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Fourier Transform Raman Spectroscopy

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Abstract: FT–Raman spectroscopy with a near-IR laser is shown to provide a universal solution to the problems of fluorescent interference in Raman spectroscopy. Data have been obtained on systems exhibiting extremely high fluorescent signals under visible excitation. Rayleigh line filtering is described for interferometric detection, and the possibilities for spectral subtraction with Raman data are shown.

The major limitation to the routine application of Raman spectroscopy is the interference caused by fluorescence, either of impurities or of the sample itself. Several methods have been developed to circumvent this problem and the parallel process of thermal degradation. Among them are time-resolved techniques,[1] nonlinear optical methods,[2] UV Raman and resonance Raman measurements,[3] and SERS experiments.[4] All have shown some success for certain samples, but none offer a universal approach to the problem. In order to completely avoid the absorption process which gives rise to the fluorescence, the Raman experiment should be done with a long-wavelength near-infrared laser, for example, a Nd/YAG system lasing at 1.064 μm (9395 cm^{-1}).[5] Unfortunately, the Raman scattering cross section is decreased by a factor of 16 from that at 5145 Å due to the λ^4 dependence. Additionally, the available detectors for this spectral region are much noisier than photomultipliers. Initial studies by Hirschfeld and Chase[5] and Jennings et al.[6] showed that reasonable Raman spectra could be obtained in this region with a multiplexing spectrometer. In this work we have shown that the fluorescent background problem is nonexistent for near-IR FT–Raman spectroscopy and that spectral subtraction techniques popularized by the FT–IR systems can be easily and accurately applied to these Raman data.

Experimental Section

Conventional Raman spectra were obtained with a J–Y Raman microprobe (MOLE) with 180° back-scattering collection. The spectral band-pass was 3.8 cm^{-1} at 5145 Å. A Spectra Physics 171-19 argon laser was utilized with an RCA C31034A photomultiplier and photon-counting detection. The instrument was operated in a step scan mode with 1 s integration time at each point (1-cm^{-1} steps).

FT–Raman data were acquired with a Nicolet 7199 interferometer equipped with a quartz beamsplitter and a Judson germanium detector, 1 mm^2, $D^* = 1.5 \times 10^{11}$. The interferometer was operated with a mirror velocity of 0.1 cm/s, resulting in modulation frequencies of 1 to 2 kHz. Each interferogram consisted of 10 896 data points which corresponds to a nominal resolution of 4 cm^{-1}. Two times zero filling was used in the Fourier transform, and a weak apodization function,[7] F3, was applied. Since the interferogram corresponds to a weak discrete line emission spectrum, conventional phase correction could not by employed. Instead, the power spectra were calculated. A Spectron SL50 Nd/YAG laser was used operating in a TEMoo mode. The output power fluctuations were 2% RMS. Plasma line filtering was accomplished with an Anaspec C1000 filter monochrometer. The laser was focused onto the sample with a 200 mm f.l. lens to a spot size of 350 μm. Collection optics are shown in Figure 1. A 75 mm diameter paraboloid (Special Optics f.l. = 17 mm) was used to collect and collimate the 180° backscattered radiation. This collected beam was passed directly into the modulator. Rayleigh line filtering was done with a three stage dielectric filter (Omega Optical 1.064 long wave pass filters) with spatial filtering as shown in Figure 1.

Results

The key to the success of an FT–Raman experiment is the effective optical filtering of the intense Rayleigh scattered radiation. Since the intensity of this line can be 10^{10} stronger than the Stokes shifted lines in the Raman spectrum, a filter with an optical density of approximately ten at the laser frequency is required. In order to obtain the maximum information available in the Raman spectrum, the filter should have a sharp transition from extinction to high transmittance at a wavelength which is only slightly shifted from the laser line. Initial studies showed that absorptive color filters could be used with both Krypton and Nd/YAG lasers and suitably high optical densities were achieved, but the transition to the nonabsorbing region was too gradual and Raman scattering below the 900 cm^{-1} Stokes shift was absorbed by the filter.

