Nonlinear terahertz signal generation

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Material-specific spectral signatures are produced in a new methodology that enables simpler standoff detection.

Terahertz (THz) spectroscopy can be used to probe the low-energy modes of molecules and longer-range intramolecular modes, and thus yield a set of molecular fingerprints for detection of explosives. A promising attribute of THz spectroscopy is the capability of penetrating and detecting non-metallic items, which is useful for detecting hidden or concealed objects. Terahertz time-domain (THz-TDS) spectroscopy is a common technique that involves a pump–probe method. This technique provides linear spectral signatures of explosives and related materials. However, the use of THz-TDS for standoff detection (where the operator is physically separated from the sample) has so far been investigated with little success.

There are several challenges associated with the use of THz spectroscopy for explosives detection. These challenges include the widths of the resonances, the sensitivity of the resonance frequencies and widths to matrix and mixture materials, interference from barrier or concealment materials (e.g., envelopes and clothing), the surface roughness of the samples, as well as water vapor or humidity in the air.

As an alternative signature-generation method, we have investigated nonlinear THz spectroscopy, for standoff detection in particular. We have also investigated this approach to try and solve some of the challenges associated with THz-TDS. Applied electromagnetic waves of moderate intensity can induce nonlinear effects. For example, frequency conversion in light scattered from energetic materials can be achieved without triggering chemical decomposition. This offers a mechanism for non-ionizing identification of explosives.

In our technique, we obtain the frequency spectrum of the far-field scattered light. We calculate this from the Fourier transform of the energetic sample’s total dipole moment second time derivative. We have used molecular dynamics (MD) simulations to compute the THz frequency conversion tensor as a function of the input and emitted frequencies. Diagonal components of the tensor correspond to Rayleigh scattering, whereas off-diagonal components correspond to Raman scattering. We have also

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simulated the simplest air-explosive slab system and computed the absorption spectra, frequency-conversion tensors, and far-field response as a function of input electromagnetic amplitude, frequency, and polarization. Depending on the magnitude of the applied field, we find that the incident pulse can simply force the molecular system to make nonlinear excursions without inducing chemical reactions or triggering decomposition that would lead to deflagration and detonation.

As part of our study, we investigated two representative energetic materials—pentaerythritol tetranitrate (PETN) and ammonium nitrate (AN)—in a benchmark test for detection capability with the use of THz signals. Representative orthoscopic views of the materials can be seen in Figure 1(a) to (d). For our MD simulations we used ReaxFF (reactive force field)—a commonly used polarizable interatomic potential for energetic materials—to model the light—matter interactions in the PETN and AN, as illustrated in Figure 1(e). We note the asymmetry in the molecular structure along each crystallographic direction. With these MD simulations, we integrate the classical equations of motion, with forces that are calculated from an intrinsically anharmonic potential energy surface (which describes both the products and reactant species). Unique THz signals of interest are generated when molecules (and their associated dipole moments) are forced to oscillate far from their equilibrium positions on this potential energy surface. To achieve this generation of signals, we use Gaussian-shaped light pulses with variable carrier frequencies. The dipole accelerations thus undergo Fourier transformation, which yields the full frequency response to the particular THz pulse. Each carrier frequency provides a unique output signal (a row in the frequency conversion tensor). Our simulations are relatively cheap to perform and it is therefore possible to study several input light pulses.

By comparing the collected conversion tensors, we can identify which THz frequencies may be used to differentiate between the two molecular crystals (i.e., PETN and AN). These calculated conversion tensors are shown in Figure 2 for a THz pulse polarized along the x-direction—Figure 2(a) and (d)—and along the y-direction in Figure 2(b) and (e). A total emission for all the polarization directions is shown in Figure 2(c) and (f). The color in Figure 2 corresponds to the strength of the emitted signal with respect to the amount of energy that is absorbed during the pulse duration. As expected, we find that the Rayleigh emission is the strongest signal for both materials. To our surprise, however, we clearly see the third-harmonic emission, but only for a handful of carrier frequencies. In addition, we observe Raman active modes near 160 and 275 cm$^{-1}$ for PETN. These strongly emitting modes can be used to help fingerprint such materials in the THz domain.

In summary, we have developed a nonlinear signal-generation process that produces spectral signatures for standoff detection. Although our predictions are limited, in a sense, to the choice of the interatomic potential used, our method of

\begin{figure}[h]
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\caption{(Left) Average emission signals for output polarizations of impulses applied in the [100] direction for PETN (A) and AN (D). (Middle) Average emission signals of field pulses in the orthogonal [010] direction for PETN (B) and AN (E). (Right) Total emission signals for all absorption and exit polarizations for PETN (C) and AN (F).}
\end{figure}
generating material-specific, nonlinear THz emission (and the simulation geometries used) is universal. This benefit is particularly intriguing because the cost of these simulations will diminish with time as more powerful computers are made available. A systematic prediction of these THz fingerprints is therefore not beyond reach. We emphasize the importance of these results because they will be within the realm of experimental validation when new THz sources are created. Our nonlinear THz signal-generation process also enables a simpler standoff detection methodology than for current THz methods. We are now working to experimentally confirm these predictions and to develop the method for potential field use.

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