A Novel Method for Remotely Detecting Trace Explosives

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The development of a technique with the ability to detect trace quantities of explosives at a distance is of critical importance. In numerous situations when explosive devices are prepared, transported, or otherwise handled, quantifiable amounts of the explosive material end up on surfaces. Rapid detection of these chemical residues in a noninvasive standoff manner would serve as an indicator for attempts at concealed assembly or transport of explosive materials and devices. We are investigating the use of a fluorescence-based technique to achieve the necessary detection sensitivity.

» **Events in recent years have led to an** increased need for improvements in our abilities to detect explosives. In numerous situations, the capability to detect explosives sensitively, accurately, and rapidly could have great benefit to national security both at home and abroad. Some of the homeland situations that would benefit from improvements in explosives detection include screening passengers and luggage at airports and other sensitive locations, and screening vehicles and people along the perimeters of high-value installations such as federal buildings. Abroad, the improvised explosive device (IED) problem is clearly in need of creative solutions to mitigate the devices' very damaging effects. Much research has been conducted to help solve these problems; however, it is unlikely that any one solution will suffice.

If we view the problem of explosive devices as a timeline, from the initial planning to construction of the devices and ultimately to their detonation, we can see that it is preferable to detect the activities as early in the process as possible. The term "left of boom" derives from displaying the explosives creation-to-detonation timeline from left to right and is sometimes used to refer to the concept of early explosives detection. Figure 1 shows a graphical representation of this process.

To address these concerns, we have begun several efforts to both understand and help solve the difficult problem of explosives detection. In particular, we are focusing on a solution for rapid and remote detection of trace amounts of explosives, with the idea that such a capability would significantly improve our ability to respond left of boom. As we discuss later, bomb making is a messy process
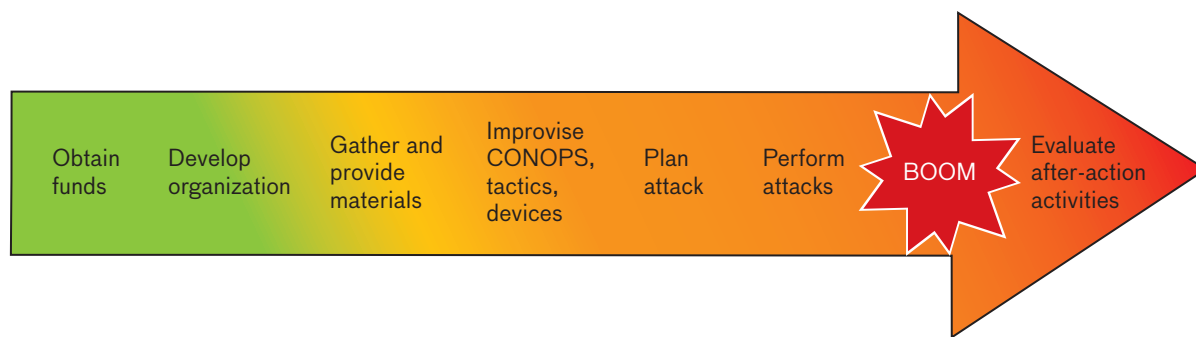
FIGURE 1. The interest in detection of explosives is focused on the early timeline activities, including the planning stages, although after-action post-detonation evaluation could determine the detonation products for forensic purposes. After-action activities on the part of the perpetrators would include evaluating the effects of the explosion. CONOPS stands for concept of operations.

that leaves behind quantifiable residues on a variety of surfaces. Trace-detection techniques could thus be used forensically, identifying devices and bomb-related activities, such as assembly, earlier in the process and thus preventing the need for more difficult countermeasures later on. To be practically useful, the technique must be rapid and sensitive. Additionally, long-range capabilities that could scan from distances of at least ten meters open up numerous possibilities in which large areas of interest could be rapidly assessed for indications of explosives activity. For a brief explanation of the issues we face in trace detection of various explosives, see the sidebar "Explosives and Their Characteristics" on page 30.

We have been investigating a multistep technique in which the first step is a dissociation of polyatomic materials into diatomic molecules. The technique is known as photodissociation followed by laser-induced fluorescence (PD-LIF). The laser powers required for this technique are significantly lower than those of some other methods, and there is a good possibility of successful detection by using eye-safe lasers. When nitro-bearing explosives are illuminated with ultraviolet (UV) light within their absorption band (see Figure 2) and of a sufficient intensity, the molecules dissociate (the PD step of PD-LIF), creating, among other things, fragments of nitric oxide (NO). Identification of this NO photofragment through laser-induced fluorescence (LIF) forms the basis of our detection technique. NO (not to be confused with nitrous oxide, N_2O) can be found in smog. There is, however, a very important difference between the NO produced in the dissociation of explosives and that which can occur as a pollutant. The atmospheric pollutant exists in its ground state, while the NO produced

in the photodissociation process is initially produced with excess vibrational energy. This excess energy is extremely significant in that it not only allows us to distinguish explosives from smog, but also, as we show later, allows us to devise a detection scheme that should be relatively immune to many common types of optical clutter (see the sidebar "Optical Clutter" on page 34).

We have performed extensive studies [1] of the bomb-making process to determine the sensitivity levels necessary for detecting microscopic explosives residues. When explosive devices are prepared, transported, or otherwise handled, quantifiable amounts of the explosive material end up on both people and related surfaces. The primary vectors of transport are the hands and feet of the bomb makers and bomb handlers. Even when people do not directly contact explosive material, they may transfer quantifiable amounts of residue that they pick up via secondary transfer. Such a transfer occurs when someone directly handling explosives touches a surface such as a countertop or door handle, and then someone else touches that surface. The second person will pick up a quantifiable amount of explosives upon contact with the surface and may then transfer it to additional surfaces.

We carefully quantified the amounts that were transferred to surfaces under a variety of conditions. These surfaces, such as vehicles, luggage, clothing, walkways, and doors, could potentially be used as early indicators of activity. Although we identified large variability in the amount of explosives residues transferred to surfaces, in most instances, a majority of surfaces of interest had quantities of at least 1 $\mu g/cm^2$. We use this quantity as a rough estimate of the required sensitivity for a foren-

sic technique. Note that this areal coverage amounts, on average, to only a few monolayers of explosives.