The current filtering arrangement is shown in Figure 1. Three dielectric long pass filters (OMEGA OPTICAL) are used in series with spatial filtering to minimize the collection of filter fluorescence. A total extinction of 10^{10} was achieved at 1.064 (9395 cm^{-1}) μm, and the transmission curve is shown in Figure 2. This curve can be used to correct the observed Raman spectrum for relative intensity fluctuations due to filter absorption. With this filter, Raman data can be obtained down to 250 cm^{-1} Stokes shift. It should be noted that the filters go through a secondary extinction near 7400 cm^{-1} (2000 cm^{-1} Stokes shift). When data are needed in this region, a second spectrum is obtained with a color filter (Glendale Optical). A typical low-frequency spectrum is shown in Figure 3. The strong Ta–Cl stretches are easily resolved, and Raman bands are observed down to 200 cm^{-1}.

It is possible to obtain Raman data with less than complete filtering of the Rayleigh line, so long as detector or A/D saturation is avoided.[8] The effects of such incomplete filtering are not limited to the intensity of the Rayleigh line but are mainifested as an increase in noise throughout the entire spectrum. Due to the distributive property of the Fourier transform, fluctuation noise on a single strong line is redistributed throughout the frequency domain. For the case of a single strong line amidst several weaker lines, the noise performance of a multiplexing instrument can be degraded. Figure 4 shows Raman data obtained on a sample with triple, double, and single stage optical filtering of the Rayleigh line. In no case was the dynamic range of the instrument exceeded. The results obtained with single stage filtering (curve A in Figure 4) are clearly useless. Both double- and triple-stage filtering produce reasonable spectra, but a scale expansion of the data, shown in Figure 5, shows that reduced filtering (curve A in Figure 5) gives rise to an increased noise level throughout the entire

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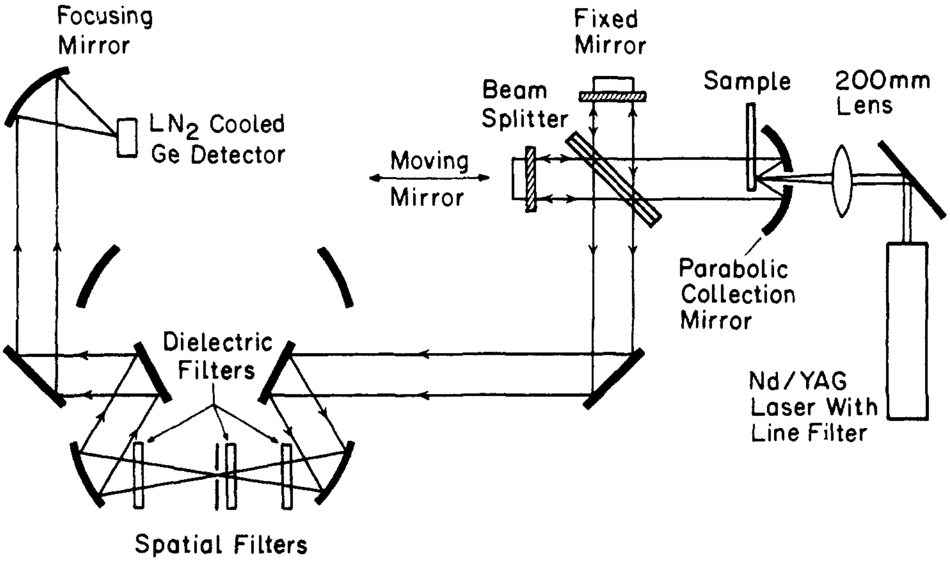

Figure 1. Collection optics and filtering optics for the FT–Raman experiment.

