

UV RESONANCE RAMAN SPECTROSCOPY: A NEW TECHNIQUE FOR SPECIATION OF AROMATICS IN COMPLEX MATRICES.

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Vibrational spectroscopic techniques such as IR and Raman are exquisitely sensitive to molecular structure. These techniques yield incisive results in studies of pure compounds or for rather simple mixtures, but are rarely used for the analysis of complex systems. Indeed, IR can be utilized for quantitative investigations in special cases for complex systems if the analyte of interest shows an infrared absorption spectrally resolved from that of other species in the sample.

Recent advances in laser and optical detection instrumentation permit the development of major new spectroscopic techniques. One of these, UV resonance Raman spectroscopy (1), appears to be uniquely suited for studies of aromatic species in fuels, coal liquids and in petroleum fractions(2,3). It is possible to selectively excite the vibrational spectra of particular ring systems in a complex sample to separately determine the types and concentrations of conjugated rings present in a sample. Our laboratory has pioneered the development of this spectroscopy over the last few years and this report reviews our accomplishments and presents our view of the future.

PHENOMENOLOGY

Excitation of a molecule with monochromatic light results in an induced dipole moment proportional to the magnitude of the electric field of the incident light and to the polarizability of the molecule. The induced dipole moment which oscillates at the frequency of the incident light derives from oscillating charges which are accelerating and decelerating in time. An accelerating charge must radiate light and this induced moment is responsible for the elastic Rayleigh scattering observed for molecules in the gas or condensed phase. Molecular vibrations modulate the molecular polarizability. The molecular vibration couples and beats against the oscillations of the induced dipole moment. This results in a component of oscillation which has a frequency offset from the monochromatic light source by a vibrational frequency of the molecule. This is the origin of Raman scattering (4).

The proportionality between the intensity of Raman scattered light and the intensity of incident light is measured by the Raman cross section, σ . The Raman cross section is proportional to the fourth power of the frequency and to the square of the

Raman polarizability. The Raman polarizability is a strong function of excitation frequency. Excitation within a molecular electronic absorption band can result in a Raman cross section increase of as much as seven orders of magnitude. This occurs because of an increase in the magnitude of the induced moment oscillating at the Raman frequency. This increase occurs because of the dramatic polarizability increase of the molecule for excitation frequencies within the molecular electronic absorption band. Excitation in "resonance" with an absorption band results in a resonance Raman spectrum.

The excitation frequency dependence of the Raman cross section can be utilized to selectively enhance the vibrational Raman spectrum of one component within a complex mixture provided excitation can selectively occur within a discrete absorption band of the analyte. Over the last few years we have examined the factors which permit this selective enhancement. We have developed new instrumentation, clarified the spectroscopic fundamentals, and have begun to apply this new analytical technique to polycyclic aromatic hydrocarbons (PAH's).

INSTRUMENTATION

We recently described the construction of a UV and visible wavelength Raman spectrometer which is continuously tunable from 217 to 800 nm and which is discretely tunable at shorter and longer wavelengths using stimulated Raman shifting in a hydrogen cell (5,6). A block diagram of the instrument is shown in Figure 1. The excitation source derives from a Nd-YAG laser whose 1064 nm output is frequency doubled or tripled or quadrupled by using nonlinear optical techniques. The frequency doubled or tripled Yag excitation pumps a dye laser giving tunable light from 370-800 nm. UV light is generated by either frequency doubling the dye laser output or by combining the doubled dye laser output with the YAG fundamental. Excitation further in the UV derives from Raman shifting of the quadrupled Yag in hydrogen.

The UV excitation beam is diffusely focused on the sample which either flows through the excitation beam in a stream free of any sample walls, or flows in a quartz capillary. The Raman scattered light is collected by reflective optics to avoid lens chromatic aberrations and this light is focused onto the entrance slit of a Spex Triplemate spectrometer-spectrograph. The double spectrometer stage rejects the Rayleigh scattered light by using subtractive dispersion. The spectrograph stage disperses the Raman scattered light onto an EG&G PAR OMA II intensified Reticon array. This optical multichannel detector simultaneously detects the entire Raman spectrum dispersed across its active surface and avoids the signal-to-noise limitation associated with the pulse-to-pulse fluctuations in effective pulse energy of the laser. Except in the case of nonlinear phenomena the signal-to-noise-ratios for typical signal levels appear to be limited by photon shot noise.

