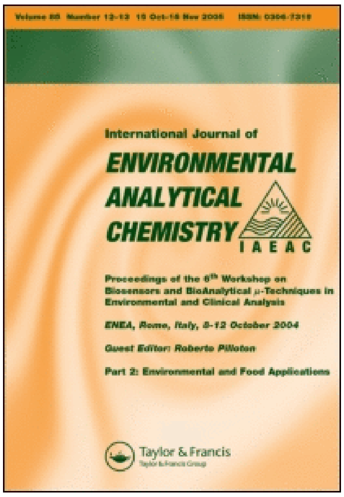

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Quantitative Measurements of Individual Polycyclic Aromatic Hydrocarbons in a Mixture by Coherent Anti-Stokes Raman Spectrometry

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Coherent anti-Stokes Raman spectroscopy (CARS) was used to obtain Raman spectra of selected polycyclic aromatic hydrocarbons (PAHs) composed of between three and seven fused rings when the compounds were pumped in the resonance and pre-resonance regions, a simple mixture of three PAHs could be optically separated through the wavelength selectivity of the resonant enhancement process. The spectrum from a component in the mixture and the spectrum of each pure component showed no significant differences when pumped at the same wavelength. Finally, lineshape analysis performed on the CARS spectra facilitated comparisons between classes of compounds and for quantitative purposes.

INDEX HEADINGS: CARS, PAHs, lineshape analysis.

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INTRODUCTION

Since the first report of coherent anti-Stokes Raman spectroscopy (CARS) by Maker and Terhune in 1965,[1] nonlinear spectroscopic techniques have been used to obtain Raman spectra of highly luminescent species. Resonance enhanced CARS allows one to probe Raman-active vibrational modes in fluorescent molecules which are not amenable to the resonance Raman technique. Furthermore, the sensitivity of CARS in the condensed phase is increased several orders of magnitude due to resonance enhancement so that concentrations as low as 5×10^{-7} M have been examined.[2,3] This additional sensitivity of resonance CARS has allowed it to be used in a multi-detector scheme for HPLC[4-6] in which UV/visible absorption, fluorescence excitation-emission, and resonance CARS detectors were connected in series to an HPLC system to obtain a wide variety of spectroscopic information about each eluting peak.

In the present study, Raman spectra in the rigorous resonance and pre-resonance region have been generated for thirteen highly fluorescent polycyclic aromatic hydrocarbons (PAHs) containing between three and seven fused rings. Also, a simple mixture of three of those PAHs has been analyzed successfully using only the wavelength selectivity of resonance enhanced CARS. This avoids the 10–20 fold dilution of the sample that is characteristic of the chromatographic process. Finally, use of lineshape analysis has been demonstrated to simplify comparisons of spectra and to facilitate quantitative measurements.

EXPERIMENTAL

Reagents and chemicals

All solvents used in this study were Baker reagent grade and were used without further purification. The PAHs were obtained from two sources: Aldrich Chemical Co. (Milwaukee, WI) and Analabs (North Haven, CT). The PAHs were specified at better than 95% purity and were used without further purification.

Instrumentation

The UV/visible absorption spectra were recorded on a computer-controlled instrument that has been described.[4] It consists of a GCA-McPherson spectrophotometer (EU-700 series) interfaced to a Digital Equipment Corp. PDP 11/34 computer. The computer also controls the dye laser and monochromator slewing, mirror and detector positioning, and data acquisition. A schematic diagram of the computer-controlled CARS set-up[3] is shown in Figure 1. The output of a nitrogen laser (Molectron UV-1000) is split into two beams by a 2:1 beam splitter. These beams pump two dye lasers (Molectron DL-200) to produce the ω_1 (pump) beam and ω_2 (probe) beam. The pump and probe beams are crossed and focused onto the sample by a lens, L_2. The sample is contained in a standard melting-point capillary tube.

