AOTF Raman spectrometer for remote detection of explosives

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Abstract

A spectrometer based on acousto-optic tunable filters is developed for use in measuring Raman spectra as part of a detection system that is low-cost, reliable, and field-portable. The system is coupled with a fiber optic bundle to carry the excitation laser light to the sample and to collect the Raman scattered light. Spectra of the explosives trinitrotoluene (TNT), cyclotrimethylenetetranitramine (RDX), cyclotetramethylpentanitramine (HMX) and nitroguanidine (NQ) were obtained in very short times and are in good agreement with those taken with conventional Fourier transform Raman spectrometers. Spectra of mixtures of explosives were also obtained and show no overlap of their characteristic Raman bands. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Techniques for detecting explosives are extremely important in areas susceptible to terrorist activity (such as aviation transport), as well as for cleaning decommissioned military bases and detecting unexploded ordinance. Explosive compounds, which consist mostly of methylene and nitramine groups, have similar structures. Thus, accurate experimental techniques are needed not only to detect them but also to distinguish them in mixtures. So far, the techniques used include X-ray diffraction, chromatography, mass spectrometry, and Fourier transform infrared (FTIR) and Raman (FTR) spectroscopy. Although these methods are well established and routinely used, they are time-consuming and require sample preparation and handling, which limits them to laboratory use.

In applications where instantaneous and noninvasive measurements and identification are required, Raman spectroscopy offers an alternative technique with advantages over other previously used methods [1]. It is very accurate, allows the measurement of molecular signatures of chemicals and their mixtures in various environments, and does not require sample preparation. Furthermore, since water has very weak Raman scattering, chemicals can be detected in aqueous

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solutions without overlap of their spectra with those of water (as happens with the FTIR technique). The Raman technique is also complementary to FTIR and is useful for chemicals whose IR spectra are weak and thus hard to measure. One drawback of Raman spectroscopy is the laser-induced fluorescence (LIF) background that is exhibited by absorbing compounds. This problem can be greatly reduced by the use of near-IR wavelength excitation, reduction of the exciting laser power, or mathematical subtraction of the LIF background during post measurement data analysis. In recent years, Fourier transform Raman (FTR) spectroscopy has been used to characterize various explosives and drugs [2−5]. Although FTR is an important improvement over other techniques, the equipment is bulky and requires optical alignment and maintenance that is not practical outside the laboratory.

For field applications, robust, compact, and vibration-insensitive equipment is needed to carry out the necessary measurements. Acousto-optic tunable filter (AOTF) based spectrometers are ideal instruments for use in combination with Raman spectroscopy. The development of AOTFs, as a result of recent advances in AO technology, allows the fabrication of a robust, portable spectrometer that offers very fast sequential or random tuning over a wide wavelength range from the ultraviolet (UV) to the infrared (IR) [6]. Such a spectrometer has no moving parts and can be used in the field without requiring any maintenance or special handling.

In an AOTF, a radio frequency (rf) acoustic wave is applied to an anisotropic, birefringent crystal through a piezoelectric transducer attached to it. A light wave traveling in the crystal is diffracted by the acoustic wave through the acousto-optic effect when the phase-matching condition between the incident light and the acoustic wave is satisfied. The wavelength of the diffracted light is selected within a narrow bandwidth by tuning of the rf frequency [7–11]. The bandpass of the AOTF has a sinc^2 lineshape. The out-of-band transmission (sidelobes) of the filter can be significantly reduced [8].

AOTFs can be of collinear or noncollinear types depending on the AO crystal used to make the AO cell. In the collinear configuration (with a crystal such as quartz), the light and acoustic waves travel in the same direction, and the diffracted beam is separated from the incident beam by polarizers, since the beams have orthogonal polarizations. In the noncollinear type (with crystals such as TeO₂ or Hg₂Cl₂), the incident and diffracted beams travel in different directions from the acoustic wave. In this case, the diffracted and undiffracted beams are spatially separated as they exit the crystal. The length of the AO interaction in the crystal and the difference between its ordinary and extraordinary refractive indices determine the resolution of the AOTF.

In this work, we have combined the Raman spectroscopic technique with an AOTF spectrometer and fiber optics to develop a Raman sensor that is field portable, easy to use, and less expensive than regular spectrometers. This paper describes the AOTF Raman measurement setup for remote sensing coupled with fiber optics. We discuss the measured spectra of the explosives cyclotetramethylenetetranitramine (HMX), cyclotrimethylenetritritramine (RDX), trinitrotoluene (TNT), nitroguanidine (NQ), and their mixtures are discussed.

