



Raman Signatures and Cross Sections of Explosives

The ability to detect explosives using non-contact technologies is an important capability for the U.S. Army due to the threat posed by improvised explosive devices. In order to achieve this capability, a variety of different optical techniques are being examined. Raman spectroscopy is potentially a valuable technique since it provides a high degree of molecular specificity. However, there are potential drawbacks including low signal levels and fluorescence interference. To try to overcome these limitations, we are using a range of excitation wavelengths ranging from the deep-ultraviolet through the near-infrared.

Raman signatures and cross sections are being measured for a variety of explosives such as ammonium nitrate, RDX, TNT, and PETN. These measurements are being carried out with excitation wavelengths ranging from 229 nm – 785 nm, with both solution phase and solid state explosives.

Fluorescence can be overcome in many cases by exciting with deep ultraviolet ($\lambda < 250$ nm) or near-infrared ($\lambda > 785$ nm) radiation. The low signal levels typically obtained in Raman spectroscopy can be mitigated by using deep ultraviolet excitation. This signal increase is due to two factors. First, non-resonance Raman cross sections scale as $1/\lambda^4$, leading to much higher signal levels with ultraviolet excitation. In addition, when the exciting radiation is in resonance with an electronic excitation of the molecule, resonance enhancement occurs which can increase the cross section by orders of magnitude. The signal levels obtained are limited by absorption, but UV resonance Raman spectroscopy could be very useful, especially for trace detection. For the solution phase measurements, acetonitrile is used as an internal standard, while for the solid phase measurements sodium nitrate or sodium sulfate are used as an internal standard. For the solid state deep ultraviolet measurements, it is necessary to use nanoparticle samples to reduce absorption bias.

These measurements provide a way to benchmark Raman-based detection instruments, as well as providing a way for testing computational predictions on the spectroscopic properties of explosive molecules both in solution and in the solid state. As such, they are important for determining the capabilities of Raman spectroscopy for detection applications.

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