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Standoff detection using coherent backscattered spectroscopy

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ABSTRACT

Intense laser pulses may be used for standoff detection of energetic materials. Coherent backscattered spectroscopy offers a tremendous advantage over other spectroscopic detection techniques in that it uses stimulated or amplified spontaneous emission from the sample to produce a minimally divergent, directional beam back to the detection platform. The characteristics of the backscattered beam depend largely on the intensity and pulse width of the laser source as well as the concentration and photo-physical characteristics of the target molecule. Different target molecules will exhibit different backscattered emission signals, allowing differential detection of energetic materials in the vapor phase. Because of the highly directional nature of the coherent backscattered beam, detection limits in the vapor of less than 1 ppm at ranges up to 100 meters can be anticipated.

Keywords: standoff detection, stimulated emission, laser spectroscopy, laser induced fluorescence

1. INTRODUCTION

The standoff detection of energetic materials has been an important and challenging problem to researchers for a number of years. Recent advances in laser technology have seen the increased application of laser spectroscopy to the problem of energetic material detection, but a robust solution has yet to be elucidated. The applications of THz wave, LIBS and UV-LIF/REMPI spectroscopy have been considered in a number of studies.

Recently, THz waves generated by femtosecond lasers pulses in p-type InAs were used to obtain reflectance spectra of RDX after propagation of the THz wave over a distance of 30 m [1, 2]. Broadband terahertz emission from laser induced plasma in air using focused femtosecond laser pulses was recently reported and has potential application to standoff detection in the THz frequency range [3]. Coherent control and detection of THz waves generated through a four-wave mixing process in laser guided filaments [4] and the detection of such waves in air [5] is a remarkable application of the latest in ultrashort laser pulse technology, but the measurements are difficult and require controlled experimental conditions and expensive laser systems for operation.

Laser induced breakdown spectroscopy (LIBS) has shown potential to be a powerful analytical tool due to its simplicity and demonstrated performance in both point detection and standoff applications. Laser induced breakdown spectroscopy has been applied to the detection of chlorine and fluorine [6], halogenated hydrocarbons [7], lead [8], bacterial spores and molds [9], molten metals [10, 11], and polycyclic aromatic hydrocarbons [12]. Numerous studies have focused on the detection of hazardous materials such as chemical and biological agents [13] and landmines [14, 15], with recent demonstrations of standoff detection of the materials [16, 17] at ranges up to 30 meters. However, the application of LIBS involves the use of high energy lasers operation in wavelength bands that are particularly dangerous to the eye (400-1100 nm) and such instruments would not be suitable for eye-safe operation in the field for stand-off detection of energetic or other hazardous materials.

The application of ultraviolet (UV) laser induced fluorescence (LIF) and resonance-enhanced multiphoton ionization (REMPI) to the detection of energetic materials, particularly nitro-substituted compounds, has seen a great deal of success in terms of sensitivity, selectivity and limits of detection. Vapor phase nitro compounds may be readily fragmented with ultraviolet radiation due to the weak bond energy of the nitro functional group (40-50 kcal/mol), resulting in free NO₂ and NO which are detected using REMPI, PI or LIF. Using ~226 nm laser pulses to fragment and

subsequently ionize the photofragments, detection limits of 8 and 24 ppb of RDX and TNT respectively were reported using REMPI [18]. A simpler method employing photoionization (PI) spectrometry following the photofragmentation process gave similar performance in detection limits with the application of low (eye-safe) UV pulse energies (10 μ J/pulse) [19]. While ionization methods may be particularly sensitive for detection of photofragments, the requirements of ultra-high vacuum-sealed sample chambers makes them inapplicable to standoff detection of energetic materials. Similar sensitivities to those achieved through photofragmentation with REMPI and PI may be obtained using laser-induced fluorescence (LIF). Following pre-dissociation of NO₂ by laser photolysis of nitro compounds, NO can be excited near 226 nm and LIF from the excited NO fragment can be detected. Detection limits of 40 ppb for TNT imbedded in soil samples can be achieved using this technique in a point detection application [20].

