

**The****SPEX**

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**Speaker****RAMAN SPECTROSCOPY AT SURFACES**

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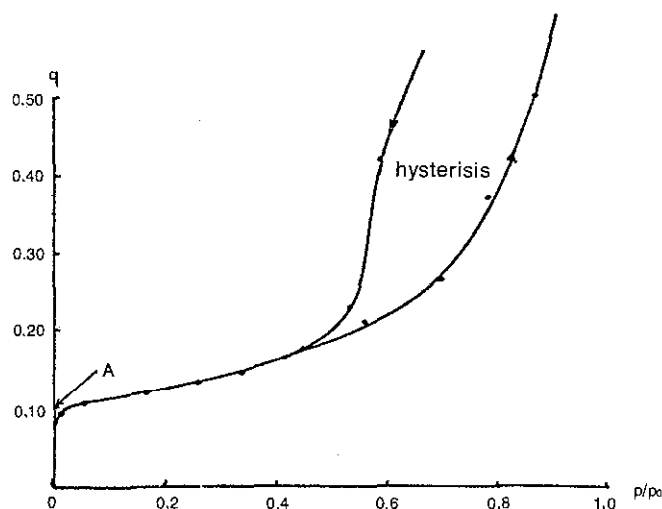
**E**VERYTHING solid or liquid with which we come in contact has, by definition, a surface! Most chemical reactions and a considerable number of physical changes occur at surfaces, yet strangely we know much less about their nature than we do about the bulk material beneath them. The reason is experimental: X-ray diffraction, electron diffraction, elemental and molecular analytical methods all readily reveal the nature and structure of the predominant species, normally the bulk substrate. At the same time, the very tiny proportion of material at or in the surface of the material is often ignored. If one is primarily concerned with coatings or layer structures, formidable analytical problems are encountered in inverse proportion to the thickness of the layer. This dilemma is particularly unfortunate because reactions at surfaces are of immense significance. Corrosion and its control comprise a major drain on the world's resources; reactions at catalyst surfaces constitute the standard method of large-scale continuous production of chemicals—"catalytic cracking" of heavy oil fragments to lighter ones or the Zeigler-Natta method of production of polyethylene and other polyolefines. Devices based on thin films semiconductors and coated optical surfaces are also essential to us.

Long before the laser appeared liquids, crystals, gases, polymers, etc. were scrutinized by Raman Spectroscopy. Lasers and modern sophisticated commercial Raman spectrometers have simply made research easier, more versatile, better in every respect. Study of the Raman spectra of species at surfaces is no exception, early publications in the field quoting mercury discharge lamp data. In 1962 Karagounis and Issa [1] reported Raman spectra of aromatic and olefinic hydrocarbons sorbed to silica and porous glass but their data were of poor quality. In the following year Pershina and Raskin, [2] working in Russia, advanced the subject a good deal further, reporting quite acceptable spectra of simple organic and inorganic molecular species adsorbed to oxides. More important, they were also able to whet our appetites by presaging, from their Raman evidence, the study of reactions between adsorbent and adsorbate at oxide surfaces. Since 1967, laser Raman spectra of a considerable range of systems have been published and it is now possible, among other things, to conduct quite thorough studies of surface-adsorbent interactions, to identify the chemical nature of surface films and layers and even to examine electrodes beneath electrolyte in electrochemical cells. We are here reviewing Raman literature on solid-solid, solid-liquid and solid-gas interfaces; an attempt is made to gaze into the crystal ball regarding future developments.

In view of the importance of surfaces, a number of experimental techniques have been especially devised for their elucidation. Low-energy electron diffraction (LEED), ESCA, Auger spectroscopy, reflectance spectroscopy all penetrate as little as possible into the surface substrate. Although these techniques command respect and hence have attracted numerous devotees they tend to be best applied to pure, chemically clean surfaces under high vacuum conditions and treated in a specially prescribed manner.

As a result other means have been sought to investigate the incredibly ill-defined surfaces frequently encountered in commercial products and practice; methods more amenable to surfaces as they are, rather than as we would like them to be.

The surface of a metal, exposed to the real world, is an inhomogeneous microcrystalline composite, more often than not, coated with a hideous mixture of grease, oxides, water, protective films and corrosion products. One or more of these identities may be of interest. Alternatively, one may wish to operate on a clean surface coated with a known molecular species. Although contamination at a metal surface can be removed, frequently it is replaced in the cleaning process by another contaminant, be it oxide or a water film. For, unless the material is cleaned and maintained under ultra-high vacuum conditions it simply will not stay clean. Ceramics and plastics suffer similarly except that, to begin with, their chemical nature is even less well defined than that of a metal and, in addition, degradation reactions will probably have occurred prior to study. Multiple layers often interact with one another thus diffusing the boundaries and further complicating measurements on them.



**Fig. 1** A typical isotherm for pyridine sorbed to a metallic oxide catalyst. Pressures 'p' are plotted as a proportion of the S.V.P. 'p<sub>0</sub>' at 25°C, the temperature at which the isotherm was determined.

Classically the true area of a surface (rather than the area apparent to the eye), and an indication of its nature, have been obtained by measuring an isotherm—a plot of quantity of volatile adsorbate on the surface against pressure of adsorbate over the adsorbent (Fig. 1). The values of 'q', the shape of the curve and the reversibil-

ity when sorbing or removing material provide an indication of the true area of material and thickness of layers. Point A is thought to represent the value of 'q' where the whole of the surface is covered with a monomolecular layer. Knowledge of the molecular cross-section then yields a surface area. Hysteresis reveals an average pore size in the material if this is appropriate. Measurements made at various temperatures offer the average value of  $\Delta H$  (interaction between adsorbate and adsorbent), and careful studies at low pressures enable us to distinguish chemisorption (where a chemical bond is formed between the surface and the adsorbate) and physisorption (where much weaker forces are involved). From isotherms for the same surface treated with a range of adsorbates we can postulate to some extent the chemical nature of the surface.

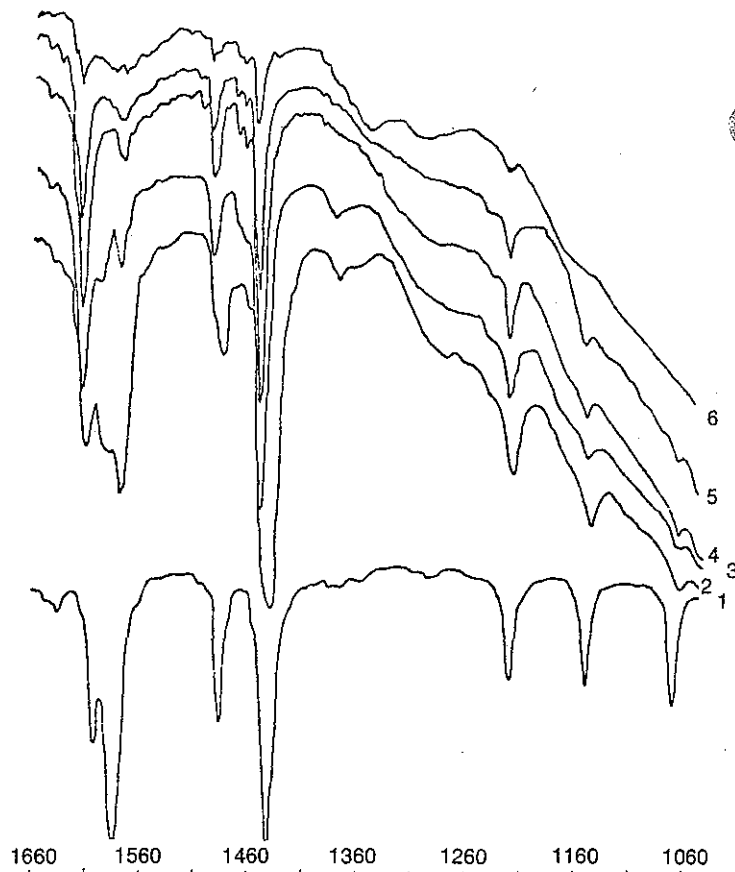
In addition to recording isotherm data, it is customary, where appropriate, to stream sorbate over the stationary surface and to monitor the chemical nature of the vapors downstream. Mass spectrometry and gas chromatography can be illuminating here. However, interpretation of the analytical data in terms of the nature of the surface is often largely intuitive. Surfaces of metals and particularly oxides can be chemically active (acidic or basic) and in favorable cases they can be monitored by titration routines in an inert solvent. Other surface films can be identified and their thickness estimated by evaporation or solution and subsequent analysis.

Another important technique in the surface field is infrared spectroscopy [3], applied in four main ways: by transmission, if the supporting material is transparent; by emission; by reflection off metal and similar surfaces; and where appropriate, by attenuated total reflectance methods (ATR) [4]. By any of these infrared methods, the total vibrational spectrum recorded will be that of the complete system sampled. In absorption experiments on thin sheets of oxide or other support, the spectrum will include the support plus the species sorbed to it. Similarly with emission experiments, characteristics of both support and sorbed species will appear in the infrared spectrogram. Reflection results sometimes prove better, the spectrum arising predominantly or even solely from material covering the surface. For purely experimental reasons reflectance methods are easier to apply to thick films but in principle they are almost universally suitable.

The interface is where the action is! Provided it can be isolated, its spectrum will be that of the molecules actually present (the spectrum providing an excellent fingerprint for identifying the chemical nature of the interfacial species) perturbed by exposure to the unique environment of the interface. Theoretically, this perturbation can be interpreted to tell us much about the nature of the surface itself. Further, in all infrared methods other than ATR, where the surface is covered with a tightly fitted prism, reactions can be monitored while the intensity of absorption or emission of radiation can yield some data on film thicknesses and the distribution of differing species present in the system.