Trace-Detection Techniques

Given the characteristics detailed in the sidebar on explosives, what sorts of techniques are possible, if we keep in mind the constraint that we require something rapid, sensitive, and remote? A number of techniques are currently in use for point detection (at a location), including ion-mobility spectrometry (in use in many airports), gas-chromatography mass spectrometry (generally a laboratory technique), and a somewhat newer technique based on the fluorescence quenching of polymers. The detector employing the latter is known as Fido. The Fido explosives detector is built by Nomadics, Inc. (a business unit of ICx Technologies, Inc.) and is based on a proprietary technology developed by Timothy Swager at MIT. The product is so named because its level of detection is comparable to that of a highly trained explosives-detection dog. All these techniques can detect minute quantities of explosives (generally in the pg-to-ng range). However, they all share one common property that makes them ill suited for standoff detection. They all require ingestion of the explosives into their detectors. In other words, they must come into direct physical contact with the explosive molecules themselves. Given the vanishingly low vapor pressures of explosives (Figure 2), it does not appear feasible for us to operate these techniques remotely.

We found that, in general, a useful detection technique must fulfill two potentially conflicting requirements. First, it must have high sensitivity: it must be able to detect a signal generated from as little as a single monolayer of material. For the technique to operate remotely, this signal must be accessible from several meters' distance. None of the above techniques appears to us to be able to meet this distance requirement. Second, the technique must have high specificity. The signal generated by explosives should be readily distinguishable from the signal generated by other common materials. We use the term chemical clutter to refer to nonexplosive materials with optical characteristics similar to those of explosives. In our case, these materials might include other NO-containing compounds. False alarms may also occur as the result of optical clutter (see the sidebar "Optical Clutter"). We use the term optical clutter to refer to photons that are
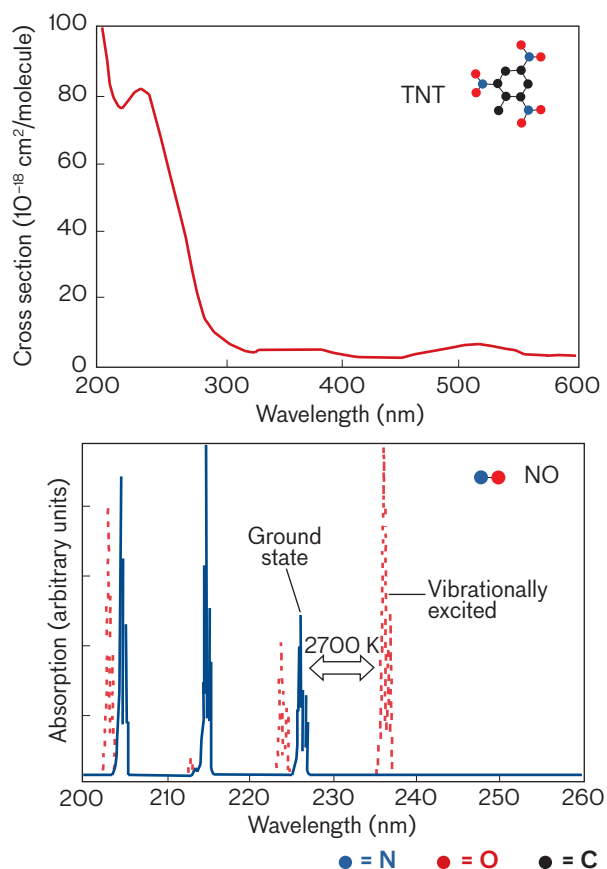

FIGURE 2. The analysis of explosives is improved with the detection and distinction of NO units. These optical absorption spectra of molecular species show the improvement. The top graph is of TNT, a polyatomic molecule in the solid phase. Note that the optical absorption spectra of other organic nitro-bearing explosives are generally similar to that of TNT because they have a broad peak in the deep ultraviolet (UV). The bottom graph is of nitric oxide (NO), a diatomic molecule in its gas phase. Both the absorption spectra of the ground (solid lines) and the first vibrationally excited (dashed lines) states are shown. Photodissociation, the first step of the photodissociation laser-induced fluorescence (PD-LIF) process, creates the distinct NO spectrum from the generally featureless spectrum of TNT. Also note that PD-LIF creates NO in an excited state, which allows for a low-clutter detection technique to be applied.

generated by a source other than explosives and that do not share the same optical characteristics as our signal. While optical clutter can be addressed via optical filtering techniques, chemical clutter could pose a more serious difficulty. Additional considerations for a successful technique include its practicality—the system should have a minimum of components and complexity to facilitate ease of use in a real-world situation.

Explosives and Their Characteristics

Some compounds are easier to detect than others.

Explosives may be broken down into two general classes: nitro/nitrate-based and non-nitro/nitrate-based. Non-nitro/nitrate-based explosives are derived from materials such as peroxides, e.g., triacetone triperoxide (TATP), perchlorates, and azides. While these explosives clearly pose a threat, our studies focused upon the more common nitro-based explosives. The military primarily uses these types of explosives; they include compounds such as nitroglycerin, 2,4,6-trinitrotoluene (TNT), and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), the active component in the plastic explosive C4. These materials make up a large percentage of the explosives used in improvised explosive devices.

