UV Resonance Raman Characterization of Polycyclic Aromatic Hydrocarbons in Coal Liquid Distillates*

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Ultraviolet resonance Raman spectroscopy has been used to characterize the polycyclic aromatic hydrocarbon composition of a series of distillates of coal-derived liquids. The UV Raman spectra easily monitor changes in the polycyclic aromatic hydrocarbon composition as a function of distillation temperature. Specific species, such as pyrene, can be determined by judicious choice of excitation wavelength.

Index Headings: **Fluorescence; Analysis for PAH; YAG lasers; Luminescence; Raman spectroscopy.**

INTRODUCTION

There is intense interest in the development of analytical techniques to characterize highly complex samples. Often major advances are possible with techniques that yield only qualitative or semiquantitative molecular information. In the case of naturally occurring samples, such as petroleum and coal, or for man-made samples, such as coal liquids, a major desire is to ascertain the levels of certain ring systems and the level of aromaticity present in the sample.

Recently our laboratory demonstrated the potential utility of UV resonance Raman spectroscopy as a new analytical technique for the study of complex samples and directly demonstrated the capability of the technique for studying coal-liquid samples.[1–4] We demonstrated that the Raman spectra of polycyclic aromatic hydrocarbons could be enhanced in coal-liquid solutions and that different ring systems could be selectively enhanced, depending upon the excitation wavelength. The earlier correlations suggested that longer excitation wavelengths selectively enhanced the Raman spectra of larger fused-ring systems; the increased size of the conjugated system results in longer wavelength absorption bands. We also showed that polycyclic aromatic hydrocarbons such as pyrene could be detected in pure solutions at ppb concentrations.[2] Further, we recently realized that our demonstrated detection limits are far from the ultimate detection limit, since our earlier measurements were limited by optical saturation phenomena from our pulsed-laser excitation source.[5,6]

In this report we show that UV Raman studies of distillates of coal liquids allow the identification of pure compounds. The Raman intensities are directly proportional to the concentrations of the analytes in the sample.[2] Indeed, given the measured Raman cross section of the analyte and the measured cross section of the solvent, we can determine the analyte concentration present in the coal-liquid sample.

EXPERIMENTAL

The coal-liquid samples were obtained from the Department of Energy, Pittsburgh Energy Technology Center. These heavy-distillate coal liquids were prepared by thermal hydrocracking of an Illinois No. 6 bituminous coal (Run 245) at the advanced liquefaction facility operated by Catalytic, Inc., at Wilsonville, AL. The heavy distillate (650–950°F) was collected from the plant and subsequently vacuum distilled at the Pittsburgh Energy Technology Center in a Podbielniak distillation apparatus to the atmospheric pressure equivalents of 50°F boiling-range cuts between 650–700°F, 700–750°F, and 750–800°F. These samples have been described previously.[7] The aromatic fractions were obtained by preparative alumina chromatography[8–10] of the distillate fractions. The pure polycyclic aromatic hydrocarbon samples and solvents used were obtained from Chem Services (West Chester, PA) and Burdick and Jackson Co., respectively.

The Raman spectra were measured by the use of a tunable Raman instrument which was described in detail previously.[11] The spectrometer utilized a Nd:YAG laser-pumped dye laser as excitation source. Nonlinear harmonic generation techniques were used to extend the dye laser output into the UV spectral region. A Spex Triplemate monochromator was used to disperse the scattered light onto the photoactive surface of an EG&G Princeton Applied Research Model 1420 Reticon multichannel array detector connected to an OMA II detector controller. The samples were dissolved in acetonitrile (0.6 mg/mL) and pumped through a narrow jet nozzle.[11] Ninety-degree scattering was used and the laser beam was defocused on the sample to minimize nonlinearities in the measured Raman intensities.

