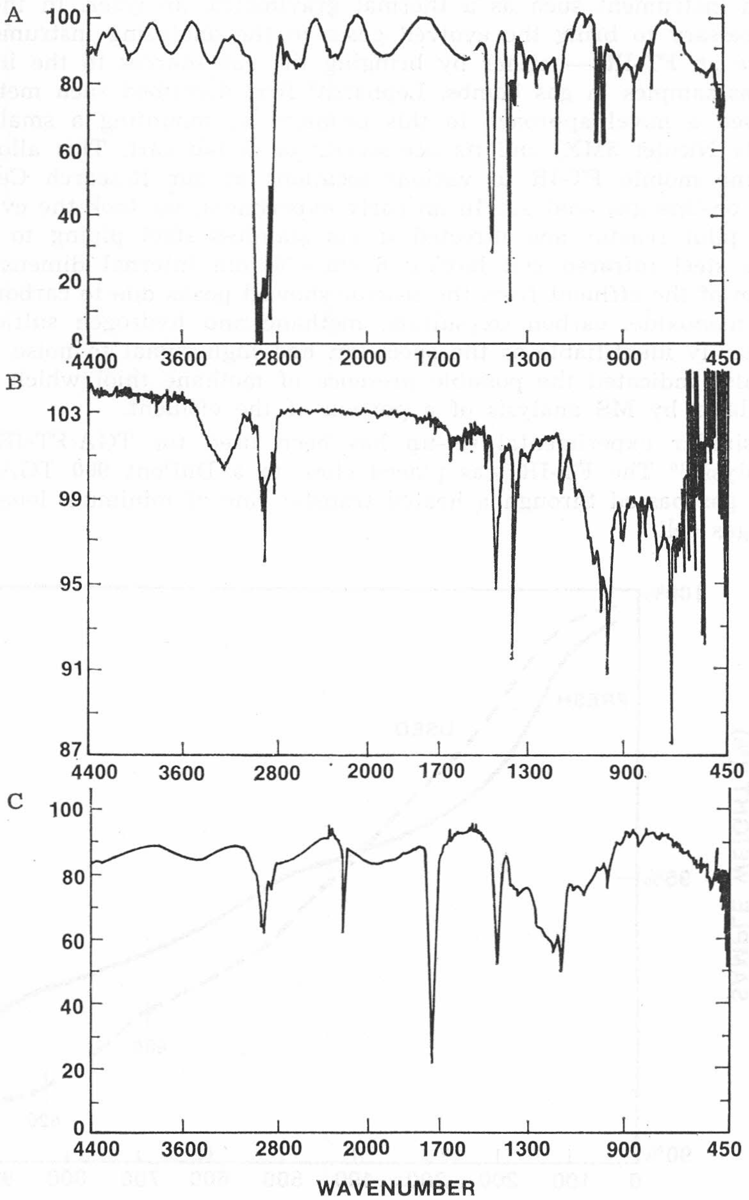

Figure 3. FT-IR spectra of a laminated film. A) ATR spectrum of one side of film. B) ATR spectrum of inner surface of outer layer. C) Transmission spectrum of middle layer.

lines between the chromatograph and the IR. Examples of capillary GC/FT-IR and of GC/LC/IR are now appearing rapidly.[8]

The term »evolved gas analysis« covers a wide range of applications such as the analysis of reactor effluent, engine exhaust, or the effluent gas from an instrument such as a thermal gravimetric analyzer. In the past, it was necessary to bring the evolved gases to the analyzing instrument — in this case an FT-IR — either by bringing the gas sources to the instrument lab or as samples in gas bombs. Lephardt[9] first described such methods. We have used a novel approach to this problem by mounting a small, rugged FT-IR (a Nicolet 5MX) and its accessories on a lab cart. This allows us to wheel the mobile FT-IR to various locations at our Research Center and provide on-line gas analysis. In an early experiment, we took the evolved gas from a pilot reactor and directed it via stainless steel piping to a heated stainless steel infrared cell having 6 cm × 6 mm internal dimensions. The spectrum of the effluent from the reactor showed peaks due to carbon dioxide, carbon monoxide, carbon oxysulfide, methane and hydrogen sulfide. These were readily identifiable as the spectrum had high signal to noise. The spectrum also indicated the possible presence of methane thiol which was confirmed later by MS analysis of a portion of the effluent.

