



Real-time stand-off detection of improvised explosive materials using time-gated UV–Raman spectroscopy

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Abstract. A transportable, trolley-mounted stand-off explosive material detection system based on the time-gated Raman spectroscopy was developed and tested in our laboratory. This system is capable of identifying the explosives and improvised explosive materials located up to a distance of 30 m. A frequency tripled Nd:YAG, nanosecond pulsed laser (355 nm, 6 ns) operated at 10 Hz was used as an excitation source to induce Raman spectra of explosive materials under investigation. A reflected type 200 mm aperture telescope designed using Zemax optical design software was used to collect the backscattered Raman signals. Raman signals were recorded using the gated intensified charge coupled device (ICCD) spectrograph. A LabVIEW-based data acquisition and analysis software for real-time identification of materials was developed and used. It gives audio as well as text alarm to the operator about threat identification.

Keywords. Stand-off detection; improvised explosive materials; time-gated UV–Raman spectroscopy.

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1. Introduction

Stand-off detection of explosives has become very important in the last few decades because of the increasing terrorist activities at crowded places in several cities worldwide [1–3]. Terrorists have targeted humans and properties with explosives and improvised explosive devices (IEDs) [2,4,5]. Early detection of explosives and improvised explosive (IE) materials saves lives and properties. The detection and identification of explosives and hazardous chemicals from a safe stand-off distance is of critical interest for security agencies. However, it is a great technological challenge for rapid and reliable identification of all kinds of explosives and IE materials from a safe stand-off distance [6–8]. Rapid, reliable, sensitive, compact and transportable stand-off detection systems are required for accurate and early detection of explosives of all types for protecting lives and properties.

Raman and laser-induced breakdown spectroscopy (LIBS) are two main laser-based stand-off detection techniques. LIBS provides the elemental information of the sample [9,10] while Raman spectroscopy provides a molecular fingerprint of the sample [11]. Time-gated

Raman spectroscopy is an ideal laser-based technique for the rapid stand-off detection of explosives, IE materials and potentially hazardous substances because it is a non-invasive technique and vibrational spectra provide ‘molecular fingerprint’ that facilitates the rapid chemical identification in real time without any need of tunable laser. Also, the possibility of direct and distant access to suspicious materials by stand-off Raman measurements makes this laser-based spectroscopic technique an important tool in operational scenarios.

Raman signal strength is inversely proportional to the fourth power of the wavelength of incident laser light. To get strong backscattered Raman signal from stand-off distances, UV laser pulses were used to induce Raman signature of the materials. The main advantages of Raman spectroscopy are that it is a non-destructive technique and provides high selectivity. The disadvantage of Raman spectroscopy is that it gives very weak signal. To overcome this problem, we have used pulsed UV laser for strong Raman scattering and intensified charge coupled device (ICCD) to intensify the collected backscattered Raman signal of the explosive materials. UV–Raman cross-sections are many folds greater than those excited in near-infrared and visible spectral

regions [12]. Raman scattering is instantaneous. Thus, if we illuminate the sample with a nanosecond laser pulse, all the Raman scattered photons will be generated during the pulse only. In order to remove the huge solar background and other ambient light, suitable delay and gate width were used in ICCD to open it only during the time when the backscattered Raman light from the sample materials arrived at gated ICCD coupled spectrograph. For this purpose, the arrival time of Raman scattered signal was calculated by distance measurement of the target. Time delay after the laser shot was applied manually to the gate of ICCD, depending on the stand-off distance to the target. By this method, almost all the background noises were successfully removed and even sunlight and ambient light could not make any contribution or very low contribution to the data acquisition. To further improve the signal-to-noise ratio of the collected weak Raman signal of the trace amount of explosive materials, the intensifier tube of the ICCD was kept at a high-gain value. We performed stand-off experiments with explosive materials and IE materials by putting the samples at different distances ranging from 5 to 30 m.

IED is a home-made bomb, fabricated in an improvised manner and constructed from military or non-military components. An IE may be any chemical or mixture of chemicals capable of an explosive reaction. IED materials are typically inorganic salts containing molecular bound oxygen, such as nitrates (e.g. ammonium nitrates, potassium nitrates), chlorates, perchlorates or organic compounds with nitro-, nitramine- or nitrate groups or peroxides. Here, our focus is to detect and identify the fertiliser-based non-military components used in home-made bombs.

