Vibrational spectroscopy of chemical warfare agents

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The infrared and Raman spectral signatures of chemical threat agents can be used to develop remote sensing chemical-warfare detection systems.

Countering potential terrorist attacks requires a diversified array of detection capabilities designed for a wide range of deployment scenarios.^{1,2} There is also increased awareness concerning the vulnerability of civilian food and water supplies to deliberate contamination by chemical warfare agents (CWAs), typically assumed to target only military personnel and installations. Hence the urgent need for analytical technologies capable of detecting a wide variety of CWAs as well as their hydrolysis and degradation products in complex environments.

Among the analytical techniques available for the detection and identification of chemical agents,^{2–11} vibrational spectroscopy (infrared or Raman) has the advantage of providing accurate chemical information. It also has a potential for remote sensing applications. Raman spectroscopy is especially useful due to its inherent ability to distinguish between molecules that have a high degree of similarity. In our work, we use vibrational spectroscopy to characterize CWAs and also seek to develop a remote sensing technology based on the Raman spectroscopic signature of these chemical threat compounds.

One of our approaches is based on acquiring the Raman spectra of CWAs and their degradation products using different excitation wavelengths. By varying the excitation at the same laser power, we can identify the laser line producing the best Raman signatures for the threat compounds studied. In a series of recently investigated chemical warfare agent simulants (CWASs), optimum excitation was achieved at a laser power of 25mW using the 488 and 532 nm lines. Typical spectra are shown in Figure 1 for 1,6-dichlorohexane. Remote Raman telescope experiments were also performed on CWASs using 488nm-excitation at a distance of seven meters. We were able to

Figure 1. Raman spectra of 1,6-dichlorohexane obtained at different excitation lines. Arb: Arbitrary.

record well-resolved single spectra of dimethyl methyl phosphonate as a function of laser power and integration time, as shown in Figure 2.

Infrared spectroscopy experiments were also carried out on trace compounds deposited on various surfaces. Figure 3 shows the fiber-optic coupled-grazing angle probe Fourier transform infrared (FOC-GAP-FTIR) spectra of 5 and 10 $\mu\text{g}/\text{cm}^2$ of 2-chloroethyl ethyl sulfide deposited on a stainless steel surface. Results clearly show that limits of detection as low as nanograms/ cm^2 (milligrams/ m^2) are achievable. This methodology also has the advantage of being able to detect CWAs on surfaces as varied as metal, plastic, glass, wood and others.^{12–14}

In other experiments, the spectra of CWAs and their degradation products were measured using Raman spectroscopy, liquid and gas phase FTIR, FOC-GAP-FTIR, as well as Raman excitation in the near infrared (785nm), visible (532, 514 and 488nm)

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Figure 2. Raman spectra of dimethyl methyl phosphonate as a function of laser power (single acquisitions).

Figure 3. Fiber-optic coupled Fourier transform infrared (FTIR) spectra of 2-chloroethyl ethyl sulfide (2-CEES) deposited on a stainless steel surface.

and deep ultraviolet (244nm). The spectra yielded clear and strong signatures suitable for chemical detection in the near or far field, potentially leading to vehicle-borne or man-portable detection systems for use by defense and security agencies or combat troops. Further, we evaluated a method for the detection and quantification of chemical warfare agent simulants on surfaces as proof of concept. In addition, we showed that the technique could be used for the decontamination and cleaning validation processes of these highly toxic compounds.

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