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Deep Raman spectroscopy for the non-invasive standoff detection of concealed chemical threat agents

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ABSTRACT

Deep Raman spectroscopy has been utilized for the standoff detection of concealed chemical threat agents from a distance of 15 m under real life background illumination conditions. By using combined time and space resolved measurements, various explosive precursors hidden in opaque plastic containers were identified non-invasively. Our results confirm that combined time and space resolved Raman spectroscopy leads to higher selectivity towards the sub-layer over the surface layer as well as enhanced rejection of fluorescence from the container surface when compared to standoff spatially offset Raman spectroscopy. Raman spectra that have minimal interference from the packaging material and good signal-to-noise ratio were acquired within 5 s of measurement time. A new combined time and space resolved Raman spectrometer has been designed with nanosecond laser excitation and gated detection, making it of lower cost and complexity than picosecond-based laboratory systems.

1. Introduction

Raman spectroscopy is a valuable analytical technique that has seen broad applications in research, industrial and biomedical settings. It has been demonstrated as a powerful noninvasive detection technique that provides information on the molecular composition of chemical substances and can be readily performed on liquids or solids. With sufficient energy intensity, Raman can also be applied for the detection of unconcealed chemical threat agents from a marked stand-off distance [1–7]. However, in traditional standoff Raman spectroscopy the interrogated chemical threat must be present on a surface or concealed within a transparent packaging (e.g. clear glass container) [8–11]. When depth-resolved information is required, Raman spectroscopy represents an ideal candidate. This is due to the fact that, when conducting Raman spectroscopy on diffusely scattering materials, excitation photons penetrate the sample and propagate into its successive layers. The different interactions between the penetrating photons and the different layers within the sample can be monitored [12,13]. This key feature, along with the recent technological advances in laser excitation sources and detection technologies, have transformed Raman spectroscopy into a practical tool for depth profiling in real life investigations [14–16].

A modern deep Raman technique that enables recording spectra from layers several millimetres below the sample surface is spatially offset Raman spectroscopy (SORS) [17–20]. In this technique, the illuminated spot on the surface layer of a double-layered system is space resolved by an offset distance (ΔS) from the Raman collection point. When an excitation laser beam interacts with a double-layered system, the excitation photons propagate into the second layer in a random walk-like fashion. Due to the random scattering of the photons within the sample material, the excited area within the sample increases with increasing depth [21]. In SORS, the return radiation collected at zero offset distance from the illuminated spot is always rich in Raman and fluorescence photons from the surface layer. When the collection of the return light is made from a spot that is offset from the excitation spot, the collected spectrum becomes relatively enriched with Raman photons from the sub-layer. Therefore, the SORS setup indirectly enhances the detection of the Raman spectrum from the sub-layer [21]. SORS has been demonstrated for biomedical applications [22,23], pharmaceutical analysis [24–26], forensic and national security investigations [27,28].

An alternative Raman technique to selectively collect spectra from deeper layers, as well as efficiently eliminate fluorescence interference, is time-resolved Raman spectroscopy (TRRS) [29–32]. When a layered system is illuminated by an excitation laser, the Raman photons emitted from the surface and shallow layers arrive earlier at the detector. However, photons emitted from deeper layers arrive at the detector after a time delay that is caused by multiple scattering events experienced during their travel from the bulk of the sample to the surface of the system. This time delay can be utilized to exclude the detection of the majority of photons being emitted from the surface layer and to selectively obtain

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chemical information from a deeper layer within the diffusely scattering sample, up to several millimetres thickness [33]. Matousek et al. [34,35] demonstrated time-resolved depth profiling using picosecond Kerr gating. However the demonstrated methodology was challenging and instrumentally complex.

Time-resolved spatially offset Raman spectroscopy (TR-SORS), in a close distance mode, has been recently demonstrated as a combined technique that leads to higher selectivity towards the sub-layer and further reduction of the fluorescence and surface layer contributions [36,37]. In time-resolved SORS, a short laser pulse (picoseconds) is used as the excitation source and delayed time-gated detection of the Raman photons at an offset position from the excitation spot leads to the discrimination against the surface layer and the detection of the sub-layer Raman spectrum [33]. However, picosecond-based TR-SORS systems are mainly lab-based and cannot be easily transformed into a mobile instrument for real life detections.