Ammonium nitrate (NH_4NO_3) is a white crystalline solid used in agriculture as a high-nitrogen fertiliser. This compound is also used in IEDs. It is the main component of ammonium nitrate fuel oil (ANFO), a popular IE material. Major uses of potassium nitrate (KNO_3) are in fertilisers, rocket propellants, fireworks and IEDs. It is one of the major constituents of gunpowder (black powder) also. Urea can be used to make urea nitrate, a fertilizer-based high explosive that has been used in IEDs. In this work, we have demonstrated the detection of IE materials up to the distance of 30 m using the time-gated UV-Raman spectroscopy.

2. Instrumentation

In the following section, we shall briefly describe the design technique of the time-gated Raman spectroscopic prototype for explosives detection. A schematic diagram of the instrumentation for stand-off detection using the time-gated UV-Raman spectroscopy is given in figure 1.

This prototype consists of a frequency-tripled Nd:YAG laser, reflected-type telescope, designed using the Zemax optical design software and ICCD coupled spectrograph. The pulse laser was a third harmonic of flash lamp-pumped Nd:YAG laser (Quantel, France, Model: Brilliant-B). The laser pulse duration was of the order of 6 ns. Laser beam divergence was 1 mrad.

Raman scattered signals were collected using 200 mm aperture, reflected-type motorised telescope in coaxial geometry having UV enhanced aluminium coating on mirrors. The complete telescope assembly including rejection filter and the focussing lens was housed in a single outer unit with a fixed primary mirror and provision for changing the intermirror distance by moving the motorised secondary mirror. Intermirror separation of the telescope mirrors can be changed using the PC control software. By changing the intermirror separation of the primary and secondary mirrors, the telescope can be focussed on the illuminated area of the sample at a desired distance for proper collection of the backscattered Raman signal from the sample with minimum background noise. A motor controller for moving the secondary mirror was attached with the telescope. Data for the intermirror separation for different target distances have been stored in the telescope controller software. Depending upon the distance of the target, intermirror separation of the mirror can be changed with the help of PC control software to adjust the focal point of the telescope.

The exit of the telescope is coupled to the spectrograph with a circular bundle (bundle diameter: 1.3 mm) of 19 fibre each with a core diameter of 200 μm . Numerical aperture of each fibre is 0.22. A lens focusses the light from the output of the telescope to the bundle of the fibre. A long-pass notch filter (Semrock, USA) at a laser wavelength of 355 nm having an optical density of the order of 6 was inserted between the focussing lens and exit of the telescope to reject strong Rayleigh scattered photons. Light collected by the telescope is transmitted to the spectrograph using a fibre bundle. Linear end of the fibre bundle is coupled to the f-matcher of the spectrograph. It focusses the collected light at the motorised entrance slit (variable 10 μm to 2 mm) of the triple grating Czerny turner spectrograph (ANDOR, USA). In the present study, 20 μm slit size was used. The resolution of the system is around 15 cm^{-1} with 20 μm slit. Blazed grating of 68 \times 68 mm^2 size having 1800 lines/mm was used to record the spectra. Spectra were recorded with a thermoelectrically cooled (-20°C), gated ICCD (ANDOR, USA) having CCD sensor, 25 mm Gen II image intensifier, integrated digital delay generator and thermoelectric cooling interface. Vertical binning was performed in the measurements. The gain of the microchannel plate (MCP) in the image intensifier can be varied using

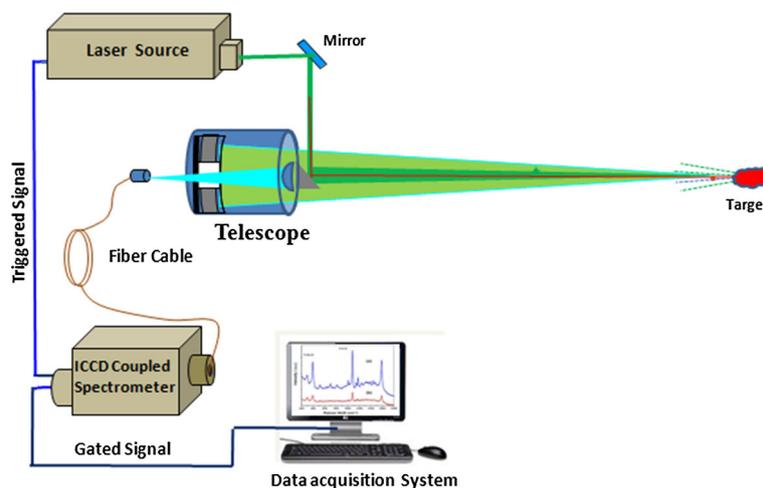


Figure 1. Schematic of stand-off detection system.

