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Narrow gated Raman and luminescence of explosives

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ABSTRACT

Narrow gated Raman spectroscopy is used to detect Raman signals of explosives, which are usually screened by their intrinsic or background luminescence. It was found that the Raman/luminescence ratio is improved by 2–10 times with gate width of 500 ps compared to the 10 ns gate. It enables in certain cases to combine the luminescence suppression by gating with higher identification ability of Raman signals achievable with green excitation.

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1. Introduction

In the manufacture and transport of improvised explosive devices (IED), there is the possibility of trace amounts of the explosive being deposited on the corresponding outer surfaces, such as vehicle. This could be due to human handling of the IED with subsequent transfer to the surface, a contaminated area used for IED manufacture, or the IED shedding trace amounts as it is being loaded into the vehicle. There are contact trace techniques for sampling and detecting this material, but the operator is put in a potentially very hazardous situation. The use of standoff non-contact techniques would greatly reduce the risk associated with trace sampling, hopefully reduce inspection time, and improve detection. The request is for any technology that meets the standoff requirement and detects explosives amounts in the range of micro-grams (or less) to tens of micro-grams per cm^2.

Raman spectroscopy, in which we can get specific shifts or signature for each molecule, is increasingly important technology for homeland defense applications. Lewis et al. [1,2] have previously shown that bulk quantities of a wide range of explosive materials can be analyzed by Raman spectroscopy using either 785, 830 or 1064 nm excitation, while 830 nm was found to be the preferred excitation wavelength. Carter et al. [3] remotely detected certain explosives using ns gated Raman spectroscopy with 532 nm excitation. The main problem in using Raman application is its low signals relative to luminescence of a substrate or the sample itself that in many cases may screen

desired signal. Using continuous wave (CW) lasers, Raman scattering is collected together with luminescence. In fact, the interaction time for Raman scattering is virtually instantaneous (less than 1 ps), whereas luminescence emission is statistically relatively slow, with a minimum time of hundreds of picoseconds elapsing between electronic excitation and radiative decay. Thus, if we illuminate a sample with a short laser pulse, all of the Raman photons will be generated during the pulse, whereas most of the luminescence photons will be emitted at much longer times after the pulse. If the detection system is gated so as to detect only those photons scattered or emitted during the laser pulse, we will collect all of the Raman photons but reject the majority of the luminescence. Ideally, such a system should achieve the highest possible rejection ratio while having high throughput and a time resolution or gating time, short enough to match the duration of the laser pulse and correspondingly the Raman flux.

Existing gated ICCD cameras and photomultipliers typically operate on nanosecond timescales, with the fastest devices reaching hundreds or tens of picoseconds. In many cases it enables to produce excellent Raman signals, which were completely obscured in non-gated spectra.

In previous work [4] we demonstrated that the detection of military grade RDX, C4 and especially Semtex, using gated Raman spectroscopy with 532 nm excitation wavelength and gate width of 10 ns, is impossible. The reason is the strong intrinsic and background luminescence that screens Raman signals of these explosives. It was also shown that UV gated Raman ($\lambda_{ex} = 248$ nm, gate width of 10 ns) is substantially better [5], but the spectra became less informative compared to visible green excitation. In this work we used gated Raman with the gate of 0.5 ns in order to suppress luminescence by narrower gating comparing to the previous experiments.

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2. Experimental

All the measurements were done using the setup described earlier [4], which includes Leopard high-energy Nd-YAG laser (532, 355 and 266 nm, pulse width 50 ps, energy 15, 8 and 4 mJ, correspondingly), ICCD camera (Princeton Instruments) with gate width down to 0.5 ns and edge filters for 532, 355 and 266 nm. We investigated the fast gated Raman on C4, PETN, RDX and Semtex on different backgrounds.

