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UV-Excited Resonance Raman Spectroscopy of Narcotics and Explosives

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ABSTRACT: A 244 nm excitation Raman microspectroscope has been developed and successfully used to investigate a range of narcotics and explosives, both pure and contaminated. The instrument is quick and simple to operate and effective in identifying these compounds. The wavelength was chosen to exploit the resonance Raman effect, thereby enhancing the band intensities beyond the normal v^4 enhancement associated with the shorter wavelength excitation. Another advantage over visibly excited Raman spectroscopy is the complete lack of any fluorescence background, even with heavily contaminated samples. The simplification of spectra caused by resonance allowed the easy identification of species contained in complex mixtures.

KEYWORDS: forensic science, spectroscopy, Raman, explosive, narcotic, criminalistics

Raman spectroscopy is a versatile technique of great potential for the field of forensic science (1–4). The appeal of this technology lies in its ability to locate and identify unequivocally many different compounds. The process is nondestructive, sensitive, fast, and repeatable. Provided a sample can be placed at the focus of the objective lens (either attached to a microscope or to a remote probe (5)) it can be investigated without sample preparation. Recent advances in computer control have also enabled operation by nonskilled staff (6).

One of the main problems limiting the widespread adoption of Raman spectroscopy in the forensic laboratory has been the strong fluorescence associated with some samples; this can completely swamp the weak Raman effect. This fluorescence may be caused by impurities or by the sample itself. Fluorescence associated with large contaminant particles can often be overcome by using confocal techniques (7) whereby a locally uncontaminated region of sample is examined. This technique offers no advantage, however, when the fluorescence is intrinsic to a homogeneous sample.

An alternative approach to combat fluorescence is to use an excitation wavelength in the infrared (IR), or in the ultraviolet (UV). Infrared excitation normally does not excite fluorescence and has been used to examine a wide range of explosive materials (1,3). However infrared excitation has the disadvantages that Raman scattering efficiencies decrease rapidly as the excitation frequency decreases, and detectors are less efficient or noisier. Correspondingly, exposure times or laser powers have to be increased to compensate (with the possibility of sample damage in the latter case).

Ultraviolet excitation Raman spectra are normally free from fluorescence because the Raman scattering occurs at much higher photon energy than the fluorescence bands (the Raman shifts are always relative to the excitation but the fluorescence is fixed in energy). It has been shown that the full Raman range (0 to 4000 cm^{-1}) is normally free from fluorescence when an excitation wavelength shorter than about 250 nm is used (8).

Ultraviolet excitation Raman spectra often exhibit resonance features. The resonance Raman effect (9) occurs when the excitation falls near to, or within, an optical absorption band of the sample. Raman scattering probabilities can increase substantially for bands coupled to the absorption. This results in much greater sensitivity, and an apparent simplification of the Raman spectra caused by the dominance of the resonantly enhanced Raman bands. In many molecular materials the electronic excitation will be located in a small part of the molecule called the chromophore.

In this paper we discuss the design of the spectroscope, and compare UV-excited and visible-excited Raman spectra from a range of materials of interest to forensic scientists.

Apparatus

We have developed a Raman instrument using 244 nm excitation from an intra-cavity, frequency doubled continuous wave (cw), argon ion (Ar+) laser (10) (Coherent Inc., Santa Clara, CA). The spectroscope is a modified Renishaw Raman Imaging Microscope (6). This comprises a single dispersive stage, with two multi-layer dielectric filters to reject Rayleigh (elastically) scattered light. The detector is a thermoelectrically cooled silicon charge-coupled-device (CCD) chip that operates as a multichannel detector (in our case a UV sensitized model is used). A 180-deg scattering geometry is employed, with a microscope objective both for illumination and for collection of the scattered light. In our case the optics were fabricated from UV-grade materials (principally fused silica and calcium fluoride), and the mirrored surfaces were protected against photo-degradation by magnesium fluoride coatings. The objective is a ×40 air-spaced compound achromat made from UV-grade materials. It is optimized for use from 200 to 450 nm, and has a NA of 0.5. The high-efficiency 3600 groove mm^{-1} diffraction

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grating gives a typical spectral range of 2150 cm^{-1}, although the spectroscope's extended scan facility (11) was normally used to give broader coverage. Spectral resolution of the instrument is 2.5 cm^{-1} (half-width, half-maximum) in the fingerprint region (500 to 1600 cm^{-1}).