2. Experiment

The Raman measurement setup consists of a quartz collinear AOTF that covers the spectral range between 400 and 800 nm [11]. The AOTF has an aperture of 10 × 10 mm², a field of view of 2°, and a spectral resolution of 7 cm⁻¹, and is equipped with a photomultiplier tube (PMT) for the detection of the Raman signal. The Raman excitation light is provided by the 514.5-nm line of an argon-ion laser (Coherent Innova 75); a power of 500 mW was used for all measurements. A three-legged bifurcated fiber bundle (Fibermode) is used to carry the light from the laser to the sample, which is in the form of a powder in a capillary tube. The central laser fiber is surrounded by six identical fibers that collect the Raman emitted light, which in turn is collimated at the entrance of the AOTF spectrometer. The fibers are 200 μm in diameter. For each sample,
the spectrum is obtained by averaging 75 scans with a measurement time of 20 s per scan. To eliminate the strong Rayleigh scattered light from the collected beam, a holographic Rayleigh notch rejection filter (Kaiser Optical) is used at the entrance of the spectrometer. This allows measurement of spectral bands to within 50 cm\(^{-1}\) of the laser excitation. The setup is shown in Fig. 1.

Fig. 1. AOTF Raman experimental setup showing fiber bundle for light excitation and collection.

![Diagram of AOTF Raman setup]

3. Results and discussion

The measured spectra of neat samples of the explosives HMX, RDX, TNT, and NQ are shown in Figs. 2 and 3 along with their molecular structures. These spectra are generally in good agreement with those obtained by the FTR and FTIR techniques [2–5]. It is however observed that the relative intensities of some of the peaks (especially in TNT) are not in agreement with those measured with FTR. This discrepancy may be partly due to the fact that the AOTF is polarization sensitive because of the two polarizers used to separate the diffracted and undiffracted beams [11]. The major Raman peaks of HMX (834, 882, 950, 1250, 1309, 2990 cm\(^{-1}\)), RDX (887, 942, 1217, 1272, 1309, 2947 cm\(^{-1}\)), TNT (818, 1204, 1351, 1532 cm\(^{-1}\)), and NQ (476, 790, 946, 1150, 1515 cm\(^{-1}\)) are very sharp and strong and can be unambiguously used to identify their respective compounds. To ensure the accuracy of the frequencies of the Raman peaks, the emission spectrum of a mercury lamp was used to calibrate the spectrometer. In FTIR spectra of these explosives, the symmetric and asymmetric stretches of the NO\(_2\) group are very strong and overlap other features in the 1200–1500 cm\(^{-1}\) region [5]. Since
the Raman intensity of the NO₂ stretch is relatively weak, other peaks are well separated and can be used to distinguish between different chemicals. In the long frequency region, we observe the peaks due to C–H stretching (2900–3000 cm⁻¹). However, as expected, NQ does not show any structure in that region; a weak structure is present around 3200 cm⁻¹, which corresponds to the N–H stretch. In the ring deformation frequency range (800–950 cm⁻¹), HMX shows the strongest activity.

Mixtures of different explosives were also measured. Fig. 4a shows the spectrum of a mixture of HMX and NQ, and Fig. 4b shows that of TNT and NQ. The mixtures were prepared by mixing the powders in a one-to-one ratio. In both cases all major features of both components are present and are well resolved. A slight overlap is observed for those peaks that are close to each other. With a resolution of 7 cm⁻¹, those peaks are still well resolved and their positions can be accurately determined, making possible the identification of the different components of explosives mixtures.

4. Conclusion

Raman spectra of various explosives were measured with an AOTF-based spectrometer that is fully automated, very fast, has no moving parts, and does not require cooling. The spectra obtained can be used as fingerprints in field applications where explosives must be detected and identified within very short times. AOTF spectrometers can be economical replacements for the much more expensive and bulky traditional spectrometers. These multipurpose spectrometers can also be used in other applications, such as drug enforcement, pollution detection, and medical diagnostics. In every area of application, a database of the species or agents investigated should be available beforehand and a computer algorithm used for comparison and identification of the measured spectra.

References