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Fluorescence-Free Scanning Raman Spectroscopy

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Abstract: We report the use of a high-power continuous wave Nd:YAG laser at 1.064 μm with a liquid nitrogen cooled germanium detector to obtain high-quality Raman spectra of normally highly fluorescent materials with a conventional scanning double monochromator. We find signal-to-noise ratios that are comparable with those obtained by Fourier transform Raman spectroscopy for similar scan times and vastly improved performance at low frequencies.

Fluorescence has been the major problem which has precluded Raman spectroscopy from being universally applicable as a vibrational spectroscopy. Although many samples suffer from intrinsic fluorescence, perhaps an even larger number of interesting materials have impurity fluorescence that overwhelms the Raman scattering. Thus, if Raman spectroscopy is to be useful in the analysis of materials like polymers, pharmaceuticals, and inhomogenous composites in general, the fluorescence problem must be eliminated. This problem has been attacked over the years with varying degrees of success. Time-resolved techniques have been tried, but since fluorescence lifetimes are comparable to the fastest switching and transit times in high-gain photodetectors, significant reductions in background cannot be expected.[1] Coherent Raman spectroscopy[2] offers reduced backgrounds, essentially through spatial filtering, but it is a difficult and expensive experiment and the high peak powers required are potentially damaging to the sample. Excitation into higher electronic states in the deep ultraviolet keeps the Raman spectrum spectrally well-separated from the fluorescence, but photochemistry can be a problem.[3] Finally, placing a molecule near a conducting metal surface will quench the fluorescence and surface-enhanced Raman scattering can be used for greater sensitivity, but the presence of the surface will necessarily perturb the spectrum.[4]

Clearly the best approach to obviating the fluorescence problem is to use a laser frequency low enough so that electronically excited states are inaccessible. Tasumi et al.[5] demonstrated the feasibility of this idea by obtaining spectra using a pulsed Nd:YAG operating at 1.064 μm. A pulsed laser, however, provides average powers that are too low for adequate sensitivity, and the high peak powers involved make sample damage a concern. Several groups have been developing Fourier transform (FT) Raman spectroscopy[6,7] in which they use a continuous wave (CW) Nd:YAG laser operating at 1.064 μm, an interferometer, and a cooled germanium photodetector to obtain high-quality Raman spectra free of fluorescence. A recent article by Chase in this journal summarizes the current progress in FT Raman spectroscopy.[8] The FT method has both its advantages and disadvantages, however, and we were interested to see if conventional scanning Raman spectroscopy using high-power CW 1.064-μm excitation offered a viable alternative.

The FT technique in general offers both a throughput advantage and a multiplex advantage over conventional techniques. It has been argued that these advantages are necessary to compensate for the factor of 20-30 reduction in cross section due to the ω^4 dependence. There is, in fact, very little throughput advantage comparing FT Raman to scanning Raman in this spectral region; since this dispersion is so low ($\sim$1 cm^{-1}/Å), very wide slits can be used with a weakly focused laser at adequate resolution. The full multiplex advantage applies only in the case of perfect rejection of the Rayleigh line; otherwise, this signal appears uniformly as noise in the interferogram. Complete rejection has been notoriously difficult to accomplish and has resulted in lower signal-to-noise ratios (SNR) as well as limited low-frequency performance. In this article, we show that conventional scanning Raman spectroscopy using a powerful CW Nd:YAG laser is a competitive alternative to FT Raman spectroscopy, providing complete fluorescence rejection, comparable (and in some cases better) SNR, and significantly improved performance at low frequencies.