3. Theoretical approach

The luminescence intensity as a function of time with decay times very close to excitation pulse duration was calculated using the rate equations in two levels system under pulsed excitation $F(t) = p_0 \exp(-t/\tau_{ex})$, with $\tau_{ex} = 50$ ps

$$\frac{dN_2}{dt} = B p_0 \exp(-t/\tau_{ex}) N_1 - N_2 A \tag{1}$$

where N_1, N_2 are the populations in the lower level and upper level (respectively), B is the Einstein coefficient for absorption, $A = 1/\tau_{lum}$ is the spontaneous emission probability and p_0 is the excitation density. The border conditions are: $N = N_1 + N_2$ is the number of atoms in the system; at $t = 0$ $N_1 = N$ and $N_2 = 0$; and in the case of low excitation density at any time $N_2/N \ll 1$. The solution is

$$N_2 = C \left[\exp\left(\frac{-t}{\tau_{ex}}\right) - \exp\left(\frac{-t}{\tau_{lum}}\right) \right] \tag{2}$$

where $C = \tau_{ex} \cdot B p_0 N / ((\tau_{ex}/\tau_{lum}) - 1)$ is a negative constant because $\tau_{ex} < \tau_{lum}$.

Simple theoretical calculation enables to evaluate the influence of luminescence with different decay times on Raman signals. Fig. 1a represents the time behavior of luminescence with different decay times in 0.4–20 ns range calculated based on Eq. (2). It may be seen that during first 10 ns after laser pulse, luminescence with decay times of 10 ns and more may be
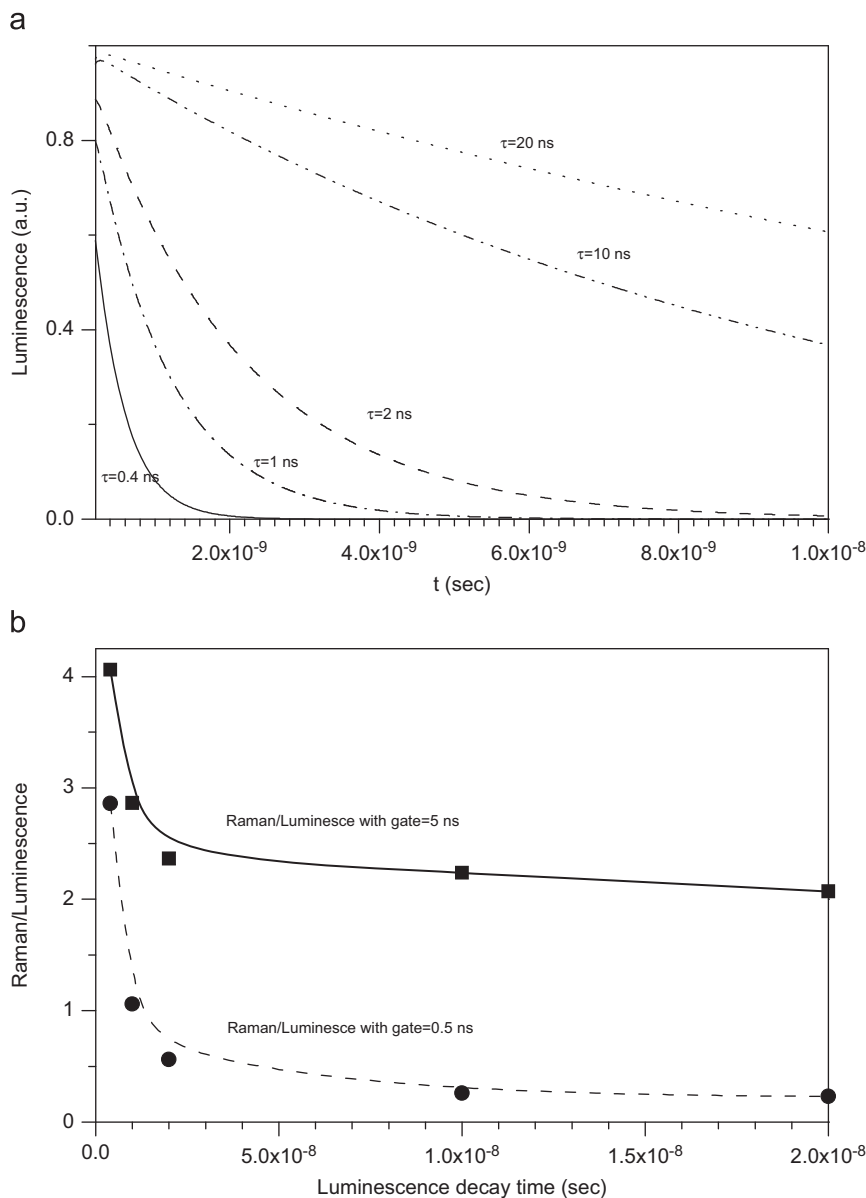