RESULTS AND DISCUSSION

Figure 1a shows the absorption spectra of the three coal liquid distillates, while Fig. 1b shows the absorption spectra of a series of pure polycyclic aromatic hydrocarbons. The increased absorption at longer wavelengths for the higher-temperature distillates occurs because of an increased concentration of larger fused-ring systems. For example, the prominent bands at ~336, 320, 273, 256, and 244 nm in the higher-temperature coal distillates probably derive from pyrene-like derivatives (compare with the pyrene absorption spectrum in Fig. 1b).

Figures 2, 3, and 4 compare the UV resonance Raman

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* Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the U.S. Department of Energy.

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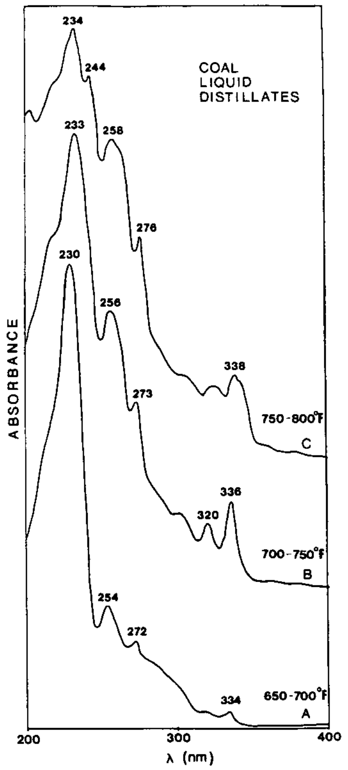

FIG. 1a. UV absorption spectra of coal-liquid distillates in acetonitrile. A, B, and C represent distillates vacuum distilled at equivalent atmospheric temperatures of 650–700°F, 700–750°F, and 750–800°F, respectively.

spectra of the distillates excited at 230, 244, and 256 nm, respectively. Each of the Raman spectra has the contribution of the acetonitrile solvent numerically removed. The small residual features that remain at ~2250 cm^{-1} are due to incomplete subtraction of the dominant acetonitrile peak at 2249 cm^{-1}. The weaker 918- and 1376-cm^{-1} acetonitrile peaks are completely removed by this numerical subtraction. The residual contribution of the 2250-cm^{-1} peak is due to a decreased self-absorption for this band compared with that for lower-frequency solvent peaks. For all excitations, the major peaks present are centered in the region of 1370 and 1600 cm^{-1}, although it is clear that the exact center frequencies, band shapes, and relative intensities depend upon excitation wavelength and the boiling range of the distillate. Figure 5, which shows representative Raman spectra of a series of polycyclic aromatic hydrocarbons, demonstrates that the strongest features observed for these compounds occur in the spectral regions 1330–1400 cm^{-1} and 1560–1630 cm^{-1}. These peaks derive from symmetric in-plane ring breathing vibrations of the conjugated ring systems. The similarities in the spectral features between the pure compounds and the coal-liquid distillates indicate selective enhancement of specific polycyclic aromatic hydrocarbons in the coal-liquid distillates.

The center frequency of the ~1370-cm^{-1} peak is a function of both the distillation temperature and the excitation wavelength. For example, for 244-nm excitation (Fig. 3) a shift occurs from 1379-cm^{-1} in A to 1412 cm^{-1} in C. Similar behavior occurs for 256-nm excitation, where a shift occurs from 1363 to 1368 cm^{-1} (Fig. 4). Frequency shifts are also evident for the ~1610-cm^{-1} bands. For example, a shift from 1615 to 1623 cm^{-1} is evident for 230-nm excitation (Fig. 2). In addition, the detailed band shape depends upon both the excitation wavelength and the distillation temperature.