A similar experimental set-up has been used for TGA/FT-IR evolved gas analysis.[10] The FT-IR was placed close to a DuPont 900 TGA and the evolved gas passed through a heated transfer line of minimum length to the heated gas cell.

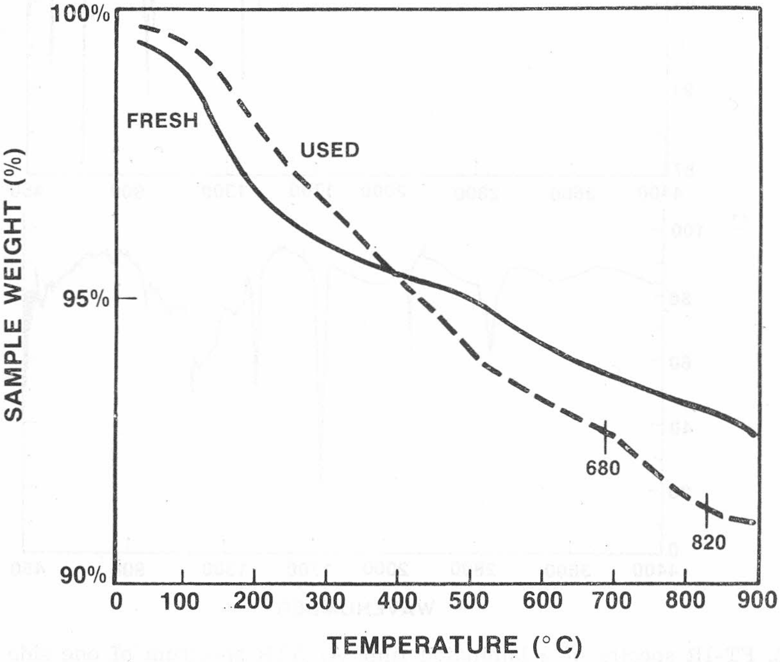

Figure 4. Thermal gravimetric analysis of alcohol synthesis catalysts.

Catalysts used to synthesize alcohols from CO/H_2 were analyzed by TGA/FT-IR to help determine the reason for their decline in activity. Figure 4 shows the TGA curves for fresh *versus* used catalyst. From 400 °C to 800 °C, used catalyst shows about 1% more weight loss than a fresh sample. Profiling

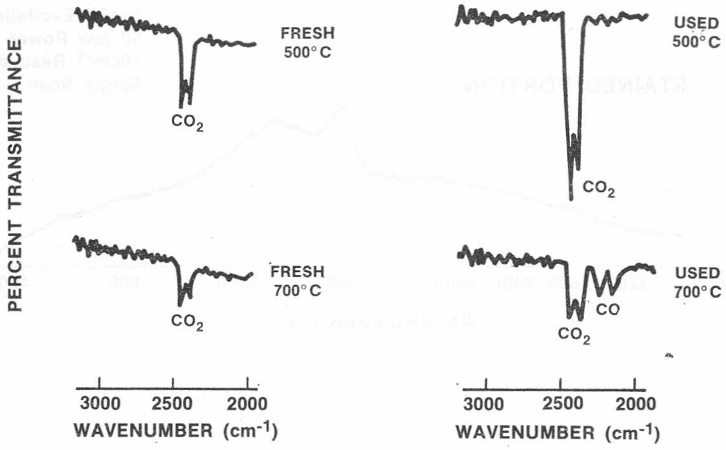

Figure 5. Evolved gas analysis. FT-IR, of alcohol synthesis catalysts.

the evolved volatiles through this temperature region using FT-IR showed that the used sample released significantly more CO_2 than the fresh (Figure 5). With some supporting data, it was conclusively shown that the activity decrease is due to formation of carbonates on the catalyst surface. TGA/FT-IR was further used to quantify the respective amounts of carbon deposited on both catalysts as CO_2 and CO. A calibration curve was prepared by decomposing various weights of calcium carbonate in the TGA and integrating the CO_2 absorbances generated by these weights. Using this calibration curve for CO_2 analysis and the TGA weight loss data for CO analysis, carbon levels calculated from TGA/FT-IR and elemental analysis were found to be in good agreement.