Experimental Section

Raman spectra were obtained using a Spex 14018 0.85-m scanning double monochromator fitted with a pair of 600 lines/mm conventionally ruled gratings blazed at 1.25 μm and scanned under computer control with a stepping motor. The dispersion at 1.064 μm is ca. 8 cm^{-1}/mm of slit width. The output of a 3-W multimode linearly polarized Nd:YAG laser (CVI C-95) was filtered through a narrow band-pass interference filter (Melles-Griot) and sent to the sample housed in a Spex UV illuminator equipped with an $f/1$ quartz lens system. The maximum laser power available at the sample is 2.3 W. The detection system comprised a cooled North Coast Optical Systems EO-817 L germanium photodetector which has an NEP of 1×10^{-15} W/Hz$^{1/2}$ at 77 K. The signal was modulated by chopping the laser mechanically at 100 Hz (EG&G PARC 196) and detected by an EG&G PARC Model 5104 lock-in amplifier whose output was fed to an IBM PC via an IEEE-488 interface. The total throughput of the system (transmission and reflection losses and detector quantum yield) is estimated to be 10%.

Results

In order to estimate the performance of the system we chose to examine the Raman spectrum of liquid benzene whose Raman scattering cross-section is well-known. The detected signal can be estimated from

$$I_{\mathrm{R}} = \rho l(\partial\sigma/\partial\Omega)\Omega P E$$

where $\partial\sigma/\partial\Omega$ is the peak differential Raman scattering cross section, ρ is the molecular density, l is the length of the laser focal region viewed by the collection optics which subtend the solid angle Ω, P is the laser power in watts, and E is the detection efficiency of the system as mentioned above. Using the value 1×10^{-30} cm^2 sr^{-1} molecule^{-1} for the Raman cross-section of the 992-cm^{-1} mode excited with 1.064-μm radiation, $l = 0.125$ cm, $\rho = 7 \times 10^{21}$ molecule cm^{-3}, $\Omega = 0.67$ sr, and $E = 0.1$ we should expect ca. 6×10^{-11} W of detected power per cm^{-1} bandwidth. If we assume that we are detector noise limited in this experiment, then we may expect a signal-to-noise ratio that approaches 10^4:1 given the detector NEP of 1×10^{-15} W/Hz$^{1/2}$ and a signal bandwidth of 1 Hz which corresponds to a lock-in time constant of 300 ms. This SNR is typical for scanning experiments using visible excitation. Figure 1 shows the Raman spectrum of benzene acquired in ca. 15 min with 580 mW of 1.064-μm radiation incident upon the sample. As shown in the insert, the SNR exceeds 100:1 but does not approach our estimate of 10^4:1. Most of this excess noise is due to the passage of muons through the detector creating huge spikes in the output. These have been partially filtered electronically but their large amplitude creates difficulty in completely filtering them out. More sophisticated filtering procedures should

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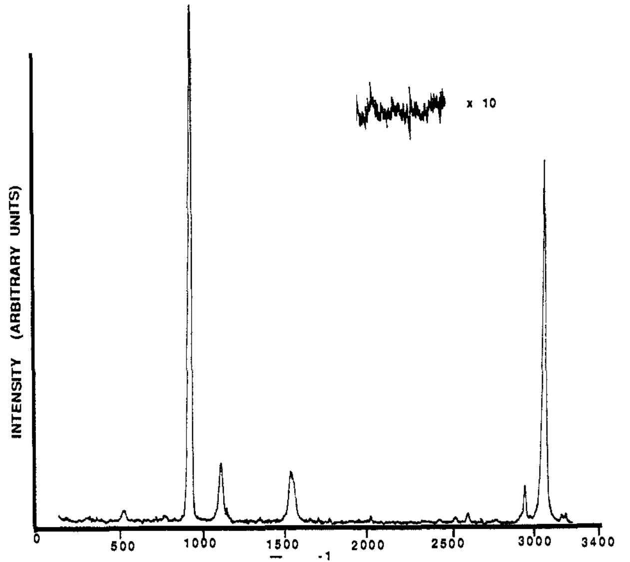

Figure 1. Raman spectrum of neat liquid benzene excited with a CW 1.064-μm Nd:YAG laser. Incident laser power was 580 mW and the slits were set for 24-cm^{-1} resolution. Scan time was 15 min.