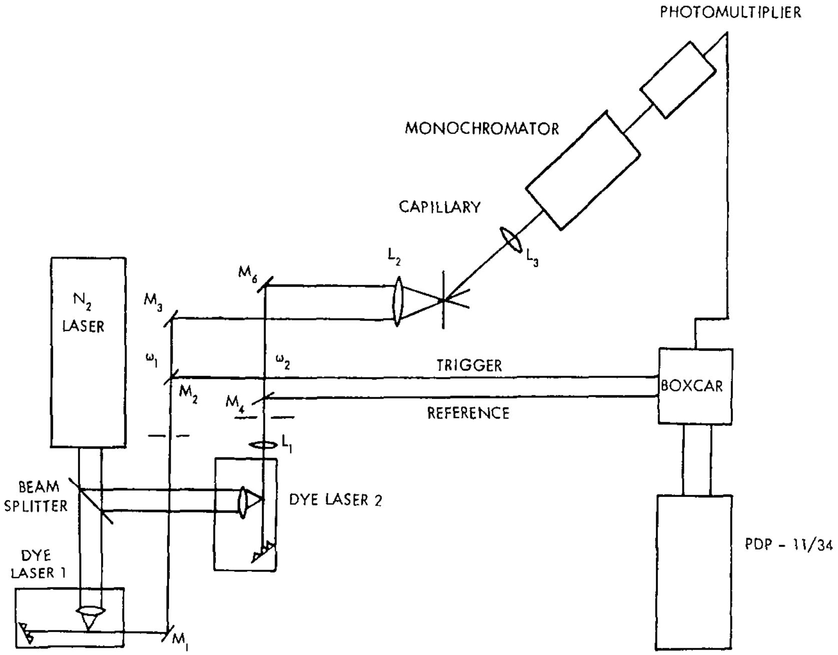

FIGURE 1 Schematic of CARS system. L_1–L_3 are lenses, M_1–M_6 mirrors.

The CARS signal generated at ω_3 is focused by a lens, L_3, onto the entrance slit of the monochromator (JY DH-20 1200 UV). The signal is detected by a gallium arsenide photomultiplier tube (RCA C31034). Signal averaging and gated detection are provided by a boxcar integrator (E. G. & G. Princeton Applied Research, Model 162) which is triggered by the ω_1 beam.

Procedure

Several milligrams of each PAH were weighed out and enough tetrahydrofuran (THF) added to completely dissolve the crystals. Serial dilutions of the original solutions were prepared when necessary. In the mixture, the concentration of each PAH approached closely the concentration used to obtain the CARS spectra when only one PAH was present.

The UV/visible absorption spectra were obtained using a 1 mm pathlength cell (NSG Precision Cells). The PAH samples were diluted with THF until the maximum absorbance reading was about 1 absorbance unit. The spectrophotometer was then scanned from 300 nm to 600 nm in 1 nm increments.

From the absorption spectra, the approximate $0 \leftarrow 0$ transition was determined for each PAH. The optimum CARS pump frequency was then determined with the pump beam, ω_1, set about halfway down the falling edge of the absorption spectrum on the high wavelength side of the 0–0 band.

The probe laser, ω_2, was scanned so that the frequency difference between the two lasers ($\Delta = \omega_1 - \omega_2$) ranged from 1,100 cm^{-1} to 1,700 cm^{-1}. This corresponds to a fingerprint region for fused-ring compounds. The pump wavelength was changed ±10 nm in 5 nm increments to determine the optimum wavelength for each PAH. If a PAH sample absorbed too much, serial dilutions of the sample were performed. The PAH mixture was pumped at each of the optimum wavelengths found for its components.

CARS spectra were recorded using pump wavelengths ranging from 365 nm to 480 nm. Generally, the spectrum was easier to obtain the further into the visible region a compound absorbed. This was due in part to increased power and longer lasting ranges from the laser dyes in the visible region.

Concentrations ranged from 3.0×10^{-2} M for pyrene to 1.5×10^{-5} M for perylene. For compounds having a strong absorption below 400 nm, only the most concentrated solutions were examined. In those cases, only the pump wavelength was changed in order to obtain an optimum spectrum. In other cases (e.g., perylene), a variety of concentrations were prepared and the best pump wavelength for the lowest concentration was chosen. Thus, the minimum concentration for those PAHs absorbing above 400 nm could be lowered to between 1×10^{-4} M and 1×10^{-5} M. In addition to those PAHs for which spectra are shown, spectra were also obtained for anthracene, 1,2-benzanthracene, 1,2,3,4-debenzanthracene, 1,2,5,6-dibenzanthracene, chrysene, 1,2,4,5-dibenzopyrene and tetracene.

Problems occurred for some of the PAHs due to photosensitivity. Tetracene, which was yellow in solution, became colorless upon extended exposure to light so that the quality of spectra were seriously affected. As a result, fresh samples were prepared every few runs, and unnecessary exposure to the laser beams and to room light was avoided. Other samples, which showed no change in solution color but did exhibit poorer spectra with time, were 1,2-benzanthracene and dibenzanthracene. Again frequent changing of the sample capillary and minimizing the light exposure was necessary to obtain good spectra.