RAMAN SPECTROSCOPY

Raman spectroscopy is not as clearly recognized as FT-IR as a practical industrial tool, although many books and papers have tried to dispel that view.[11–14]

It is often the ability to solve problems quickly, especially ones involving the identification of deposits, stains, inclusions. *etc.* that make spectroscopic instruments invaluable in the industrial laboratory.

A sample of rolled and annealed brass sheet was submitted for analysis of the dark stains. A dispute over the cause of the stains involved the possibility of an improper rolling operation, which would tend to result in surface oxidation, or a problem with the rolling lubricant or tarnish inhibitor, which would tend to produce carbonaceous deposits. Figure 6 shows the Raman spectra of the stained material compared with an unstained portion of the brass. The peaks at 1355 cm^{-1} and 1575 cm^{-1} are indicative of graphitic material.[15] The ratio of these two bands suggest that the crystallite size in the direction of the graphite plane is around 56 Å. There is no evidence of Cu_2O or ZnO. Raman spectroscopy was thus able to eliminate the rolling operation as the culprit.

The feasibility of Fourier transform Raman spectroscopy has been demonstrated, as has been the ability of this technique to provide reasonable

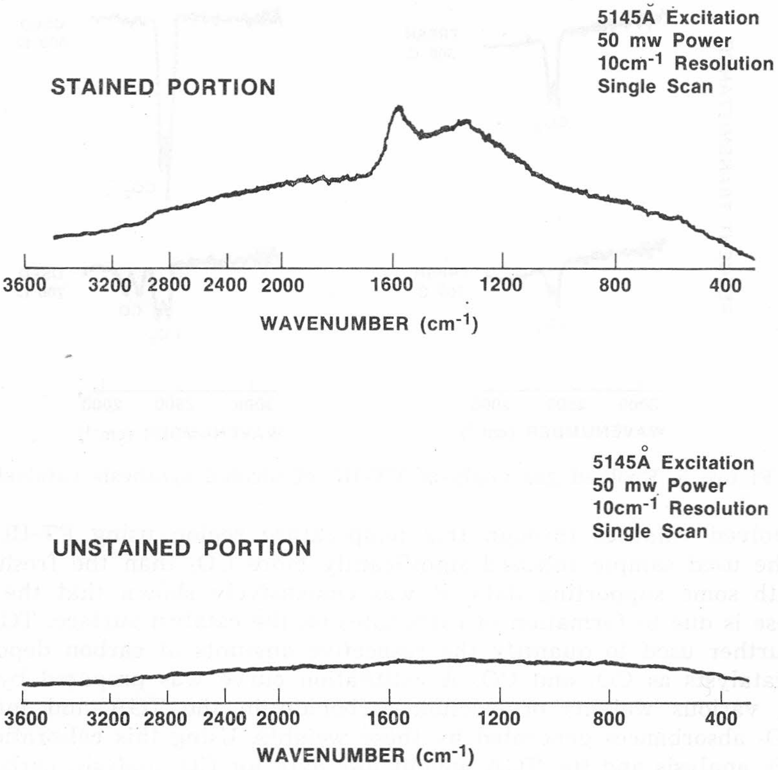

Figure 6. Raman spectra of stain on brass sheet.

signal-to-noise ratios in near-IR excited Raman.[16,17] Raman spectroscopy in this spectral region is virtually free from fluorescence interference and photochemical sample damage. A further benefit from this technique is the use of a single mainframe instrument for both IR and Raman spectroscopy using different accessories. The advantage of resolution, throughput, stability, and extensive data manipulation of FT-IR systems thus becomes available to Raman spectroscopy.

MICRO ANALYSIS

Although vibrational spectroscopy microprobes have been in existence for awhile[18], it is only recently that the development of good commercial instruments has enabled them to be used routinely for analytical applications. The obvious samples for microprobe analysis are nonhomogeneous samples exhibiting inclusions, phase segregation, bubbles, impurities, *etc.* Not surprisingly the areas of application parallel those of regular IR and Raman spectroscopy and include catalysis, corrosion, minerals, polymers, ferrography, environmental samples, fossil fuels, ceramics materials, and photovoltaic devices.[19]

In the case of laminated polymer structures, an IR microprobe can be successfully used to analyze the cross section of the laminate. This technique tends to be faster than time-consuming delamination or using FT-ATR and

FT-PAS while varying the depth of sampling. The laminate cross section of the proper thickness can be made by microtoming. The sample will float on the top of the microtome water bath and can be picked up by KRS-5 or some other water resistant crystal and analyzed without any further sample preparation. For this work, the microscope should have a rectangular aperture available in addition to the usual circular aperture.