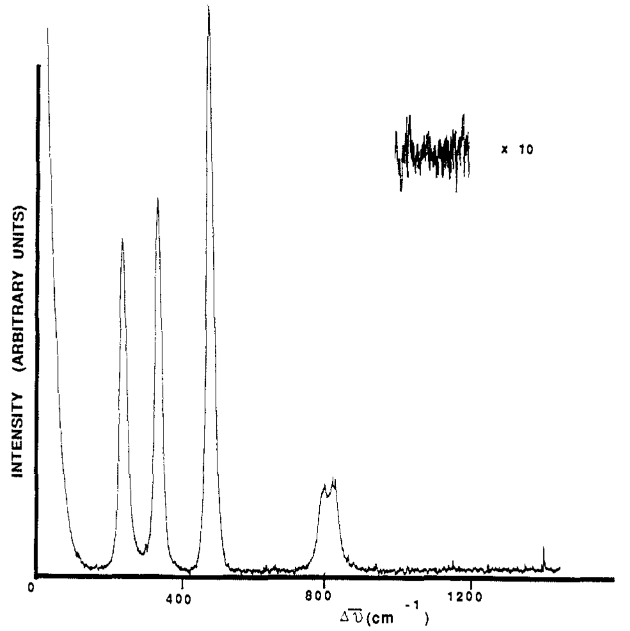

Figure 2. Raman spectrum of neat liquid carbon tetrachloride excited with CW 1.064-μm Nd:YAG laser. Incident laser power was 610 mW and the slits were set for 16-cm^{-1} resolution. Scan time was 18 min.

reduce this noise to achieve the high SNR predicted above. We found that thermal lensing is a problem with liquid samples having high-frequency C–H stretches whose third overtones are nearly resonant with the laser frequency. For these samples, either reducing the laser power or opening the slits is required, depending upon whether resolution or high SNR are most important. As a second example, we present the spectrum of CCl_4 in Figure 2. The high SNR is shown to extend into the low-frequency region, and the thermal lensing encountered with benzene is unimportant here, as evidenced by the higher resolution achieved at the same laser power. These two examples clearly show that high SNR are obtainable with a scanning instrument and relatively high-power CW near-infrared excitation.

Figure 3 demonstrates the complete elimination of fluorescence; the sample is benzene doped with 17 μM rhodamine 6G. The spectrum is virtually identical with that of neat benzene. Perhaps even more dramatic proof of the elimination of fluorescence are the spectra of neat, solid rhodamine 6G and fluorescein disodium salt shown in Figures 4 and 5. The spectra are beautifully resolved and the high SNR extends to low frequencies in constrast to spectra obtained by the FT method.

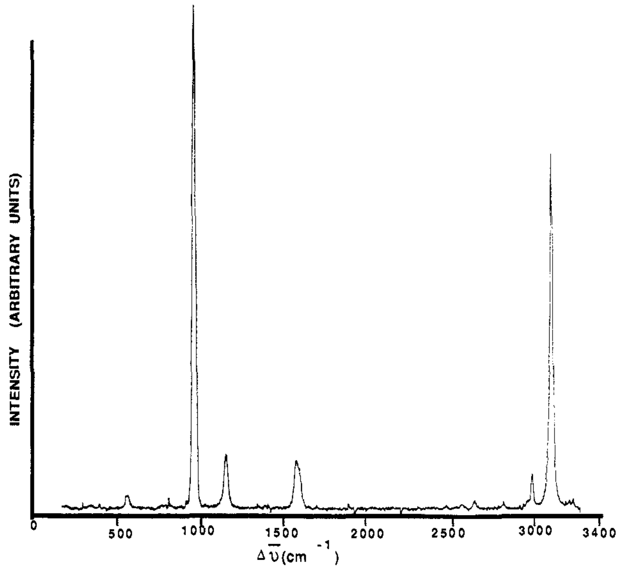

Figure 3. Raman spectrum of liquid benzene doped with 17 μM rhodamine 6G, excited with a CW 1.064-μm Nd:YAG laser. Incident laser power was 580 mW and the slits were set for 16-cm^{-1} resolution. Scan time was 15 min.