FUNDAMENTALS

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We developed a new technique to measure, for the first time, absolute Raman cross sections (7). We examined small molecules such as CH_3CN , SO_2 , NO_2 , acetone, N-methyl acetamide as well as other species and found that the intensities derived from preresonance enhancement by transitions in the vacuum UV. Species such as NO_2 and N-methyl acetamide which have clearly assigned $\pi \rightarrow \pi^*$ transitions show Raman cross sections which are essentially dominated by these strong absorptions (8). The other species show no discrete, easily assignable transitions in the vacuum UV and show Raman cross sections which increase relatively slowly (almost as ν^4). A major point of these studies is that no interference will occur from the resonance Raman scattering of small molecules for excitation at wavelengths greater than 210 nm. For example, the carbonyl functional group of acetone and the amide functional group of acetamide show $n \rightarrow \pi^*$ transitions between 200 and 280 nm; however, these absorptions result in negligible resonance Raman scattering. It is clear that species containing these functional groups will not congest the Raman spectra of mixtures. It should be realized, however, that the signal-to-noise ratio of the spectra will decrease to the extent that the excitation beam is absorbed by the absorption bands of these species.

Little resonance Raman intensity is evident from the 260 nm absorption spectrum of benzene (9). Indeed, the Raman intensity observed for benzene with visible wavelength excitation derives from excited states in the far vacuum UV spectral region. Major increases in benzene Raman intensity occurs only for the ν_1 , symmetric ring stretch at 992 cm^{-1} . This enhancement which appears to derive from both the B_{1u} and E_{1u} transitions is only evident for excitation below 230 nm. Thus, benzene is a relatively weak Raman scatterer in the 215-300 nm spectral region. Substituted benzene derivatives, in contrast, show strong resonance enhancement from their L_u (in benzene B_{1u}) transitions (10). The aromatic ring modes increase in intensity by a factor of 1000 compared to that in benzene excited between 215-240 nm. This occurs primarily because ring substitution breaks the ring symmetry and allows many ring vibrations to be Raman allowed. Figure 2 compares the resonance Raman spectra of benzene, toluene and phenylalanine with 230 nm excitation. The shaded peaks derive from Raman bands of the solvents. Obviously, selective enhancement is present for substituted benzene derivatives.

Substituted benzene derivatives such as phenol, p-cresol, tyrosine, phenolata and tyrosinate have strong absorption bands shifted to longer wavelength than that of alkyl substituted benzenes (10,11). The oscillator strengths of the absorption bands increase and a large increase occurs in their UV Raman intensities. Indeed, the L_u transitions of p-cresolate, tyros-

inate, and phenolate are shifted to 240 nm and excitation in these absorption bands result in large resonance Raman intensities.

Polycyclic aromatic hydrocarbons show strong absorptions in the UV (12). In general, the maximum wavelength for absorption increases as the number of fused conjugated rings increase. Although the longest wavelength absorption bands often show modest oscillator strengths the second and higher singlet transitions are strong. Figure 3 shows the absorption spectra of a variety of polycyclic aromatic hydrocarbons. The absorption spectrum of a solution of a coal liquid in water is shown as the topmost spectrum. The broad strong absorptions of the coal liquid sample derive from the numerous polycyclic hydrocarbon ring systems present in the sample. Figure 4 illustrates the UV resonance Raman spectra displayed by the different PAH's at excitations close to their absorption spectral maxima.

The different PAH's can be selectively studied by utilizing their unique vibrational spectral features and by selectively exciting each PAH in its relatively unique absorption band (12). Ring substitution alters the Raman spectra as can be seen by comparing the UV Raman spectra of naphthalene and its 1- and 2- hydroxy derivatives (Fig. 5). Thus, the spectra are diagnostic of ring substitution patterns. Indeed, the substitutional isomers show absorption spectral shifts which can be utilized to separately and selectively excite the individual derivatives in mixtures.

The magnitude of resonance enhancement for these derivatives is huge. For example, the Raman cross section for pyrene excited at its 240 nm absorption spectral maximum is significantly greater than 4×10^{-23} cm²/sr molc. This compares to a cross section of close to 10^{-27} cm²/sr molc for an alkane in this spectral region. Thus, a dramatic selectivity exists for resonance enhancement of polycyclic aromatic hydrocarbons versus saturated hydrocarbons and nonaromatic ring systems. As discussed later, our values for the cross sections of pyrene are underestimates because saturation phenomena have prevented the penultimate measurements of the cross sections. It is, however clear from figure 6 that the detection limit for pyrene in acetonitrile solution is less than 20 ppb. Recent improvements have decreased the detection limit to less than 1 ppb. This limit derives from optical saturation phenomena due to the high laser peak powers, and is not the ultimate detection limit.