Fine focusing and scanning of a laser beam makes it possible to do high spatial resolution Raman and scanning/mapping Raman experiment (MOLE). Microscopes, generally equipped with TV monitors, are available in both dispersive slit instruments and OMA-based instruments. Applications of micro Raman are well documented in the literature.[20]

The use of a diode array detector in optical multichannel analyses brings a new dimension to Raman spectroscopy.[16] OMA instruments are characterized by fast data collection (current state-of-the-art is 10 milliseconds/scan) and improvement in S/N by the use of multiplexing and signal averaging, which give similar results to FT-IR and FT-NMR. OMA instruments have high energy throughput, working with wide apertures typically in a Cassagrain configuration. Because of this, however, OMA spectrometers are more susceptible to stray light problems than conventional instruments. For samples where data close to the Rayleigh line is important, it is better to use a conventional instrument with slits. This is also true for high resolution work.

IN SITU ANALYSES

In situ experiments are increasingly important in many research areas today where it is important to obtain data under dynamic and real world conditions for a better understanding of kinetics and mechanisms of important processes. Such experiments have been especially useful in the field of heterogeneous catalysis for evaluating surface and bulk properties of the inorganic solid catalysts.

Of all the molecular and surface spectroscopies, Raman is the easiest for *in situ* work. This is so because of the ease of getting visible laser radiation in and out of the cell, which can be made of glass or quartz. But Raman suffers from the weakness of the scattering effect and this can be a significant problem with poor scatterers, such as the majority of solid catalyst materials. An *in situ* cell also will reduce the observed signal. Since most materials are sensitive to laser radiation, one cannot simply increase the power of the incident radiation. The ways to cope with this problem include: sample spinning (or rapid beam scanning), wide slits (or wide collection apertures such as a Cassegrain collector), cooled photomultipliers, photon counting, optical multichannel detection (OMA), and computerized data acquisition with signal averaging.

Figure 7 illustrates a very simple set-up used for study of heterogeneous catalysis (solid-gas interface).[21,22] It consists of a quartz tube in a ceramic furnace which can be heated to 650—700 °C. Most of the radiation backscattered from the catalyst is collected by a 45° mirror for spectral analysis.

Bismuth molybdates (α-$Bi_2Mo_3O_{12}$, β-$Bi_2Mo_2O_9$, and γ-Bi_2MoO_6) and related compounds have been extensively studied for many years because of their importance in selective oxidation and ammoxidation of olefins. Raman spectra of the stoichiometric compounds are shown in Figure 8. Disproportionation of