The aim of this current work is to extend the application of TR-SORS for the non-invasive standoff detection of chemical threat agents. We demonstrate a TR-SORS spectrometer that uses nanosecond excitation coupled with nanosecond gated detection for deep Raman profiling of concealed chemical threat agents from 15 m. The nanosecond-based TR-SORS spectrometer described in this paper is lower in cost and less complex than picosecond-based laboratory systems, which makes it competent for real life measurements. For comparison, the new spectrometer was used for screening the threat agents by standoff SORS as well as standoff TR-SORS. Our results confirm that using TR-SORS leads to higher selectivity towards the concealed substance and higher signal to noise ratio than obtained by SORS alone.

2. Experimental

2.1. Instrumentation

A schematic diagram of the developed TR-SORS spectrometer is shown in Fig. 1. The excitation was carried out using a second harmonic 532 nm Q-switched Nd:YAG laser source (Brilliant EaZy, Quantel, USA). The laser source has a pulse length of 4 ns and a repetition rate of 10 Hz. The return light was collected using an eight inch Schmidt-Cassegrain telescope (Celestron, U.S.A.). The light was filtered through a 532 nm long-pass filter (Semrock, U.S.A.) and collected by a fibre–optic bundle cable that consists of nineteen 200 μm diameter optical fibres (Princeton Instruments, USA). The bundle was directed to an Acton standard series SP-2300 imaging spectrograph. A PIMAX 1024RB gated ICCD camera (Princeton Instruments, USA) was used to detect the return light. The detector gate width was set to 4 ns. The laser and ICCD detector were synchronised to ensure that the maximum Raman signal was measured. To achieve this condition, the initiation of the gate opening was first set to overlap with the triggering of the laser pulse and then the 4 ns gate was shifted in time using steps of 50 ps to increment the delay. To obtain TR-SORS spectra, 50 laser pulses of 35 mJ laser energy were focused on an area of 20 mm^2 that was offset from the telescope axis by a distance (ΔS). The detection gate was shifted in time using 50 ps increments to enhance the selectivity towards the sub-layer. The SORS measurements were carried out using gated detection, however the ICCD gate was not shifted in time. To create the spatial offsets, the excitation beam was adjusted on the container wall surface to different offset distances of zero, 6, 11 and 15 mm from the telescope axis. For the standoff measurements at 15 m with a spatial offset of 15, the Raman collection area on the sample was 150 mm^2. In order to acquire reference spectra of the tested threat agents, the spectrometer was setup in the conventional back-scatter geometry (direct Raman mode) and pure standards of the chemical substances were screened in a quartz cuvette. All the spectral measurements made using the various Raman modes (direct Raman, SORS and TR-SORS) were carried out under fluorescent light within the lab environment. All spectra are presented as acquired without spectral processing.

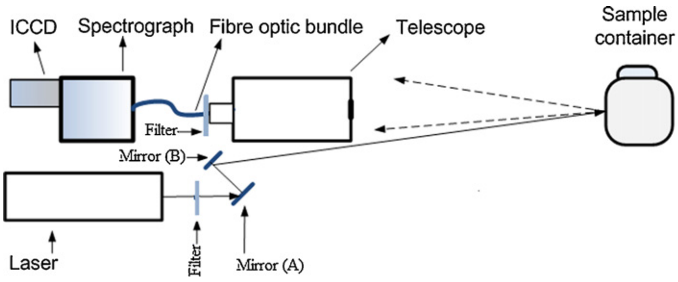


Fig. 1. Schematic diagram of the developed Raman spectrometer for the standoff detection of concealed substances.

2.2. Chemicals

Ammonium nitrate (NH_4NO_3 ≥98%), barium sulfate ($BaSO_4$ ≥99.9%), nitromethane (CH_3NO_2 ≥99%), 2,4-dinitrotoluene ($CH_3C_6H_3(NO_2)_2$ ≥97%) from Sigma were screened by the unit. For all sample measurements, barium sulfate, ammonium nitrate, 2,4-DNT and nitromethane were concealed within a white opaque container made of high-density polyethylene (HDPE) (with a wall thickness of 1.5 mm).