To develop and/or assess the utility of a trace-detection technique, we have to understand some of the physical characteristics of these explosives. Figure A shows the chemical structure and vapor pressure of some of the more common nitro-based explosives. Other key characteristics of explosives are the following:
• Explosives have extremely low vapor pressures, ranging from parts per million to less than parts per quadrillion, in the case of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX). Low vapor pressure places severe limitation on a technique that relies on the ambient vapor above the material for detection. The solid residue itself holds much more potential signal than the vapor phase.
• Nitro-based explosives all have at least one NO_2 group. When nitro-based explosives detonate, one of the ultimate end products is N_2 gas, which is very stable due to its N-N triple bond. The formation of this low-energy product from the higher-energy starting material is

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We concluded that optical techniques appear to have the greatest potential for remote-detection capability. A variety of approaches to optical detection have been attempted [2], and we found it instructive to examine them in the context of the above-mentioned constraints. UV illumination of explosives induces a relatively strong fluorescence signal. However, it is not very specific to explosives, since many materials fluoresce under UV illumination and their fluorescence spectrum is often nonspecific. Thus this technique does not fulfill the specificity constraint; optical clutter would be a significant problem. Other techniques generate a reflection signal based on the absorption peaks in explosives. Again, optical clutter appears to be a problem because the spectra are broad and not necessarily unique to explosives. Furthermore, only a very thin layer of material (monolayer) is being interrogated; thus it will not absorb much light beyond the ultraviolet. Additionally, and perhaps more importantly, the explosives distribution is nonuniform, such that much of the reflected signal may not be dominated by the explosives themselves but by the surface upon which they reside.

A more promising technique utilizes Raman spectroscopy. It has been known for some time that there is a weak but distinct interaction between photons illuminating a material and the vibrational modes (phonons) of the material. The result of this interaction is a scattered photon with either slightly more or less energy than that of the incident photon, depending upon whether a phonon has been absorbed or created. This inelastic scattering process creates a spectral fingerprint of the material specific to its vibrational structure; thus it is expected to have reasonably low clutter. While these Raman energy shifts are successfully used to identify materials at very close range in the laboratory, the scattered signal is so weak that detection at long range would require the combination of large collection optics and long integration times.

An alternate approach, which removes many of the difficulties associated with the indistinct spectra of the materials themselves, is to dissociate the materials and use instead signals related to their constituents. Laser-induced breakdown spectroscopy (LIBS) is one such technique, which in its most common incarnation analyzes

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accompanied by the release of a sizable amount of energy. Note that inorganic nitrate-based explosives have NO_3 groups instead of NO_2 groups (ammonium-nitrate fuel oil is one such example). Our initial work focused on organic materials that contain NO_2 groups.

• The explosives residues relating to bomb activities can be, on average, only a few monolayers thick. However, they are nonuniform, taking the form of mounds or clumps at the microscopic level. This nonuniformity means that some percentage of a surface of interest may be bare, containing no explosive material at all.

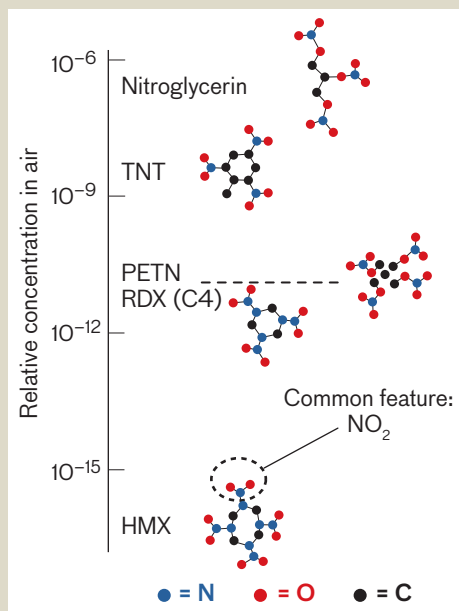• The optical absorption spectrum (Figure 2 in the main text) of nitro-bearing explosives is

broad and nondistinct. There is a broad absorption peak in the ultra-violet (UV), and the explosives will fluoresce in the visible as a result of UV illumination.

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a. National Research Council, *Existing and Potential Standoff Explosives Detection Techniques* (The National Academies Press, Washington, D.C., 2004).

b. J. Steinfeld and J. Wormhoudt, "Explosives Detection: A Challenge for Physical Chemistry," *Ann. Rev. Phys. Chem.,* vol. 49, 1998, pp. 203–232.

FIGURE A. The vapor pressures of some nitro-bearing explosives are quite low and span orders of magnitude, indicating the difficulties of trace detection of vapors [a, b]. TNT is 2,4,6-trinitrotoluene, RDX is hexahydro-1,3,5-trinitro-1,3,5-triazine, PETN is pentaerythritol tetranitrate, and HMX is octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocane.

the atomic constituents. LIBS uses tightly focused, high-energy laser pulses to dissociate the materials into their constituent atoms via the formation of a microplasma. The atomic emission spectra allow identification of the atoms and estimation of their relative abundances. A nitrogen/oxygen ratio consistent with explosives is used as an indicator of the presence of a specific explosive. While the LIBS signal is strong, the relative ratios can be easily obscured by the existence of other nitrogen and/or oxygen-bearing materials present on surfaces. In other words, LIBS is highly susceptible to clutter [3, 4]. In addition, there is the disadvantage of using high-intensity lasers that aren't eye safe.

Photodissociation Followed by Laser-Induced Fluorescence

PD-LIF is a dissociation-based technique in which the polyatomic materials are dissociated into diatomic molecules, as opposed to the atoms produced via LIBS. The laser powers required for the PD-LIF process are significantly lower than those of LIBS, and there is a good

possibility (as we discuss later) that successful detection can occur if eye-safe lasers are used (again in contrast to LIBS). When nitro-bearing explosives are illuminated with UV light within their absorption band (see Figure 2) and of a sufficient intensity, the molecules dissociate and create, among other things, fragments of NO. Identification of this NO photofragment forms the basis of our detection technique. As mentioned earlier, the NO product of PD has excess vibrational energy when compared to the potential chemical-clutter components of NO in smog, for example.