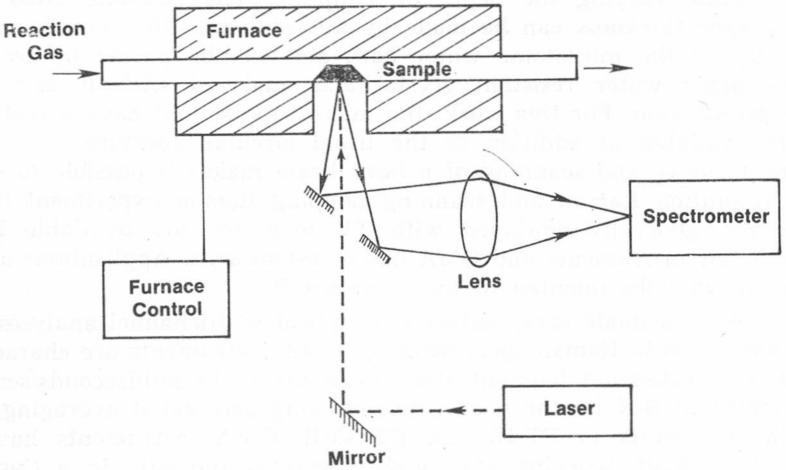

Figure 7. *In situ* Raman experiment — schematic of heated cell

β-$Bi_2Mo_2O_9$ into the more stable α- and γ- forms occurs in a redox cycle. *In situ* Raman study provides direct spectroscopic evidence for this process. Figure 9 clearly indicates that β-$Bi_2Mo_2O_9$ disproportionates under cyclic reduction with propylene and reoxidation with air at 430 °C. This restructuring of single phase β-$Bi_2Mo_2O_9$ is a slow process. Although β-$Bi_2Mo_2O_9$ is metastable up to 500 °C it disproportionates at lower temperature due to the presence of α- and γ- forms that act as nucleation centers. Under similar conditions α-$Bi_2Mo_2O_{12}$ and γ-Bi_2MoO_5 do not change. After disproportionation, the material kinetically behaves as the γ-Bi_2MoO_6 form via a surface restructuring.[23]

Over the years one of the major applications of specular reflectance has been to study polymer coatings on metal surfaces.[24] Both *ex-situ* and *in situ* studies can yield valuable information, as shown by the following example. The two substrates studied were untreated cold-rolled steel and cold-rolled steel with a conversion coating of zinc phosphate. Initial studies were performed *ex-situ* on samples which had been cured at a variety of temperatures. Further studies were done *in situ* under both air and nitrogen atmospheres.

The *ex-situ* studies showed that polymer behaviour was not affected by the substrate. The only spectral differences were due to the phosphate itself and to the water present either in the polymer or between the polymer and the substrate. The phosphate conversion coating is initially present as the tetrahydrate. As the temperature of cure increased, the waters of hydration were lost, resulting in crystallinity changes and hence spectral changes. At the higher temperatures (200 to 260 °C). the spectra showed a small amount of water left in both systems, presumably between the polymer and the steel. However, there is more of this water in the system with cold-rolled steel without the conversion coating. Since the system with the conversion coating shows much better wear characteristics, it is clear that the coating is important as a corrosion inhibitor. It is possible that additional spectral changes seen as a function of temperature might correlate well to other changes in physical properties. And from these data we might even infer a method of cohesion and its importance to the physical properties of the system.

Experiments were performed *in situ* on the same systems. Experimental conditions were not duplicated exactly; that is, the sample was not immediately brought from room temperature to a given cure temperature within the IR spectrometer. Rather, the sample was placed in the spectrometer at room temperature and the temperature was programmed at 10 °C per minute up to 260 °C, with interruptions at several specific points to allow spectra to be collected. Although spectra could have been collected continually, this was a low throughput experiment which required the co-addition of scans in order to achieve good signal-to-noise spectra. Taking the spectra at a