3. Results and discussion

3.1. TR-SORS vs SORS

To study the selectivity of TR-SORS towards the Raman photons from the sub-layer, barium sulfate in an opaque HDPE white plastic container was screened, as a model sample, from a standoff distance of 15 m. Standoff SORS measurement of the concealed barium sulfate sample was also carried out at the same distance for comparison purposes. HDPE was chosen to represent the surface layer as this material is frequently encountered in real life scenarios as a packaging material. We have previously demonstrated depth profiling by TR-SORS spectroscopy through other container materials such as PE, polypropylene, coloured cellulosic fabric, paper packaging as well as coloured pharmaceutical capsule shell made of gelatinous material [27,28,39].

For TR-SORS measurements, the excitation beam was first offset from the telescope axis by 15 mm then successive detector gate delays were introduced. For both of the SORS and TR-SORS detections the measurement time was kept constant at 5 s. For the TR-SORS measurement, the gate delay was successively progressed until it reached a value where the intensity of the sub-layer signal was optimised and the intensity of the surface layer was suppressed. The results are shown in Fig. 2a and b. As indicated by the figures, the Raman spectra from both the SORS and TR-SORS measurements consisted of spectral contributions from both the HDPE wall material (container) and the barium sulfate sample (sub-layer). In real life measurements the spectral signature of the container material may not be known. This problem which is experienced in conventional direct Raman measurements causes the discrimination between the bands originating from the surface layer and the bands originating from the sub-layer (chemical substance) to be extremely difficult. However our results show that when the spatial offset (in SORS measurements) or the detector gate delay (in TR-SORS measurements) was increased, the band intensities between 1000 and 1500 cm^{-1} (arising from the