The advantage of using all-optical methods of detection is the potential to employ coherent laser stimulated processes to enhance the intensity and directionality of the emitted signals from UV generated excited states or photofragments. Combined with the fact that UV lasers are rated eye-safe up to several millijoules per pulse, the use of UV excitation for standoff detection of energetic materials is a potentially feasible option. Stimulated processes have been observed since the invention of the laser. Some of the earliest observations included stimulated Raman scattering from organic liquids and vapors. Stimulated Raman scattering from benzene, nitrobenzene, toluene, 1-bromonaphthalene, pyridine, cyclohexane, and deuterated benzene was first characterized using a Q-switched ruby laser [21]. Early studies also noted the existence of both forward and backward stimulated Raman scattering [22]. Backscattered emission is particularly applicable to standoff detection methodologies in which the signal generated at a distance returns to the detection platform. Backward-stimulated Raman pulses from CS₂ liquid were characterized in terms of pulse energy, pulsewidth and linewidth [22]. It was found that the Raman pulses emitted in the backward direction had different pulse characteristics than those emitted forward. The development of picosecond laser pulses contributed to increased stimulated Raman generation with milder pulse energies and the observation of stimulated Raman pulses in gaseous hydrogen, deuterium and methane [23].

In this report we demonstrate the use of intense ultraviolet laser pulses to generate coherent backscattered emission from vapors at ranges up to 15 meters. The characteristics of the backscattered emission will be discussed. Application of the methods used here for detection of luminescence from ambient vapors is challenging, but the ideas developed in this report can be extended to sampling methodologies that involve preparation of the vapor environment by target ablation or thermal desorption which may be followed up with backscattered laser induced luminescence for analyte identification.

2. EXPERIMENTAL

Absorption spectra of vapor samples were collected using a sealed 5 cm path-length quartz cell containing a small droplet or a few crystals of the sample material. Vapor samples for laser experiments were generated by bubbling dry nitrogen gas through pure liquids or over solid crystals of the materials of interest. Benzene, toluene and acetone spectroscopic grade solvents were purchased from Aldrich and used without further purification. Naphthalene (99%) crystals were purchased from Aldrich and used without further purification. Vapor samples were pumped into cylindrical glass tubes of different diameters and lengths, all without windows. Vapor was confined to the sample cell by the use of small vacuum inlets at the ends of the cell that were evacuated using a small laboratory vacuum pump. The outlet of the vacuum pump was directed to a custom lab ventilation system to prevent the accumulation of potentially hazardous levels of vapor in the laboratory space. Partial pressures of vapor under these sample conditions range from 10⁻³ to 1 torr, depending on the sample. Concentrations were determined by measuring the transmission at 266 nm along the sample tube in relation to the transmission of a saturated cell of vapor sample of which the vapor pressure at room temperature is known.

Ultraviolet laser pulses at 266 nm and 213 nm were obtained from the 4th and 5th harmonic of a Q-Switched Nd:YAG laser operating at a repetition rate of 10 Hz and having an 8 ns pulse duration. Typical pulse energies for the experiment were 1-50 mJ. The beam diameter at the output of the laser was 6 mm and was focused within the sample using a 100 cm focal length fused silica lens. The UV laser pulses were launched down the center of the sample tube using a harmonic separating beam splitter. Backscattered radiation from the sample was observed through the back of the beam splitter, collinear with the pump axis of the incoming laser pulse. A beam dump at the outlet of the sample tube captured remaining pump laser radiation.