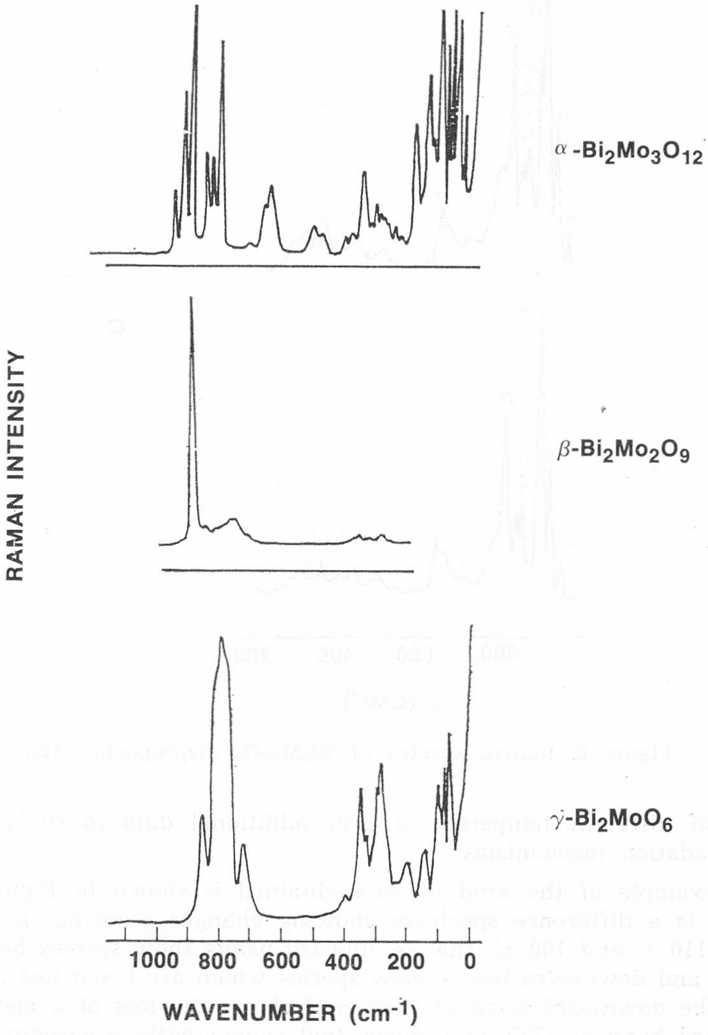

Figure 8. Raman spectra of bismuth molybdate phases.

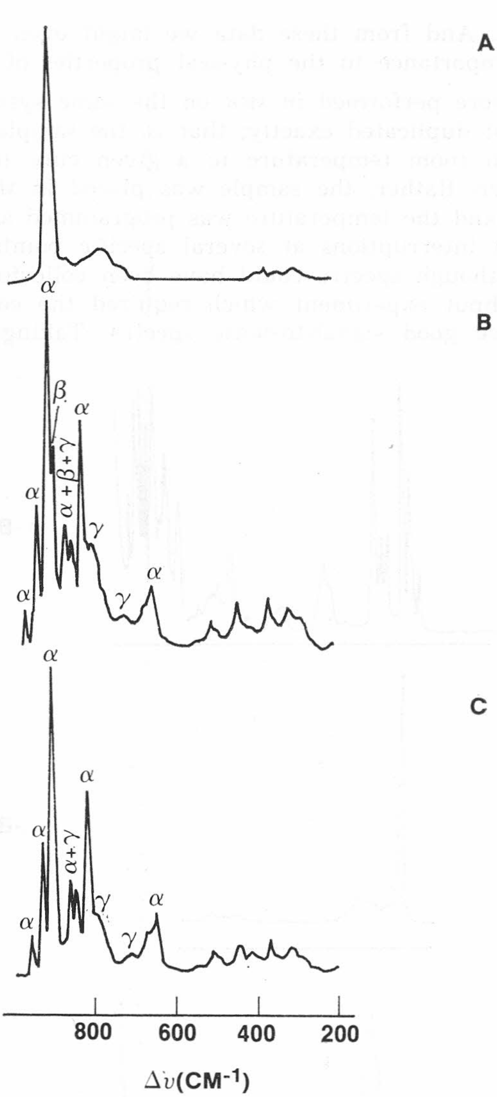

Figure 9. Raman spectra of $Bi_2Mo_2O_9$ disproportionation.

number of different temperatures gave additional data to study both cure and degradation mechanisms.

An example of the kind of data obtained is shown in Figure 10. This spectrum is a difference spectrum showing changes occuring in the system between 110 °C and 100 °C; that is, upward bands show species being formed at 110 °C and downward bands show species which are being lost in the same period. The downward band at 1332 cm^{-1} shows the loss of a methyl group; the upward band at 1725 cm^{-1} shows that concurrently a carbonyl species is being formed. In addition, a shoulder on the low frequency side of the upward

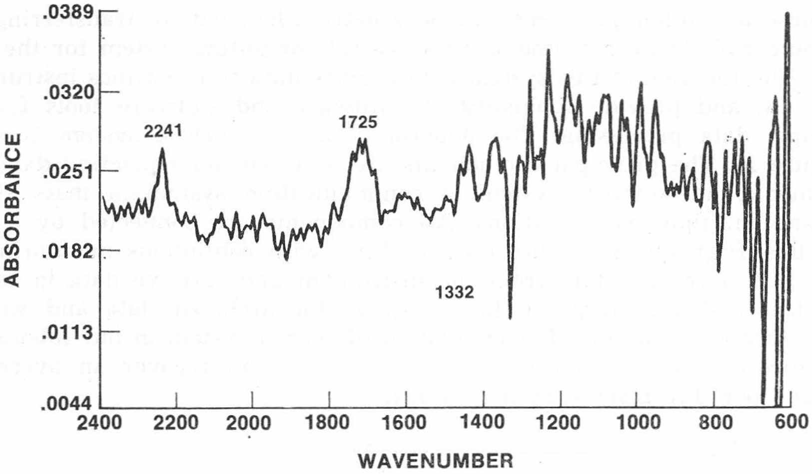

Figure 10. Polymer coating on steel substrate, *in situ* Raman spectrum, Subtraction: 110 °C spectrum minus 100 °C spectrum.

band at 2241 cm^{-1} shows that an unsaturated nitrile species is being formed.