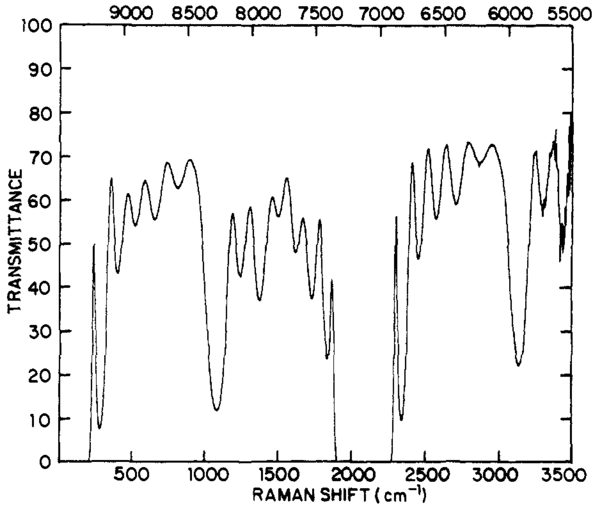

Figure 2. Transmission curve for the three-stage dielectric filter.

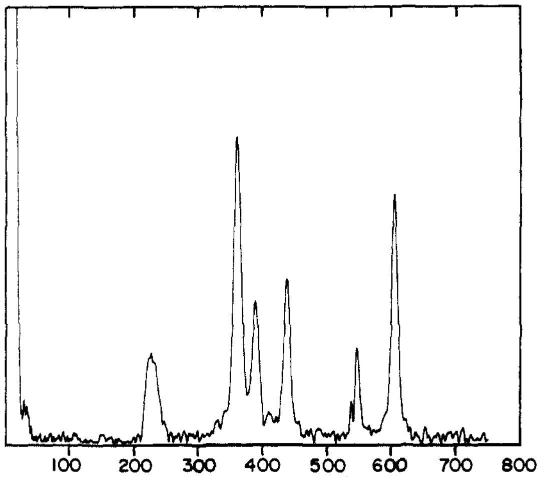

Figure 3. FT–Raman spectrum of tantalum cyclopentadienyl tetrachloride.

spectrum. The slight reduction in transmission (75%) caused by the introduction of a third filter is more than compensated for by the improved noise performance. For strong scatterers, it appears that the current dominant noise source is laser power fluctuations (currently 2% RMS). By stabilizing the power output, a further improvement of 10× is expected.

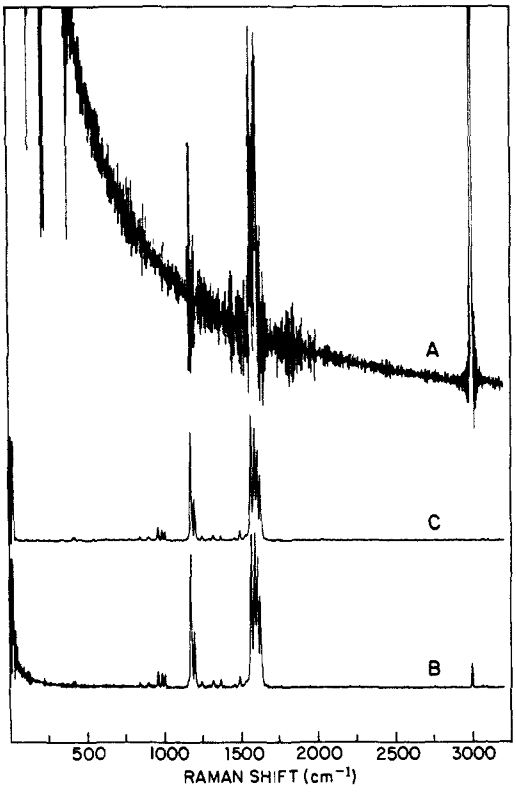

Figure 4. FT–Raman spectrum of bis(phenylimino)terephthaldehyde (BPT) with (A) single, (B) double-, and (C) triple-stage filtering.