Characterization of the backscattered vapor emission was carried out using beam profiling, luminescence spectroscopy and kinetics measurements. The emission was profiled using a CCD array equipped with a quartz camera lens. Narrow band-pass filters were used to isolate the sample luminescence from background emission from the laser. To obtain luminescence spectra the backscattered emission was collected and focused onto a fiber optic bundle and sent to the input slit of a 300 mm spectrograph. Kinetics measurements were carried out using a photomultiplier tube detector with an instrument response function of 8 ns. A narrowband interference filter was used to isolate the emission from the sample against background emission from the laser fundamental and scattered radiation from the optics.

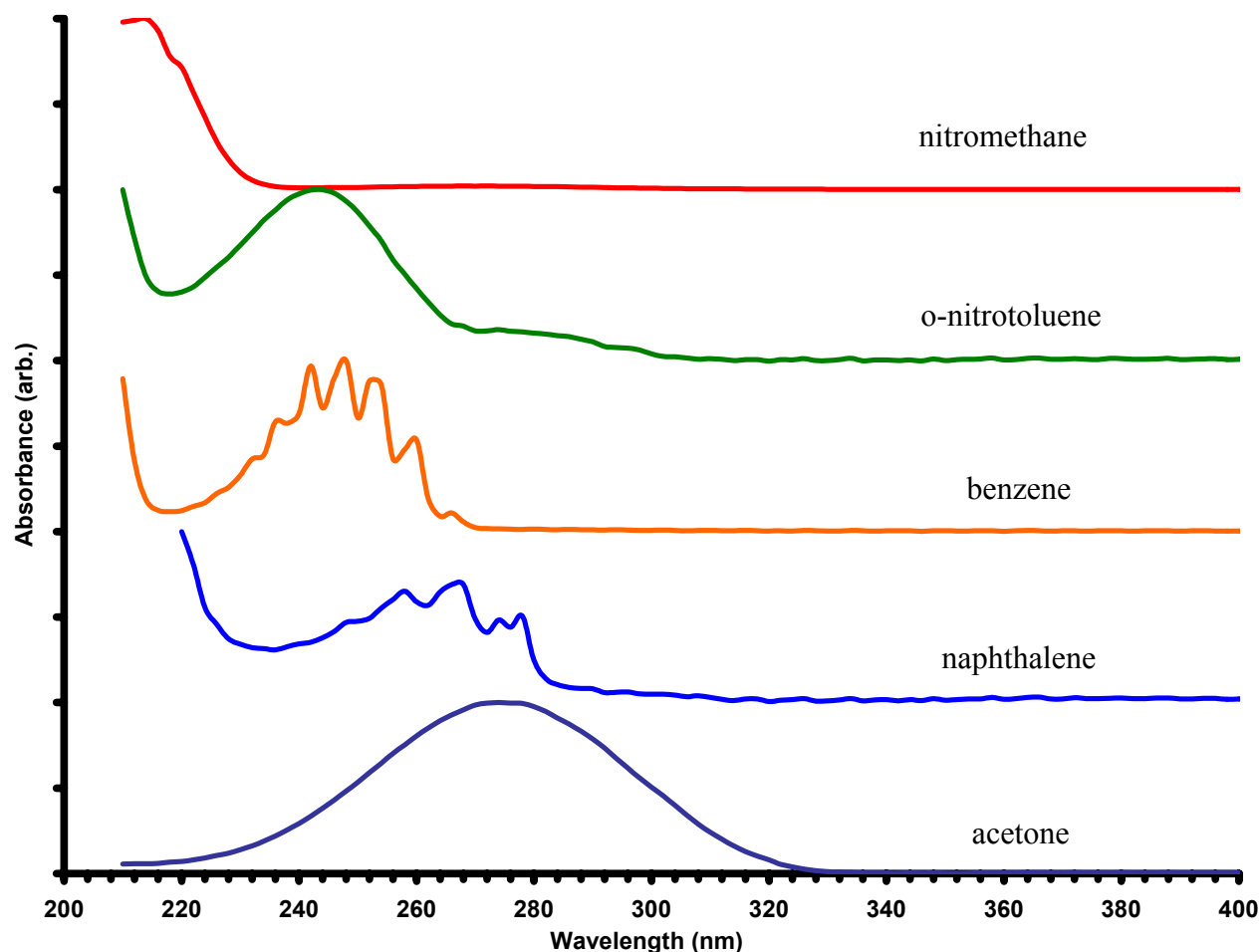


Figure 1. Ground state absorption spectra of some target organic vapors at room temperature.