**T**HE Raman spectrum of an organic species adsorbed to a bulk material such as an oxide should be similar to its infrared counterpart. One would expect severe interference from the support, the relatively small proportion of adsorbate contributing little or nothing to the whole. Like its IR counterpart, the intensity of Raman bands would be expected to be enhanced when originating from a porous surface where the volume of adsorbate is high. From the first reports to appear in the field, however, it became encouragingly clear that in this branch of Raman spectroscopy the problems were not as severe as in IR spectroscopy. Witness:

1. The spectra produced from carbon tetrachloride, pyridine, bromine, *trans* dichloroethylene and many other species on silica and silica gel were those of the organic adsorbate, no characteristics of the adsorbent being apparent [5]. As a result, spectra are clearly recognizable over the entire vibrational range and the problem demonstrated in Fig. 2 is not encountered.



**Fig. 2** IR spectrum of pyridine adsorbed on alumina (pretreated ~ 550C in vacuo), Spectrum 1 — pyridine (liq); 2 — sorbed; 3 — after evacuation to remove excess pyridine; 4 — heated to 150C; 5 — to 250C; 6 — to 375C. Note: — the IR transmissive "window" closes near 1000 cm<sup>-1</sup>.

2. Almost always the spectra were identical with those of the liquid adsorbate. Where reaction between the surface and adsorbate was likely, good fingerprint spectra of the chemisorbed species or the altered product were found [6].
3. On white surfaces little or no evidence was encountered of significant sample heating by the laser beam.

Two problems were, however, quickly identified: sensitivity of the technique was poor and fluorescence emerged as a major problem. Using the then current He-Ne lasers at around 50 mW, work was strictly confined to the study of white adsorbents of high area (> 60 m<sup>2</sup>g<sup>-1</sup>) treated with excellent Raman scatterers. Under these conditions, recognizable spectra could be obtained down to ~ 1 monolayer coverage. To be of interest, most adsorbents require pretreatment frequently by evacuation under heating. A typical recipe might require roasting at 500C for 2 hours under a pumped vacuum of better than 10<sup>-4</sup> Torr. In early experiments it became clear that these were just the conditions to enhance fluorescence to a level which made Raman work impossible. Here, obviously, conditioning treatment had to be modified. Although progress was slow fortunately it was continuous and now sensitivity is vastly improved and fluorescence partially tamed.

The current technique at Southampton is [7]:

Samples in powder, pellet, crushed lump or any convenient form are placed in a tube similar to that illustrated in Fig. 3. Normally about 1 g of sorbate is ample, the total weight of the cell being ~ 80 g. Suspending the cell on a fine nichrome wire from a conventional chemical balance, adsorbent quantities down to ~ 2 mg with a precision of ± 0.5 mg can be identified and measured. The sorbate is held in the tube with a silica wool pad.

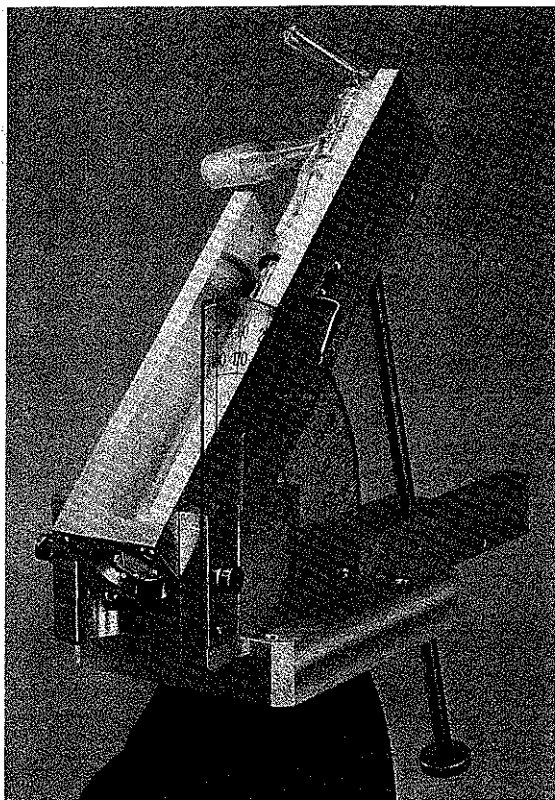


Fig. 3 Sample cell containing ~ 1g catalyst against the optical flat at the lower end of the tube held in a holder suitable for Raman work. The laser is imaged from below onto the flat. Scattered light collected to the left by the spectrometer.

The cell is heated and pumped to clean the adsorbate. We tend to avoid the temperature range 200 to 800C to minimize fluorescence\*. Sheppard *et al* recommend heating in a stream of O<sub>2</sub> and have found that temperatures up to at least 500C are accessible in this way [8].

After weighing, adsorbate is added and the pressure over the surface recorded after equilibration in a thermostatted environment. Raman spectra are then taken with the cell mounted kinematically. (No sample alignment is carried out during a series of Raman experiments.) When satisfied, a further aliquot of sorbate is added, a new pressure measurement made and a further Raman spectrum recorded. Equally easy, of course, is the reverse scan, adsorbate being removed between successive experiments. Thus, Raman spectra are recorded at precisely known positions on the isotherm. Further, the sample can readily be maintained at any realistic temperature. Designs for flow cells based on Fig. 3 have also been tried with no apparent problems.

A good double (or better a triple) spectrometer is required. To minimize the risk of sample heating by the laser, we use < 150 mW of laser power normally at 5145 or 4880A and slightly defocus the laser spot on the sample tube. First-class laser stability is essential because weak Raman signals are often being measured against a heavily zero-suppressed background. As adsorbed species tend to give relatively broad spectral bands and sensitivity is always at a premium we normally operate at 2-5 cm<sup>-1</sup> slit width. From preliminary measurements made at Southampton it looks as if computer averaging has considerable potential and this is discussed later.

\*Sheppard has suggested that the fluorescence so frequently encountered results from getting of the cell system by the newly cleaned adsorbate. As a consequence, grease is sorbed to the surface, then decomposes to produce fluorescent products. We agree with Sheppard and not with Careri *et al* [8] who contend that the intense background emission arises from water molecules excited by a Raman-like process chemisorbed to the surface.

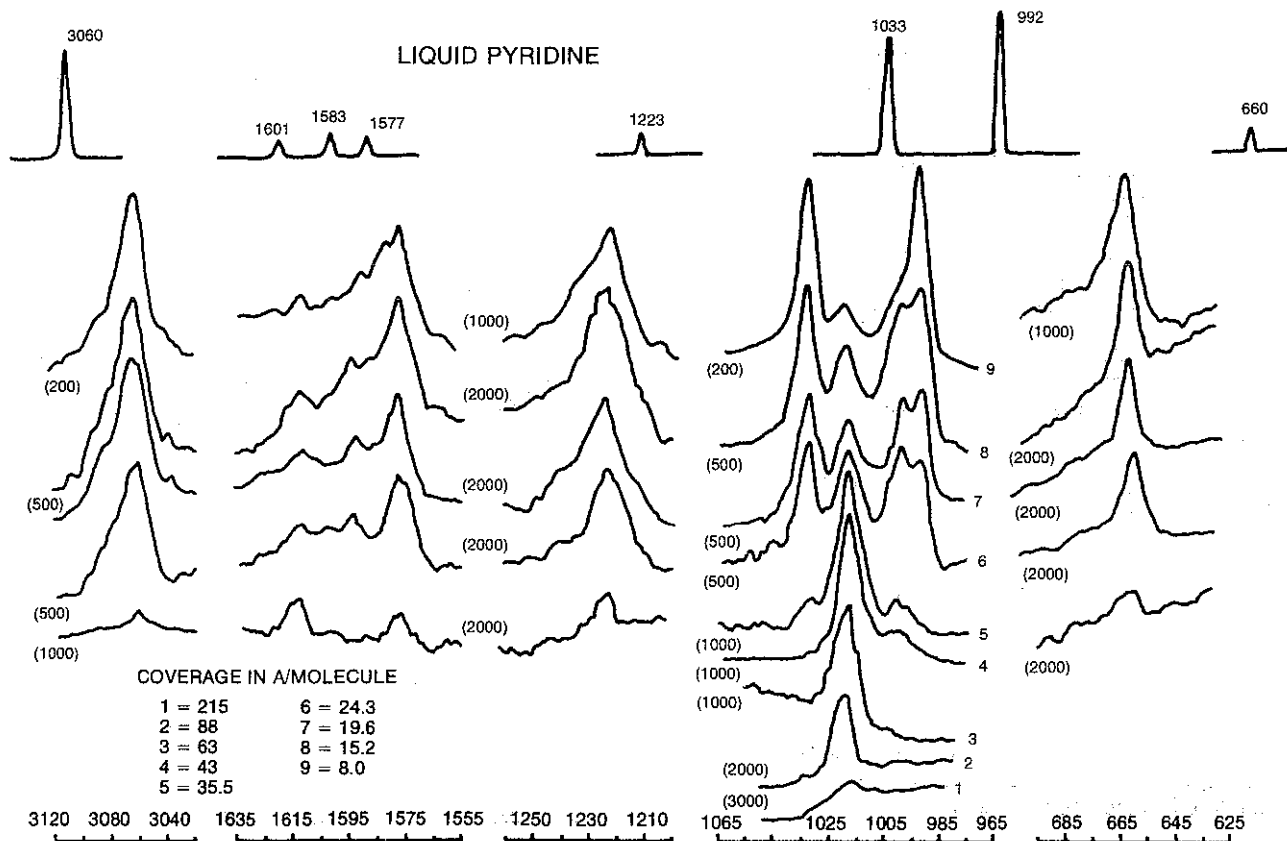
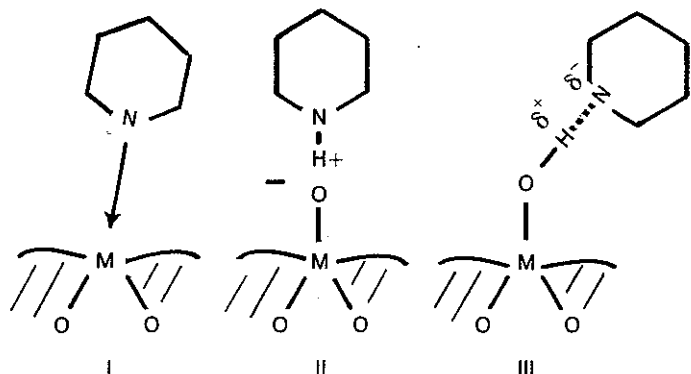