As mentioned previously, one primary reason for the development of FT–Raman spectroscopy was to overcome the problem of sample (or impurity) fluorescence. The effectiveness of this approach can be readily seen in the following examples. Figure 6A shows a Raman spectrum of a sample of anthracene obtained on our conventional instrument with 150 mW of 5145-Å radiation and a total measurement time of 1 h. The severe fluorescent background is probably due to impurities or some small amount of sample degradation. Figure 6B shows an FT–Raman spectrum obtained on the identical sample with 1500 mW of 1.064-μm radiation and 30 min measurement time. There is no detectable excitation of fluorescence. The signal to noise is drastically improved over the conventional spectrum where the shot-noise component of the fluorescent signal dominates. This sample was irradiated at that power level for 2 h with no sign of thermal

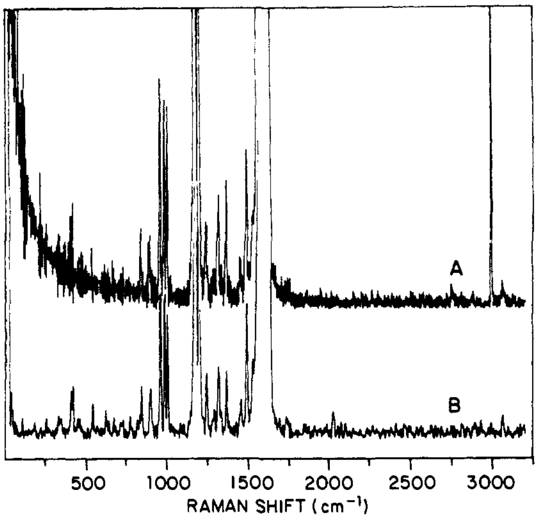

Figure 5. FT-Raman spectra of bis(phenylimino)terephthaldehyde (BPT) (scale expanded): (A) double- and (B) triple-stage filter.

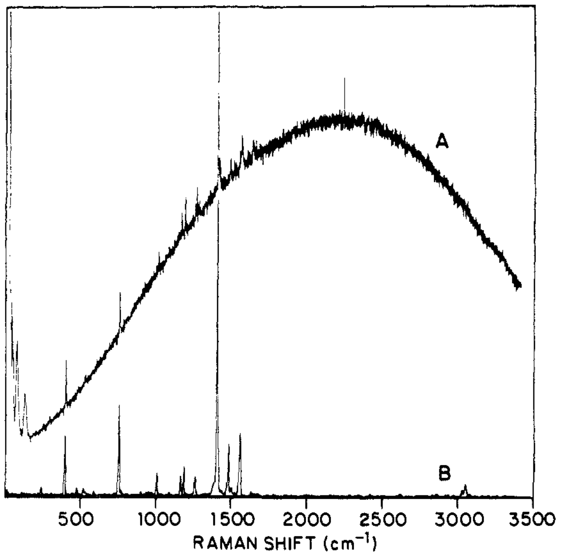

Figure 6. (A) Conventional Raman spectrum of anthracene. (b) FT-Raman spectrum of anthracene.

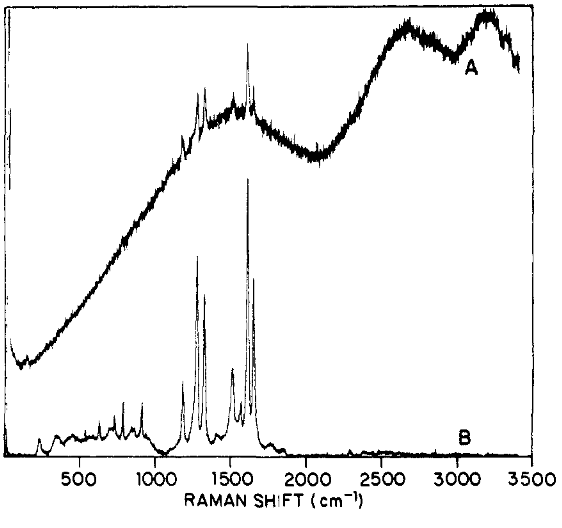

Figure 7. (A) Conventional Raman spectrum of poly(*p*-phenylene)-terephthalimide. (B) FT-Raman of poly(*p*-phenylene)terephthalimide.