3. RESULTS AND DISCUSSION

Ground state absorption spectra of some target organic vapors are shown in Figure 1. Many of the materials of interest have strong resonances in the ultraviolet which are accessible with the 4th or 5th harmonic of a Q-Switch Nd:YAG laser. Producing pulse energies of 10-100 mJ for the 4th and 5th harmonic, such sources can potentially produce high excited state densities within the interaction volume and may lead to amplified and directed luminescence from the excited state materials. Even weakly luminescent materials can be detected using these laser induced fluorescence techniques. The absorption and laser-induced fluorescence spectrum of acetone vapor is shown in Figure 2. Acetone is

known to have low quantum efficiency for luminescence, reportedly owing to its very short-lived lowest excited singlet state [24-27]. However, with the excited state densities produced by intense laser excitation ($\sim 10^{25} \text{ m}^{-3}$) it is possible to detect its luminescence, even without the use of intensified and gated CCD arrays.

One advantage gained by using amplified luminescence for backscattered standoff detection is illustrated in Figure 3a. The surface plot in Figure 3a shows the backscattered luminescence profile of naphthalene vapor excited with an intense 266 nm laser pulse. A CCD camera was positioned along the pump axis to observe backscattered emission at a distance of 3 meters from the sample position. Luminescence was filtered through a narrowband interference filter centered on the maximum of the luminescence of naphthalene. In the image obtained along the pump axis shown in Figure 3a, the signal intensity is well over 1000 counts/pixel across the middle cross section of the backscattered image. Similar measurements were taken perpendicular to the pump axis at the same range for comparison. In the perpendicular