Fig. 1. Theoretical estimation for the temporal behavior of luminescence with different decay times during first 20 ns after laser pulse (a), and for Raman/luminescence ratio for different decay times with 0.5 and 5 ns gates (b).

effectively removed by gating, while luminescence with decay times of 2 ns and less are mostly detected during this time window. Fig. 1b represents Raman/luminescence ratio for different decay times of luminescence with 0.5 and 5 ns gates. Raman signal intensity is proportional to integral of the excitation pulse duration, so $I_{Raman} = p_0\tau_{ex}$ while the luminescence intensity is equal to integral in time interval of the signal registration Δt (in our case it is the time gate) of Eq. (2) $I_{lum} = \int_0^{\Delta t} AN_2 dt$.

It was calculated taking integral under decay curves with widths of 0.5 and 5 ns. It may be seen that starting from decay time of 10 ns and more, this ratio is approximately one order of magnitude higher, for decay times between 5 and 10 ns it is approximately 5–7 times higher, for 1 ns it is three times higher and for 0.4 ns it is approximately only 1.5 times higher.

4. Results and discussion

Fig. 2 demonstrates Raman spectra of C4 and Semtex with 532 nm excitation wavelength and gate widths of 0.5 and 5 ns. C4 spectra are very pure from background, demonstrating strong Raman spectra of RDX, which is the main component of C4. We did not found significant intrinsic luminescence of C4 and correspondingly dependence of C4 Raman spectra on gate width (Fig. 2a). This result strongly contradicts to excitation by 532 nm with 6–8 ns pulses, where very strong intrinsic C4 luminescence has been detected, preventing in many cases Raman lines detection. From the other side, for Semtex the effect of the shot gating is seen very clearly. We have not been capable to detect Raman spectrum of Semtex using excitation by 532 nm with 6 ns pulse width, while it is clearly seen with 50 ps pulse width and 0.5 ns gate (Fig. 2b).

Nevertheless, substantial luminescence background still presents in spectra taken with 0.5 ns gate. Evidently luminescence components with very short decay time exist. Calculated decay times (τ) of intrinsic luminescence of the studied explosives are presented in Table 1, decay times of several backgrounds typical for real life scenarios are also included. Fitting of τ was done using one or two-exponential decay where in most cases two-exponential decay is better than the one-exponential.
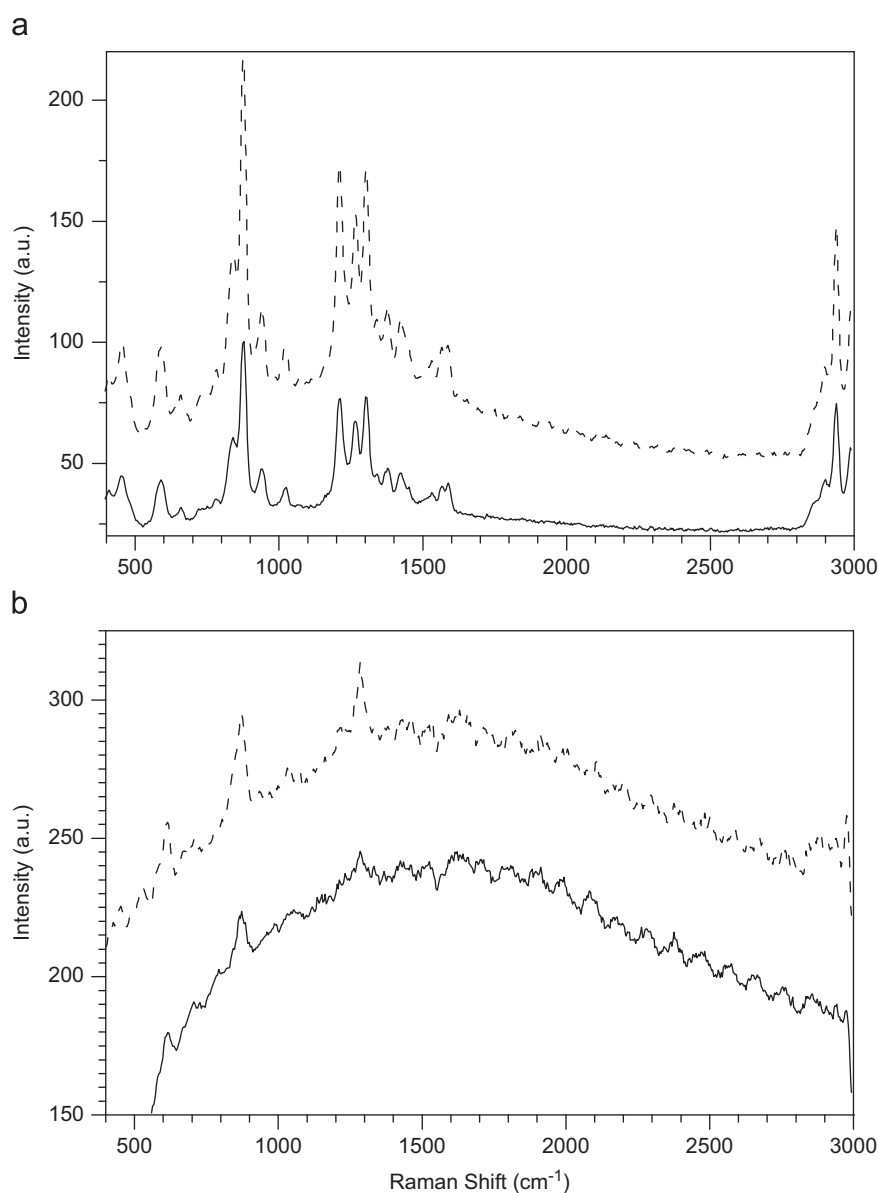