APPLICATIONS

We are able to selectively enhance polycyclic aromatic ring systems in complex samples of industrial analytical interest. For example, our recent UV Raman study (2,3) of a coal liquid dissolved in acetonitrile demonstrates that the spectra are characteristic of the polycyclic ring systems present in the coal liquid samples (Figure 7). Different excitation wavelengths result in spectral changes which reflect alterations in the

selective enhancement of the polycyclic aromatic ring systems in the sample. The fact that UV Raman measurements of these ring systems is possible indicates that UV Raman spectroscopy is apparently immune from the fluorescence interference phenomena which plague normal visible wavelength Raman measurements of typical environmental and industrial samples. This immunity stems from the fact that few, if any, compounds show fluorescence below 250 nm in condensed phase matrices (2).

The future is especially bright for the application of UV Raman measurements to petroleum and coal liquid samples. Information is available on conjugated fused ring systems. As libraries of data become available on model systems it will become practical to analyze typical samples for aromatic ring content and overall substitution patterns. Unfortunately, the technique is relatively insensitive to the exact structure of the ring substituent unless it is unsaturated and conjugated with the ring. The spectra are, however, sensitive to the ring substitution position.

Extraordinarily complex samples will require pre-separation prior to spectral identification of individual components. The high sensitivity of UV Raman measurements can be effectively utilized in the detection of polycyclic aromatic hydrocarbons eluting from an HPLC column as is illustrated in figure 8.

The utility of UV Raman spectroscopy for studies of fuels is just now being investigated. Many of the ongoing studies focus on characterizing the spectroscopic phenomena involved and relating spectral data to detailed ring structure. Other studies involve developing new sampling methodologies. The present UV laser excitation sources are pulsed with low duty cycles. These pulses which are typically less than 5 nsec in duration have extraordinarily high peak powers. These high peak powers can result in peculiar optical phenomena which limit spectral sensitivity and/or result in the creation and observation of photochemical transient species (11). For example, recent studies of tyrosine and phenol displayed spectral features assignable to phenoxy and tyrosyl radical species which were formed due to photon absorption from the incident laser pulse. A subsequent photon from the same excitation pulse was resonance Raman scattered from the transient radical species. It was interesting that the phenoxy radical forms only transiently and decays back to ground state phenol with a milli- to micro-second lifetime.

A more insidious limitation of the high peak power excitation pulses is optical saturation phenomena (13). Figure 9 shows three resonance Raman spectra of pyrene in acetonitrile. The acetonitrile peaks are shaded. The differences between the spectra derive from changes in the incident excitation pulse power density. The important feature to note is that the

relative pyrene intensities compared to acetonitrile intensities increase dramatically as the pulse power density decreases. Indeed, no intensity is evident for the acetonitrile at the lowest laser excitation power. The acetonitrile intensities are directly proportional to laser power. Thus, the acetonitrile cross sections do not depend on the excitation power. In contrast, the pyrene cross sections are obviously decreasing as the excitation power density increases. Thus, the optimal cross section for pyrene would occur for low power excitation. Unfortunately, this condition is accompanied by low net Raman intensities, poor signal-to-noise ratios and high detection limits.

We are in the process of developing a quasi-CW UV laser excitation source to improve the sensitivity of UV Raman spectral measurements. The likely detection limits for pyrene in pure acetonitrile solutions, for example, are likely to be in the part per trillion range. It should be realized that this represents less than a femtogram of pyrene in the sample volume probed by the laser. Further, we are in the process of examining cryogenic sampling methodologies such as Shpol'skii and matrix isolation. These techniques will lead to increased sensitivity and selectivity. Increased selectivity derives directly from narrowing of vibrational Raman bands which permit finer resolution between Raman bands of different species, and also the narrowing of the Raman excitation profiles which permit higher resolution excitation for the Raman spectra of individual species. Increased sensitivity derives from the accompanying dramatic increases in Raman intensity due to decreased homogeneous and inhomogeneous linewidths of the electronic absorption bands.