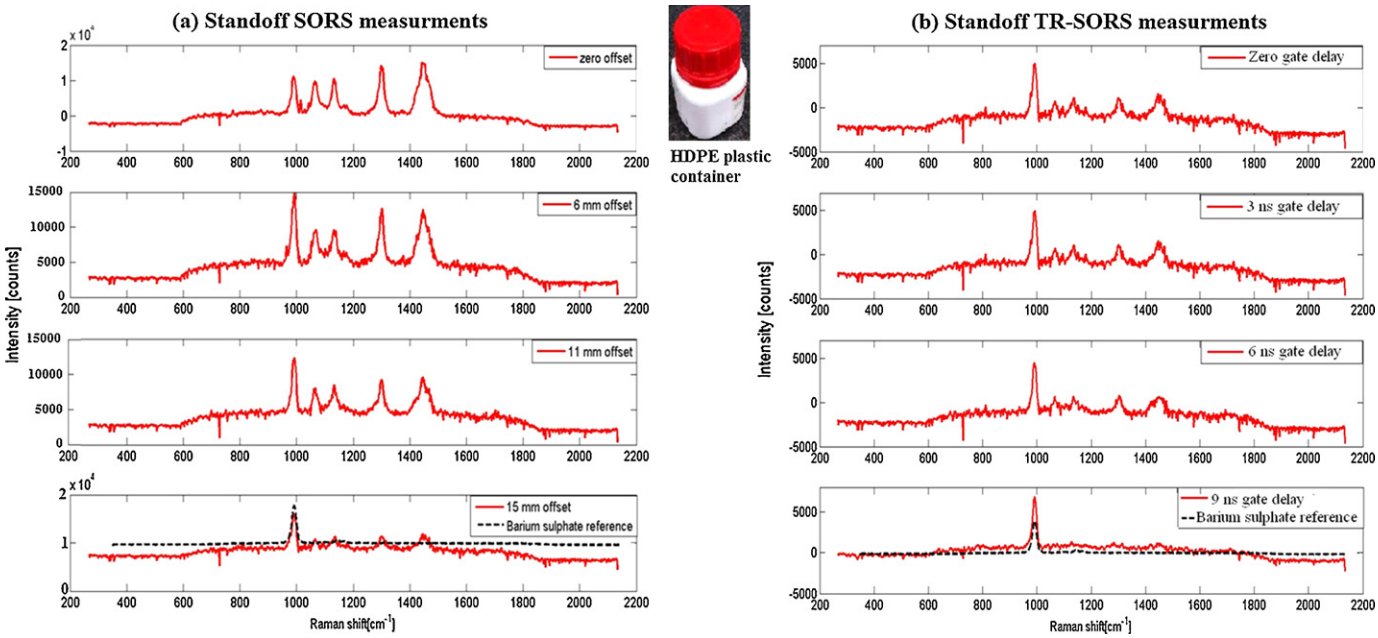


Fig. 2. Standoff Raman spectra of barium sulfate concealed in an opaque HDPE plastic container (a) Standoff SORS measurements (SNR = 5.9), and (b) Standoff TR-SORS measurements (SNR = 13.5). Measurements were carried out from standoff distance of 15 m.

container wall material) decreased significantly. On the contrary, the band intensity at 980 cm^{-1} (from $BaSO_4$) decreased at a lower rate until it became the predominant spectral line within the spectrum. Therefore, by observing the relative reductions in signal intensities and the change in the spectral profile with increasing spatial offset or detector gate delay, a positive identification of the spectral lines from the chemical substance present in the sample becomes possible, enabling the identification of the unknown concealed substance. This can be achieved without the need for prior knowledge of the spectral signature of the packaging material or the concealed substance [15,27].

The signal intensity ratios of $BaSO_4$ at 980 cm^{-1} (representing the sub-layer) to HDPE plastic material at 1450 cm^{-1} (representing the surface layer) were calculated for the measurements made by SORS and TR-SORS. The change in the signal intensity ratios with the spatial offset (SORS mode) and the detector gate delay (TR-SORS mode) is shown in Fig. 3a and b. As indicated by Fig. 3b, the change in the intensity ratio ($BaSO_4$ to HDPE material) was higher in the TR-SORS measurements when compared to that in the SORS measurements. The significant change in the intensity ratios within the TR-SORS measurements is due to the combined effects of time and space resolve. This result is in agreement with the recent findings of research groups in the art where they demonstrated that combining time and space resolve leads to higher selectivity towards the sub-layer in TR-SORS when compared to SORS [36,39].

Petterson et al. [36] demonstrated close range time-resolved SORS using picosecond pulsed laser excitation with a narrow ICCD gate width of 250 ps, in order to achieve good temporal resolution and suppress fluorescence and surface layer contributions [33]. However, using a very narrow gate width may reduce the signal intensity and, therefore, result in a low signal to noise ratio (SNR) particularly for large standoff distances. To overcome this