The spectroscope is confocal (7) and, with the ×40 objective used in this study, has a collection volume less than 1 μm across; the mass of the material contained within the illumination/collection volume is typically 1 pg. This small volume can result in high power densities sufficient to cause photo-degradation of the samples; therefore neutral density filters were used to reduce the laser power on the sample to <1 mW, rather than the maximum 30 mW.

A simple monochromator consisting of a prism and a pinhole was used to prefilter the laser light before it entered the spectroscope. This prevented laser discharge tube plasma lines from entering the instrument and overwhelming any weaker Raman features of the same wavelength.

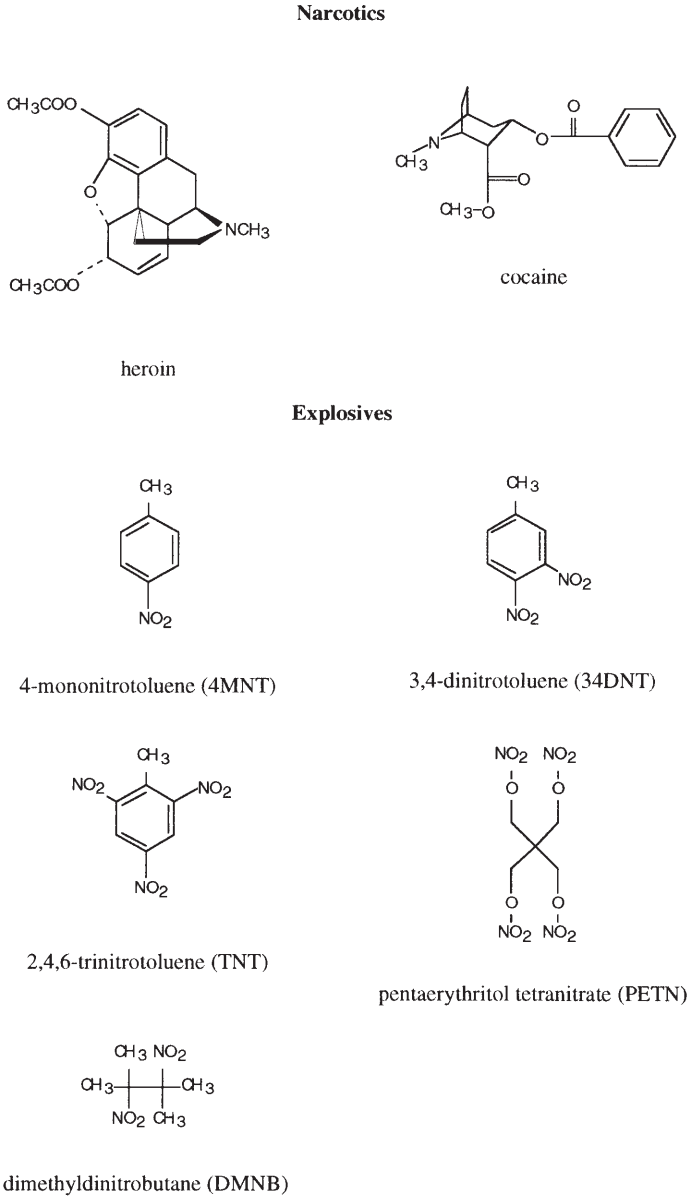

FIG. 1—*Chemical structures of the materials studied.*

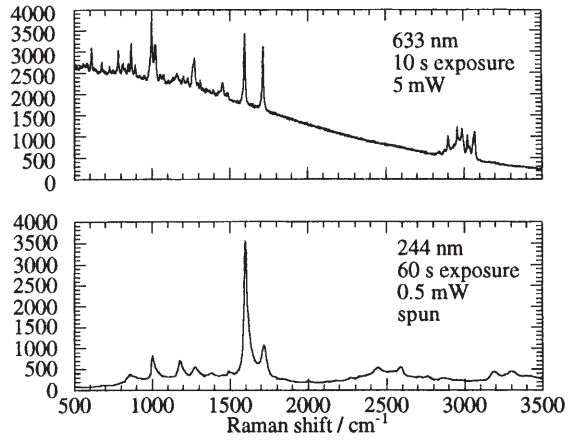

FIG. 2—*Raman spectra of cocaine hydrochloride, taken with 633 nm and 244 nm excitation.*