Fig. 4 Part of the Raman spectra of pyridine over alumina. Figures in parentheses indicate relative gain factors. All spectra recorded using 5 cm<sup>-1</sup> slits and 4880A radiation. Raman bands at 1019 cm<sup>-1</sup>, Lewis-coordinated pyridine; 999 cm<sup>-1</sup>, H-bonded and 992 cm<sup>-1</sup>, liquid (physisorbed) pyridine.

With these methods or ones closely related to them, the sorption of pyridine and substituted pyridines over acidic metallic oxides has been studied *ad nauseum* [9]. Acidity at this type of surface is thought to originate in a variety of surface species including Lewis acid sites I, Brønsted acid sites II and surface alcohol groups III all of which can interact with the weak base such as pyridine as follows



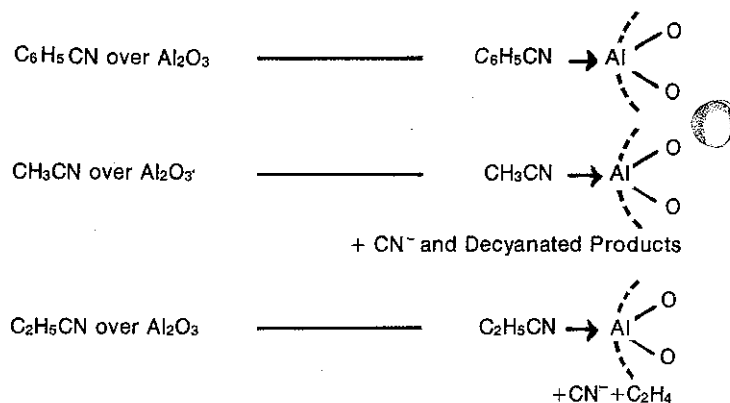
The Raman spectrum of pyridine over oxides\* contains bands characteristic of some of the above and can be used to assay the acidity of the surface (Fig. 4). It is also possible to refine the measurements further by monitoring the effect of a second base on the Raman spectrum of the oxide coated with the first. If the pK is widely different, the competition between the two can be most illuminating. Examples of Raman spectroscopy applied to the interaction between sorbates and many aromatic molecules are listed in Table 1.

**Table 1. Examples of Raman spectroscopy applied to sorbed species on oxides**

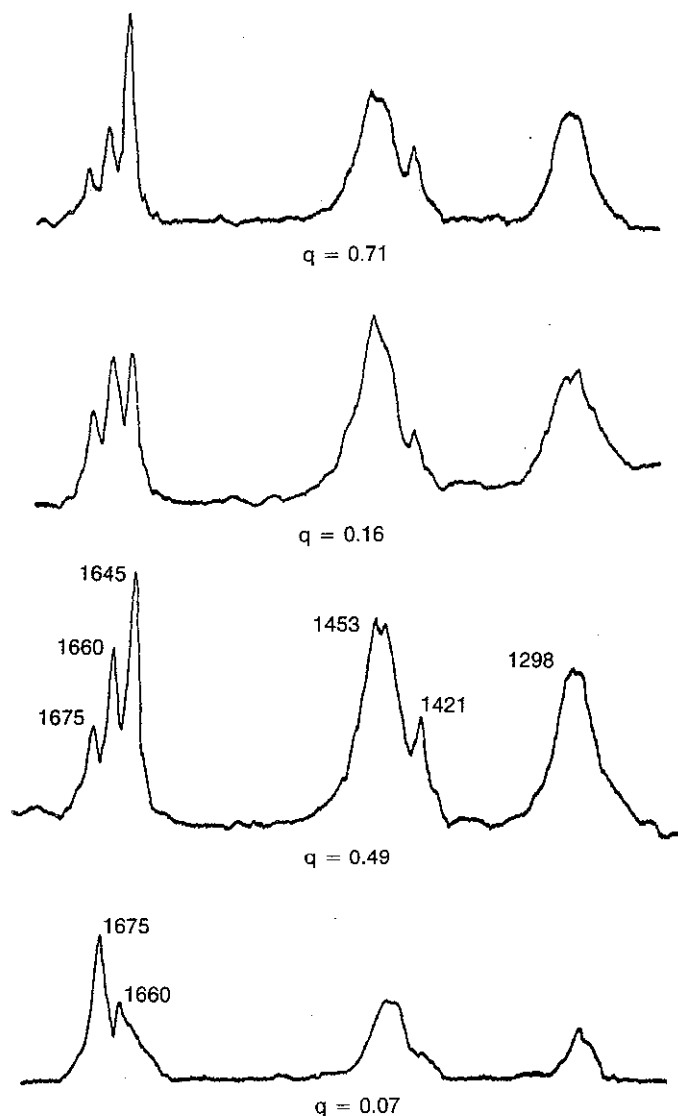
Adsorbate	Adsorbent	Authors/ref
Pyridine	numerous	numerous 9
2-Chloropyridine	SiO <sub>2</sub>	Kagel 9
Acetone	Al <sub>2</sub> O <sub>3</sub>	Winde and Denime 10
Nitrobenzene	porous glass, Al <sub>2</sub> O <sub>3</sub> , zeplites	
Acetaldehyde	SiO <sub>2</sub> gel	
Benzene	Vycor glass	ref. 6
Benzene/ethylene/propylene	Vycor glass, molybdenum oxide, uranium oxide, zeolites	Sheppard 8
Carbon monoxide	Pt-porous glass	Buechler and Turkevich 11
Silanes	glass and silica	
Olefines and diolefines	alumina and silica/alumina	Turner 12
Nitriles CH <sub>3</sub> CN		
C <sub>2</sub> H <sub>5</sub> CN		
C <sub>6</sub> H <sub>5</sub> CN		
CH <sub>3</sub> CN	zeolites	Angell 13
Propylene		
Acrolein		
Pyridine, piperidine and Thiophene	Silica	Cooney 14

Recently it has been shown that reactions at surfaces, like nitrile with alumina and silica-alumina and the isomerization of olefins, can be monitored as they occur (Fig. 5).

\*Accessible oxides certainly include high-area samples of silica, silica gel, titania, magnesia, some zeolites,  $\beta$ ,  $\gamma$  and  $\eta$  aluminas, some silica-aluminas and porous glass.



In these cases, the spectrum can be recorded over a range of pressures and temperatures. In addition, some of these reactions occur at a fairly pedestrian rate at room temperature so spectra can be recorded in a few minutes repeatedly and kinetic data accumulated (Fig. 5b).



**Fig. 5 Raman spectra of species reacting at surfaces.**

a) spectra for 4 coverages of hexene-1 over alumina at 25°C. The Al<sub>2</sub>O<sub>3</sub> has been pretreated by evacuating at 950°C. Bands at 1645 cm<sup>-1</sup> hexene-1, 1660 cm<sup>-1</sup> *cis* hexene-2 and 1675 cm<sup>-1</sup> *trans* hexene-2.