Fig. 2. Luminescence spectra of C4 (a) and Semtex (b) on Al background excited by 532 nm and gate width of 5 (solid) and 0.5 ns (dash).

Fig. 3 represents the experimental results for the ratio between Raman and luminescence for 0.5 and 5 ns gate widths. In accordance with theory, shorter gate reveals better ratios and as the luminescence decay time is getting longer the ratio gets higher.

Similar effects have been found detecting explosives on different backgrounds, which are characterized by very strong luminescence under excitation by 532 nm. Fig. 4 represents C4 Raman spectra deposited on green car. Very weak Raman signal may be detected with 5 ns gate width, while it is much clearer with the shorter gate.

To evaluate the narrow gated Raman ability with UV excitation, several explosives were studied using excitations by 355 and 266 nm (3rd and 4th harmonics of Nd-YAG). The fourth power dependence of Raman intensity on incident frequency means that it increases by about 16 times when using UV laser radiation at 266 nm instead of the 532 nm. Since Raman frequency shifts depend mainly on the identity of the molecule, not on the frequency of the excitation laser, infrared, visible, and ultraviolet lasers produce the same set of Raman shifts for a specific molecule.

An additional increase in Raman intensity may be achieved due to the dependence of Raman cross-section on excitation frequency. When the excitation frequency is close to an electronic transition of the molecule, strong enhancement of the particular

Fig. 4. Raman spectra of C4 on green painted car with 5 (solid) and 0.5 ns (dash) gate widths.

Raman vibration mode may occur and as a result strong enhancement of particular Raman lines will be observed. Resonance Raman takes place for explosives materials and up to 200 times enhancement occurs in the deep UV [5]. Another advantage of excitation in the UV range is the possibility to move the Raman information out of the luminescence region. In the UV range, with very energetic photons, the Raman lines are very close to the incident exciting frequency, while in this spectral range luminescence is still very weak because of its inherently large Stokes shift.

Fig. 5 represents Raman spectra of PETN and C4 with 355 nm excitation wavelength. Intrinsic luminescence background appears in PETN case, but Raman lines are mostly spectrally separated. Besides, gating with 0.5 ns (Fig. 5b) leads to luminescence background which approximately three times lower compared to gating with 5 ns (Fig. 5a). In the case of RDX explosives with 355 nm excitation, even chemically pure RDX demonstrates strong luminescence, which becomes approximately twice weaker with gating of 0.5 ns compared to gating of 5 ns. Such luminescence background becomes much stronger in military grade RDX with additional binders and Raman lines are barely visible even with gate width of 0.5 ns. The situation is even worse in C4 case where Raman lines are absolutely invisible on luminescence background both with 5 ns (Fig. 5c) and 0.5 ns gate widths (Fig. 5d). Similar situation takes place in HMX case. It was found that Raman spectroscopy with excitation by 355 nm is not good for Semtex and TNT. The first one has extremely strong luminescence, which covers the Raman lines even with gating of 0.5 ns, while the second one exhibits an extremely weak Raman signal. The last result is unexpected and very unusual, because TNT Raman lines demonstrates deviation from classical λ^{-4} dependence of Raman cross-section and actually totally disappear with UV excitation by 355 nm. The possible reason is that different Raman lines derive from different electronic transitions and disappear when the excitation energy exceeds the corresponding resonance energy [5].