software. By increasing the gain, the voltage across the MCP is increased and hence the signal reaching the CCD sensor is amplified. CCD array has 1024×256 pixels, where each pixel size is $26 \times 26 \mu\text{m}^2$. The 256 pixels were binned and acquired on a PC as a single spectrum to enhance the sensitivity. ICCD has an in-built electronic card. Gate delay with respect to transistor-transistor logic (TTL) pulse and the gate width of ICCD can be controlled using the software. The gated detection was carried out by triggering (external trigger mode) the ICCD camera using Q-switched 5V-TTL pulse from the laser. Depending on the laser pulse duration and stand-off distance to the target, suitable gate width and delay were used in ICCD. All measurements were carried out in daylight. The resulting spectra were acquired and analysed using the LabVIEW-based software.

The Raman spectrum of molecules provides an excellent fingerprint, which can be used for the identification of the species. The analysis of Raman spectrum manually is a time-consuming process and security personal cannot afford it in a real scenario. Automation of acquisition and analysis of Raman signal for identifying the sample is required for operations in a real scenario. The LabVIEW-based user-friendly software was developed and used to acquire and process the spectra obtained by ANDOR spectrometer on illuminating the explosive sample by 355 nm laser. Reference Raman spectra of several explosives, IED materials and hazardous materials were acquired to build a library of the software of the explosives detection system. The software automatically performs the following major functions: capturing the data from the spectrometer, spectrum data processing, peak picking, Raman shift measurement in wave number and signature matching (Raman shift) with a reference library and displaying the name of identified explosive along with audio alarm in real time. Software

data library is upgradable and the user can save spectra of new reference materials. Acquisition and analysis software performs data analysis in real time to identify the materials. The particular high sensitivity reached in the detection of explosives was due to the specific optical design and electro-optics components adopted. The sensor was successfully tested on many explosives and hazardous chemicals.

3. Experimental procedure

Experiments were performed on ammonium nitrate, potassium nitrate and urea sample from the stand-off distances of 5–30 m. Telescope focal point was aligned at the sample position using red pointing fibre-coupled laser diode (power 5 mW). For each stand-off distance, the intermirror separation of the telescope was adjusted using PC control software to collect the proper Raman signal with minimum environmental noise. The UV-laser beam was aligned with the optical axis of the telescope, and the illuminated area of the sample was located at the centre of view area of the telescope at a desired stand-off distance. For each measurement, Raman signals of 20 shots of laser pulse were accumulated. For each stand-off distance, the control values of ICCD camera, i.e. gate delay from the laser pulse and laser pulse energy, were modified for optimised detection from different distances.

4. Result and discussion

Figures 2–4 illustrate the recorded Raman spectra of a powder sample of 1 mg of ammonium nitrate, potassium nitrate and urea using ANDORE software from a

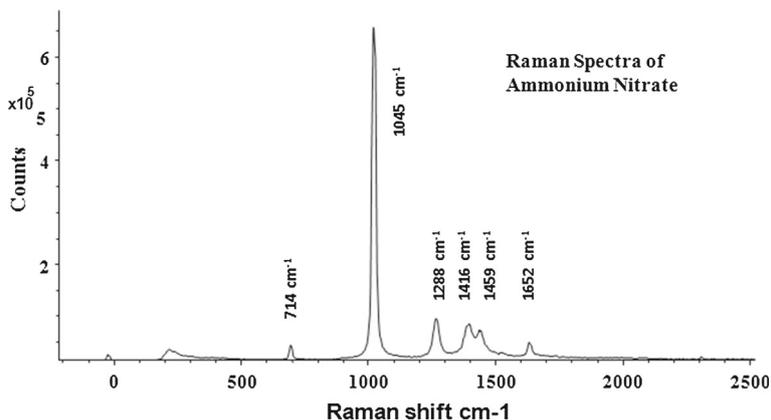


Figure 2. Recorded Raman spectra of ammonium nitrate from 30 m.