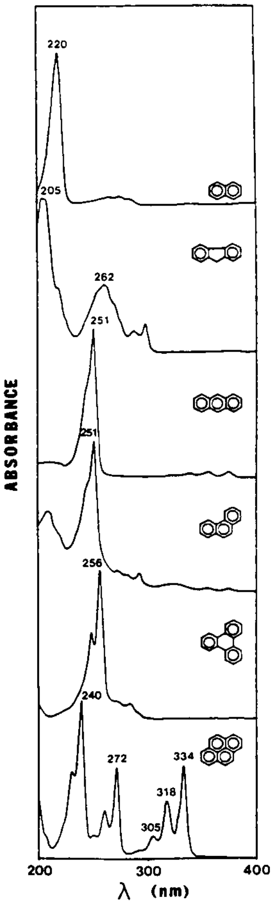

FIG. 1b. UV absorption spectra of representative polycyclic aromatic hydrocarbons, including naphthalene, fluorene, anthracene, phenanthrene, triphenylene, and pyrene. Adapted from Johnson and Asher.[3]

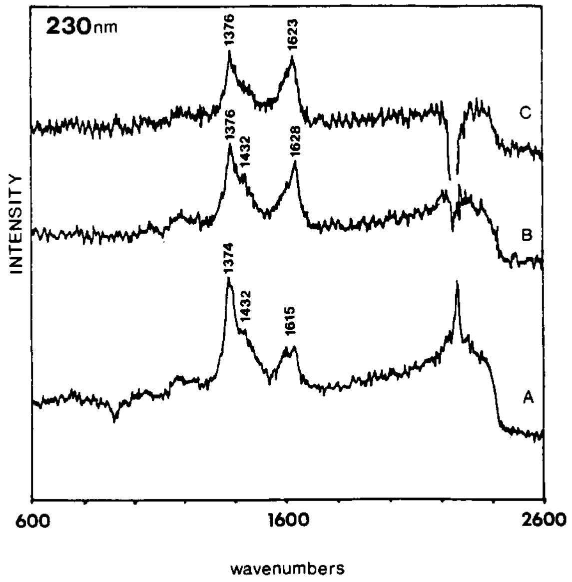

FIG. 2. UV Raman spectra of coal-liquid distillates with excitation of 230 nm. A, B, and C label the 650–700°F, 700-750°F, and 750–800°F distillates, respectively.

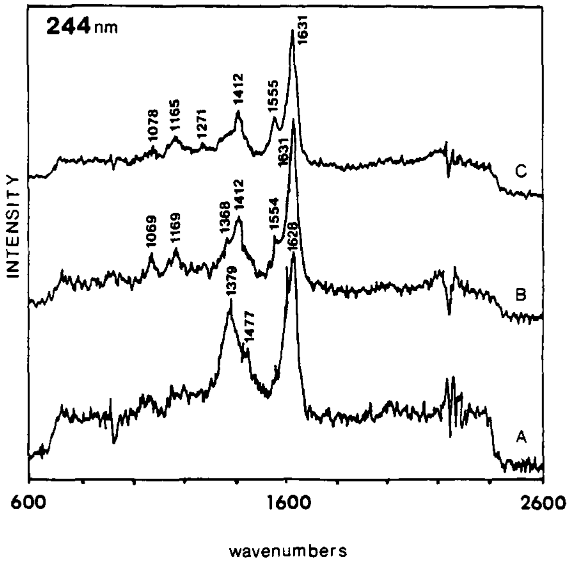

FIG. 3. UV Raman spectra of coal-liquid distillates with excitation of 244 nm. A, B, and C label the 650–700°F, 700–750°F, and 750–800°F distillates, respectively.