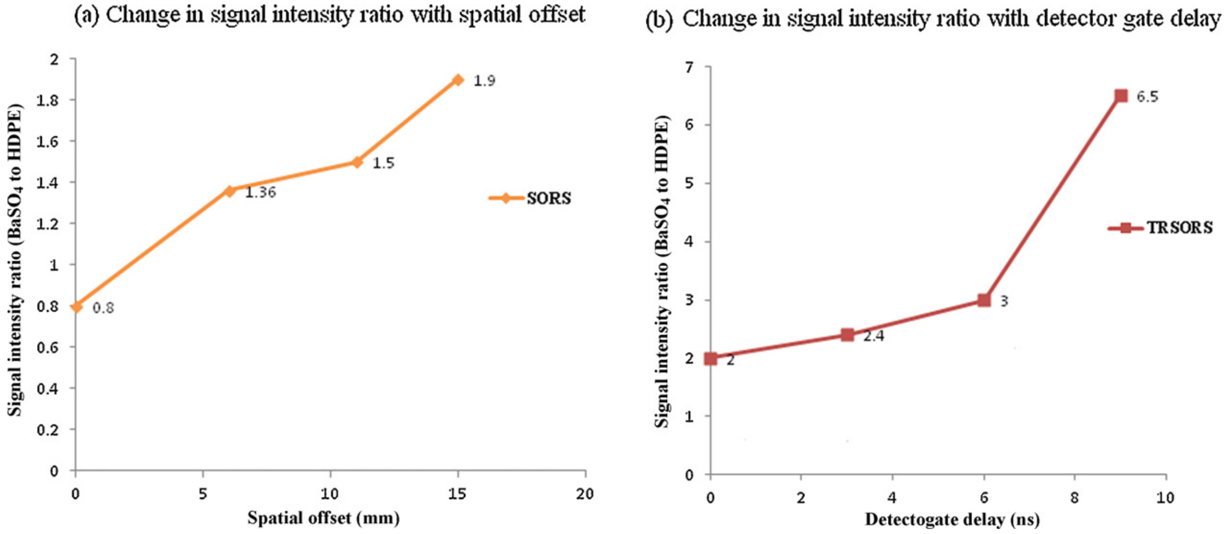
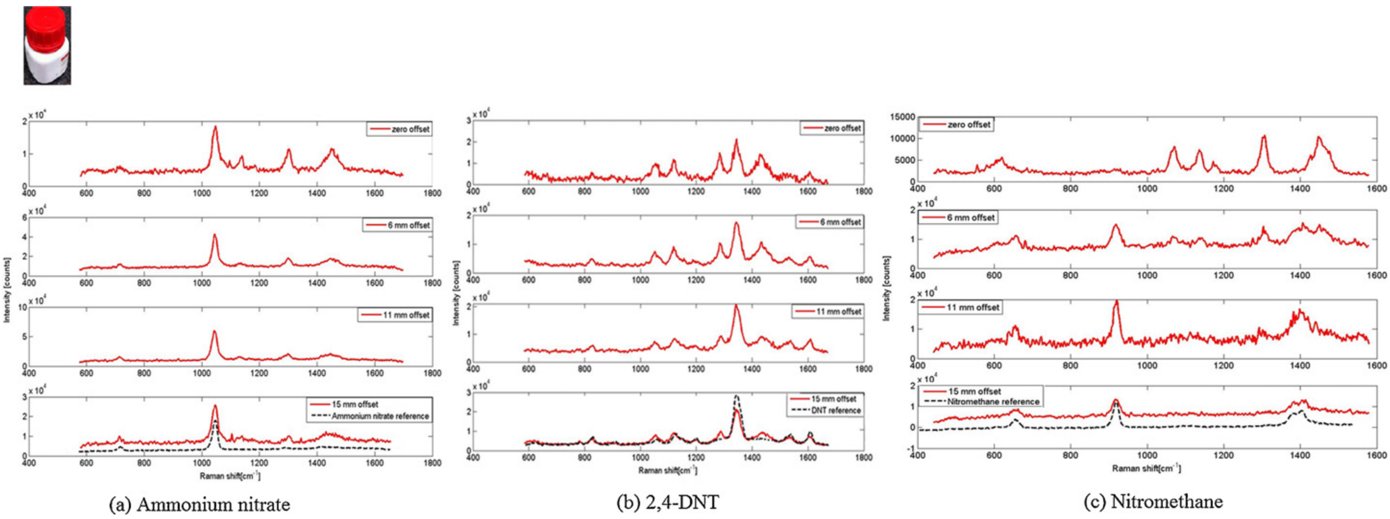


Fig. 3. Change in the signal intensities ratio of barium sulfate (at 980 cm^{-1}) to HDPE plastic material (at 1450 cm^{-1}) with (a) the change of the spatial offset (standoff SORS detection mode) and (b) the change of detector gate delay (standoff TR-SORS mode).



(a) Ammonium nitrate (b) 2,4-DNT (c) Nitromethane

Fig. 4. Standoff SORS measurements of (a) ammonium nitrate (SNR = 26), (b) 2, 4-DNT (SNR = 21.2) and (c) nitromethane (SNR = 8.5). The chemical substances were concealed in HDPE plastic container and measurements carried out from standoff distance of 15 m.