Excitation by 266 nm enables to separate Raman and luminescence signals substantially, but it was found that RDX and all RDX containing explosives may not be detected evidently for the same reason as for TNT not being detected using excitation by 355 nm.

Table 1
Luminescence decay time (τ) for various materials, explosives and backgrounds.

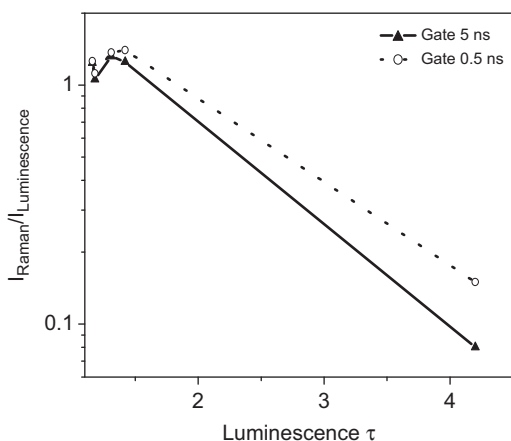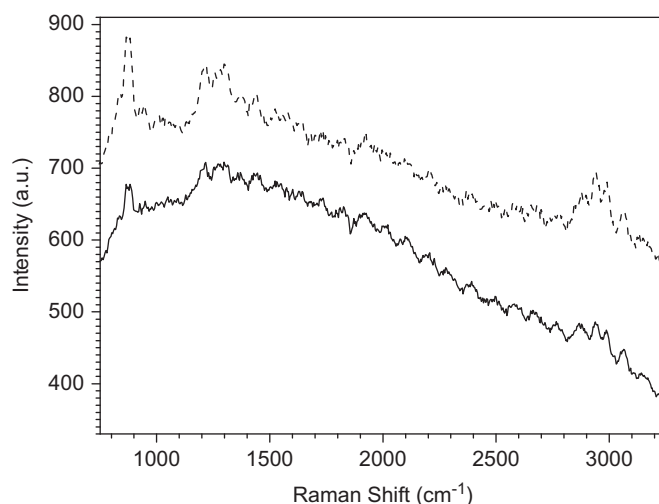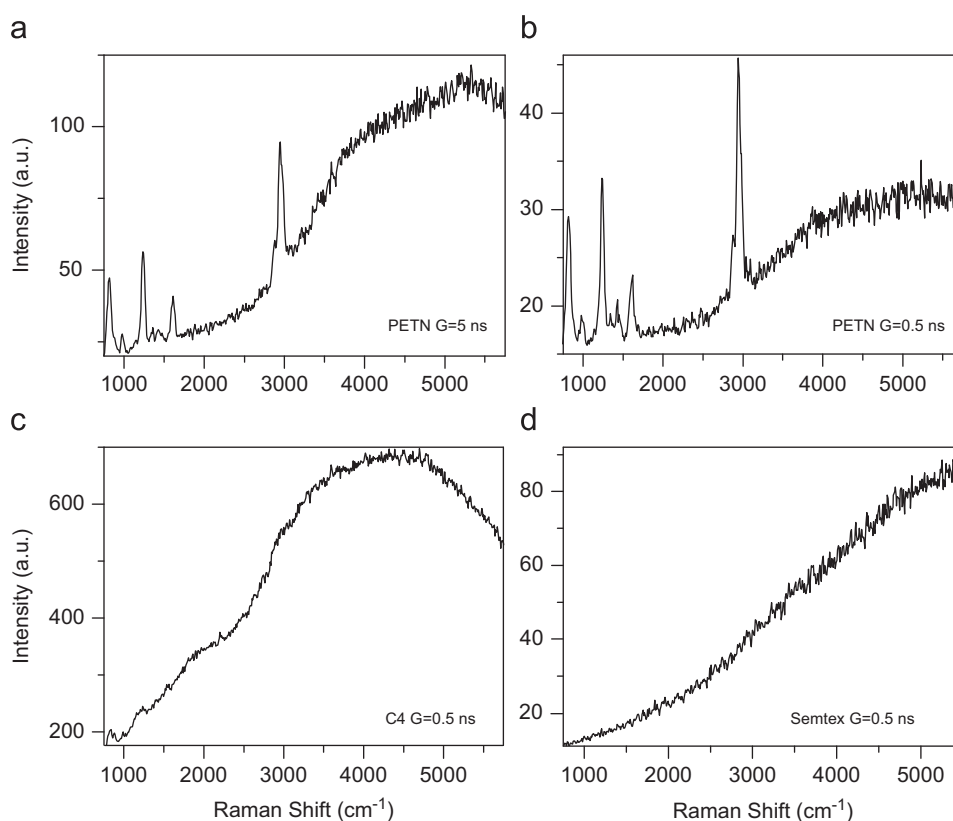| Material	Single decay τ (ns)	Double decay	
		τ_1 (ns)	τ_2 (ns)
C4 ($C_3H_6N_6O_6$)	1.7	0.56	3.25
HMX ($C_4H_8N_8O_8$)	0.98	0.71	1.31
PETN ($C_5H_8N_4O_{12}$)	0.89	0.55	1.42
RDX3 ($C_3H_6N_7O_8$)	0.82	0.55	1.18
RDX5 ($C_3H_6N_7O_8$)	0.66	0.62	1.16
Semtex (RDX+PETN)	1.65	0.72	4.2
Silver painted car	3	1	6
Cotton-1	1	0.44	1.8
Cotton-2	1.85	0.75	4
Polyester-1	2.15	–	–
Polyester-2	2.05	–	–