We expect the next few years to result in major new advances in the demonstrated utility and utilization of UV Raman spectroscopy as a technique for the study of PAH's in complex samples. In addition to an increased understanding of the fundamental spectroscopic processes involved, the development of a library of spectral data, and the development of simple sampling methodologies we expect major improvements in instrumentation which will make the technique routine and permit the commercialization of a reasonably priced instrument.

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ACKNOWLEDGEMENTS

We gratefully acknowledge partial support of this work from NIH grant 1-R01GM30741-04 and by EG&G Princeton Applied Research. Sanford A. Asher is an Established Investigator of the American Heart Association; this work was done during the tenure of an Established Investigatorship of the American Heart Association and with funds contributed in part by the American Heart Association, Pennsylvania affiliate.

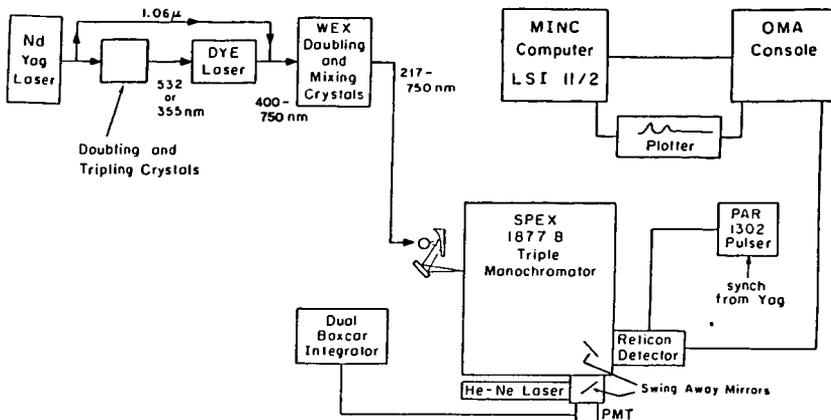


Fig 1. Block diagram of UV Raman Spectrometer. Taken from reference 1.

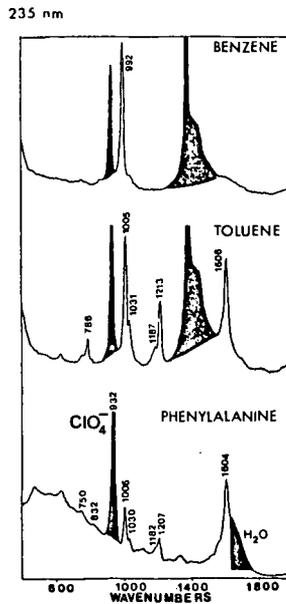


Fig 2. UV resonance Raman spectra of solutions of benzene and toluene in acetone and phenylalanine in water excited at 235 nm. The dashed peaks derive from the solvent and ClO_4^- anion. Adapted from reference 10.

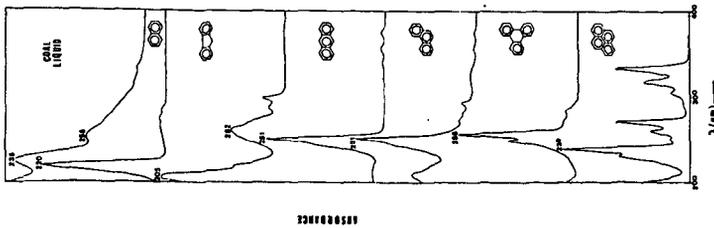


Fig 3. Absorption spectra of various polycyclic aromatic hydrocarbons in acetone. Taken from reference 3.

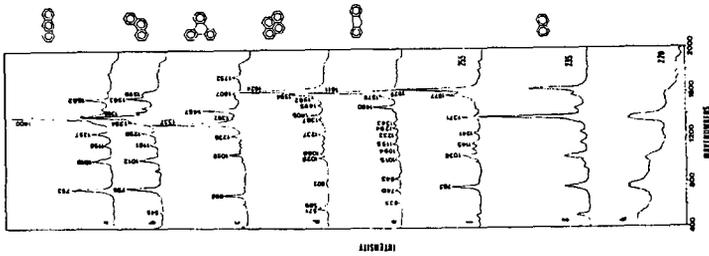


Fig 4. UV resonance Raman spectra of various polycyclic aromatic hydrocarbons in acetone. Except where explicitly indicated excitation occurred at 235 nm. Taken from reference 3.