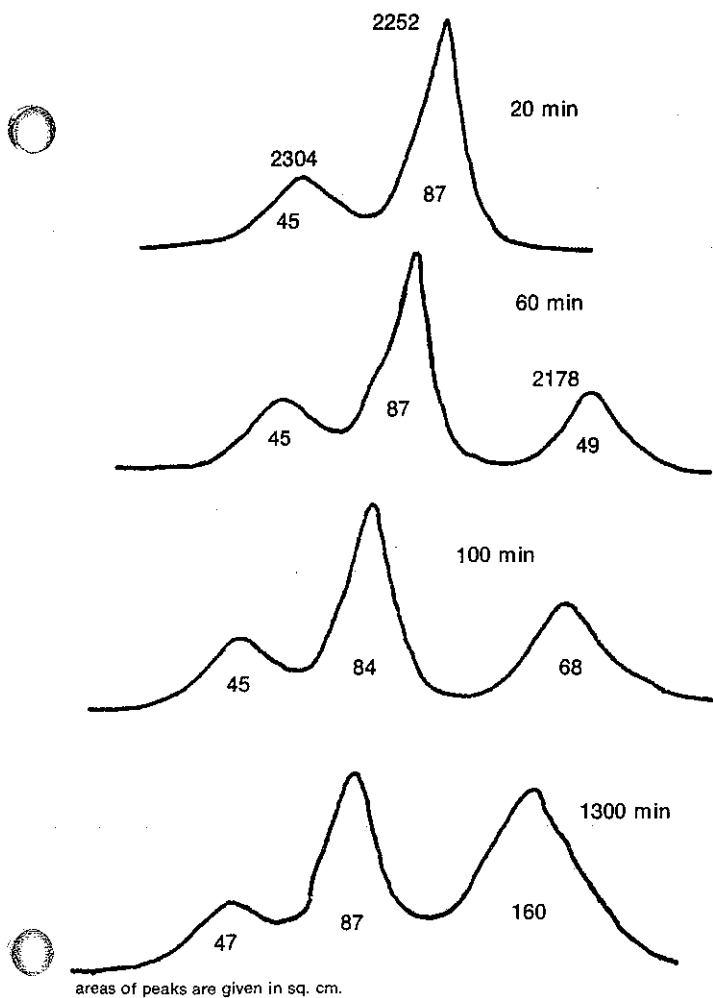


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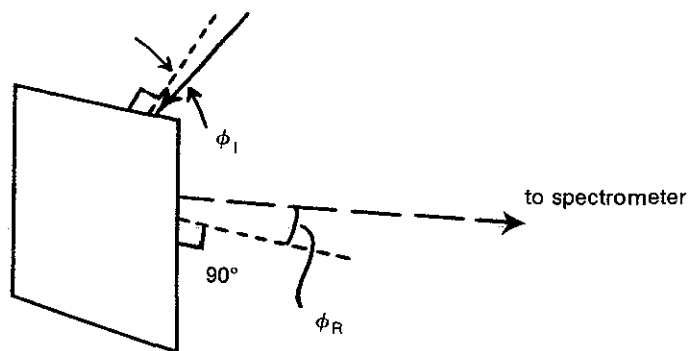
b) propionitrile over a similar alumina to above. In this case the effect of time was observed. Bands at  $2252\text{ cm}^{-1}$  liquid physisorbed propionitrile,  $2304\text{ cm}^{-1}$  Lewis coordinated propionitrile and  $2178\text{ cm}^{-1}$   $\text{CN}^{-}$  ion.

IN Table 1 several examples were cited of studies on Vycor or similar porous glasses. Optically these materials are fairly clear and yet have high intrinsic surface areas because they have been deeply etched. Infrared studies of this type of material abound and it seems that corresponding Raman measurements are quite possible. Unfortunately, glass is not a functional catalyst and reactions at the surface of microporous glass and/or the nature of species at the surface are of mainly academic interest. On the other hand, the surface of conventional (non-etched and hence smooth) glass, is of considerable technical significance but tends to have a low surface area. To overcome this limitation, Shih [15], in a study of the surface interaction of glass and silicones (with particular reference to the properties of glass/polymer composites), chose glass microspheres and glass fibres\*. Raman analysis of fibres was straightforward. A small fibre bundle was held in the laser beam at a slight inclination to it and the scattered radiation collected at a right angle to the illumination direction. Multiple reflections of the laser beam within the fibre tend to enhance the detected Raman signal favoring this method of studying surface interactions at glass, quartz or even organic polymer surfaces. Glass microspheres ( $\sim 50\mu$  diameter) also provide a sufficiently large surface area for Raman work.

Transparent thin film coatings on opaque substrates quite easily provide good spectra. It takes only focusing the laser into the specimen if the film thickness is of the same order as the diffraction-limited laser spot diameter, typically between 5 and  $40\mu$ . As a consequence, film layers of thickness in the microns range over metals are quite approachable. Paradoxically, unsupported thin films can be more troublesome. When they are not

supported on a substrate, laser radiation absorption can cause catastrophic heating of the film. Immersion in water often prevents overheating. Of obvious value are such investigations of paint to metal bonding or adhesion of paint to lower paint layers. In forensic science, characterization of minute chips of paint can constitute essential evidence. The small diameter of the laser spot makes the Raman technique particularly attractive. Unfortunately, however, there is a tendency for this type of specimen to have a fluorescence level which is quite overpowering because fluorescence in polymers is frequently associated with oxidative degradation at or near surfaces. It is a fact, however, that the base pigment common to most modern paints — titania — has a very intense Raman spectrum and this can be detected very easily.

Research projects, on the other hand, often require analysis of films over reflective metallic surfaces far thinner than those discussed above. Greenler and Slager [16] have considered the theory and practice of a situation where the laser illuminates a specimen of metal coated with an organic layer less than 100A thick. They were able to show that 'best' results over silver with blue lasers are obtained if the angle of incidence  $\phi_i$  is large (typically  $70^\circ$ ) and the collection angle  $\phi_R$  near  $60^\circ$ .



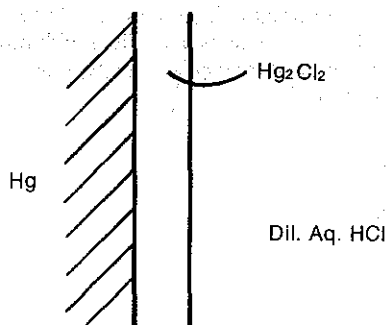
A spectrum, admittedly of poor S:N ratio, was shown of benzoic acid over silver with a film thickness of only 50A excited with a laser of only 60 mW. More recently, Ikeshoji et al [17] have attempted to carry out a Raman experiment closely analogous to Attenuated Total Reflectance in the infrared. Focusing the laser through a glass hemisphere onto the interface between the plane surface and liquid carbon disulfide at angles of incidence in excess of the critical angle of total reflection (in this case  $70.8^\circ$ ), they were able to collect Raman radiation emanating from molecules very close indeed to the glass/carbon disulfide interface. Finding the signal strength in their preliminary measurements disappointing, they resorted to repeat scanning and computer averaging techniques. Since they were handicapped by a helium-neon laser of low power and multiple reflection and other instrumental improvements are sure to be developed, the method shows considerable potential for problems involving the interface between glasses and other transparent solids and liquids.

IN recent years there has been a considerable increase in research into the reactions which occur at electrode-electrolyte interfaces. The quest for fuel cells and storage batteries with high capacities and the control of metallic corrosion stimulated by commercial applications and the space program have added urgency to this effort while the energy crisis has added another turn to the screw. Our knowledge of the reactants and final products in an electrochemical process and of the electrical parameters involved (current, voltage capacitance, etc.) is excellent but the structure of the electrode-electrolyte interface and the mechanisms of reactions at the interface are only poorly understood. This data, if available, would certainly improve prospects for the invention and development of significant new devices.

\*P.R. Reed at Spex Industries successfully detected siloxane coatings on glass fibres  $20\mu$  in diameter. Such coatings are industrially important for bonding glass to rubber in the manufacture of tires.

Already mentioned, X-ray, electron diffraction and related techniques are not applicable under electrolytic conditions. Optical methods of analysis at the electrode-electrolyte interface are normally unfeasible. Although some success has been achieved with ultraviolet/visible absorption/reflection techniques and ellipsometry, the data from these methods are not too specific so they are unlikely to be developed very enthusiastically. Infrared methods show promise but in aqueous electrolytic cells are almost impossibly difficult due to the intensity of water absorption. Infrared attenuated total reflectance has been tried for infrared transparent germanium electrodes [18].

Raman, on the other hand, would appear to be an attractive approach. Since water is both a poor scatterer and does not absorb in the visible region, its interference with Raman spectra should be minimal. The first successful experiments to be reported [19] related to this Hg surface interface.



The electrode, especially contrived to maximize the surface area, was placed in the Raman spectrometer with the laser beam impinging at glancing incidence, thus illuminating a considerable area of its surface, which consisted of very finely divided droplets of mercury adhering to a platinum substrate. As the electrode potential was cycled, the Raman-scattered spectrum of calomel ( $\text{Hg}_2\text{Cl}_2$ ) could be made to appear and vanish. Spectra of  $\text{HgO}$  and  $\text{Hg}_2\text{Br}_2$  could be found if nitric and hydrobromic acid were used as electrolyte. All three species identified,  $\text{HgO}$ ,  $\text{Hg}_2\text{Cl}_2$  and  $\text{Hg}_2\text{Br}_2$  are strong Raman scatterers but the experiment did demonstrate the feasibility of examining the electrode-electrolyte interface in this way.

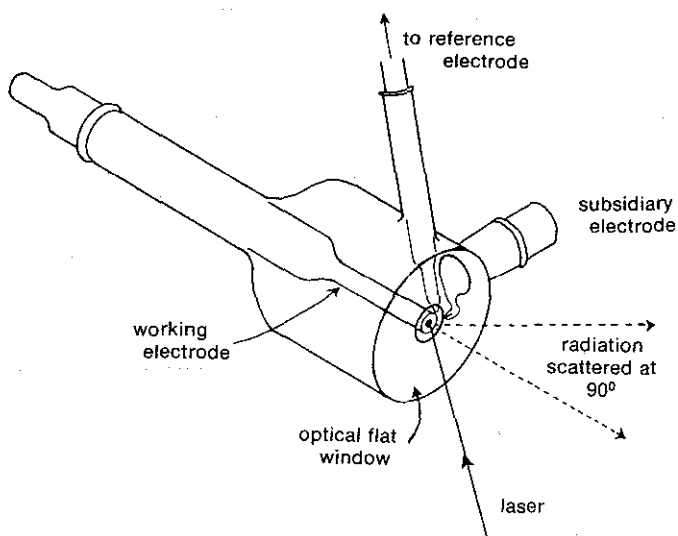


Fig. 6 In this thin-layer cell a mercury drop only  $\sim 1$  mm in diameter is extruded through the hollow working electrode holder against a glass optical flat. The subsidiary electrode is a platinum wire ring surrounding the mercury drop.