An additional advantage of having produced the NO molecule via photodissociation is that we are now dealing with a gas-phase diatomic molecule (as compared to a solid-phase polyatomic molecule), which has a much more distinct spectrum that can be used as an identifying fingerprint. The lower portion of Figure 2 displays the absorption spectrum of NO. Note the distinct lines, as compared to the broad spectrum of 2,4,6-trinitroluene (TNT). Also note the different spectra for the ground and excited states of the molecule. As can be seen from the
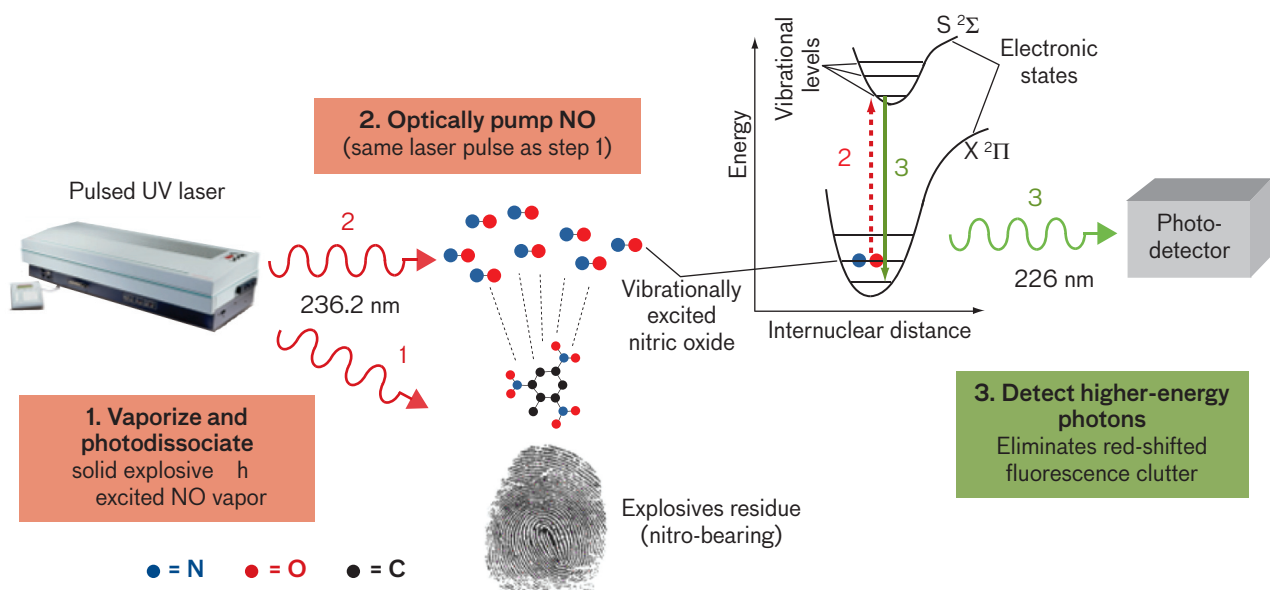
FIGURE 3. The PD-LIF explosives-detection technique can be understood as a three-step process. In the first step, a material with a distinct signature is created by vaporizing and dissociating solid explosives and forming gaseous NO fragments. In the second step, these fragments are optically pumped to a higher-energy state. Finally, the higher-energy fluorescence emission is detected. The wavelength of the fluorescence and the wavelength required to induce fluorescence are both very precise, which provides the specificity of the technique.

figure, the energy difference between the two is ~2700 K: thus the excited state is not occupied under standard ambient temperatures. In PD-LIF, detection of the vibrationally excited NO is achieved via laser-induced fluorescence. Here, a photon further pumps the vibrationally excited NO fragment into an electronically excited state. The electronically excited NO molecules rapidly fluoresce as they return to their ground states. Because of the initial excess of vibrational energy, this fluorescence occurs at a shorter wavelength (226 nm)—i.e., higher energy—than the exciting laser photons (236.2 nm). Signal photons that are of shorter wavelengths, or shifted toward the blue end of the spectrum relative to the laser photons, are critical to minimizing optical clutter. A schematic of this multistep (photodissociation/vaporization—photoexcitation—fluorescence) detection process is shown in Figure 3. In brief the steps are the following:

1. The first photon is absorbed by the explosives and very rapidly (<<1 ns) vaporizes and dissociates the explosives' components into fragments including the vibrationally excited NO.

2. A second photon pumps the vibrationally excited NO to an electronically excited state. This pumping must happen within a few ns, which is the lifetime of the vibrationally excited

state in a standard atmosphere.

3. The resulting NO fluorescence, which occurs at a shorter wavelength than that of the laser, is used for detection.

Note that all these steps occur within a single laser pulse. The exquisite specificity of this technique derives from the precise wavelengths involved in the LIF process. It is highly unlikely that many other materials will produce photons at precisely 226 nm in response to illumination at precisely 236 nm, since few will share the exact spectral structure of the excited NO. Thus we can utilize a narrow-wavelength source and a narrowband detector to specifically detect these NO fragments with a high degree of sensitivity and specificity. We note also that it is fortuitous that the nitro-bearing explosives absorb quite well at the UV wavelength needed to pump NO. Because of this absorption, we can accomplish the multiphoton process with a single laser pulse, significantly simplifying the necessary equipment.

Advantages of this detection method include a relatively strong fluorescence signal—which can be generated by using eye-safe excitation-laser intensities—and a low false-alarm rate. The low false-alarm rate is expected because relatively few processes produce light at shorter wavelengths than the source laser. In contrast, most other

processes, such as scattering or traditional fluorescence, are single-photon processes in which each incident photon yields another of equal or lesser energy. The PD-LIF process involves multiple photons, the first of which creates a molecule with excess energy and the second of which further excites that molecule. As the molecule relaxes to its ground state (see Figure 3), photons are emitted with *greater* energy than that of the incident photons. As such, this technique isn't susceptible to false alarms from traditional fluorescence processes, for which the resultant photons typically are at longer wavelengths. The sidebar on optical clutter shows how these higher-energy emitted photons are distinguishable from typical fluorescence coming from the surfaces on which the explosives reside.