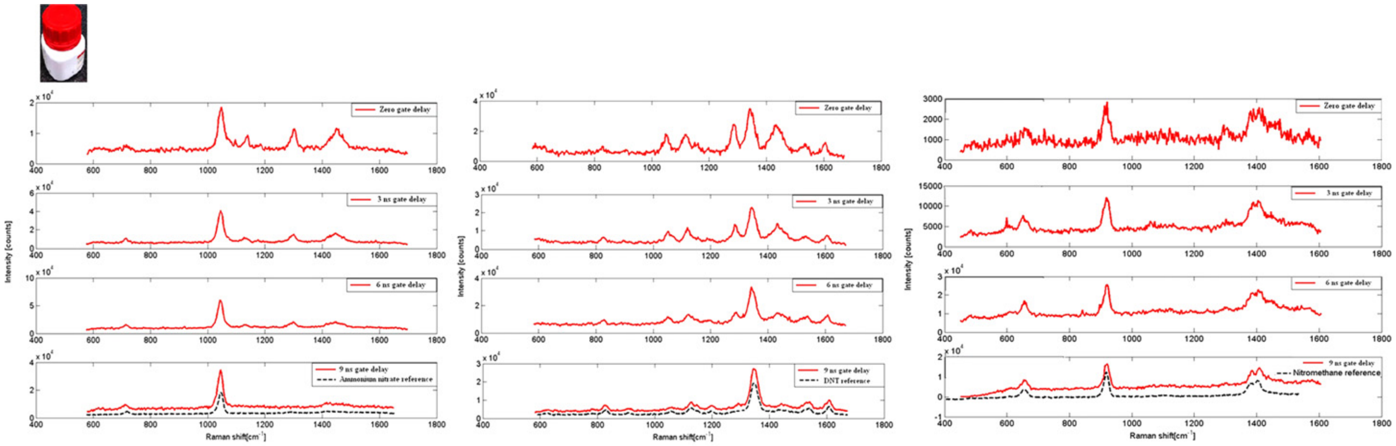
limitation of picosecond-based systems, we used nanosecond laser excitation coupled with nanosecond gated detection for conducting standoff detection of the concealed chemical threat agents. Using our developed system to screen barium sulfate, we recorded a signal to noise ratio of 13.6 with TR-SORS (Fig. 2b). Petterson et al. [36] reported a signal to noise ratio of 9.7 for the depth profiling of a 2 mm polyethylene layer hidden behind a 7 mm Teflon layer by TR-SORS (using a picosecond-based system). For our measurement of barium sulfate by SORS (Fig. 2a), we recorded a signal to noise ratio of 5.9. This result is in agreement with the findings of Zachhuber et al. for the change in signal to noise ratio of the sub-layer [8]. They used a nanosecond-based system (under a standoff SORS configuration) to detect isopropanol hidden inside a polyethylene plastic container from a standoff distance of 12 m and reported a limited increase in the signal to noise ratio of isopropanol with the increase of the spatial offset distance (ΔS) from zero to 10 mm.

3.2. Standoff SORS measurements

The SORS spectra of ammonium nitrate (represented by the Raman frequency at 1050 cm^{-1}), nitromethane (represented by the Raman frequencies at 650 cm^{-1}, 915 cm^{-1}, 1400 cm^{-1}) and 2,4-dinitrotoluene (represented by the Raman frequencies at 836 cm^{-1}, 1055 cm^{-1}, 1122 cm^{-1}, 1200 cm^{-1}, 1346 cm^{-1}, 1533 cm^{-1}, 1605 cm^{-1}) at 15 m are shown in Fig. 4a–c. The Raman spectra collected from the successive offset points show progressive increase in the population of the Raman photons from the sub-layer as well as a rapid decrease in the surface-layer contribution (represented by the Raman frequencies at 1140 cm^{-1}, 1303 cm^{-1}, 1450 cm^{-1}). As indicated by the figures, at a spatial offset of 15 mm (between the excited spot on the surface of the sample and the axis of the telescope) the Raman signals from the hidden chemical threat dominated the acquired Raman spectrum. These observable differences are attributed, in part, to the lateral fading of the photons generated from the excited spot on the surface layer [37,38]. At 15 mm spatial offset, the contributions of the surface layer Raman photons in the SORS spectrum are substantially suppressed while the contributions from the sub-layer are promoted. Therefore, a Raman spectrum revealing the concealed chemical substance is acquired. However, it can be seen that the acquired signals still suffer from a considerable background caused by the interfering fluorescence photons that reach the detector. These photons are generated from the surface layer upon excitation and were not efficiently rejected under the SORS setup. This was also evident from the relatively low signal to noise ratios (SNR) observed in the standoff SORS measurements of the screened samples.