Electrochemists have an almost insatiable attraction for the plane mercury surface. Unfortunately this is far from ideal for Raman work because it has little area and mercury surfaces wobble! Confined in the cell drawn in Fig. 6, the surface can be kept still, the thin film of electrolyte between the metal and the glass flat being adequate to complete the cell. Using this device, admittedly unbelievably bad but recognizable spectra of calomel ( $\text{Hg}_2\text{Cl}_2$ ) can be recorded and, as before, their intensity is potential-sensitive this time demonstrating the feasibility of the Raman method in a situation really well studied by the classical electrochemical, mercury polarographic system. Very recently a new system has yielded significant and much more detailed results. It is an electrochemically etched silver electrode with a high surface area.

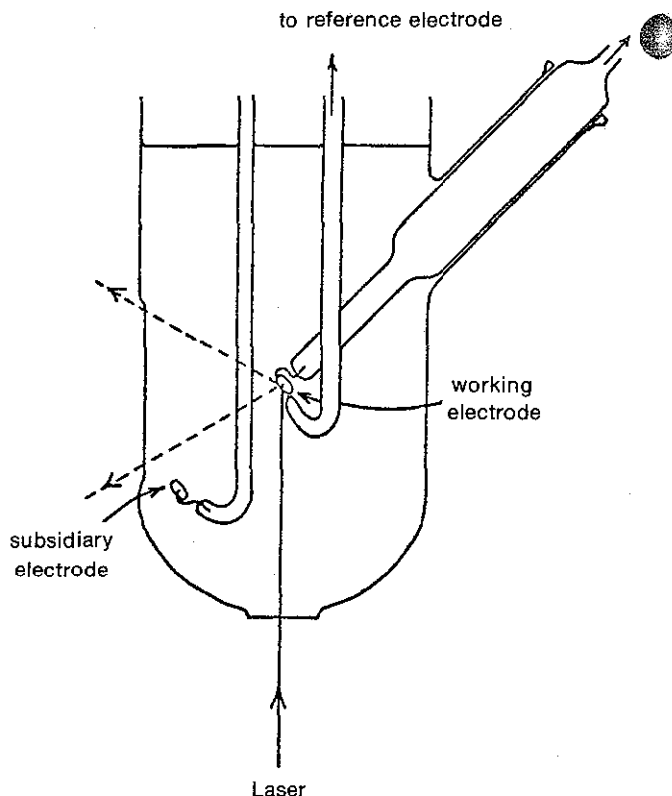
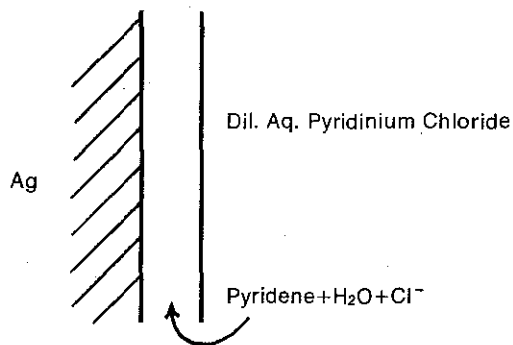
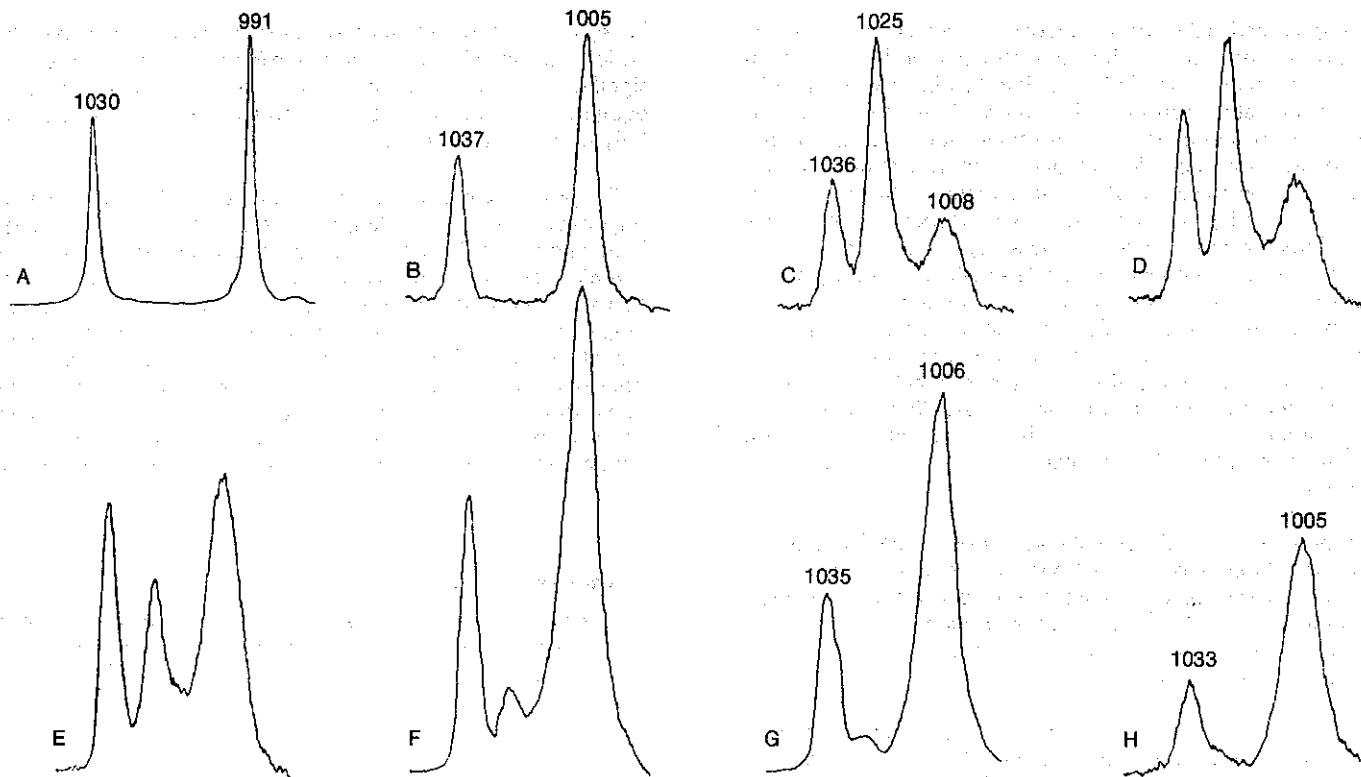


Fig. 7 An electrochemical cell for Raman experiments. The working electrode can be supported in a glass tube blown onto a modified hypodermic syringe or fitted into a machined Teflon sleeve.



**Fig. 8** Spectra at a silver-electrolyte interface. The electrolyte used was aqueous 0.1M KCl and 0.05M analytical grade pyridine.

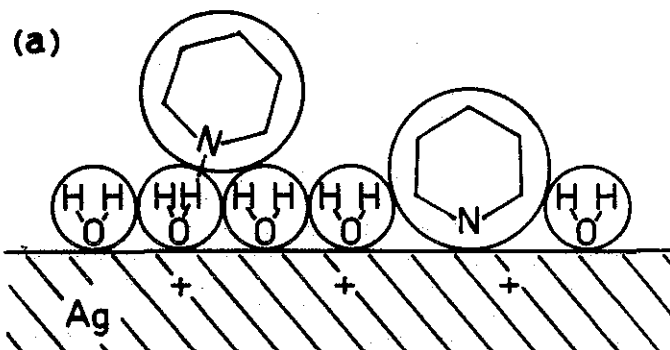
- |   |                |
|---|----------------|
| <b>A</b> liquid pyridine                    | <b>E</b> -0.4V |
| <b>B</b> 0.05 M aqueous pyridine            | <b>F</b> -0.6V |
| <b>C</b> silver electrode at 0.0 V (S.C.E.) | <b>G</b> -0.8V |
| <b>D</b> -0.2V                              | <b>H</b> -1.0V |

Bands 1025  $\text{cm}^{-1}$  — Lewis coordinated pyridine, 1005-8 — H-bonded coordinated pyridine.

The cell and the spectra produced as the electrode potential is varied are shown in Fig. 7 and 8; the identity of the bands given in the caption to Fig. 8. The appearance of pyridine molecules Lewis-coordinated to silver atoms is not unexpected but the behavior of the hydrogen-bonded species is of considerable interest. As the potential is made more cathodic it would appear that sorption maximizes near the "potential of zero charge" but also that the ring breathing mode frequency shifts. At the anodic potentials, the frequency is intermediate between that characteristic of hydrogen-bonded pyridine in water and the pyridinium ion. At cathodic potentials the frequency is close to that of the aqueous hydrogen-bonded heterocycle. We interpret this as follows: at anodic potentials, the water molecules are oriented with the oxygen atom towards the electrode and the pyridine is bonded to the surface layer of water molecules. At cathodic potentials the water molecules reverse in orientation and at least one further water molecule must be inserted between the metal and the pyridine (Fig. 9).

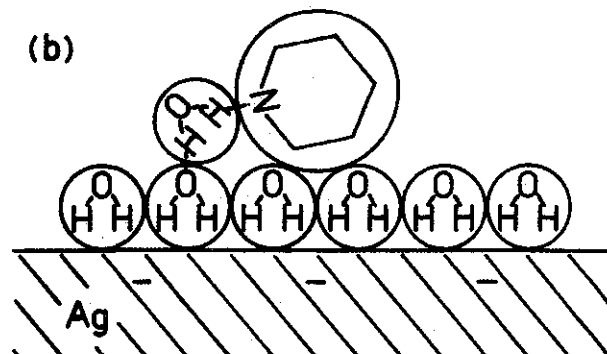
Success has also been achieved with other aromatic amines. Further, preliminary measurements suggest that the deformation vibration of the water molecules close to the surface of the electrode is perturbed significantly by the immense potential gradients within the electrical double layer.

