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Detection of bacteria, chemicals or explosives with Raman scattering is fast, noncontact, does not require chemical supplies and is adaptable to robotic vehicles; making Raman ideal for many military and civilian applications. In this technique, a laser is used to illuminate an area which may contain the sought after substance. Some of the laser light is absorbed by the molecular vibrational and rotational states of the substance, and is re-emitted (scattered) at wavelengths slightly different than the wavelength of the illuminating laser.

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SWOrRD: Swept-Wavelength resonance-Raman Detection of Bacteria, Chemicals & Explosives

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Introduction: Detection of bacteria, chemicals, or explosives with Raman scattering is fast, non-contact, does not require chemical supplies, and is adaptable to robotic vehicles – making Raman ideal for many military and civilian applications. In this technique, a laser is used to illuminate an area which may contain the sought after substance. Some of the laser light is absorbed by the molecular vibrational and rotational states of the substance, and is re-emitted (scattered) at wavelengths slightly different than the wavelength of the illuminating laser. The spectrum of this scattered light is unique to the substance's molecular bond structure, forming a signature that can be used for identification. But, the fraction of laser light that is Raman scattered is very small, leading to insufficient sensitivity in many practical situations. Furthermore, the illuminated area may contain many different substances, each scattering its own Raman spectrum. What is measured is the sum of these spectra, which can be quite complex, so that the ability to identify the constituent substances, i.e. the method's specificity is degraded. There remains a continuing need to improve the specificity and sensitivity of Raman detection.

When the photon energy of the illuminating laser matches one or more of the energies of the substance's vibrational and rotational states, the laser is said to be in resonance with the substance, and the scattering process is called resonance-Raman. In resonance, the amount of absorbed laser light is significantly greater, and so is the amount of scattered light: Light scattered through resonance-Raman is 100 to100,000 more intense than light scattered through a Raman process. Thus, we expect that resonance-Raman detection would result in a much better sensitivity (~ ppm for Raman in ideal environments) or equivalently, allow much larger distance from which detection can be made. But, this is hard to realize in practice. Current detectors use lasers operating at a single laser wavelength, which are not necessarily in resonance with the bonds of the sought after substance, or are resonant with bonds of one substance, but not with those of another.

Swept-Wavelength Optical resonance-Raman Detection: The potential for increased sensitivity of resonance-Raman can be achieved if a way is found to illuminate the sample with more than one wavelength, chosen to be resonant with the substance's rotational and vibrational states. And, as will be discussed below, illuminating with more than one wavelength adds another important capability – increased selectivity in complex environments, i.e., environments which contain many different substances.

We are developing two technologies to enable practical multi-wavelength resonance-Raman detection.[1,2,3] The first technology is SWOrRD, Swept-Wavelength Optical resonance-Raman Detection, a multi-wavelength resonance-Raman system that sequentially illuminates an area with a laser tunable from deep-ultraviolet to near-infrared and acquires resonance-Raman spectra at each illumination wavelength with a two-stage tunable spectrometer. All components of the SWOrRD system are synchronized, under computer control, and switching wavelengths takes less than one second. The laser has certain unique characteristics that make it especially suitable for detection: narrow bandwidth, low peak power, and high average power (see Fig.1).

A comparison of a multi-wavelength resonance-Raman signature of the explosive HMX and a resonance-Raman signature of HMX acquired by illuminating with a single wavelength is shown in Fig. 2. Looking at the single illumination wavelength signature, it is easy to imagine how the distinctive features of this signature are lost once noise and the signatures of other substances are superimposed on it, resulting in a loss of specificity. The multi-wavelength signature is composed of multiple spectra, each produced by illumination with a distinct laser wavelength, which are assembled to form a two-dimensional signature, the two independent dimensions being laser-illumination wavelength and scattered wave numbers. In addition to the information contained in the single spectrum, this two-dimensional signature contains information reflecting variations in resonance cross sections with illumination wavelength. It is therefore much more robust and harder to confuse, resulting in better specificity, especially in complex environments containing many different substances.

Figure 3 shows the two-dimensional signatures of a few explosives, and Figure 4, two-dimensional signatures of selected bacteria.

The second technology we are developing is a set of algorithms which will enable automated identification of substances from their two-dimensional resonance-Raman signatures, even when the substances sought after are mixed with many other substances, i.e., when they are present in a complex environment. The algorithms are based on ORASIS, the Optical Real-time Adaptive Spectral Identification System,[4] a class of algorithms based on the linear mixture model that was originally developed for analysis of satellite and aerial hyperspectral imagery, where it was used to identify objects in complex scenes that contained many objects in addition to the one being sought. ORASIS will be adapted to SWOrRD detection because the application is similar, namely, identifying the spectral signature of a particular substance within a spectrum originating from many different substances. The algorithms are used as follows: First two-dimensional signatures of pure substances are measured and stored in a digital library. A signature measured in the field, and assumed to be a linear combination of some of the signatures that are stored in the library, is introduced to the code. In a process analogous to an inverse Fourier transform, the code determines which library signatures make up the field-measured signature, and thus identifies the chemical present as well as their amount.

Conclusion: We are currently working on developing SWOrRD technology to the point where it is practical to field, and are also adopting it for medical applications. Two-dimensional signatures of bacteria, explosives, chemicals used to manufacture explosives, pharmaceuticals, and assorted chemicals that may occur in the environment are being measured. The ORASIS code is being adopted so it can take a measured signature of a complex mixture and decompose it into constituent signature, such as those shown in figures 3 and 4.

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Figure Captions:

Figure 1: Average laser power of the SWOrRD laser as a function of wavelength. The laser runs at 1kHz, has a line width of about 4cm^{-1}, and is tunable in less than one second in 0.1nm steps.

Figure 2: One and two-dimensional resonance-Raman spectra of the explosive HMX. Top right: A spectrum acquired by illumination with 261nm laser light. Bottom left: A spectrum acquired by illuminating with multiple laser wavelengths from 210 to 270nm.

Figure 3: Two-dimensional spectral signatures of acetonitrile, TNT, RDX, HMX, and PETN. The horizontal axes are the resonance-Raman shift wavenumbers and the illumination wavelengths, and the vertical axes are spectrum intensities.

Figure 4: Bacterial signatures. Two-dimensional resonance-Raman signatures of E. coli (top row), Y. rohdei and S. epidermidis (middle row), with B. cereus and B. thuringiensis (bottom row). The horizontal axis in each frame is the Raman shift, from 900 to 1800 cm^{-1}, relative to the excitation laser wavelength. The vertical axis is the laser wavelength from 210 to 270 nm. Colors represent the relative amplitude of resonance-Raman scattering from the bacteria.

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