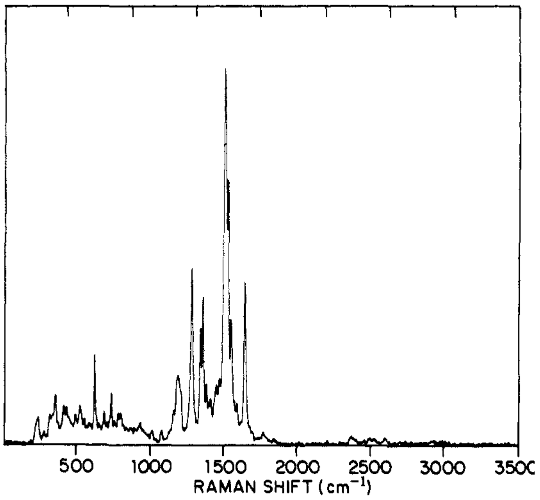

Figure 8. FT-Raman spectrum of rhodamine.

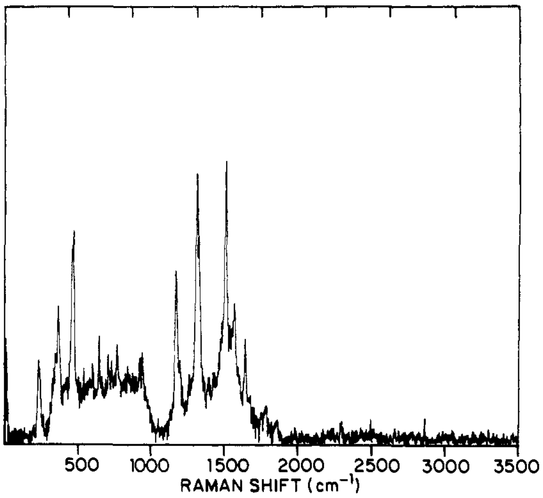

Figure 9. FT-Raman spectrum of fluorescein.

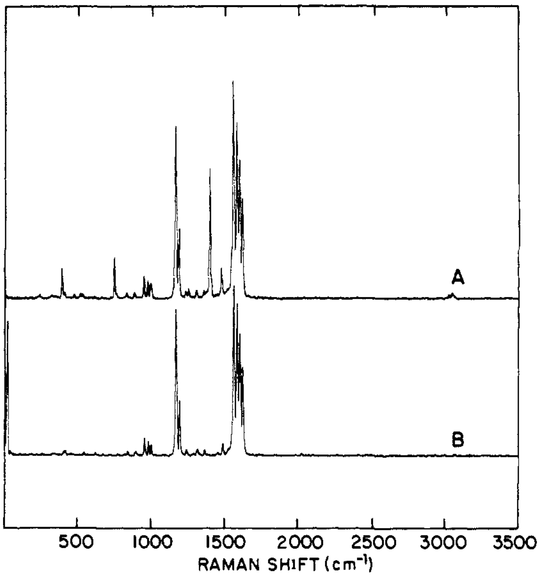

Figure 10. (A) FT-Raman spectrum of anthracene/BPT mixture. (B) FT-Raman spectrum of BPT.

degradation. Even higher power levels could have been employed, reducing the measurement time. Figure 7 shows similar data obtained on poly(*p*-phenylene)terephthalimide with the conventional Raman instrument (curve A) and the FT-Raman instrument (curve B). Again, the suppression of the fluorescent background is complete.