The Samples

The samples consisted of a range of narcotics and explosives (Fig. 1). The cocaine and heroine samples were taken from police seizures and were impure, whereas the explosives were purchased from the manufacturer and were nominally pure. The samples were prone to laser damage and had to be moved under the focal spot. This was achieved by mounting them on a plate attached to the shaft of a small electric motor. This rotated the samples (at about 1 revolution s^{-1}) so that a ring of material (approximately 5 mm diameter) was exposed to the laser.

It was necessary for the samples to be sufficiently flat so that the surface remained approximately in focus at the objective as it was being rotated (because the spectroscope is highly confocal). Therefore the samples were prepared by dissolving them in acetone, and then allowing the solution to recrystallize on a microscope slide. This resulted in thin films of relatively uniform thickness.

Results and Discussion

The two main differences between the Raman spectra obtained using 633 nm excitation and 244 nm excitation are clearly illustrated in the case of cocaine hydrochloride (Fig. 2). The 633 nm excited Raman spectrum (Fig. 2, top) is superimposed on a broad fluorescent background. The fluorescence is absent from the 244 nm excited spectrum because, if it is generated, it always occurs at the same absolute wavelength (that is, a shift of 26,000 cm^{-1} from the 244 nm excitation) well away from the region of the spectrum with the Raman bands.

The other major difference between the spectra is that only a subset of the 633 nm excitation Raman bands is apparent in the 244 nm spectrum, most notably those at 1605 and 1718 cm^{-1}. These vibrations are associated with the phenyl ring of the cocaine. The 244 nm laser light is absorbed by the phenyl ring, the chromophore of the molecule, exciting the π electrons in the ring. This causes a resonant enhancement of some of the Raman bands associated with vibrations of the atoms on which these electrons are located. The nonenhanced bands associated with the rest of the molecule are relatively so weak that they do not appear above the noise on the 244 nm spectrum. The additional bands on the 244 nm cocaine spectrum (2450 cm^{-1} and above) are overtones and combinations of the lower wavenumber bands.

The fluorescence background of the 633 nm excitation heroin

spectrum (Fig. 3, top) is associated with impurities in the field taken seizure, and is especially strong. It completely masks any Raman bands, making it impossible to identify the sample as heroin. The 244 nm excited spectrum has no fluorescent background, and clear Raman bands. These are associated with the aromatic ring, and are resonantly enhanced.

Resonant effects are also apparent in the case of 2,4,6-trinitrotoluene (TNT) (Fig. 4). The two major resonantly enhanced bands in the 244 nm excitation spectrum (Fig. 4, bottom) are associated with the phenyl ring 1617 cm^{-1}), and with the NO_2 groups (1356 cm^{-1}). The sample was nominally pure and does not have a strong fluorescent background. The 633 nm excitation spectrum (Fig. 4, bottom) is very similar in appearance to the 1064 nm excitation FT-Raman spectrum obtained by other workers (12), although their laser power was higher (300 mW), their exposure time longer (18 min), and their spectral resolution lower (4 cm^{-1}).