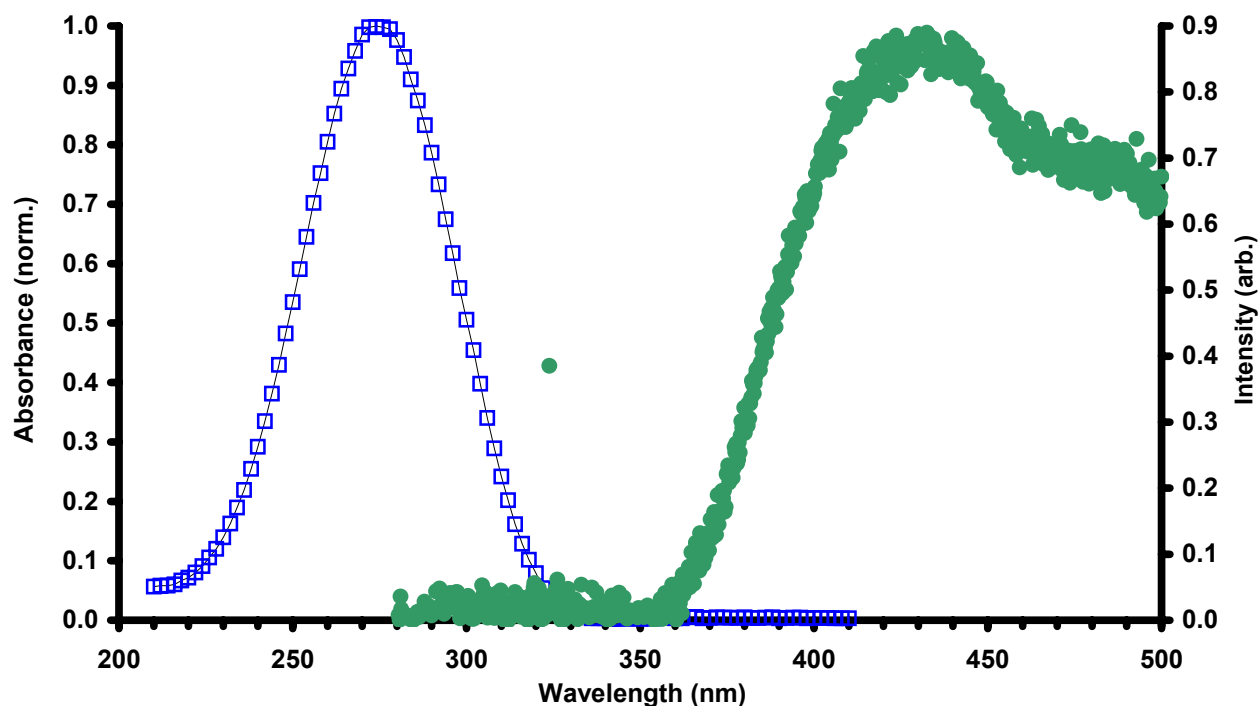


Figure 2. Absorption (open squares) and laser induced luminescence (closed circles) spectra of acetone vapor at room temperature. Laser induced luminescence collected using 40 mJ, 266 nm Q-Switched Nd:YAG laser pulses.

detection geometry, the luminescence intensity was barely discernable above the noise, giving at most 100 counts per pixel across the entire length of the sample (dark counts ± 30 counts/pixel). In general, the enhancement gained will be proportional to L/d where L and d are the length and diameter of the excited state volume produced by the pump laser.

While this may seem as trivial as choosing the correct detection geometry, the advantage gained in this method is only realized using the correct pump laser pulse to generate the excited state volume. The pulse-width of the laser can dictate the path-length of the excited states in the vapor, and a significant path-length is required to achieve a bright, spatially coherent image of the luminescence back at the detection platform. This idea is illustrated in Figure 3b, which shows the minimum effective path-length of excited states produced by different pump laser pulse-widths. Depending on the concentration, lifetime and luminescence efficiency of the sample, some laser pulses, no matter how intense, will not produce a spatially bright image of the luminescence at standoff range. We have investigated the backscattered luminescence from a number of vapor samples using UV pulses of all three pulse-widths shown in Figure 3b. For

samples such as benzene, toluene and naphthalene, the luminescence in the backscatter geometry is intense and spatially coherent for all laser pulses utilized. Acetone vapor behaves differently, giving intense signal only with the use of 8 ns pulses from a Q-Switched Nd:YAG. The intensity from a 35 ps pulse is significantly less than that of the 8 ns and with 150 fs pulses the luminescence is not detectable. Acetone is different from the other probes investigated in this study in that its backscattered luminescence is “pulse-width determined” rather than “life-time determined”. As mentioned, the first excited singlet state lifetime of acetone in the vapor phase is < 200 fs, shorter than the pulse duration of the pump lasers utilized in this study. This means that the path-length of the interaction volume for acetone vapor will be strictly determined by the laser pulse-width as illustrated in Figure 3b, whereas the path-length for benzene, toluene and naphthalene could potentially be longer than that dictated by the laser pulse-width up to a maximum determined by the lifetime of the lowest excited singlet state. For benzene, toluene and naphthalene, the excited state lifetimes are 20-200 ns, longer than the pulse-width of the lasers used in this study. The quality of the backscattered luminescence obtained for vapors of benzene, toluene and naphthalene can be illustrated in Figure 4. The vapor pressures used were 10^{-3} torr (~ 1 ppm) and the spectra presented here were collected at a distance of 15 m from the sample through a 3 mm aperture collection optic using 40 mJ, 266 nm laser pulses. Given this range and size of the aperture stop, we can anticipate that similar signals as shown in Figure 4 would be observable at 100 m using a 20 mm collection optic.