Obviously, these spectral frequency changes must be associated with differences in the composition of the different distillates and changes in the selectivity for enhancement of the spectra of particular polycyclic aromatic hydrocarbons with different excitation wavelengths. Figures 6a, 6b, and 6c show the ratio of the intensities of the ~1400-cm^{-1} and 1600-cm^{-1} bands to that of the 918-cm^{-1} acetonitrile band as a function of both excitation wavelength and distillation temperature. Since the Raman cross section for the 918-cm^{-1} band of acetonitrile

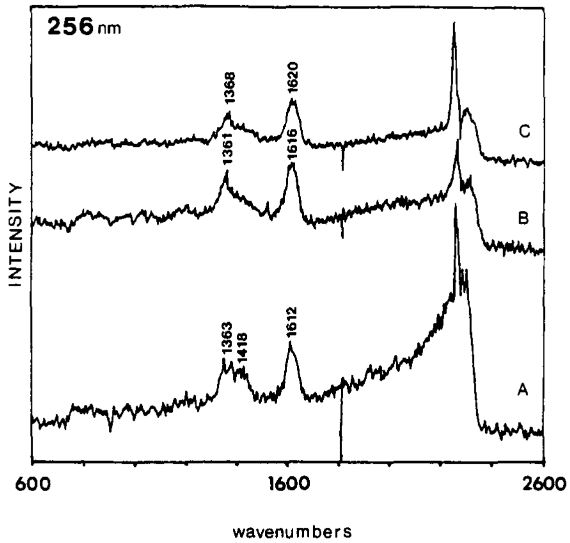

FIG. 4. UV Raman spectra of coal-liquid distillates with excitation of 256 nm. A, B, and C label the 650–700°F, 700–750°F, and 750–800°F distillates, respectively.