PD-LIF Detection Measurements

Previous studies by others [5] have examined the PD-LIF signature from explosives vapors. We, however, probed the solid and liquid explosives themselves [6, 7] as they offer the potential for much greater signal, since the vapor pressure of explosives is very low. The four main components in single-laser PD-LIF laboratory experiments shown in Figure 4 are the excitation laser, the photodetector, the bandpass optical filters, and the samples being tested. In our studies, the laser was a tunable pulsed Continuum 9030 system, which provides variable laser output from 215 to 310 nm. The laser output was an ~1 cm^2 beam of 7 ns pulses, emitted at a rate of 30 pulses per second, with energies of 2 to 3 mJ per pulse. The spectral linewidth was 0.03 to 0.04 nm around the wavelengths of interest. All wavelengths reported are the values in air (approximately 0.03% less than the wavelengths in a vacuum).

The fluorescence detection subsystem consisted of a solar-blind (tuned to eliminate the background solar radiation) photomultiplier tube (PMT) with narrowband filters. Narrowband filters are essential in these experiments because they are needed to suppress the scattered laser light. The Perkin Elmer cesium-tellurium channel photomultiplier had single-photon sensitivity, negligible dark counts, and a quantum efficiency of 10% near the signals of interest (220 to 230 nm). The PMT was used in both a photon-counting and linear mode (dependent upon photon flux) and was calibrated for short laser pulses at various cathode voltages in order to ensure a linear response at a given flux level. Experiments were performed primarily in a close-range geometry, so that the PMT and filters were positioned 6 cm directly above the sample. No collection or collimation optics were used in the close-range configuration. In this geometry, we estimate a collection efficiency of 4×10^{-7} of all emitted signal photons.

A variety of explosives in a variety of morphologies were studied. The explosives included 2,6-dinitrotoluene (DNT), TNT, pentaerythritol tetranitrate (PETN), and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). DNT, as received from Sigma-Aldrich, was in the form of small granules roughly the size of salt crystals. Studies were performed on macroscopic mounds (several milligrams)
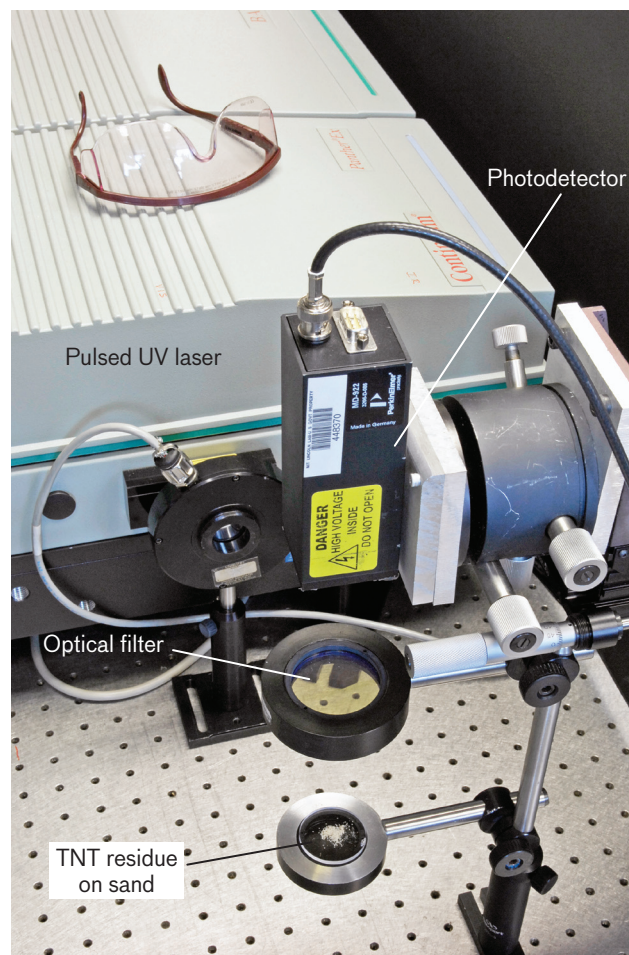

FIGURE 4. The four primary components of the experimental detection setup are shown: the pulsed UV laser, the high-rejection optical filters (which are normally attached directly to the photodetector and allow only signal photons to reach the detector while blocking the scattered laser photons), the photomultiplier tube photodetector, and the sample being tested (here it is sand covered with traces of TNT).

Optical Clutter

Reduce the effects of clutter on false-alarm rates by taking measurements where spurious fluorescence isn't.

Detection of spurious radia- tion, or optical clutter, causes an increase in false-alarm rates. Potential sources of optical clutter can be either ambient or laser-induced radiation, as shown in Figure A.

Ambient Clutter. While solar radiation is a dominant source of clutter in the visible and near infrared, and thermal radiation can be problematical in the infrared, the deep ultraviolet (UV) is quite clutter free. Below approximately 300 nm (the solar-blind region), the absorption due to atmospheric ozone prevents almost any light from reaching the surface of the earth [a]. This

fact opens up the possibility of operation of a detection system that relies upon a very small number of signal photons (perhaps as few as one) for detection. The PD-LIF detection system we are pursuing operates in the deep UV and thus aims to utilize just such single photons.

Laser-Induced Clutter. Laser-induced clutter can be subdivided into three broad spectral categories: laser scatter, i.e., photons at the laser wavelength; red-shifted clutter (photons with less energy and longer wavelengths than the laser); and blue-shifted clutter (photons with more energy

and shorter wavelengths than the laser). Generally, the scattered photons (at the laser wavelength) are the strongest source of clutter. Fluorescence processes (the dominant form of red-shifted clutter) can yield signals as strong as ~10% of the laser scatter, depending on the material and wavelengths chosen. Note that many materials fluoresce when irradiated with UV light (just visit your local roller rink). Photons that are created with more energy than the energy of incident photons are quite rare because they require the addition of excess energy. Thus blue-shifted clutter is much weaker than in either of the other two

of these solid granules, in addition to a liquid form, which was obtained by heating the granules to 80°C. With the exception of the liquid DNT measurements, all other measurements were performed at room temperature under ambient atmospheric conditions. Military-grade TNT was studied in a solid pellet form, as a trace coating on sand, and dropcast from a dilute acetone solution. Military-grade PETN was studied in the form of a white powder. RDX was studied both as a trace coating on sand (8% by weight) and as the dominant component (~90%) in the putty-like C4 plastic explosive.