The importance of pulse-width is not only limited to controlling the length of the interaction volume, it can also dictate the types of processes observable and exploited for standoff detection. For energetic materials of interest such as nitro-aromatics, the parent molecules themselves are very weakly luminescent and it is unlikely that luminescence from the parents can be used for any reasonable detection application. However, the photo-fragments produced from these materials can luminesce quite intensely. Photo-fragmentation followed by subsequent laser-induced fluorescence of the fragments would require two consecutive UV photons of the correct energy and delayed in time enough to capture the

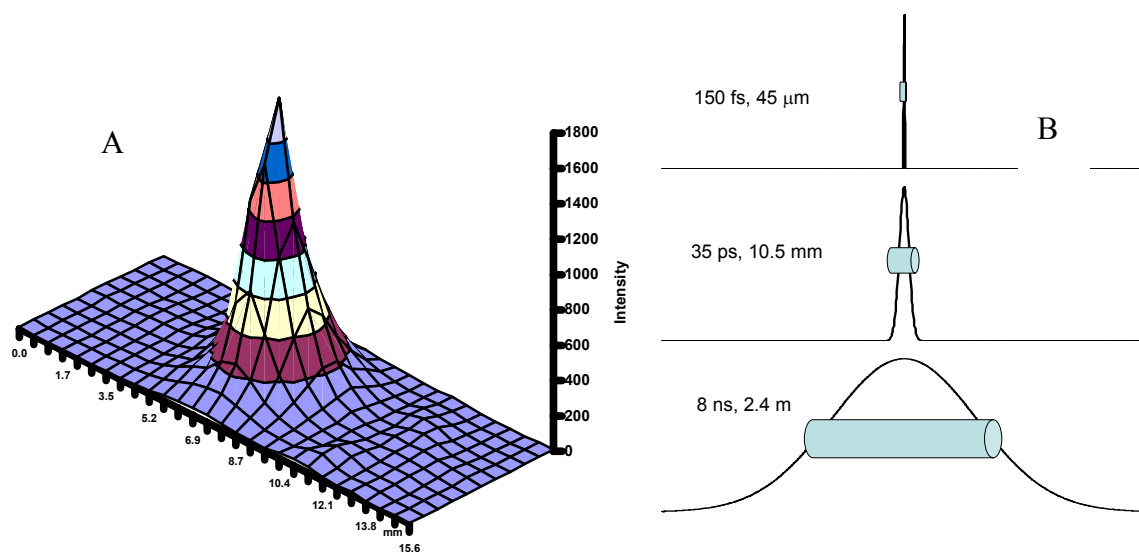


Figure 3A. Profile of the backscattered laser induced luminescence from naphthalene vapor at room temperature. Pump laser characteristics: 40 mJ, 266 nm, 2 mm beam waist. Figure 3B. Representation of the effective minimum path-lengths of excited states produced by pump lasers with the different pulse widths used in this study.

photo-fragment after it has dissociated far enough from the reaction center to be considered a free species. With picosecond and sub-picosecond pulses, this condition cannot be met within a single pulse envelope and would require two separate pulses delayed electronically or mechanically from one another. The use of an 8 ns pulse of 213 nm radiation to generate a spatially coherent image of the laser-induced fluorescence from o-nitrotoluene vapor at a range of 3 meters is shown in Figure 5. The emission spectrum seen here consists of fluorescence from both the NO_2 and NO photo-fragments known to be present upon photo-fragmentation of nitrotoluenes at room temperature [28].

4. CONCLUSION

We have demonstrated the standoff detection of organic vapors and energetic simulants using intense ultraviolet laser pulses at distances up to 15 m using coherent backscattered spectroscopy. The careful selection of laser pulse parameters, including pulse-width and laser wavelength can determine the relative enhancement of the backscattered intensity. Continuing studies will include the use of pulse combinations and sensitive gated detection schemes to lower the detection limit and discrimination ability of the technique. Sampling methodologies that include ablation or thermal desorption of analytes from surfaces followed by coherent backscattered laser induced fluorescence of the liberated vapors will extend the application to more types of analytes and enhance the detection abilities of standoff spectroscopy.