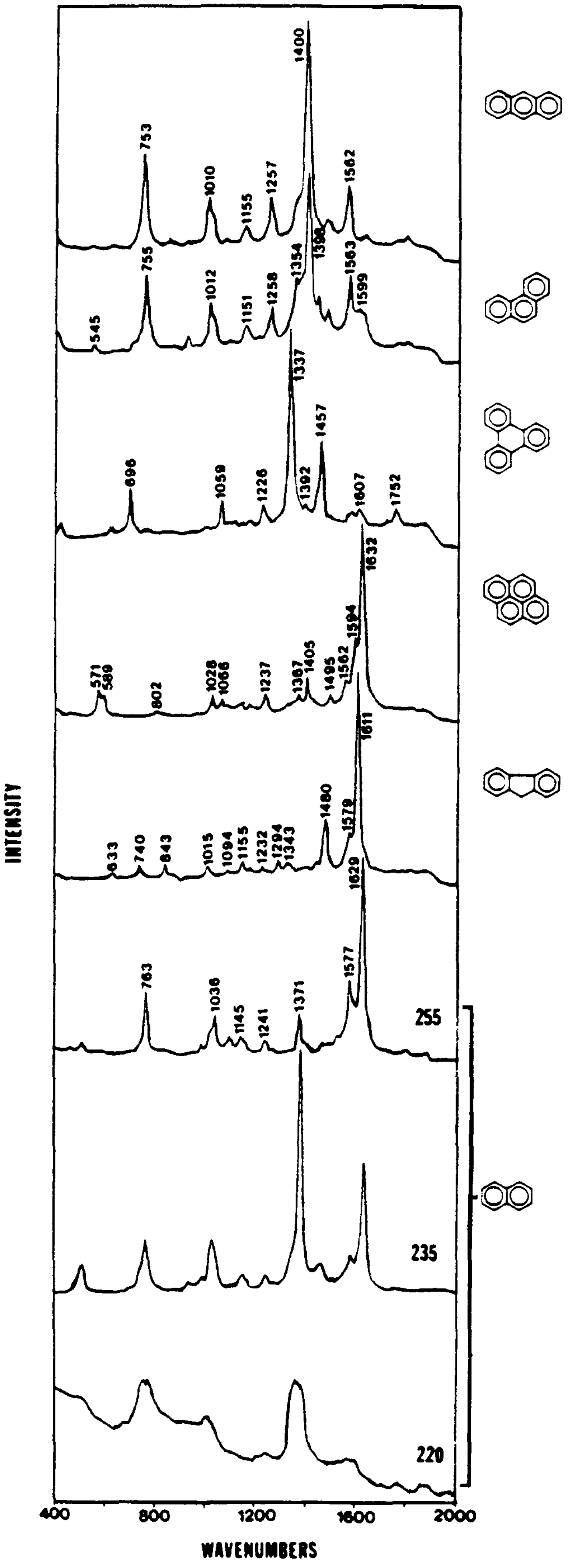

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FIG. 5. UV Raman spectra of representative polycyclic aromatic hydrocarbons including anthracene, phenanthrene, triphenylene, pyrene, fluorene, and naphthalene at 255 nm excitation. Naphthalene is also shown at excitations of 235 and 220 nm. Adapted from Johnson and Asher.[3]

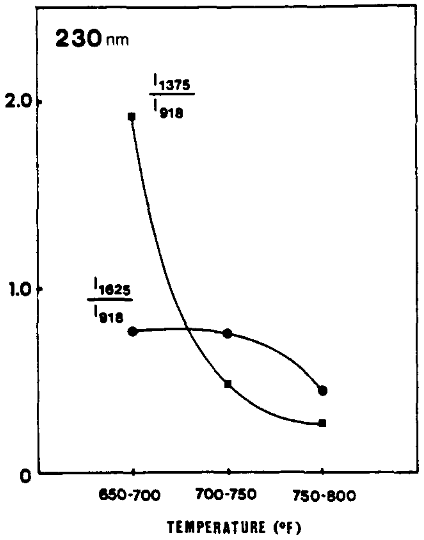

FIG. 6a. Intensity of the ~1375-cm^{-1} and 1625-cm^{-1} Raman bands to acetonitrile's 918-cm^{-1} band at 230-nm excitation as a function of distillation temperature.

shows only a frequency to the fourth dependence upon excitation wavelength,[12] the ratios plotted in Fig. 6 are directly proportional to the product of the concentration and the Raman cross section of the contributing analytes.

Figure 6a, which shows data for 230-nm excitation, indicates that the ~1375-cm^{-1} band relative intensity is a maximum in the lowest temperature distillate and decreases dramatically for the higher-temperature distillates. In contrast, the intensity of the ~1625-cm^{-1} band shows a weaker dependence upon distillation temperature. Figure 6b, with 244-nm excitation, shows that the 1630-cm^{-1} intensity is a maximum in fraction B, while the 1375-cm^{-1} band intensity shows only a weak dependence upon sample distillation temperature. The 1410-cm^{-1} intensity shows a strong maximum for distillate B. The 256-nm excited data show that both the 1610-cm^{-1} and 1360-cm^{-1} intensities are at a maximum in the 700–750°F distillate (Fig. 6c).

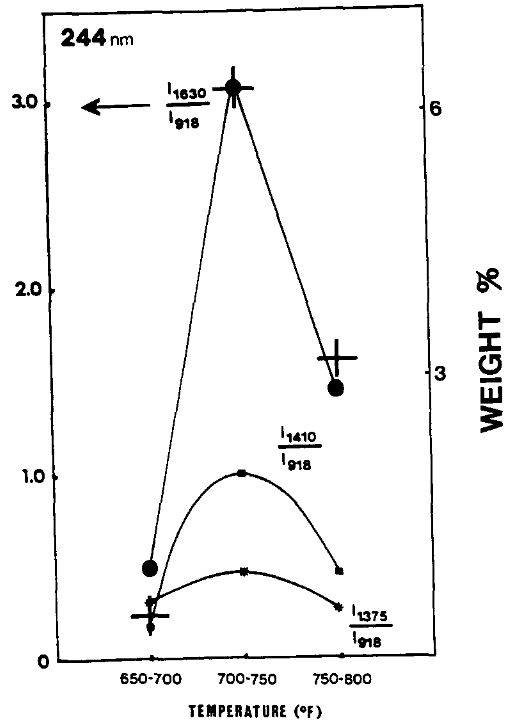

FIG. 6b. Intensity ratios of the ~1375-cm^{-1}, 1410-cm^{-1}, and 1630-cm^{-1} Raman bands to acetonitrile's 918-cm^{-1} band at 244-nm excitation as a function of distillation temperature. Also shown in the weight percent pyrene (+) calculated from low-voltage, high-resolution mass spectral studies of the 202 *m/e* band. See text for details.