Absorption spectra showed that four of the PAHs (pyrene, benzo(e)pyrene, coronene, and chrysene) did not absorb significantly above 360 nm. While resonance CARS has been performed in the wavelength region below 360 nm,[7] its use further complicates the experimental set-up. Commercially available dye lasers are generally tunable only in the wavelength range from 360 nm to 740 nm. In order to effectively pump these four compounds, one would need to frequency-double the laser radiation. However, instead of going to lower pump wavelengths, more concentrated samples were used, and they were pumped in the preresonance region with the result that the spectra had poorer signal-to-noise ratios than those pumped in a resonance region. The sample still exhibited strong fluorescence, and one of them (coronene) has shown fluorescence even when pumped in the red.[8]

CARS spectra are composed of three different lineshapes; positive Lorentzian, negative Lorentzian and dispersive lineshapes. These lineshapes originate from the equation for the absolute square of the third order susceptibility, $\chi^{(3)}$, which is proportional to the intensity of the CARS signal. Fitting these lineshapes with a Jacobian least squares algorithm allows one to solve for the real, R, and imaginary, I, parts of the Raman susceptibility. From the R and I terms, one can construct a spectrum, without fluorescence interference, that corresponds to the spontaneous Raman spectrum.

In those reconstructed spectra, the heights of the peaks were proportional to the concentrations. For quantitative purposes, the relative standard deviations of the peak heights were determined from different initial estimates of the Raman frequency and halfwidth for each peak.

RESULTS AND DISCUSSION

Examination of the CARS spectra showed that all of the PAHs gave qualitatively different CARS spectra. Thus, one could distinguish very easily between structural isomers having the same number of fused rings. For example, benzo(e)pyrene could be distinguished from benzo(a)pyrene, and both of these could be distinguished from pyrene.

Qualitative examinations of PAH spectra can be greatly facilitated by lineshape analysis.[9] Figure 2(a) shows the CARS spectrum for perylene over the frequency range 1,200–1,400 cm^{-1}. The smooth line in Figure 2(b) is the fitted line for the spectrum and Figure 2(c) is the reconstructed spectrum for perylene. Likewise, for the example of the pyrenes, the differences between the spectra are clearly seen in Figure 3. Thus, lineshape analysis can be very useful when comparing spectra within a class of compounds.

Lineshape analysis may also be used to facilitate quantitative measurements for spectra of the same compound at different concentrations. Because the relative contribution of each lineshape type varies differently with concentration,[3] the characters of the spectra also change with concentration. This is evident in Figures 4(b) and 4(c) where the samples of perylene differed in concentration by a factor of sixteen. Although the original CARS spectra were radically different, the reconstructed spectra, after lineshape analysis (Figure 5), were nearly identical. In that example, the concentration of perylene in the dilute sample was so low (1.5×10^{-5} M) that the broad peaks in the background due to the solvent had to be taken into account in the following way. Figure 4 shows the fitted lines for the spectra of pure THF, dilute perylene both in THF, and concentrated perylene. By including the two broad solvent peaks at

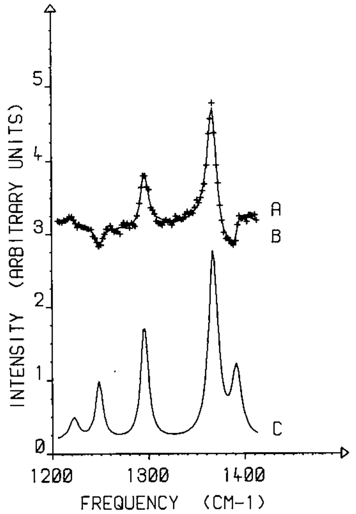

FIGURE 2 Lineshape analysis applied to the CARS spectrum of perylene over the range 1,200–1,400 cm^{-1}; (a) raw data (+), (b) Jacobian least squares fit over the raw data, (c) reconstructed CARS spectrum after lineshape analysis.