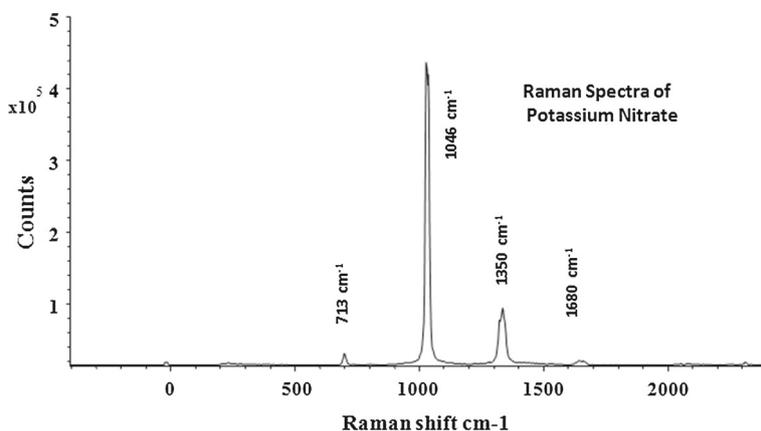


Figure 3. Recorded Raman spectra of potassium nitrate from 30 m.

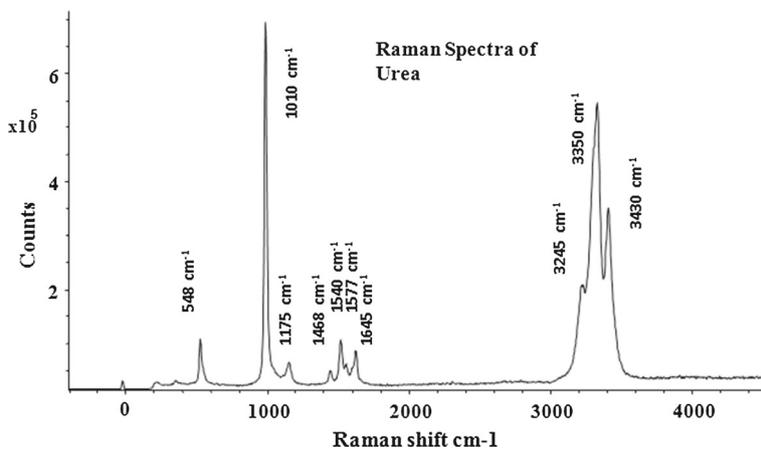


Figure 4. Recorded Raman spectra of urea from 30 m.

distance of 30 m using 355 nm excitation wavelength, 30 mJ pulse energy and 20 integration pulses. ICCD gate width and time delay of 10 and 200 ns were used for 30 m distance. Raman lines of the recorded spectra were analysed using the available literature data [13–19].

In the Raman spectra of ammonium nitrate, the weak band at 714 cm⁻¹ and very strong Raman band at 1045

cm⁻¹ are attributed to the internal covalent vibration of the NO₃⁻ ions. The band at 1045 cm⁻¹ originates from the totally symmetric NO₃⁻ stretching vibration. Very low intense line around 714 cm⁻¹ is due to in-plane bending of nitrate ion (NO₃⁻). The 1416 cm⁻¹ band came from the asymmetric NO₃⁻ stretching. Very

weak Raman vibration band at 1459 cm^{-1} is due to NH_4^+ (ammonium ion) present in ammonium nitrate.

Both ammonium nitrate and potassium nitrate contain NO_3^- ions. Raman vibration lines of KNO_3 at 713, 1046 and 1350 cm^{-1} are attributed to different internal covalent vibrations of NO_3^- ions. Raman vibrational modes of NH_4NO_3 around 714, 1045 and 1228 cm^{-1} are analogous to 713, 1046 and 1350 cm^{-1} of KNO_3 . Strong Raman peak around 1046 cm^{-1} is due to the symmetric stretching of NO_3^- ions.

The strongest Raman peak in the spectrum of urea was found at 1010 cm^{-1} . This feature is attributed to the CN symmetric stretching vibrations. Raman band at 1468 cm^{-1} is attributed to the CN antisymmetric vibration of NCN. The NH_2 symmetric rocking vibration band was observed around at 1175 cm^{-1} . The Raman band at 548 cm^{-1} corresponds to CO deformation vibration. The Raman vibration band located at 1645 cm^{-1} is attributed to the NH_2 symmetric deformation vibration and the Raman band located at 1540 cm^{-1} is due to the CO symmetric stretching vibration.

5. Conclusion

A stand-off detection system based on nanosecond-gated UV-Raman spectroscopy for explosive materials and IED materials was developed. Using this system, we were able to detect and identify explosive materials in real time up to the distance of 30 m. Experiments were performed at stand-off distance in the presence of ambient background and it is found that the nanosecond-gated Raman spectroscopic technique is very efficient in identifying explosive materials in the presence of ambient background. The result of the present work demonstrates that the time-gated Raman technique is a potential and very promising laser-based spectroscopic technique for stand-off detection of explosives. The experimental results indicated that the UV time-gated Raman system was very effective in identifying the explosives from safe stand-off distances.

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