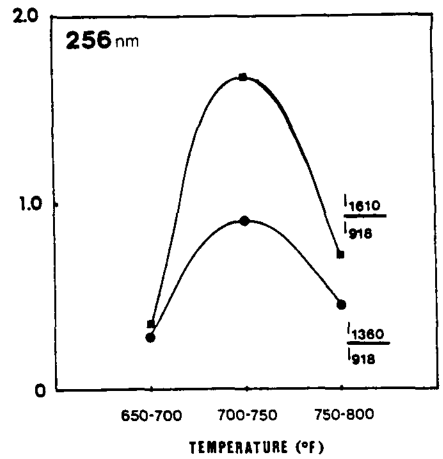

FIG. 6c. Intensity ratios of the ~1360-cm^{-1} and 1610-cm^{-1} Raman bands to acetonitrile's 918-cm^{-1} band at 256-nm excitation as a function of distillation temperature.

The dependence of the band frequencies upon the distillation fraction clearly indicates that a complex mixture of different species is contributing to the spectra from each distillation fraction. One would require a library of both Raman spectra and excitation profiles of the contributing species to be able to completely determine the species giving rise to the major features in the observed spectra; however, from the data shown in Fig. 5, the lowest-temperature distillate appears to have a large contribution of species that give rise to spectra reminiscent of naphthalene. Both the peak frequencies and the relative intensity changes with excitation wavelength are similar to those for naphthalene. For example, Fig. 7 shows a plot of the relative intensity ratios of the ~1400-cm^{-1} and 1600-cm^{-1} bands as a function of distillation boiling range at the three excitation wavelengths. The lowest temperature distillate shows the largest change in relative intensity as the excitation wavelength increases from 230 to 256 nm. This behavior is identical to the relative intensity changes observed for naphthalene in the bottom portion of Fig. 5. The 2.9 relative intensity ratio observed for this distillate with 230-nm excitation is close to that expected for naphthalene with this excitation. Indeed, the cross section for naphthalene should be high at this excitation wavelength, since it is in resonance with the strong 220-nm absorption band. At longer wavelength excitation, the ratio is expected to decrease, but also to have a smaller contribution from naphthalene; the relative contribution of naphthalene must dramatically decrease as excitation occurs farther from resonance. This predicted behavior is consistent with the 244-nm excited Fig. 7 data, where the relative intensity decrease and the large frequency shift (Fig. 3) indicate a decreased contribution of the naphthalenic

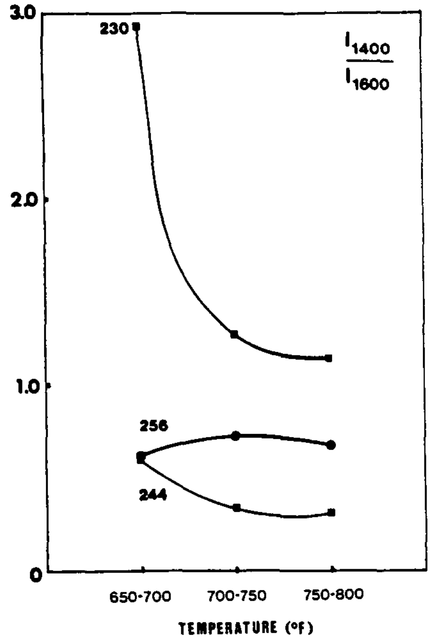

FIG. 7. Relative intensity ratios of the ~1400-cm^{-1} to the 1600-cm^{-1} band as a function of excitation wavelength and distillation temperature.