The structurally specific nature of these preliminary results is unique and we feel invaluable in electrochemistry. In particular, a classical study alone of the pyridinium chloride/silver system would have given little hint of the importance of Lewis adsorption or of the role pyridine must play within the electrical double layer. There is no reason in principle why Raman data cannot now be taken of numerous significant electrochemical systems to acquire discrete analytical and structural information of electrode surfaces.



**Fig. 9** Possible models for the structure of the electrical double layer between Ag and a KCl solution containing pyridine.

a) Situation at potentials positive with respect to the potential of zero charge. Pyridine in this case is sorbed via the nitrogen atom to the silver in an "aqueous acidic environment."



b) As above but at more negative potentials. Here the pyridine can be said to be in an "aqueous environment."

As emphasized in the first section of this article, Raman methods have solved real, significant interfacial problems but the effort exerted internationally in this field has been very small indeed. Unfortunately, sensitivity is at a premium and, as a consequence, the few researchers who are active have been inclined to forfeit reality for acceptable S:N ratios! If more instrumental sensitivity could be found, those elusive plane surfaces could be examined and orientations of sorbate with respect to them measured; colored catalysts could also be analyzed, an immense area including the poorly understood Zeigler-Natta olefine polymerization process and reactions at the oxide-supported metal and mixed heavy-metal-oxide catalysts. Carbon blacks are also amenable to Raman study probably because of their very great specific surface area [5]. To date, interaction of carbon black with rubber, chlorohydrocarbons and other technically significant systems has not been subjected to Raman methods but hopefully will be soon. Again progress will require enhanced sensitivity and a mastery of fluorescence.

Someone should, and certainly will, look at the fundamental mechanism of operation of electrodes, especially the plane mercury surface. The effect of crystal face on electrochemical interactions at metals would also be a soluble problem if current Raman sensitivity were improved. Corrosion mechanisms on metals should also be accessible.

The instrumental improvements needed to advance the work are already available or under development. Triple monochromator systems reduce stray light so that at high sensitivity, apparent S:N ratios are better than with the older double monochromators. Computer interfacing with the output signal and wavenumber scan of Raman spectrometers permits far more sophisticated analyses of data than heretofore. For example, incremental counting, digital background subtraction or suppression and repeat scanning and averaging of noise are all feasible now and only await application to surface studies. To date laser powers have been kept relatively modest (to minimize the risk of heating the sample) and this is obviously wasteful. Spinning sample accessories now quite common, may be modified to accept sorbed species or electrochemical cells. Absorption of radiation by the sample then ceases to be a problem up to two or three watts of laser power.

Recently, it has become clear that the principle of "resonance enhancement" of Raman signals has a very wide application. In this type of experiment, one deliberately tunes a laser so its exciting wavelength is close to an absorption maximum. In favorable cases, the absolute intensity of the Raman radiation can thus be increased by up to  $10^6$  times. Since absorption occurs, the sample must be moved beneath the laser focus if it is not to suffer, thus the development of spinning sample accessories. Although not yet applied to surface species, this technique will definitely prove to be of value in the near future, particularly since laser manufacturers are now producing convenient, reliable and powerful continuously tunable dye laser systems enabling us to "tune" the laser wavelength precisely to the samples' absorption characteristics. Not only does resonance result in great enhancement, it is often specific. When a mixture is to be analyzed, one can often choose an excitation frequency corresponding to the absorption of a particular compound, thus relegating the Raman spectra of potentially interfering substances to the background.

Fluorescence remains a major problem which a number of groups including Spex researchers have been making determined efforts to reduce. The most generally successful approach starts with a train of pulses from a laser attempting to analyze the detected signal temporally. If the pulses are short and sharp enough, the virtually instantaneous Raman scatter will appear on top of the fluorescence which will then decay exponentially. With electronic switching such as the Box-Car detector, the decaying emission can

be rejected and thus the level of fluorescence integrated over long periods can be reduced relative to the Raman signal collected. Very significant progress has been made in this field but the exotic equipment required is not truly commercially available yet. Hopefully it will be very soon.

The proven feasibility of many significant surface chemistry and physics experiments, with improvements in the offing, indicate that both fundamentally inclined and commercially oriented chemists, chemical engineers, physicists and metallurgists will be finding Raman an expedient tool. In this connection, an outstanding example comes from researchers at IBM. Under the direction of Nobel laureate L. Esaki, the significance of Raman spectroscopy in developing a promising new class of semiconductors has been demonstrated [20]. Where other techniques have failed, Raman has succeeded in the analysis of alternating layers of different substances laid down as thin as 500Å each by epitaxial methods.

### Acknowledgments

Much of the work reported and discussed in this article was completed by the author's co-workers at Southampton including Drs. E. J. Loader, I. D. M. Turner and A. J. McQuillan.

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# RAMACOMP SUBROUTINES

The Spex RAMACOMP is a computerized Raman system consisting basically of the Spex RAMALOG 4, a dedicated computer, interactive teletype and pertinent software tailored to the needs of Raman spectroscopy. A laser, for which provision is made in the RAMALOG console, is required to operate the system. Additional memory, sub-routines, Linc magnetic tape drives, etc. are available as accessories.

## Hardware

**RAMALOG 4**, with the exception of a laser, includes all items required for the analysis of liquids by Raman spectroscopy.

**Computer**, Interdata Model 716 with 16 KB of memory, ASR 33 Teletype, Spex interface module.

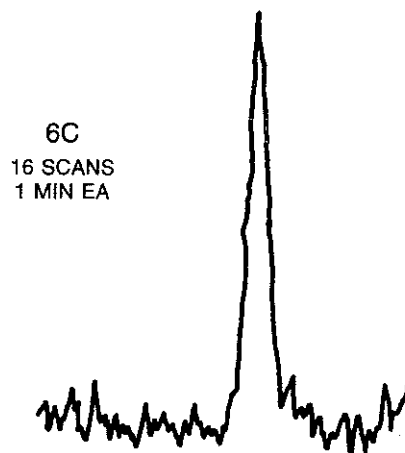
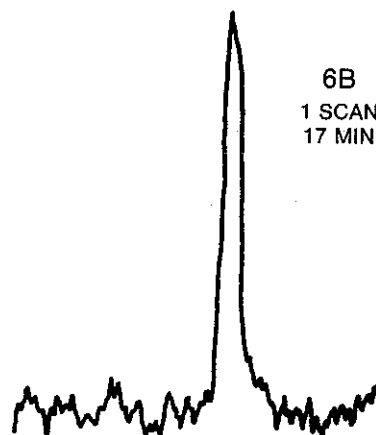
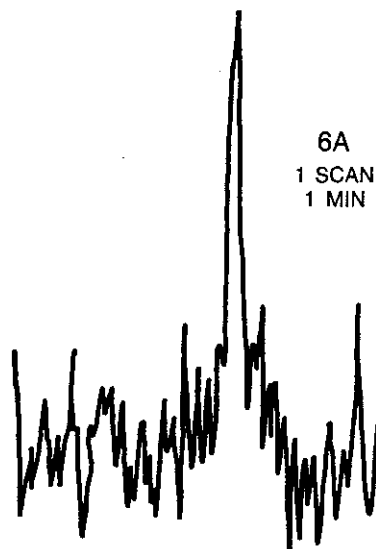
**Software**, Subroutines include the following:

1. **Spectrometer Driving.** Starting and stopping points can be typed as instructions; the computer will then drive the spectrometer to the starting point, (taking up backlash in the process) scan at parameters set by the operator, and stop at the end. The scan increments can be made linear in wavelength or wavenumber.
2. **Repeat Scan.** The above operation can be repeated up to 999 times.
3. **Photon Counting.** The digitized signal from the photon counter is processed by a scaling register.
4. **Parameter Selection.** The operator may select maximum and minimum counting times and photon counts at each spectral data point. These control automatic variation of the scanning speed in order to optimize signal-to-noise ratio.
5. **Recorder Driving.** The paper drive of the recorder can be driven during scan. It is slaved to the scanning speed so that the presentation is linear irrespective of varying scan speed.
6. **Signal Averaging.** A spectrum representing the average of many identical scans can be produced.

Statistically, it is well known that the signal-to-noise of any measurement is proportional to the square root of the time of measurement. Slow speed scanning, however, has its drawback. Any long-term drift in the system, whether in intensity of the source or in the measuring instrumentation, can seriously offset or even negate the predicted improvement. Catting (computerization to average transients) also known as multichannel averaging — repetitive scanning at normal speeds followed by averaging of the intensity data — has turned out to be a better, more universal way to improve the data.

The Spex catting subroutine is illustrated by the  $992\text{ cm}^{-1}$  line structure of benzene. Benzene dissolves in water to the extent of less than 0.1% so its detection by laser Raman spectroscopy in the presence of water is difficult. In 6A, a single one-minute scan is shown. In 6B, a 17-min single scan and in 6C, 16 1-min scans are averaged.

To achieve this dramatic improvement in S:N, the spectrometer (Spex 1401) must be capable of precise reproducibility of frequency from one scan to the next. Backlash is first removed to achieve the highest inherent precision. This is done in the computer program much as it is done manually: The region of interest is scanned at the selected speed; at the end of each scan, the motor is reversed at slow speed, the mechanism scanned to a frequency about  $50\text{ cm}^{-1}$  below the starting point; next, the motor is once again reversed but still kept at the slewing speed until the starting frequency is reached; the second scan is then started at the preselected motor speed. The computer digests intensity information at each data point, averaging the old and new figures after the preselected number of scans. After 16 scans, improvement in S:N is 4 times, as predicted statistically.



