A Difference-Frequency Based Mid-IR Broadband Source for Surface Spectroscopy of Explosives

Lora Nugent-Glandorf*, Tyler W. Neely, Todd A. Johnson, and Scott A. Diddams *NIST Time and Frequency Division, Mail Stop 847, 325 Broadway, Boulder, CO 80305 *presenting author: lng@boulder.nist.gov*

Abstract: We describe a 2.8 – 4.4 µm tunable difference-frequency based mid-IR broadband source. With a FWHM of 170 nm centered at 3.3μ m, we have investigated the C-H stretch signatures of solid-phase trace explosives on surfaces.

Mid-infrared (MIR) laser sources originating from femtosecond fiber lasers have gained recent attention as promising sources for molecular spectroscopy [1-4], combining broad spectral bandwidth and high resolution. In this study we also utilize the high brightness and power of a MIR laser to probe trace amounts of solid explosives on a surface using backscattered spectroscopy. A diagram of the MIR source is shown in Fig. 1(a). The 2.8 W amplified output of a Yb fiber laser, with 130 fs pulses and a 100 MHz repetition rate, is separated into two beams with a polarizing beamsplitter. A Raman-shifted soliton is formed in one arm by launching a portion of the power into a photonic crystal fiber (PCF). The soliton center wavelength can be tuned from 1.36 - 1.66 µm depending on the input power and polarization into the fiber [5]. MIR light is generated via simple difference frequency generation (DFG) in a 2-mm long fan-out periodically-poled lithium niobate (PPLN) crystal. The combination of the original laser output at 1.03 μ m and the Raman soliton results in an idler tunable from 2.8-4.4 μ m, with a FWHM spectral width of \sim 170 nm, and average output power of up to 100 mW. Resulting MIR spectra are shown in Fig. 1(b).

Figure 1: (a) Experimental setup. PBS polarizing beam splitting cube, PCF photonic crystal fiber (1 m, 3.2 µm core, 945 nm zero-dispersion wavelength), DBS dichroic beam splitter, PPLN periodically-poled lithium niobate. The path length of the pump (orange) must be adjusted to compensate for the signal delay due to the PCF. (b) MIR tuning range achievable with the laser system. The system was tuned to a center wavelength of 3.3 μ m for examining the explosive samples.

 While this system has applications for high-resolution precision trace-gas spectroscopy [6], the low vapor pressure of explosives under typical environmental conditions makes the detection of outgassed molecules impractical for field applications [7]. We have thus begun to investigate the broadband spectroscopy of trace amounts of explosive residues deposited on surfaces, by examining the spectroscopic signature of MIR light scattered off the samples.

By tuning the MIR laser center-wavelength to 3.3 μ m the C-H stretch spectral region common to many organic molecules can be investigated. In particular, we have examined the high explosives RDX, HMX, Tetryl, and PETN. Starting with a solution of 1 mg explosive dissolved in 1 ml of solvent (typically a 1:1 ratio of methanol and acetonitrile), we deposit one drop at a time onto either a gold mirror or roughened aluminum plate, allowing the solvent to evaporate. Each drop contains $\sim 20 \mu g$ of solid material, which allows us to simulate first-generation fingerprint quantities of $\sim 20{\text -}200 \text{ }\mu\text{g/cm}^2$ [8]. An image of the prepared gold mirror is shown in the inset of Fig. $2(a)$.

 The optical system used to image scattered light from the explosive samples is shown in Fig. 2(a). The light from the laser system is directed at the solid sample, and a $CaF₂$ lens system is used to image scattered light to the input slit of a monochromator with a 4 nm spectral resolution. Fig. 2(b) illustrates how the spectra are recorded. A background is obtained by focusing the laser on a blank spot on the mirror. The mirror is then moved so that the laser interacts with the solid sample. Absorption spectra are found by taking the difference of the light-scattered spectrum from the sample and the background, as shown in Fig. 2(b) for a 10 -drop (200 µg) sample. Spectra of the four explosives mentioned above are shown in Fig. 2(c), using only one drop of sample (20 µg). Despite the ubiquitous nature of the C-H stretch region in organic molecules, the spectroscopic results show utility in using this spectral range in identifying explosive compounds, as each compound exhibits unique features when crosscompared with the other spectra. In order to extend the usefulness of this technique, the standoff distance must be increased. Detection at larger distances is primarily limited by the amount of scattered light detected and atmospheric absorption. However, the amount of scattered light is scalable with increased laser power and improvements to the detection system, both currently under development in the lab.

Figure 2: (a) Imaging system used for collecting scattered light. The specular MIR beam is not shown and does not propagate through the imaging system. *Inset:* Explosive samples prepared on a gold mirror, with each drop containing ~ 20 µg of material. (b) *Top panel:* Scattered light spectrum from focusing the MIR source on a blank mirror (red) and a sample (black). *Bottom panel:* Absorption signal resulting from subtraction of the signal scatter from the background scatter. (c) Resulting MIR spectra from interrogating four explosive samples. PETN is known to react quickly with air and thus the fresh sample looks significantly different than a sample that has been sitting in air for some time.

[1] F. Adler, et. al., "Phase-stabilized, 1.5 W frequency comb at 2.8-4.8 µm," *Opt. Lett.* **34**, 1330-1332 (2009).

[3] D. Winters, et al., "Subpicosecond fiber-based soliton-tuned mid-infrared source in the 9.7–14.9 μm wavelength region," *Opt. Lett.* **35**, 2179- 2181 (2010).

[4] A. Schliesser, et al., "Frequency-comb infrared spectrometer for rapid, remote chemical sensing," *Opt. Exp.* **13**, 9029-9038 (2005).

[5] F. Mitschke and L. Mollenauer, "Discovery of the soliton self-frequency shift," *Opt. Lett.* **11**, 659-661 (1986).

[6] T. Johnson and S. Diddams, "Mid-IR frequency comb upconversion spectroscopy," CLEO/QELS postdeadline paper CPDB11, (2010).

[7] J. Steinfeld and J Wormhoudt, "Explosives Detection: A Challenge for Physical Chemistry" *Annu. Rev. Phys. Chem.* **49**, 203–232 (1998).

[8] F. Fuchs, et. al., "Imaging standoff detection of explosives using widely tunable midinfrared quantum cascade lasers," *Opt. Eng.* **49**(11), 111127 (2010).

^[2] C. Erny, et al., "High-repetition-rate optical parametric chirped-pulse amplifier producing 1-µJ, sub-100-fs pulses in the mid-infrared," *Opt. Lett.* **17**, 1340-1345 (2009).