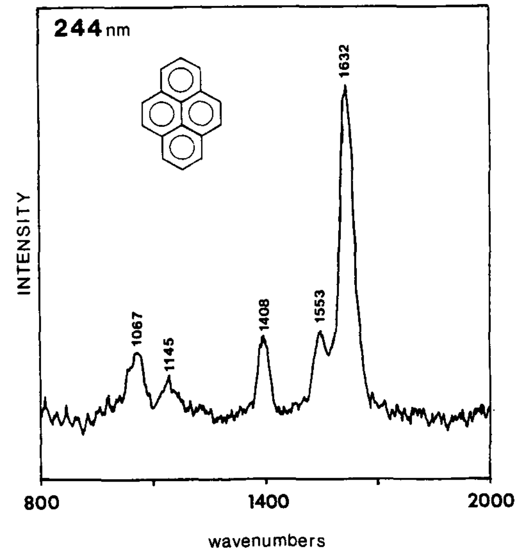

FIG. 8. UV Raman spectra of pyrene in acetonitrile with 244-nm excitation. Acetonitrile Raman bands have been subtracted.

species that dominate the shorter wavelength excitation data.

Lower-molecular-weight polycyclic aromatic hydrocarbons are expected to predominate in the lower-temperature distillates. Although naphthalene has a lower boiling point (424°F) than that of the lowest-temperature distillate, a number of alkyl naphthalenes would have boiling points in the correct range to occur in distillate A. It should be noted that hexahydropyrene, which has the same aromatic carbon skeleton as naphthalene, has a boiling point of 701°F.[13] Furthermore, phenyl naphthalene derivatives have boiling points around 650°F. The phenyl groups will not show ring vibrations, because they are not conjugated with the naphthalene ring.[12]

Excitation at 244 nm occurs at the maximum of the resonance Raman excitation profile of pyrene;[14] at 244 nm pyrene shows a cross-section value of 48 barns/str, which is the largest resonance Raman cross-section observed to date.[6] Indeed, with 244-nm excitation, the spectrum of the highest boiling fraction shows a spectrum almost identical to that of pyrene (Fig. 8), indicating that the pyrene Raman bands dominate. A comparison of these results with the low-voltage, high-resolution mass spectra of these distillates[15] is quantitatively consistent with this assumption. If we monitor the m/e 202 peak and assume that it is due entirely to pyrene, we conclude from the mass spectral data that the 650–700°F, and 700–750°F, and 750–800°F distillation fractions contain 0.4, 6.2, and 3.3 weight percent pyrene, respectively. This quantitatively agrees with our Raman results if we assume that all of the 1630-cm^{-1} intensity derives from pyrene. This is illustrated by the mass spectral results plotted in Fig. 6b. We recognize that the mass 202 peak could have some contribution from polycyclic aromatic hydrocarbons such as fluoranthene.

As the excitation occurs at longer or shorter wavelengths, the relative pyrene contribution decreases and the Raman frequencies shift away from that of pyrene. Thus, we conclude that we selectively excite pyrene in these fractions, and that the absorption spectral shoulder observed at 244 nm in the highest boiling distillate derives from pyrene. This is consistent with the features at ~336, 320, 272, and 260 nm observed in the absorption spectra (compare Figs. 1a and b). Pyrene appears to be responsible for the longer wavelength absorption bands.

CONCLUSIONS

Ultraviolet resonance Raman spectroscopy can be easily used to monitor changes in polycyclic aromatic hydrocarbon composition as a function of distillation temperature for coal-liquid distillates. Specific species can be separately excited and determined by a judicious choice of excitation wavelength. We were only able to identify pyrene uniquely in this study, because an extensive library of UV Raman spectra of polycyclic aromatic hydrocarbons does not yet exist. We are in the process of constructing a portion of this library.