Figure 5 displays the results of fluorescence detection measurements of DNT, TNT, C4 (RDX is the active component), and PETN. Data were taken at a fluence of 10 mJ/cm^2/pulse (1-mJ pulses over 0.1-cm^2 area). Data points represent 6-pulse averages, with the exception of the background measurements on the bare silica substrate (shown as the open squares in the top graph) for which the data points are 60-pulse averages. All

explosives samples display the same multipeak structure with a maximum signal at the excitation wavelength of 236.2 nm and a shoulder near 236.3 nm. They also display a secondary peak at 236.9 nm, again with an accompanying shoulder.

The similarity of these signatures implies that all nitro-bearing explosives can be detected via this technique without the need to fine-tune the laser parameters to each individual explosive type. The vapor pressures for these compounds differ significantly—by over four orders of magnitude at room temperature—while their signal strengths are within one order of magnitude. These measurements indicate that the observed signal is not related to the ambient vapors of the materials, but rather the condensed phase itself. This is an important point in our consideration of solid-phase analysis: a technique that relies upon detection of the ambient vapors of the explosives will be severely limited due to their very low vapor pressures [8, 9].
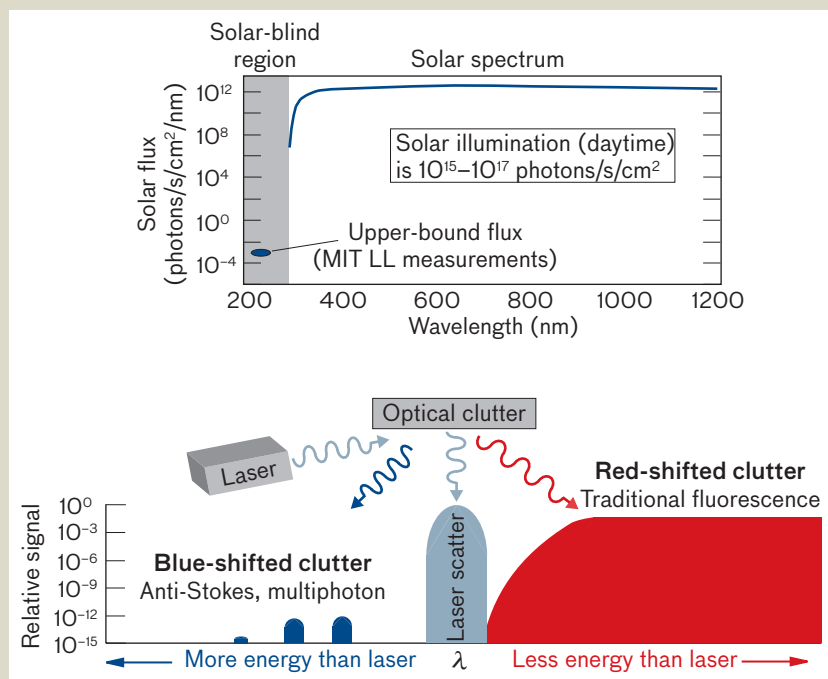
FIGURE A. Ambient clutter is present whenever the system is in an environment where sources other than the laser are present. Such clutter is shown In the upper image, specifically for solar-induced scatter. The laser-induced clutter exists in three wavelength regions. The laser scatter (at the laser's wavelength) and the lower-energy red-shifted scatter do not affect the PD-LIF measurement, which occurs at a higher-energy blue-shifted wavelength.

regions. Anti-Stokes Raman scattering involves excess energy that comes from the vibrational energy (phonons) of the material scattering the light. Processes that involve the simultaneous absorption of more than one photon (multiphoton processes such as our PD-LIF) can also produce a blue-shifted signal. The cross sections for all these processes are exceedingly weak, and thus this regime offers a useful portion of the spectrum in which to do low-clutter detection.

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The bottom graph of Figure 5 displays the predicted fluorescence spectrum of NO, assuming the PD-LIF excitation (excitation from the first vibrationally excited state of its electronic ground state to the vibrational ground state of its first electronically excited state). We obtained these results by using the LIFBASE software package [10, 11]. Comparison of the experimental data to the computed NO spectrum provides clear evidence that the measured signal is generated by excited NO species.

We used calibrated quantities of explosives dissolved in acetone to demonstrate trace-level detection. These explosives were dropcast on silicon wafers to yield areal concentrations of 2 μg/cm^2 (shown in Figure 6), similar to concentrations expected from fingerprint residues. We investigated both RDX and TNT in this manner and measured signals roughly half of those measured for the bulk materials. Laser-induced photolysis of the trace material is evident in the top portion of the left-hand figure. For laser fluences of 10 mJ/cm^2/pulse and a wavelength of 236.2 nm, complete photolysis of TNT takes about 10 laser pulses, as shown on the right in the figure. On the basis of these results, we can estimate that in our specific experimental configuration we were detecting 20 ng TNT with each laser pulse (2 μg/cm^2 times 0.1 cm^2/10 pulses). Also displayed in Figure 6 is the photo response from a control sample (the bare silicon wafer), which is significantly weaker than that of the TNT, indicating a relatively high signal-to-noise ratio for detection.