Spectrum of BENZENE IN H<sub>2</sub>O  
 Instrument RAMACOMP  
 Quantity CAPILLARY Temperature RT  
 Excitation SIYS A Power 600 MW  
 Slit Width 200 microns (4  $\text{cm}^{-1}$ )  
 Scan  $\text{A}/\text{cm}^{-1}/\text{min}$ . Chart cm/10/min  
 Scale 0.5 cm⁻¹/data Period 10  
 Log/Linear DC / Photon Counting / Lock-In  
 Zero Suppress Scale Expand  
 Detector CW8V Voltage 1900 Temp. -30

7. **Spectra Relations.** Two spectra can be compared by ratio or subtraction, with recorder display or paper tape output.

Interpretation of complex Raman spectra (a difficult task in its own right) is often further complicated by the presence of solvent bands and general background due to the solvent. Removal of such interferences is a simple task for the RAMACOMP. A saturated aqueous solution of triptophan (an amino acid) was chosen for the demonstration.

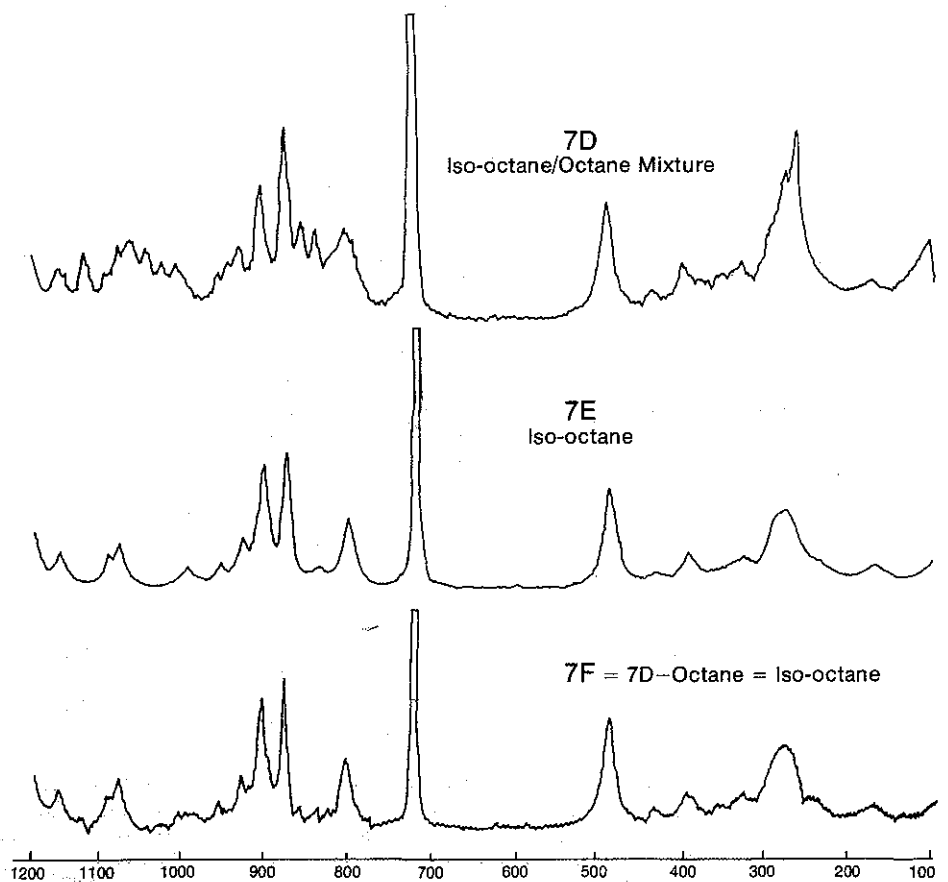
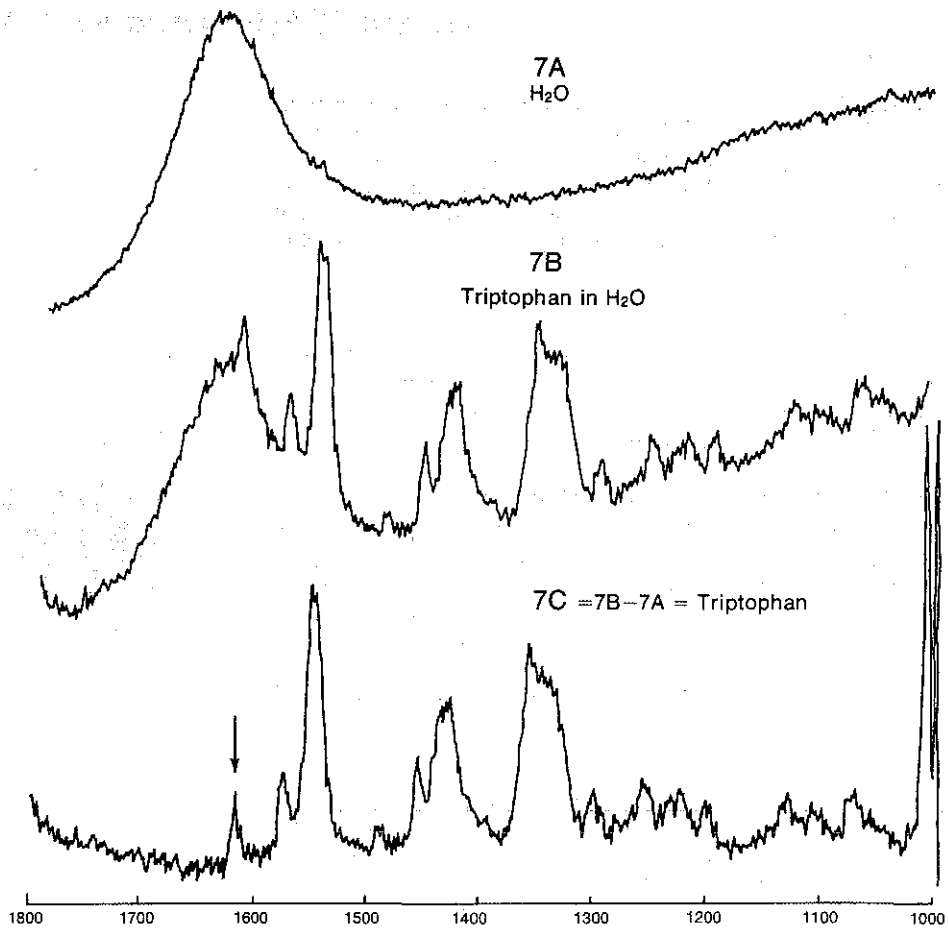
First, a water spectrum was generated covering the region  $1000-1800 \text{ cm}^{-1}$  and stored in one of the memory arrays of the RAMACOMP (at the same time it was recorded on the stripchart as spectrum 7A).

Next the solution of triptophan in water was run, under similar conditions, and stored in another computer array (while it was being recorded on the stripchart as spectrum 7B).

Finally, the computer was directed to subtract 7A from 7B and record the result, which is spectrum 7C. It is interesting to note that in 7C the line at approximately  $1610 \text{ cm}^{-1}$  becomes a "real" feature as opposed to being of "questionable" character in spectrum 7B. The background in the region  $1000-1200 \text{ cm}^{-1}$  has also been attenuated considerably.

Another example is more dramatic in that the two materials, octane and iso-octane (mixed 1:1), are so similar in their physical and chemical characteristics as to make peak identification virtually impossible by the naked eye.

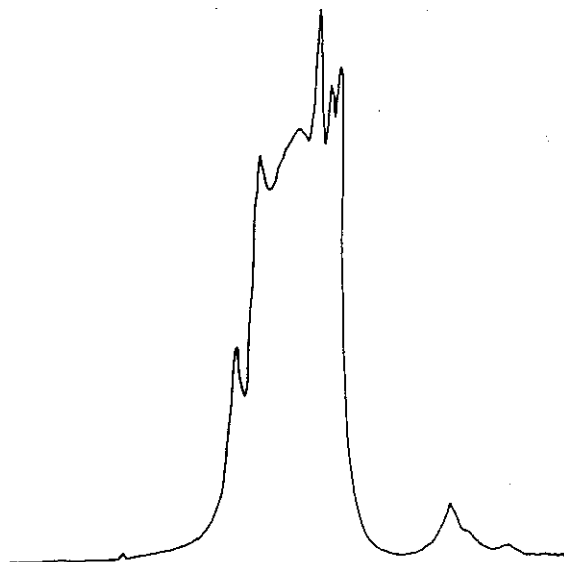
Thus, spectrum 7D is a real-time trace of the mixture (spectrum is also stored in the computer memory). Spectrum 7E is a real-time trace of iso-octane (spectrum not stored in computer memory). Spectrum 7F is the iso-octane spectrum generated by the computer after subtracting an already-stored spectrum of octane. There can be little doubt that 7E and 7F are the same compound. Incidentally, the subtraction of spectra was done without benefit of normalization. Had the spectra been normalized the "match" between 7E and 7F would be even better.