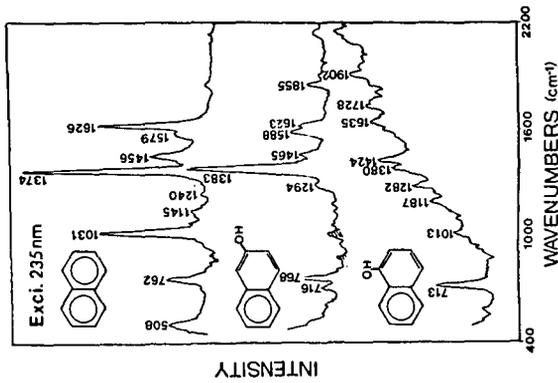


Fig 5. UV resonance Raman spectra at 235 nm of derivatives of naphthalene dissolved in acetonitrile. The bands of the solvent have been numerically subtracted.

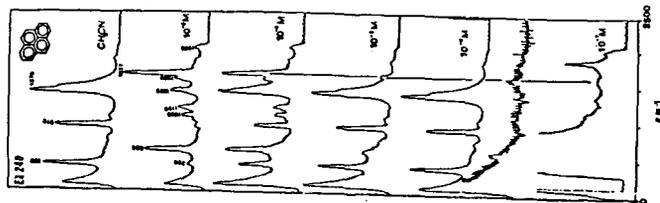


Fig. 6. UV Resonance Raman spectra of Pyrene in acetone/nitrile at different concentrations. Top spectrum is that of a 10⁻⁴ M solution of Pyrene in acetone/nitrile while the bottom spectrum is of 10⁻¹ M solution of Pyrene in water. The second from the bottom spectrum is from the 10⁻² M solution after subtraction of the spectrum from the 10⁻¹ M solution. Excitation is at 240nm. Taken from reference 12.

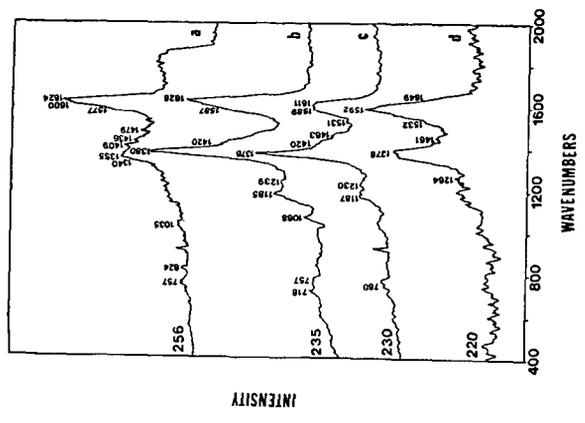


Fig. 7. UV resonance Raman spectra of a solution of a coal liquid sample dissolved in acetone/nitrile at various excitation wavelengths. Taken from reference 3.

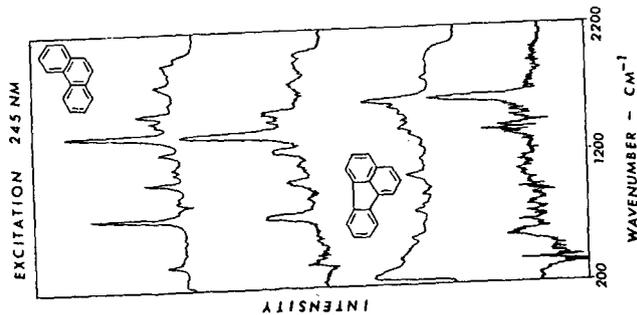


Fig B. UV resonance Raman spectra of phenanthrene and fluorene eluting in real time from an HPLC column. The top spectra are from pure samples in static solutions while the shaded spectra were measured during the elution. The components eluted from the column. Scan duration 58 one minute.

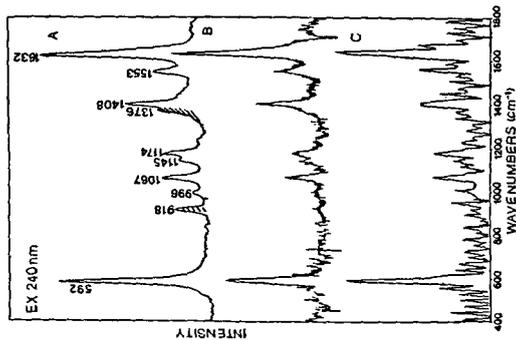


FIG P. UV resonance Raman spectra of a 10^{-4} M pyrene solution in acetonitrile as a function of laser power. A, maximum pulse energy; B, 50 % of maximum; C, 30 % of maximum. Acetonitrile bands are shaded in the figure.