Remote Detection Projections

Our trace-detection results along with the spectra of the different explosives indicate a technique with the required sensitivity to detect the trace amounts of interest. Keeping in mind the eventual application of PD-LIF to the stand-off detection of these residues, we need to estimate the detection range of a notional system. For a first step, we calculate the relative efficiency of this process, compared to the alternative of Raman spectroscopy. (While compar-
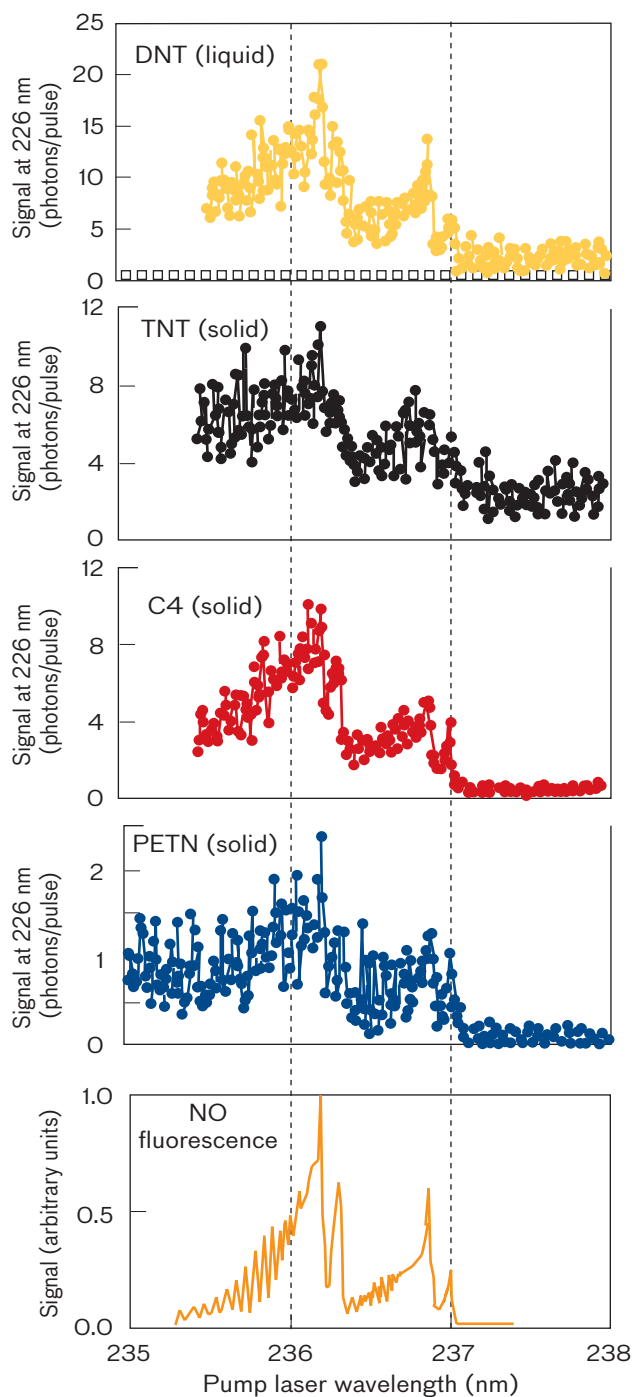
FIGURE 5. The response of NO-based materials to pump laser wavelength is selective. The shifted peaks and shoulders show a marked response to the NO first excited state. The top graph also includes a background measurement of the response of the silica substrate without explosives (open squares). The bottom graph is the predicted fluorescence of NO, assuming excitation from its first vibrationally excited state. Note that the emission from these materials is actually at the higher-energy blue-shifted 226 nm wavelength.

ison to LIBS is also possible, PD-LIF and Raman-based detection have in principle similar low false-alarm rates.) The Raman cross section for TNT has been reported as 2×10^{-31} cm^2/sr/molecule for visible excitation and 10^{-28} cm^2/sr/molecule for ultraviolet resonant excitation, and therefore the angle-integrated values are 2.5×10^{-30} cm^2/molecule and 10^{-27} cm^2/molecule, respectively [12, 13]. The spontaneous Raman scattering process is linear in fluence, and therefore the cross section is a constant. In contrast, the PD-LIF is nonlinear in fluence because it is a multiphoton process. A cross section will therefore be fluence dependent. Furthermore, it will be an effective parameter rather than a true molecular property.

By analogy to a linear process such as Raman scattering, the number of fluorescence photons collected in our experimental setup, N_{photon}, can be expressed as follows:

$$N_{\text{photon}} = F n \sigma_{\text{eff}} \eta,$$

where F is the laser fluence (in photons per unit area), n is the number of molecules being irradiated, σ_{eff} is the effective cross section of the overall PD-LIF process, and η is the experimental collection efficiency. We have estimated the PD-LIF cross section, σ_{eff}, on the basis of our dropcast results at a fluence $F = 10$ mJ/cm^2/pulse (1.25×10^{16} photons/cm^2). At this fluence, we collect $N_{\text{photon}} \sim 10$ photons/pulse. We can estimate the number of irradiated molecules, n, by using the areal density of the dropcast TNT (2 μg/cm^2), the laser spot size (0.1 cm^2), and the molecular weight of TNT (227 g/mole).