For some samples, the fluorescence and thermal decomposition problems are so severe no spectra can be obtained with conventional instrumentation. Laser dyes are a prime example. Figures 8 and 9 show Raman spectra obtained on Rhodamine and

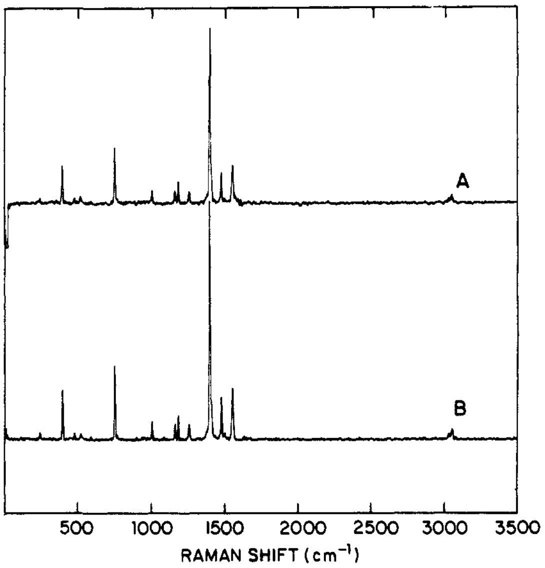

Figure 11. (A) Subtraction result from Figure 10. (B) FT-Raman spectrum of anthracene.

Fluorescein, respectively. As a further example, the material whose Raman specrum is shown in Figure 3 has a measured fluorescence quantum yield of 1% at 5145 Å. The ability to use higher power levels in the near-infrared coupled with the multiplex and throughput advantages of the interferometer compensates for the loss in scattering cross section. This approach offers a universal solution to the problem of fluorescence in Raman spectroscopy.

An additional advantage offered by interferometric Raman spectroscpy is the possibility of spectral subtraction. The frequency precision of a laser referenced interferometer is quite high, approximately 0.01 cm^{-1}. This high precision ensures that two spectra can be arithmetically combined without introducing artifacts or features due to a lack of frequency registration. This process of spectral subtraction has been done previously in conventional Raman spectroscopy, but great care must be taken in instrument alignment and calibration. Figure 10A shows the FT-Raman spectrum obtained on a physical mixture of anthracene and bis(phenylimino)terephthaldehyde (30:70). The spectrum shown in Figure 10B is that of pure bis(phenylimino)terephthaldehyde.

By adjusting a subtraction factor to remove features in the composite spectrum which are due solely to component A, the spectrum shown in Figure 11A was obtained. Figure 11B is a reference spectrum of pure anthracene. The agreement between the subtraction result and the reference is excellent.

Conclusions

It has been shown that by using a multiplexing spectrometer and a near-infrared laser, high-quality Raman spectra can be obtained in reasonable measurement time. The problem of fluorescence background is totally circumvented with this approach, and the problem of thermal decomposition is minimized since the only absorption mechanism involves excitations of vibrational overtones and combinations. The high frequency precision of the interferometric instrument allows accurate spectral subtractions to be performed. The problem of effective Rayleigh scatter removal can be addressed by the use of multistage dielectric filters, and Raman data can be obtained down to within 250 cm^{-1} of the exciting line.

Registry No. BPT, 14326-69-3; tantalum cyclopentadienyl tetrachloride, 62927-98-4; anthracene, 120-12-7; poly(*p*-phenylene terephthalamide), 24938-64-5; rhodamine, 12676-92-5; fluorescein, 2321-07-5.

Transmethylation Reactions of L-Carnitine in Energized Condensed Phase[1]

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Abstract: The FAB spectra of L-carnitine negative ions provide unique data concerning the chemistry of the sampled molecule in energized condensed phase which can be correlated to some extent with those obtained in vivo or under conventional laboratory conditions. Demethylation of the ammonium moiety and Hoffman degradation are the base induced processes preferentially populated, while the relative intensity of $(M - H)^-$ is negligible. The chemistry of the demethylated anions in the gas phase has been investigated by MS/MS techniques.

Results and Discussion

The use of mass spectrometry in analyzing large involatile molecules[2-5] has been facilitated by the introduction of desorption ionization techniques such as FAB[6]. Since the formation of secondary ions depends on the chemistry of the analyte/solvent system in the energized condensed phase[7], a desorption ionization spectrum displays not only protonated or deprotonated molecules but also ionic species formed both by unimolecular processes in the gas phase and by bimolecular interactions in the condensed layers.[7-9] Because of the widespread use of desorption ionization methods in analyzing polar materials it has become essential to

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