It might be inferred that it is impossible to differentiate similar compounds because of the simplification of the Raman spectrum caused by resonant enhancement. This is not generally true, however, and can be illustrated by referring to spectra of 4-mononitrotoluene (4MNT), 3,4-dinitrotoluene (34DNT), and 2,4,6-trinitrotoluene (TNT) (Fig. 5). A band appears in the 4MNT spectrum at 864 cm^{-1}; this is weak in the 34DNT and TNT spectra. In addition, the two dominant bands common to both spectra occur

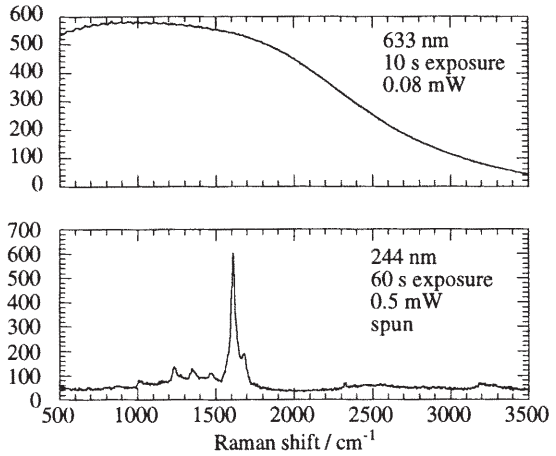

FIG. 3—*Raman spectra of heroin, taken with 633 nm and 244 nm excitation.*

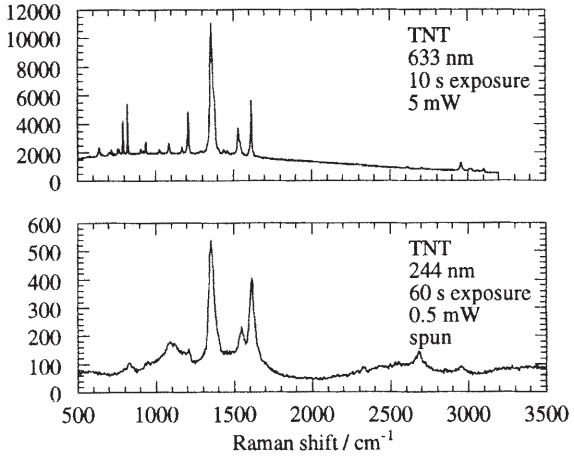

FIG. 4—*Raman spectra of 2,4,6-trinitrotoluene, taken with 633 nm and 244 nm excitation.*

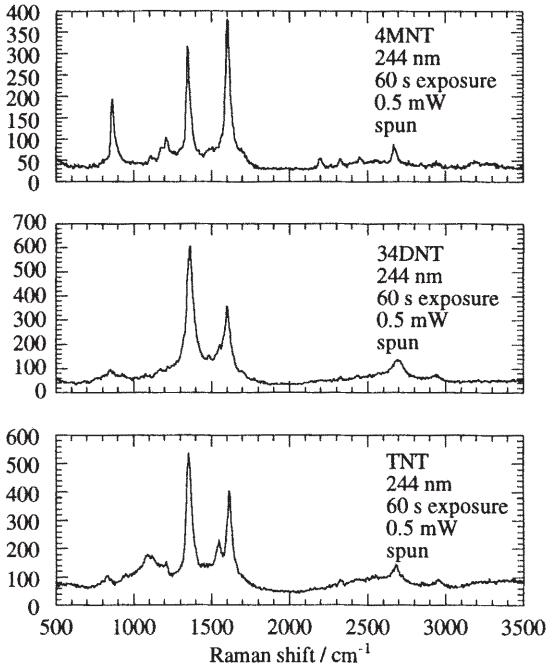

FIG. 5—*Raman spectra of 4-mononitrotoluene* (top), *3,4-dinitrotoluene, and 2,4,6-trinitrotoluene* (bottom) *taken with 244 nm excitation.*

TABLE 1—*Vibration frequencies of the two main Raman peaks of 244 nm excited 4-mononitrotoluene, 3,4-dinitrotoluene, and 2,4,6-trinitrotoluene.*

Material	NO_2 Symmetric Stretch	Benzene Ring Breathing Mode
4-mononitrotoluene (4MNT)	1350 cm^{-1}	1604 cm^{-1}
3,4-dinitrotoluene (34DNT)	1362 cm^{-1}	1604 cm^{-1}
2,4,6-trinitrotoluene (TNT)	1356 cm^{-1}	1617 cm^{-1}

at slightly different Raman shifts (Table 1). These bands are shifted because of the modification of the appropriate bond strengths by the addition or removal of NO_2 groups from the phenyl ring. The shifts are sufficiently large to be used to differentiate these molecules (the resolution of the spectroscope is 2.5 cm^{-1}).