Fig. 3. Raman/luminescence ratio for different luminescence decay times with 0.5 and 5 ns gates.

Fig. 5. Raman spectra of PETN with gate width of 5 (a) and 0.5 ns (b), C4 (c) and Semtex (d) with gate width of 0.5 ns on Al background under 355 nm excitation.
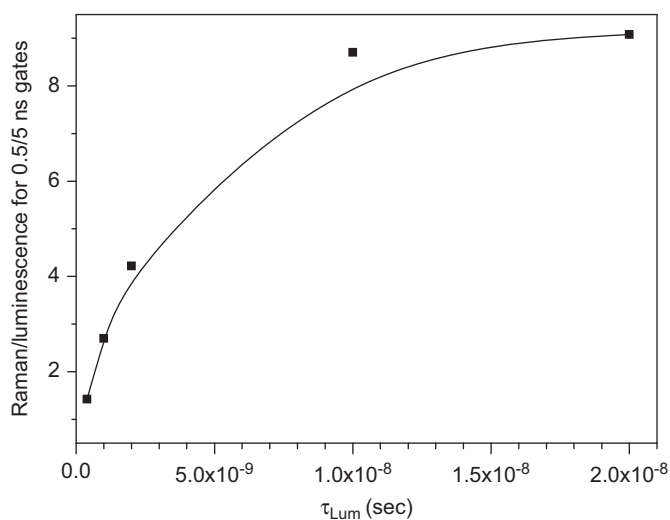

Fig. 6. Raman/luminescence improvement for 0.5 ns gating compared to 5 ns gating for luminescence with different decay times.

5. Conclusions

The main problem for Raman application is its low signals relatively to Rayleigh scattering and luminescence of a substrate or the sample itself that in many cases may blur desired signal. Military grade RDX, C4 and especially Semtex have very strong luminescence that do not allow detect these explosives, even using gated deep UV excited Raman scattering with nanoseconds pulse durations. We found that ultra fast gated Raman spectroscopy may resolve this problem. Using excitation source with 50 ps pulse duration (532 nm) and gating with 500 ps, we have been able, for example, to detect characteristic Raman lines of RDX in Semtex, which were not seen using gate of 10 ns because of strong Semtex luminescence with decay time of 5–6 ns.

Such approach enables to detect effectively luminescence signals with decay time longer than 10 ns. In such case the Raman/luminescence ratio is one order of magnitude higher with 0.5 ns gate compared to 5 ns gate. This advantage becomes less effective for luminescence signals with decay time of 1 ns and less, where gate of 0.5 ns enables only 2–3 times improvement in comparison with 5 ns gate. Fig. 6 summarizes these data.

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