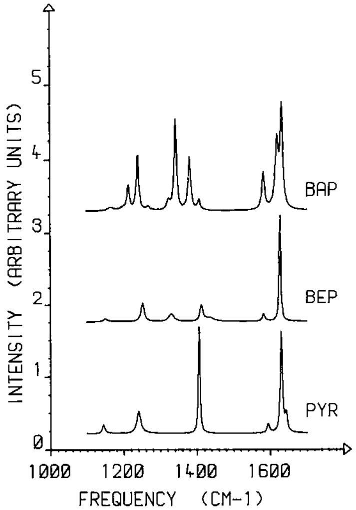

FIGURE 3 Comparison of reconstructed CARS spectra for (PYR) pyrene, (BEP) benzo(e)pyrene, and BAP (benzo(a)pyrene.

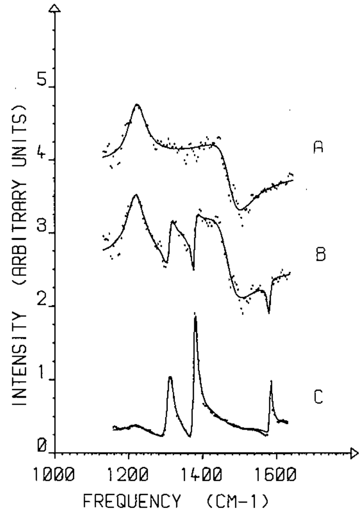

FIGURE 4 CARS spectra and Jacobian least squares fit for (a) THF, (b) perylene at a concentration of 1.5×10^{-5} M in THF, and (c) perylene at a concentration of 2.5×10^{-4} M in THF. ω_1 is 445 nm.

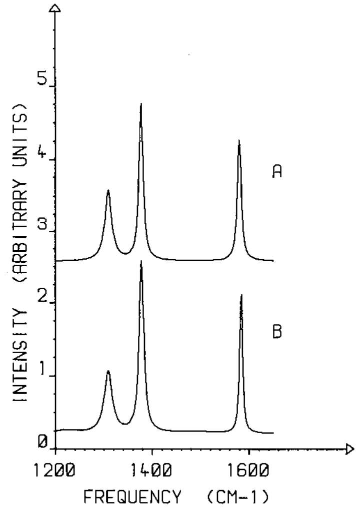

FIGURE 5 Comparison of reconstructed CARS spectra for perylene, (a) 16 × dilute spectrum, (b) concentrated spectrum.

1,220 cm^{-1} and 1,475 cm^{-1} in the lineshape analysis, a much better fit of the perylene spectra was possible so that the reconstructed spectra then gave information that was unaffected by a difference in solute concentration.

As a quantitative test, lineshape analysis was applied to perylene spectra taken at concentrations ranging from 2.5×10^{-4} M to 1.5×10^{-5} M (only one spectrum was recorded at each concentration using a pump wavelength of 445 nm). The height for the same individual peak in each reconstructed spectrum was plotted against concentration. The correlation coefficients for calibration plots of each of the three perylene peaks ranged from 0.996 to 0.999. In each case, the slope of the plot was linear and the *y* intercept was (0 ± 0.01). The relative standard deviation of the linshape analysis, when started from the beginning for a given concentration, was 4–5%.

The range of concentrations that could be examined at any pump wavelength was limited at the low end by the lowest concentration of solute that gave a spectrum distinguishable from the solvent spectrum. At the upper end, it was limited by the concentration of solute that kept its peaks on scale while giving a measurable background signal for the solvent. However, the upper limit could be shifted by changing the pump wavelength. For perylene, more concentrated samples could be examined by pumping further from resonance towards the red (e.g., 450 nm or 455 nm). Thus, quantitation of CARS spectra was possible over a relatively wide range through lineshape analysis and proper choice of pump wavelength.

Once the CARS spectra of the PAHs had been obtained, the selectivity of resonance enhancement was examined so as to determine whether one could resonance-enhance the CARS signal of one compound in the presence of other compounds. A simple mixture of three PAHs was prepared. Coronene, benzo(ghi)perylene and perylene were chosen for the mixture because they had overlapping absorption spectra (Figure 6) but well separated $0 \leftarrow 0$ transitions. In addition, none of the three compounds was found to be photosensitive. The mixture was pumped at the wavelengths used for the three pure compounds, and then the results were compared to the spectra for the pure components.