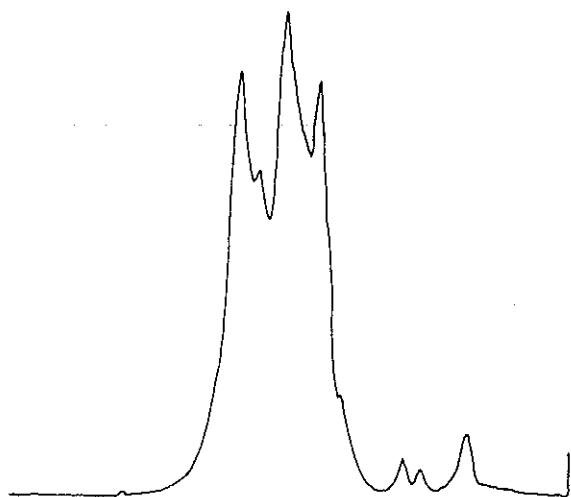
8. **Multiply by Constant and Add or Subtract.** If we examine the CH stretch region ( $3000 \text{ cm}^{-1}$ ) of the spectrum of octane (8A), iso-octane (8B) and their 1:1 mixture (8C), run under identical conditions, we note that in the latter there is no feature exclusively attributable to either of the compounds making up the mixture. Nevertheless, we would like to determine the concentration of iso-octane in the mixture.

As a first approximation let's assume that it is 50% (my, wasn't that a good choice). The RAMACOMP is directed to multiply the neat spectrum of each compound (8A), (8B) by 0.5 (divide by 2) and add the results. This is so because we know that each of the components will be present at approximately half the intensity values shown in the neat spectrum if our guess was correct. Any resulting spectra should look like (8C). In fact, the spectrum marked "Multiply by Constant and Addition" does exactly that. Another way of doing the same thing is to "normalize" spectra (8C), i.e., multiply by 2 and then subtract one of the neat component spectra. The reason for the initial multiplication by 2 is obviously to obtain, if our guess is correct, a neat spectra of the component at exactly the same intensity we had previously.

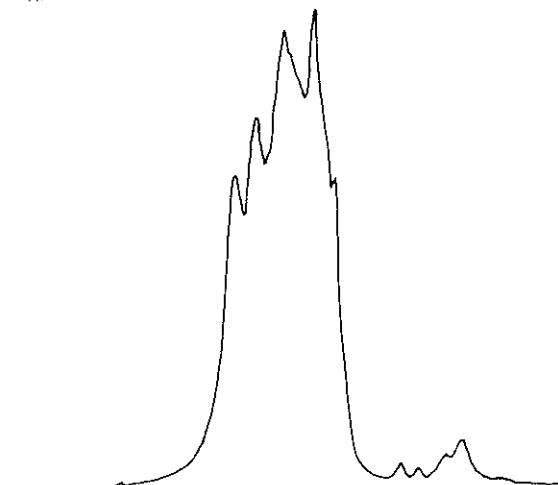
Should you want it, the RAMACOMP can generate, from the neat spectra of components, the curve resulting from any desired mixture of the two components by similar manipulations.



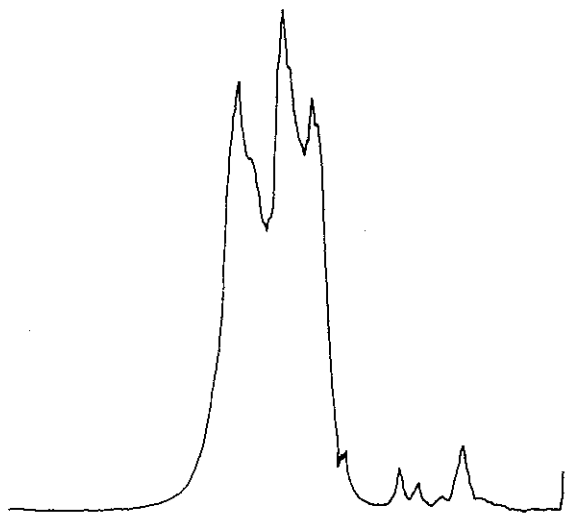
8A  
Octane-neat



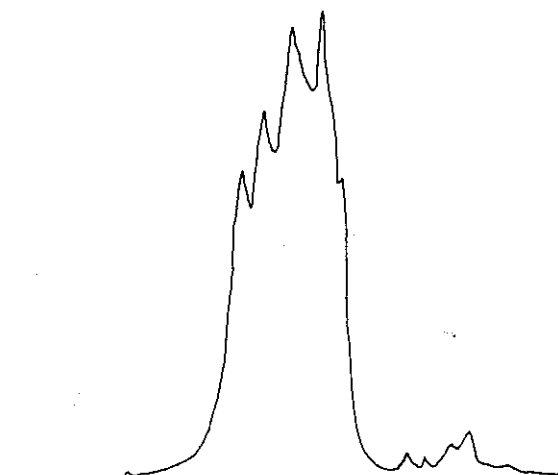
8B  
Iso-octane-neat



8C  
1:1 Mixture



Multiply by Constant  
& Subtraction  
 $2C - A = B$



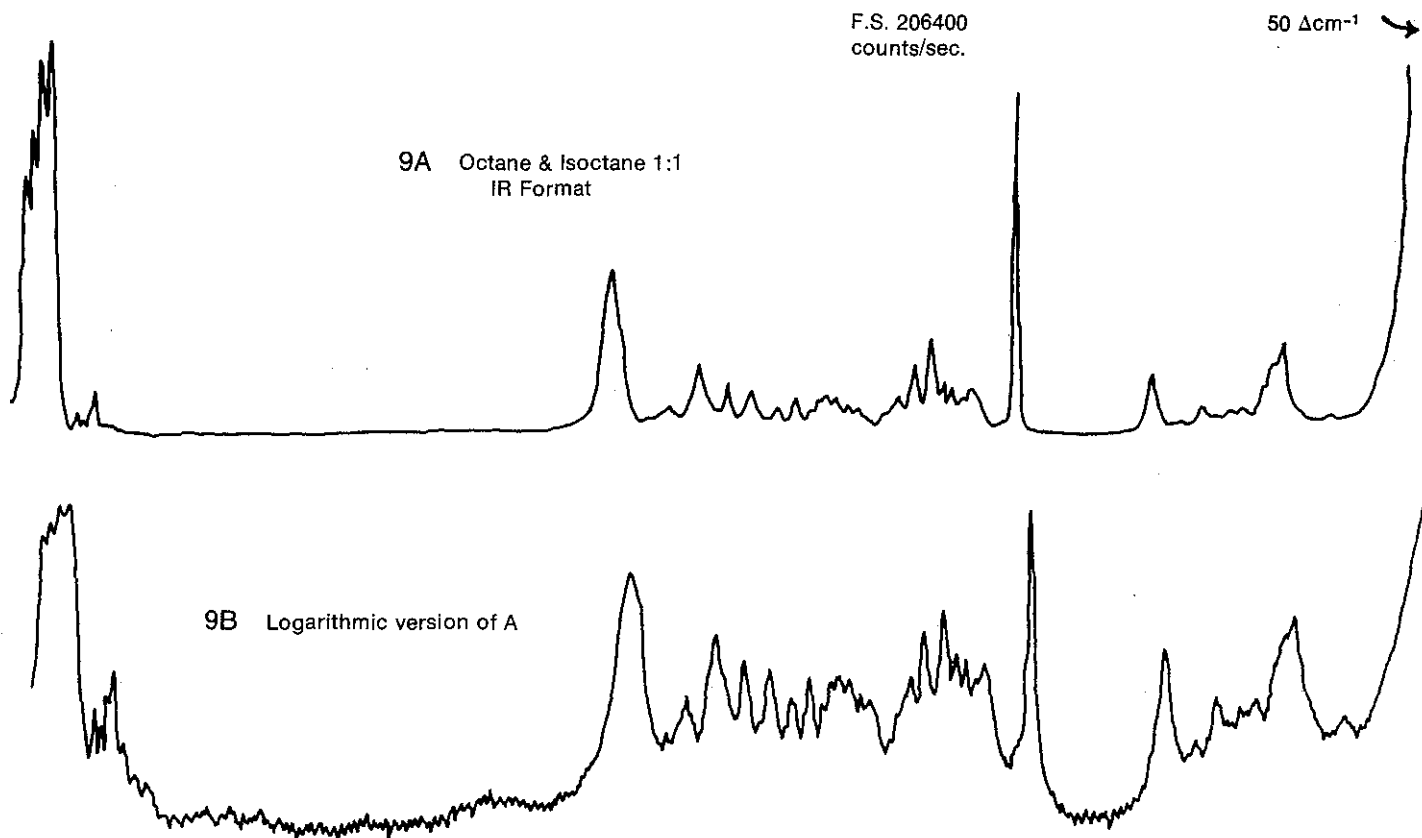
Multiply by Constant  
& Addition  
 $0.5A + 0.5B = C$

9. **Recorder Scaling.** The chart may be set to expand, compress, or shift in either the x or y-axis. Presentation in infrared-compatible format may be attained.

Because laser Raman spectroscopy and infrared spectroscopy give complimentary results, it is desirable to be able to compare spectra run on one type of instrument with another. We

call this infrared compatibility and it is demonstrated by 9A) the spectrum of octane and iso-octane mix.

Spectrum 9B) demonstrates not only the infrared compatibility (expansion along the X axis) but also the spectrum of the mixture of octane and iso-octane on a logarithmic scale.



10. **Data Storage.** Spectra can be put into memory, employing up to 3000 points. These may be divided into four smaller sections, for storing different spectra.

11. **Smoothing.** A 9-point least-squares cubic-fit smoothing routine is provided.

12. **Differentiation.** A 9-point smoothed weighting differentiating routine is supplied.

13. **Integration.** The area under the intensity curve between any two selected points is calculated; the operator can select the

points so as to reduce background.

14. **Paper Tape Output.** A punched paper tape version of the spectrum, real time or stored, can be provided.

15. **Spectral Feature Printout.** The location of spectral peaks, and their amplitude, can be printed out in order of spectral position or in order of intensity.

16. **Logarithmic Conversion.** The logarithm of the intensity to base 10 can be derived.

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