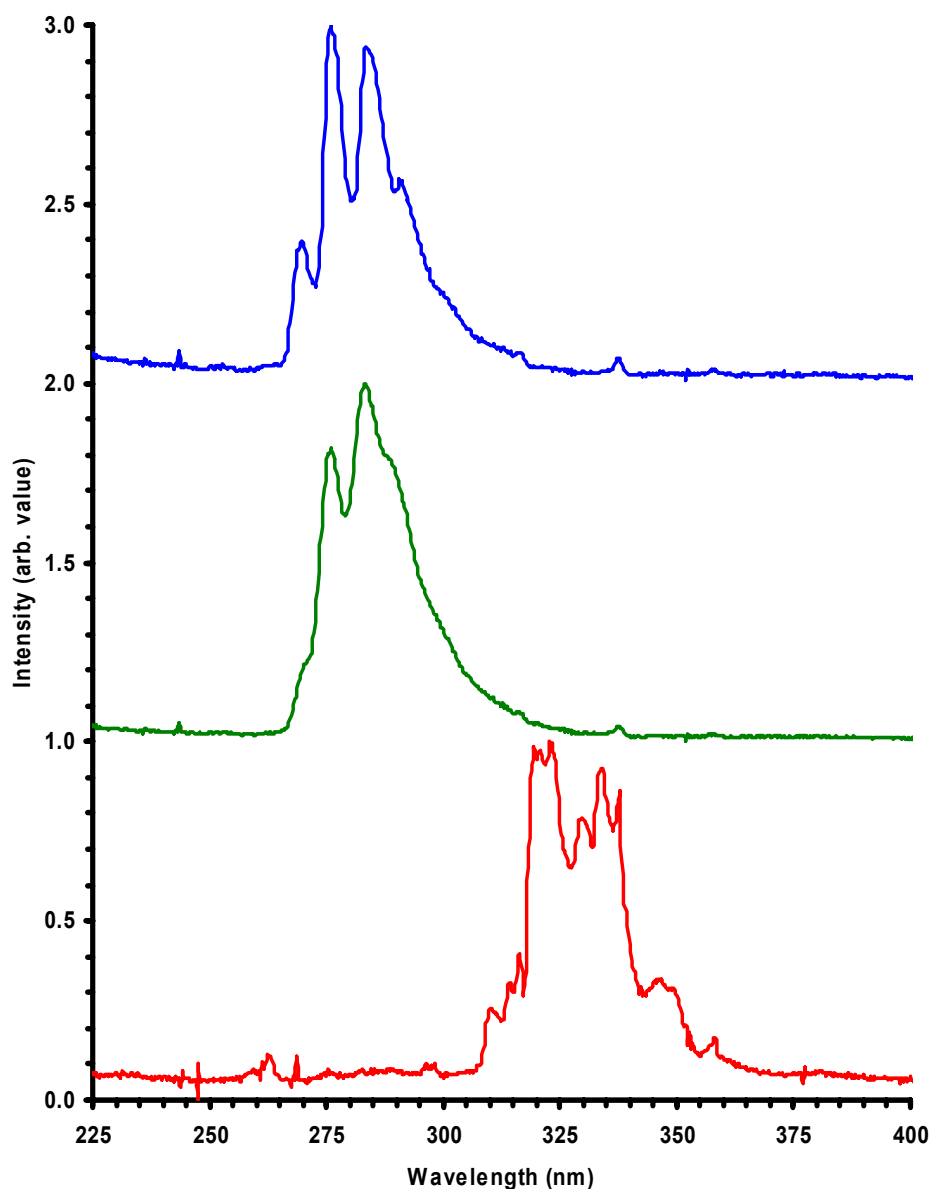


Figure 4. Backscattered laser induced luminescence from (top to bottom) benzene, toluene and naphthalene vapors ($\sim 10^{-3}$ torr in N_2) collected using 40 mJ, 8 ns, 266 nm laser pulses from a stand-off distance of 15 m.