The 633 nm excitation spectrum of pentaerythritol tetranitrate (PETN), one of the components of Semtex plastic explosive, is very similar to those taken using 1064 nm excitation FT-Raman spectrometers (3,12,13), whereas the 244 nm excitation spectrum (Fig. 6) is dominated by the resonantly enhanced vibrations of the NO_2 groups at 1293 cm^{-1} (symmetric stretch) and at 1660 cm^{-1} (asymmetric stretch). The symmetric stretch frequency differs significantly from those of the nitrotoluenes because of the different environment of the NO_2 (bonded to an oxygen, rather than to a phenyl ring).

Dimethyldinitrobutane (DMNB) is a potential additive to explosives to facilitate the detection of terrorist devices. It has a relatively high vapor pressure in comparison with many explosives and is therefore more easily detected by vapor-based detection systems such as mass spectroscopy (14). Like PETN, it differs from the other materials studied here in that it does not contain a phenyl ring. The 244 nm excitation spectrum (Fig. 7) is simplified by resonance, and primarily consists of a 1345 cm^{-1} NO_2 symmetric stretch, a 1540 cm^{-1} NO_2 asymmetric stretch, and a band at 1650 cm^{-1}. The latter band does not appear on the 633 nm excited

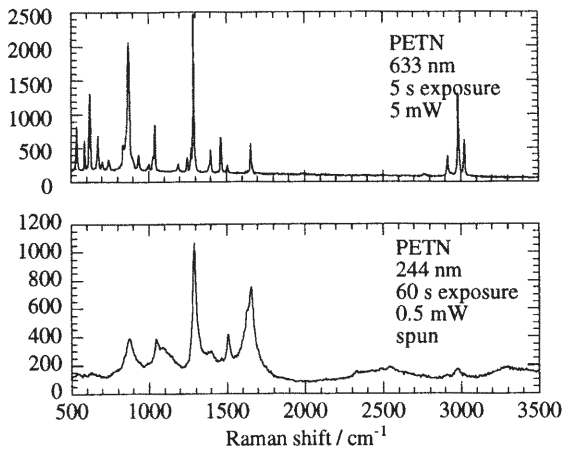

FIG. 6—*Raman spectra of pentaerythritol tetranitrate (PETN) taken with 633 nm and 244 nm excitation.*

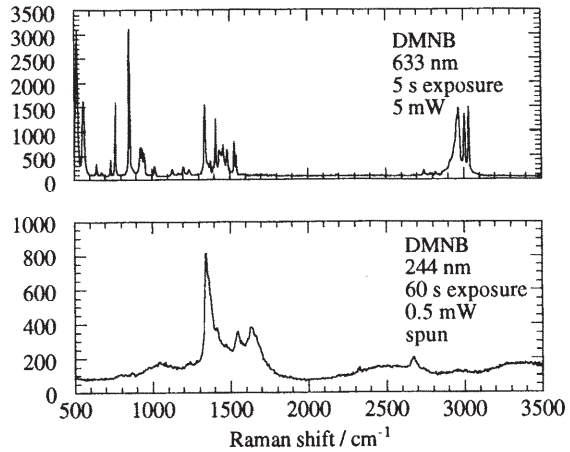

FIG. 7—*Raman spectra of dimethyldinitrobutane (DMNB), taken with 633 nm and 244 nm excitation.*

spectrum, and may be associated with carbon species produced by sample degradation.

In most practical situations contraband materials will be mixed or contaminated with others. For example, criminals usually dilute cocaine by mixing (''cutting'') it with sugar, scouring powder, or some other material. The ''cutting'' agent may be highly fluorescent, making identification of the contraband difficult.