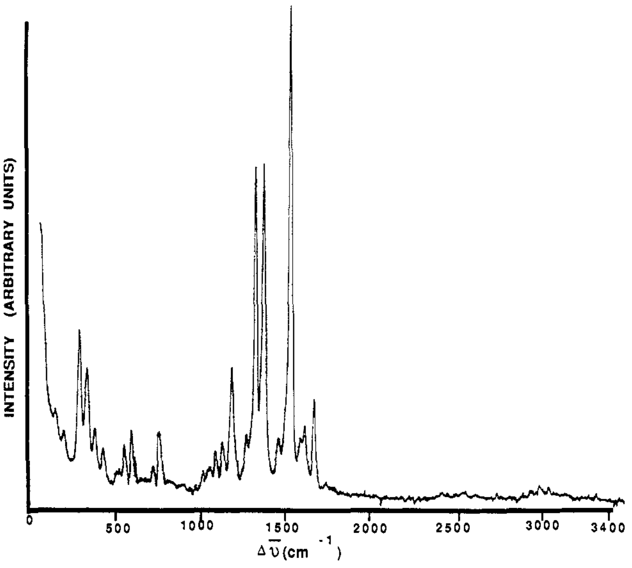

Figure 4. Raman spectrum of crystalline rhodamine 6G, excited with a CW 1.064-μm Nd:YAG laser. Incident laser power was 400 mW and the slits were set for 16-cm^{-1} resolution. Scan time was 18 min.

The superior low-frequency performance of the scanning instrument is illustrated in Figure 6, the Raman spectrum of polycrystalline sulfur. This is a classic test of instrument performance, and the spectrum presented here shows very clearly the 27-cm^{-1} phonon and that frequency shifts as low as 10 cm^{-1} should be observable. This low-frequency performance is clearly superior to that currently available in FT Raman spectroscopy and is, of course, particularly important for studying inorganic materials as well as the lattice modes of solids.

Finally, we present one example to show our estimate of the current sensitivity of the technique in the analysis of multicomponent systems. Figure 7 shows the Raman spectrum of a solution of 10% (volume) of benzene in carbon tetrachloride in which the benzene ring breathing mode and C–H stretching modes are clearly seen. The insert shows the 992-cm^{-1} ring breathing mode in a 0.1% solution, which represents the current lower limit of sensitivity. The relative sensitivity observed here is probably not too different from what would be achieved in a conventional Raman experiment with visible laser excitation; there is always

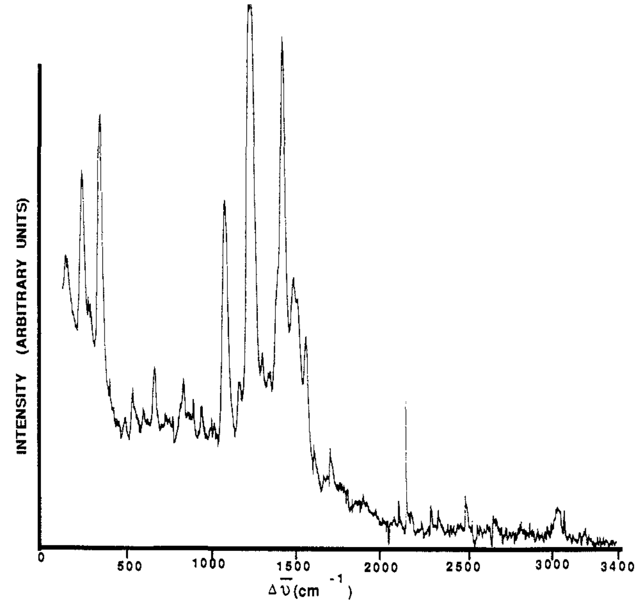

Figure 5. Raman spectrum of crystalline fluorescein disodium salt, excited with a 1.064-μm CW Nd:YAG laser. Incident laser power was 40 mW and the slits were set for 16-cm^{-1} resolution. Scan time was 18 min.