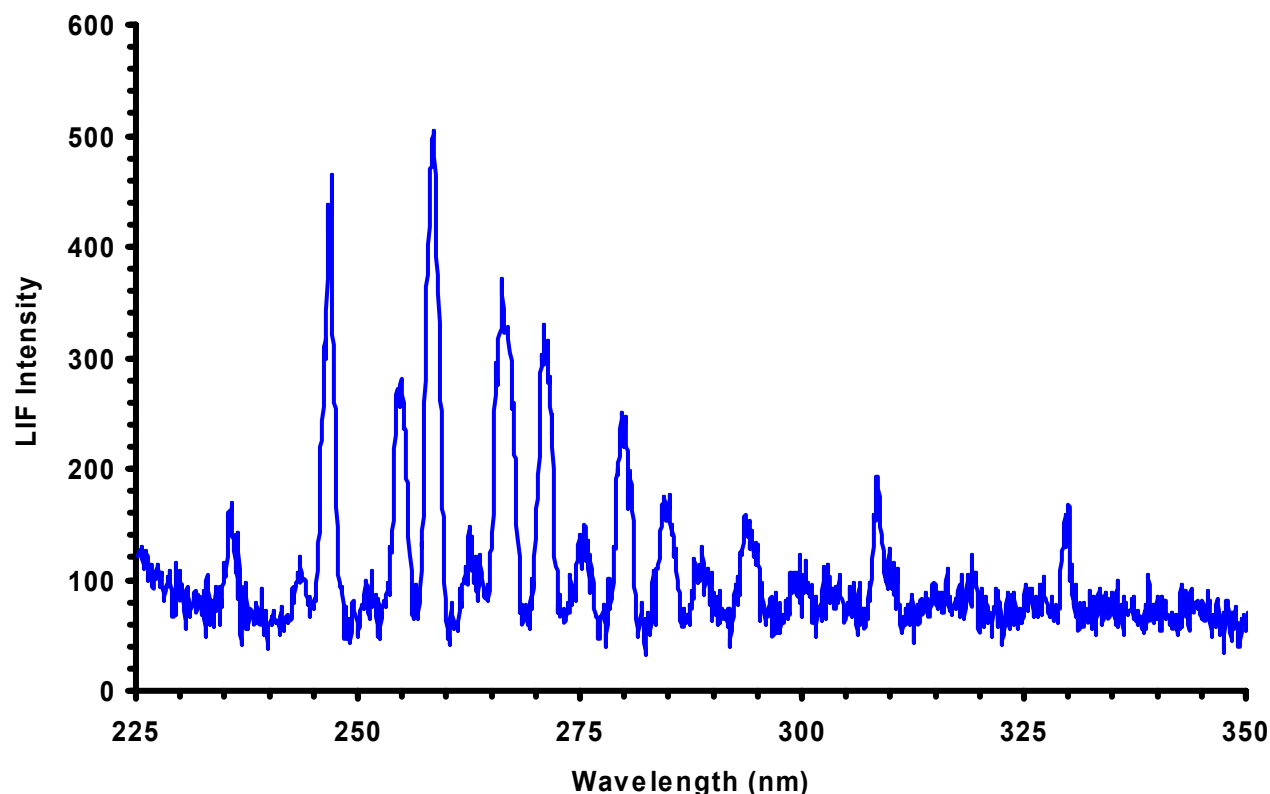


Figure 5. Backscattered laser-induced fluorescence from o-nitrotoluene vapor ($\sim 10^{-3}$ torr in N_2) collected using a 1 mJ, 8 ns, 213 nm laser pulse at a standoff distance of 3 m.

5. ACKNOWLEDGEMENTS

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