Figure 8 shows 633 nm excitation spectra of ''Q Care scouring powder'' (Robert McBride Group, Manchester, UK) containing anionic surfactant and chlorine based bleaching agent (top), cocaine hydrochloride (bottom), and a 50:50 volume mixture of the two (middle). The spectrum of the mixture is completely dominated by the spectrum of the scouring powder, consisting of a strong fluorescent background with two strong carbonate Raman bands at 710 cm^{-1} and 1083 cm^{-1}. It is not possible to infer the presence of any cocaine in the mixture from the middle spectrum.

Corresponding results for 244 nm excitation are shown in Fig. 9 (in this case the sample did not require rotating to prevent laser damage). The fluorescence background is absent from the scouring powder spectrum (top). The mixture spectrum (middle) consists primarily of Raman features from both the components of the mixture; the cocaine component can be easily identified. The presence of bands in the scouring powder spectrum that have no counterparts in the mixture spectrum (most notably at 700 cm^{-1}) is evidence of the heterogeneity of the scouring powder.

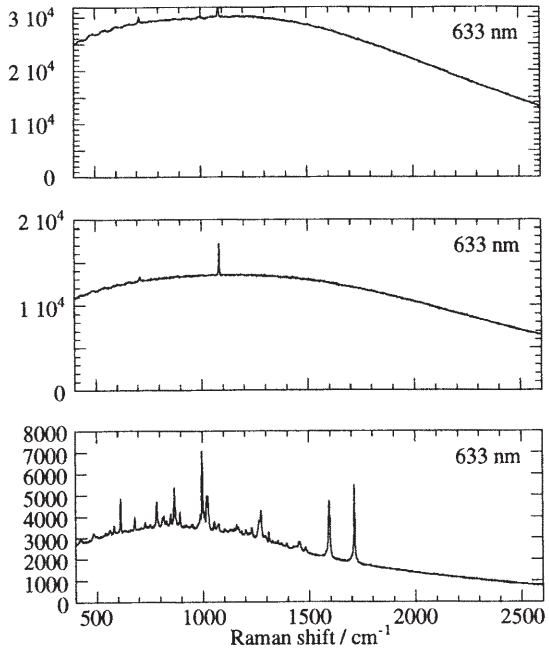

FIG. 8—*Raman spectra of scouring powder* (top, *20s exposure), cocaine hydrochloride* (bottom, *5 s exposure), and a mixture of the two* (middle, *20 s exposure), all taken with 633 nm excitation.*

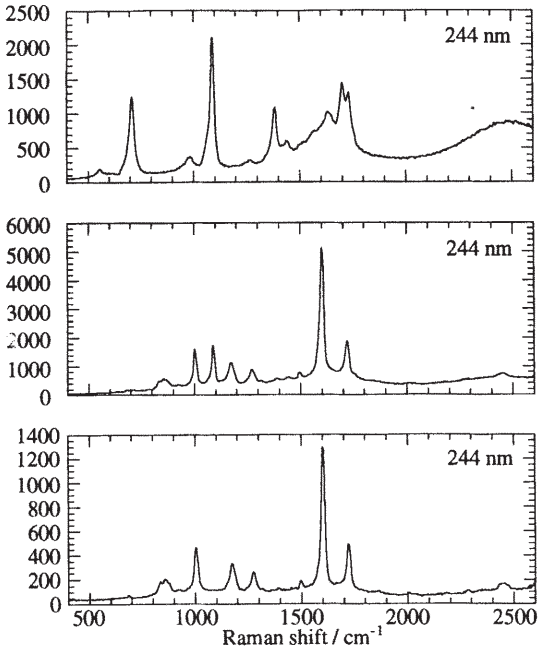

FIG. 9—*Raman spectra of scouring powder* (top, *cocaine hydrochloride* (bottom), *and a mixture of the two* (middle), *all taken with 244 nm excitation and a 30 s exposure.*

Conclusions

The result detailed in the foregoing show that UV-excitation Raman spectroscopy, like visible-excitation Raman spectroscopy, can be used to identify explosives and narcotics. UV excitation has the advantages that fluorescence interference is avoided (which often occurs when samples are contaminated or mixed with other materials), and that resonance effects enhance many of the Raman bands of interest, resulting in higher scattering intensities and simplified spectra.

Acknowledgment

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