ACKNOWLEDGMENTS

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A New Dual-Channel Frequency-Domain Fluorometer for the Determination of Picosecond Rotational Correlation Times[*]

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A new dual-channel multifrequency fluorometer is described which employs a mode-locked argon-ion laser as a polarized excitation source. The laser produces high-frequency sinusoidal intensity modulations in the MHz to GHz regime which are used to simultaneously probe the fluorescent molecules. The resulting orthogonally polarized components of the emission are collected by two opposite matched detection channels. Because both the parallel $[I_\parallel(\omega)]$ and perpendicular $[I_\perp(\omega)]$ components of the emission are collected simultaneously and at all modulation frequencies, information about the molecules' rotational rate can be rapidly deduced. With the new instrument, rotational correlation times as short as 15 ps can be routinely determined with data-acquisition times as short as 10 ms. Commonly, however, we employ collection times of several seconds to permit the averaging of between 100 and 500 scans. Examples which demonstrate the utility of the new instrument include the determination of the rotational correlation times for rhodamine 6G, fluorescein, and rubrene as a function of solvent viscosity. In addition, results are presented for the resolution of rhodamine 6G associated with beta-cyclodextrin. In the beta-cyclodextrin studies, little spectral (excitation/emission) or temporal (fluorescence lifetime) change was noted upon association. However, a significant difference exists between rotational correlation times of the free fluorophore and the fluorophore included by beta-cyclodextrin. This difference enables the formation constant for the association to be determined, a measurement which would be impossible with conventional techniques.

Index Headings: **Fluorescence; Instrumentation; Time-resolved fluorescence; Luminescence; Time-resolved spectroscopy.**

INTRODUCTION

The elucidation of molecular motions on a picosecond time scale is an area of intense scientific inquiry. Many techniques exist which allow an investigator to explore such picosecond phenomena as Brownian rotations and energy migration.[1–5] Of these techniques, fluorescence spectroscopy is perhaps the most commonly employed, because such molecular motions all occur on the same time scale as does the fluorescence phenomenon. Therefore, fluorescence provides an internal reference time by which these events can be indirectly clocked.

The excitation of a random distribution of molecules by linearly polarized light results in the selective excitation of only those molecules whose absorption dipoles are oriented along the polarization axis.[6–10] Because of this orientational selection, a nonuniform distribution (anisotropy) of excited-state molecules is generated. This induced anisotropy decays as a function of time because of molecular motion, solute-solvent interactions, and collisions. The result of this decay of anisotropy is a randomization of the molecular emission dipole(s) which manifests itself as a time-dependent depolarization of the resulting fluorescence.[6–10]

In the past, two approaches have been employed to measure this decay of anisotropy. The first is a time-domain experiment, involving excitation of the sample with a very brief pulse of polarized light, followed by measurement of the resulting fluorescence.[6–10] The fluorescence must, however, be measured in a particular manner. First, an emission polarization analyzer is placed between the fluorescent sample and the detector, to selectively detect fluorescence of a desired polarization. In operation, the emission polarizer is first aligned along the excitation polarizer's transmission axis ($I_\parallel$) and the resulting fluorescence decay curve $[I_\parallel(t)]$ collected. Following this measurement the emission polarizer is rotated 90° ($I_\perp$) and the decay curve $[I_\perp(t)]$ again collected. From these two simple measurements can be found the decay of anisotropy $[r(t)]$ for a molecule that exhibits a single exponential decay of anisotropy:

$$r(t) = \frac{I_\parallel(t) - I_\perp(t)}{I_\parallel(t) + 2I_\perp(t)} = r_0 e^{-t/\mathrm{RCT}}. \tag{1}$$

In Eq. 1, t is time; r_0 is the limiting anisotropy, which is simply the steady-state anisotropy for the fluorophore in a frozen glass; and RCT is the rotational correlation time of the fluorophore. Following proper deconvolution

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