Given that ~10 laser pulses were required to fully photolyze the film, and that the total number of molecules in the film was 5×10^{14}, we estimate that $n = 5 \times 10^{13}$ molecules/pulse were irradiated. Note that the average thickness of the dropcast TNT is ~12 nm (the density of TNT is 1.65 g/cm^3), similar to our measured photolysis rate per pulse. However, we observed experimentally that 10 pulses were required to photolyze the film, rather than one pulse, as may be indicated by the average film thickness. These results are reconciled by noting, as is evident from optical images of the films, that the films are not uniform. Rather, they consist of islands of different sizes and, presumably, thicknesses. Using our collection efficiency of $\eta = 4 \times 10^{-7}$, we calculate $\sigma_{\text{eff}} = 4 \times 10^{-23}$ cm^2/molecule for TNT at 10 mJ/cm^2/pulse fluence. This is a factor of 4×10^4 higher than that achievable with Raman scattering in the opti-
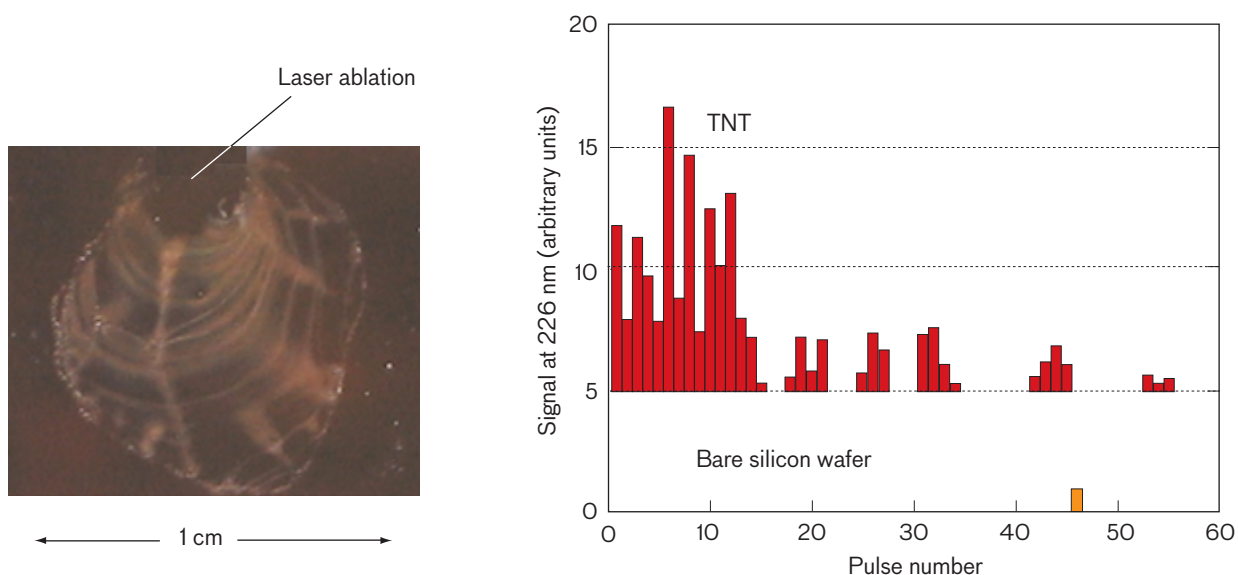
FIGURE 6. Dropcast TNT was analyzed to determine the trace-detection levels available with PD-LIF. On the left is a photo image of dropcast TNT on a silicon wafer with the laser spot (causing photolysis) labeled. On the right are time-series data displaying signal photons as a function of laser pulse (the top curve for TNT is offset for clarity from the bottom bare silicon).

mal condition of UV excitation, and ~10^7 higher than that of the more conventional visible/near-IR Raman scattering. Making the simplifying assumption that the number of molecules probed via PD-LIF is fixed at $n = 5 \times 10^{13}$ molecules/pulse, we use our data at other fluences to esti-
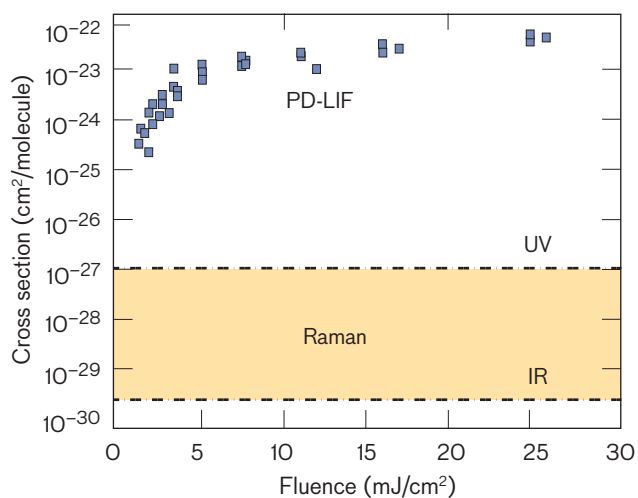

FIGURE 7. The TNT effective cross sections as a function of fluence for PD-LIF (squares) clearly outperform Raman-detection cross sections [14, 15], whose UV upper and infrared lower bounds are denoted by dashed lines. Note that PD-LIF cross-section estimates assume that the number of particles probed per pulse was constant with fluence, and equal to the measured value at 10 mJ/cm^2.

mate the fluence dependence of σ_{eff}. This dependence is compared to the Raman cross section, which remains fixed with fluence, in Figure 7. As can be seen in the figure, PD-LIF compares favorably with Raman scattering as a process enabling standoff detection of TNT and other nitro-bearing explosives. Using these estimates for the PD-LIF cross section, we estimate that it will be feasible to achieve detection of trace levels of explosives with a single pulse of eye-safe UV illumination at distances of tens of meters.

Future Work

To achieve these detection ranges (tens of meters) would require ~30 cm optics and a laser capable of producing at least 5 mJ pulses of light at 236.2 nm. While the laser used in our laboratory measurements produces nearly these pulse energies, it has several drawbacks. Its pulse repetition rate is low (30 Hz), which makes rapid area scanning impossible. It is also large and requires significant input power. Moreover, it requires precise alignment and as such is not robust enough for low-maintenance field measurements. Finally, its bandwidth (0.03 nm) is not well matched to the explosives signal peak (~0.5 nm; see Figure 5).

John Zayhowski of Lincoln Laboratory's Laser Technology and Applications Group has developed a design for a solid-state laser that would meet all these specifi-

cations. It would not only be more robust, smaller, and lower power than the commercial system, but it would also facilitate rapid area scanning and improve the system's signal-to-noise ratio (via a 0.5 nm laser bandwidth matched to the explosives' signal bandwidth). We have identified the necessary crystal family and completed preliminary fluorescence studies. These efforts should provide us with a stable high-power 236.2 nm laser source capable of the desired high standoff distances. On the basis of our examination of some nitrate-bearing materials (fertilizer, soil, and manure), which showed no evidence of a PD-LIF signal, we expect that there will be few false alarms generated by other materials—i.e., we do not expect nitrates to be a source of chemical clutter.

Although our initial work does not indicate the presence of significant sources of false alarms due to chemical clutter, extensive studies are required to verify a low false-alarm rate for a wide variety of substrates. Thus our continued efforts are twofold: testing the new equipment for standoff distance capabilities and evaluating the specificity of the technique with other materials and substrates to eliminate or at least significantly reduce the false-alarm rate.

Acknowledgments

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