In a recent report[25] external reflection Fourier transform infrared spectroscopy has been applied to the *in situ* measurement of the infrared spectra of insoluble phospholipid monolayer films that were spread at the air/water interface. The spreading conditions for the phospholipids [1,2-distearoyl-sn-glycero-3-phosphocholine (DSPC) and 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC)] were chosen to mimic those of liquid-condensed and liquid-expanded surface films, respectively. It was shown that the infrared reflection spectra can identify vibrations due to the hydrocarbon acyl chains, carbonyl ester, and phosphate groups for these monolayer films on water.

SPECTROSCOPY LABORATORY DATA SYSTEMS

Computerized instruments abound in today's industrial laboratories. Computers range from microprocessors to minicomputers equipped with moderate storage capacity and computing power. These unique computers perform three functions. First, they operate the instruments and collect data from them. Second, they are used to process the data. Third, they are used to archive the data. However, on some systems problems exist. The processing of data negates the collection of data on the instrument, leading to a situation where expensive instruments are idle for up to fifty percent of the working day, while their relatively inexpensive computers are being used. Since different computers with proprietary software may be used on the various instruments by different manufacturers, it is often difficult or imposible to program them for tailored applications involving several different spectroscopies. As an example, programs required for processing large amounts of data from dynamic experiments are not available, limiting the utility of such experiments. Proprietary reference collections are often among a corporation's more valuable assets and these should be accessible via on-line searches. Data should also be securely archived.

These and other problems can be greatly alleviated by transferring spectroscopic data from instruments to a central computing system for the laboratory. The function of this system is to acquire data from various instruments, archive it, and provide sophisticated hardware and software tools for spectroscopic data processing. The general design of such a system is shown in Figure 11. The principal components are a system for collecting data from instruments, an archival system, a communication system, a mass storage unit, and multiple work stations. All components are connected by a high-speed bus. High-speed parallel transfer lines with continuous monitoring can accept and store raw data from the instrument and retrieve data in seconds so that a real-time response to a request for archived data and working space is always available. The evaluation of such a system in our laboratories has indicated that, on a conservative basis, we can recover an average of one hour per day from such a network.[26]

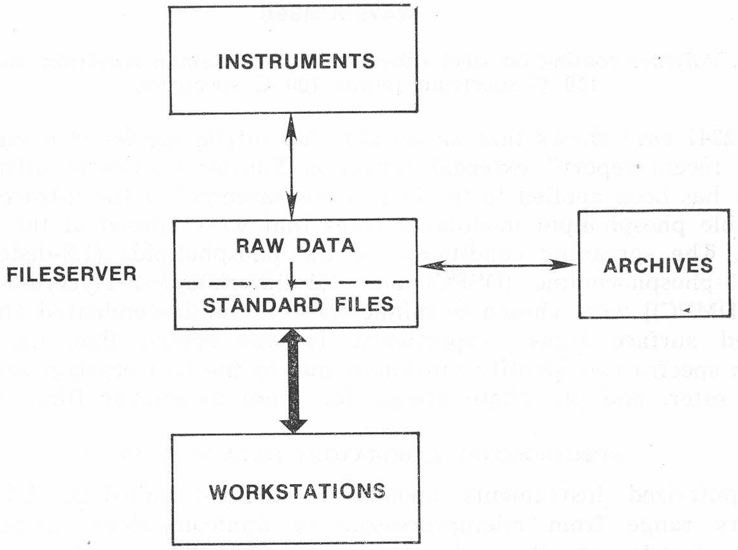

Figure 11. Schematic of a data archival — workstation computing system.