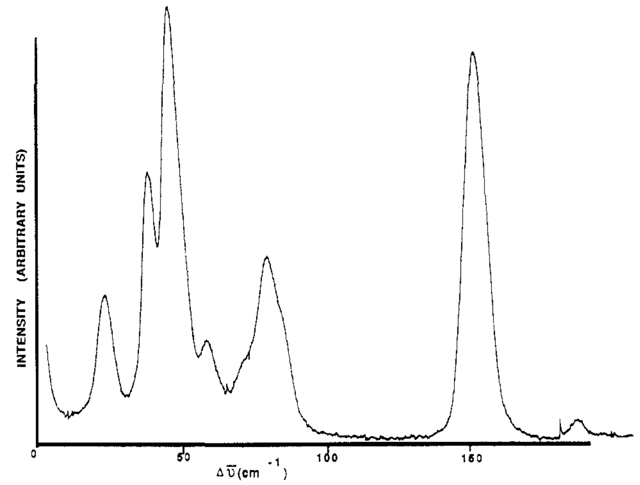

Figure 6. Raman spectrum of polycrystalline sulfur, excited with a CW 1.064-μm Nd:YAG laser. Incident laser power was 400 mW and the slits were set for 3-cm^{-1} resolution. Scan time was 20 min.

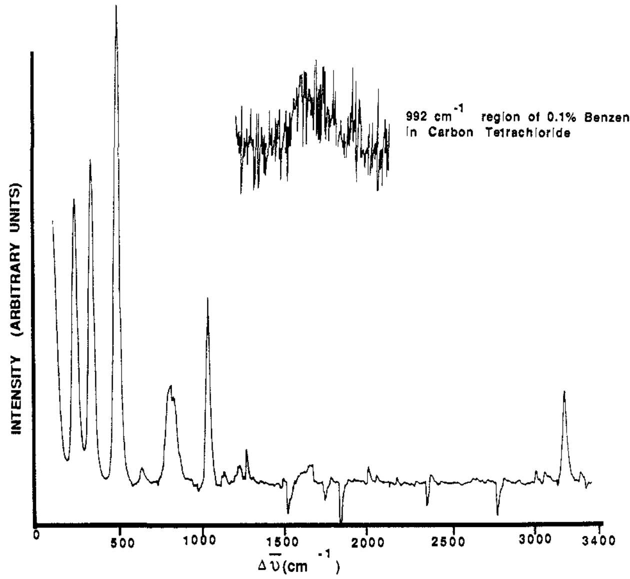

Figure 7. Raman spectrum of 10 and 0.1% solutions of benzene in carbon tetrachloride, excited with a CW 1.064-μm Nd:YAG laser. Incident laser power was 400 mW and the slits were set for 24-cm^{-1} resolution. Scan time was 15 min.

a weak continuum background of the major component present which sets the lower limit of detectability for the minor component. Spectral subtraction techniques have been employed using FT Raman spectroscopy which can retrieve the spectrum of each component in a multicomponent system separately. The high-frequency precision of the FT method would appear to be an advantage here in achieving good registry, but with the reduced dispersion in this frequency region and the precision with which the stepping motor drive can set the frequency, the scanning method should provide equivalent results for spectral subtraction.

Conclusions

We have demonstrated that conventional scanning Raman spectroscopy, using a 1.064-μm Nd:YAG laser as the source, is competitive with FT Raman spectroscopy. The method offers comparable SNR at similar scan times and laser powers, complete elimination of fluorescence, and superior low-frequency performance. We expect greater than one order of magnitude improvement in SNR using higher laser powers and more effective elimination of the muon spikes which will require either more sophisticated filtering or a different detector. Spectroscopists may well decide that which is the preferable system depends upon what is already available in their laboratories. conversion of either an FTIR or a conventional scanning system for near IR operation requires only the addition of a relatively inexpensive laser and infrared detector. There is clearly no question that freedom from fluorescence that these new techniques provide will make many new areas accessible for study by Raman spectroscopy.

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Registry No. Benzene, 71-43-2; carbon tetrachloride, 56-23-5; rhodamine 6G, 989-38-8; fluorescein disodium salt, 518-47-8; sulfur, 7704-34-9.