3.3. Standoff time-resolved SORS (TR-SORS) measurements

In order to maximize the Raman signal to noise ratio in standoff detection of concealed substances, rejection of the surface layer Raman and fluorescence photons should be maximized. To meet this requirement, we used the nanosecond-based TR-SORS detection mode as a combined approach that enables time and space resolve within the Raman measurement and leads to higher selectivity towards the sub-layer as well as significant reduction of the fluorescence background [29,36,39]. For our standoff TR-SORS measurements, we used a gate delay that is dependent, in part, on the refractive index of the concealed chemical substance. The results are shown in Fig. 5a–c. As indicated by the figures, the TR-SORS measurements of the interrogated chemical threats showed higher SNR when compared to those obtained by standoff SORS. The introduced time delays between triggering the laser pulse and detecting the return light allowed for rejecting a significant abundance of the surface layer fluorescence and Raman photons (by not detecting the return light), compared to that detected during SORS measurements. On the other hand the use of a wide gate width of 4 ns allowed for detecting a high abundance of the sub-layer Raman photons similar to that detected by the SORS setup. Consequently, less contributions from the surface layer Raman and fluorescence photons were detected while high abundance the Raman photons from the sub-layer was still detected. This led to the observed higher signal to noise ratios within the TR-SORS measurements when compared to those of the SORS measurements of the same samples at the same standoff distance. This is to say that, the high SNR is due to the efficient rejection of the surface layer Raman and fluorescence photons and the optimal recovery of sub-layer photons. The TR-SORS spectra were recorded within 5 seconds of data acquisition and suffered from minimal to no interference from the surface layer spectral lines (Fig. 5a–c). As mentioned earlier, there was no need for prior knowledge of the package material. By using TR-SORS the native spectrum of the hidden substance (sub-layer) was easily identified and retrieved. This was achieved by observing the rapid decrease of the Raman spectral lines that represent the surface layer with the progress of the gate delay. Once the Raman



(a) Ammonium nitrate (b) 2,4-DNT (c) Nitromethane

Fig. 5. Standoff TR-SORS measurements of (a) ammonium nitrate (SNR = 42), (b) 2, 4-DNT (SNR = 37) and (c) nitromethane (SNR = 19.5). The chemical substances were concealed in HDPE plastic container and measurements carried out from standoff distance of 15 m.

spectral signals of the hidden unknown substance are identified, the identity of the substance can be confirmed by comparing the retrieved TR-SORS spectrum of the sub-layer to a reference spectrum from a Raman spectral library.

Cletus et al. previously explained how the use of nanosecond pulsed-laser excitation and gated detection contributes to fluorescence rejection and the retrieval of the sub-layer signals [39]. In brief, at the start of the laser excitation a subset of incident photons from the leading edge of the laser pulse arrives at the surface layer of the sample and generates Raman photons from the surface material. Some of the incident photons will begin to propagate (by diffusely scattering through the surface layer) into the sub-layer sample. Meanwhile, fluorescence in the surface layer begins to develop (after $\sim 10^{-9}$ s) but still remains at low levels. The trailing edge of the long laser pulse continues to arrive at the surface layer and causes the Raman scattering to continue, while fluorescence from the surface layer also continues but now at high levels. However, the Raman photons from the bulk (sub-layer) are still undergoing scattering inside the concealed contents and begin travelling towards the surface. Towards the end of the pulse, the Raman photons from the sub-layer start to emerge from the bulk of the sample and travel towards the collection optics (telescope) then the detector at a delayed time. Therefore, at this point in time, the return light contains both Raman photons from the sub-layer (chemical substance) and fluorescence. The gated detection discriminates between these signals by choosing an optimal point in time where the Raman signal from the sub-layer is maximized against the fluorescence signal which contributes to the background and noise present in the acquired spectrum [39–41]. With a sufficient number of laser pulses, a significant Raman signal is collected to build up the SNR and develop a Raman signature for the sub-layer [42].

4. Conclusion

A new TR-SORS spectrometer which uses pulsed laser excitation on the nanosecond timescale has been constructed and tested for standoff detection of concealed energetic materials. The new spectrometer has higher selectivity towards Raman photons from deeper sample layers through diffusely scattering surface layers when compared to standoff SORS and conventional TRRS. Raman spectra that have minimal interference from the packaging and good SNR could be recorded with 5 s of data acquisition. The new unit has powerful potential for national security and forensic applications.

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