The benefits of software commonality between instruments was recently demonstrated in the field of X-ray diffraction. Controlled smoothing can be used to improve the signal-to-noise ratio of a spectrum without decreasing the information content, and it yields information regarding the appropriateness of the resolution used in the experiment. An IR algorithm was applied to XRD data. A study of the smoothing parameter showed that the diffractograms were over-sampled by a factor of at least five. We concluded that the collection time for survey diffractograms can be reduced from 80 minutes to 16 minutes, greatly improving the sample throughput. As a result of the central storage and distributed work station configuration, the degree of consultation between analysts is improved, increasing the knowledge base used for interpretation.

In the previous twenty years, we have gone from virtually no computing to mainframes and then to instrument computers. We are now seeing a move towards ready transferral of data with the JCAMP-DX protocol[27] having been developed to facilitate such transfer. This will further assist in making the computation independent of the instrument. Data are being securely archived with a great reduction in the manpower required. Intensive data processing has been removed from the instrument computing with a resultant increase in productivity.

Another major benefit has been in the »cross-fertilization« area. Software tools that are commonplace in FT-IR are not available in many other spectroscopies. We are now able to use them and derive more and better data than previously.

SUMMARY

The past and the present state-of-the-art in vibrational spectroscopy, especially in industry, is challenging and exciting. Some guesses on what we might look forward to in the future are shown in Table II.

TABLE II

○ More Hyphenated Techniques
○ Expert Systems/Networks
○ Stil More Difficult Problems
  — complexity
  — sensitivity
  — physical form
○ Quantitative Analysis
○ Process Control

There is little doubt we will expand our hyphenating in the near future. We will see even more elegant extensions of the coupling of separation methods and spectroscopic instruments. We can also expect to see multiple spectroscopic instruments directly on-line with the separation tools, such as gas chromatography or liquid chromatography with MS and IR and NMR! Our ability to identify smaller amounts of materials in more complex mixtures, specifically and rapidly, will be enhanced.

Spectroscopists form an information society. We have many very large databases and extensive knowledge bases. Expert systems which include interpretive capabilities are already available. In the not too distant future, we should see the development of expert systems which encompass all forms of spectroscopy. The capability to utilize data from several spectroscopic methods combined with information on the physical properties of samples should give us a total system for sophisticated molecular structure identification of materials, using pattern recognition techniques as well as artificial intelligence. Along with this use of knowledge-based expert systems, we will see the enhanced utilization of robotics and automation in the laboratory.

We are constantly pushing the capabilities of vibrational spectroscopy to address and solve still more difficult problems. Highly complex samples or those with awkward or sensitive physical forms will be analyzed with even better sensitivities for low-level components. Without question, the ability to perform *in situ* experiments at varying temperatures and pressures will contribute even more to the widespread applicability of infrared methods. Rapid scan instruments and Hadamard transform techniques are already showing practical applications.[28,29] Micro techniques have now advanced to the point that we can obtain spectra on samples with diameters close to the diffraction limits of the spectrometer. And with small apertures or microscopes, the spectra of samples in the picogram range are possible.

Advances in quantitative analysis are proceeding more rapidly than one can even follow in the literature.[30] Quality control will include quality assurance, laboratory and personnel accreditation, and a significant advance in the use of near-infrared techniques or miniaturized process analyzers for industrial applications.[31,32] Another advance in process analyzers may come from the use of IR-transmitting optical fibers for probing samples in hostile or normally inaccessible environments.[33,34]

Vibrational spectroscopy in industry today provides essential tools to help us address the evermore complex problems of the researcher. They have had a powerful impact and can anticipate an even brighter future.

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SAŽETAK

Nova era za primjene vibracijske spektroskopije u industriji

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Razmjerno novi razvoj vibracijske spektroskopije snažno utječe na sva područja tipičnog industrijskog istraživanja i razvoja. Tu se podrazumijeva Fourier-transformirana infracrvena spektroskopija, kompjuterizirana Ramanova spektroskopija, mikro-tehnike, kombinirane tehnike (uključujući separacijske i termičke metode sa spektroskopijom), te obilje novih i djelotvornih uređaja za uzorkovanje. Međutim, najznatniji je u tome razvoju dramatičan porast broja metoda *in situ,* za ispitivanje materijala ili praćenje reakcija. Bilo da se radi o katalizi, polimernoj kemiji, koroziji ili istraživanju nafte, uporaba vibracijske spektroskopije za eksperimente u realnom vremenu otvara novu eru impresivnih primjena.