Figure 7 shows coronene at a pump setting of 370 nm *vs.* the mixture at the same pump wavelength. The spectra are virtually

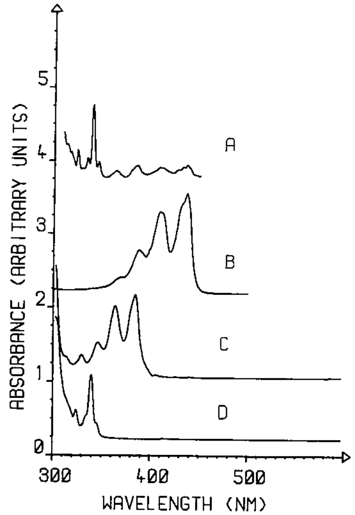

FIGURE 6 Absorption spectra in THF for (a) PAH mixture (perylene, benzo(ghi)perylene, coronene), (b) perylene, (c) benzo(ghi)perylene, and (d) coronene.

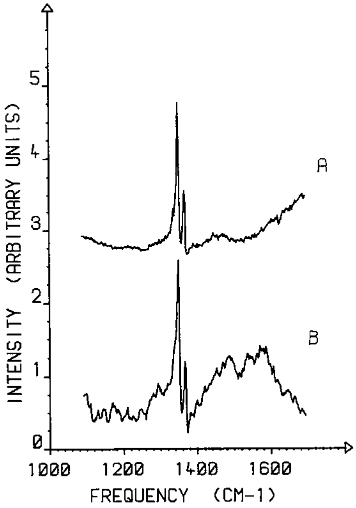

FIGURE 7 Comparison of CARS spectra for (a) coronene, and (b) PAH mixture. ω_1 is 370 nm.

identical except that the mixture spectrum had a noisier background. This was probably due to absorption of the "selective" pump, probe, and signal beams by the other PAHs present in the mixture.

In Figure 8, the spectrum of benzo(ghi)perylene pumped at 400 nm is compared to the mixture pumped at the same wavelength. There are two very weak negative peaks in the 1,350 cm^{-1} region of the mixture spectrum which are not present in the spectrum of the pure sample. These peaks were probably due to contributions of the coronene in the mixture. Overall, however, the two spectra were essentially the same.

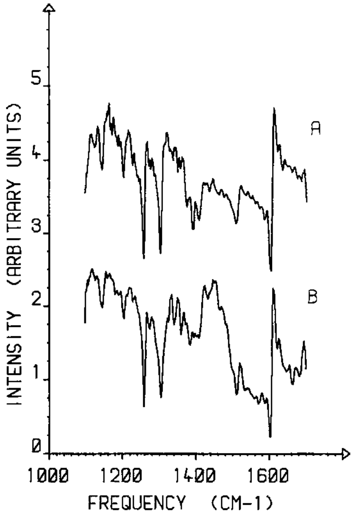

FIGURE 8 Comparison of CARS spectra for (a) benzo(ghi)perylene, and (b) PAH mixture. ω_1 is 400 nm.

Finally, Figure 9 compares perylene at 430 nm alone and in the mixture. Once again, very small differences were found between the two spectra, and the general character of the two spectra was the same.

CONCLUSIONS

CARS has proven to be an effective technique for obtaining Raman spectra that were qualitatively different for 13 highly fluorescent

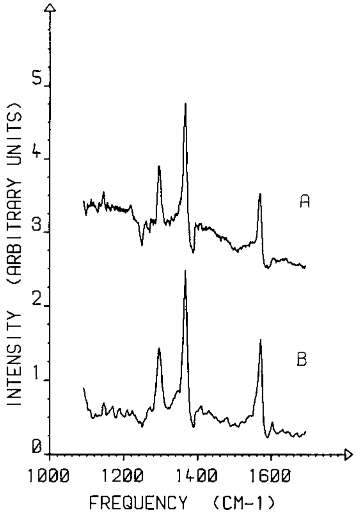

FIGURE 9 Comparison of CARS spectra for (a) perylene, and (b) PAH mixture. ω_1 is 430 nm.

PAHs. Lineshape analysis was applied to the original CARS spectra in order to construct spectra having all positive Lorentzian lineshapes thereby eliminating qualitative differences in the appearances of the original spectra due to concentration. Lineshape analysis was also shown to be useful for quantitation because the peak heights for reconstructed spectra were shown to be directly proportional to concentration.

Lastly, it was shown that one could identify each of three PAHs in a mixture by comparing the major peaks of known compounds to the peaks in the mixture. However, proper choice of the pump wavelength was critical since a 5 nm change from the optimum pump wavelength was enough to alter radically the spectral intensity of the PAHs. On the other hand, one may be able to use this sensitivity to wavelength selection to probe complex mixtures. By changing the pump wavelength over a region and comparing the spectra obtained to standard spectra of known compounds, one should be able to identify many compounds in a mixture.

Acknowledgment

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