

THz-Raman Spectroscopy for Explosives, Chemical and Biological Detection

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ABSTRACT

Raman and Terahertz spectroscopy are both widely used for their ability to safely and remotely identify unknown materials. Each approach has its advantages and disadvantages. Traditional Raman spectroscopy typically measures molecular energy transitions in the 200-5000 cm^{-1} region corresponding to sub-molecular stretching or bending transitions, while Terahertz spectroscopy measures molecular energy transitions in the 1-200 cm^{-1} region (30GHz - 6THz) that correspond to low energy rotational modes or vibrational modes of the entire molecule.

Many difficult to detect explosives and other hazardous chemicals are known to have multiple relatively strong transitions in this “Terahertz” (<200 cm^{-1} , <6THz) regime, suggesting this method as a powerful complementary approach for identification. However, THz signal generation is often expensive, many THz spectroscopy systems are limited to just a few THz range, and strong water absorption bands in this region can act to mask certain transitions if great care isn't taken during sample preparation. Alternatively, low-frequency or “THz-Raman” spectroscopy, which covers the ~5 cm^{-1} to 200 cm^{-1} (150GHz - 6 THz) regions and beyond, offers a powerful, compact and economical alternative to probe these low energy transitions.

We present results from a new approach for extending the range of Raman spectroscopy into the Terahertz regime using an ultra-narrow-band volume holographic grating (VHG) based notch filter system. An integrated, compact Raman system is demonstrated utilizing a single stage spectrometer to show both Stokes and anti-Stokes measurements down to <10 cm^{-1} on traditionally difficult to detect explosives, as well as other chemical and biological samples.

Keywords: Raman, Low-frequency Raman, THz spectroscopy, Polymorph Identification, Explosives Detection, Chemical Identification, Forensics, Volume Holographic Notch Filters

1. INTRODUCTION

Spectroscopic analysis of the molecular and intermolecular structure of a substance is of increasing importance for many applications, since these spectra can reveal unique information about the physical properties and behavior of an element or compound. Consider carbon, which can take the form of graphite, diamond, graphene, “Buckyball” or nanotube, among others, all of which behave quite differently. Such substances are known generally as polymorphs (or allotropes in the case of a single element) and their identification is critical in many applications, including formulation and analysis of pharmaceuticals, chemicals and polymers. Structural information about the entire molecule and its interaction with surrounding molecules can improve the sensitivity and accuracy of explosives detection, while revealing important clues about preparatory methods, manufacture techniques, or sources of origin during forensic analysis. However, getting access to molecular structural information via spectroscopy has typically been either difficult, expensive, and/or tethered to the laboratory.

Raman spectroscopy is a scattering technique that has been widely adopted as an economical and effective means of optically sensing and analyzing the chemical composition (or “fingerprint”) of a substance. The corresponding “fingerprint region” of the Raman spectrum ranges from about 200 cm^{-1} to 2,000+ cm^{-1} . However, it has long been known that “low-frequency” Raman (defined as a Raman shift of ~5 cm^{-1} to 200 cm^{-1} , or 150GHz-6THz in the electromagnetic spectrum) can yield rich information regarding the vibrational energies associated with molecular and intermolecular structures and features¹. Unfortunately, most Raman systems – though widely adopted in a broad range of laboratory and field uses – remain limited to capturing only chemical fingerprint information, primarily due to the use of edge or notch filters that also remove most, if not all of these low frequency signals, including the entire anti-Stokes region. Some

higher-end Raman systems can be configured to access the low-frequency regime, but these are mostly large and expensive laboratory instruments, and often have very limited throughput. Thus, most Raman systems leave out a vast region of important spectral information that could be used to improve sensitivity and accuracy, as well as yield insights into the structure of the materials they measure.

Alternatively, terahertz (THz) spectroscopy is an absorption technique that can be used to measure these structural modes by directly emitting radiation in the 300GHz to 6THz frequency range (10cm^{-1} to 200cm^{-1} region), and detecting the corresponding absorption spectrum. THz systems have the additional benefit of being able to more deeply penetrate a material or “see through” external layers (e.g. clothes, packaging, etc.) to capture the signal. Unfortunately, these systems rely on bulky and expensive laser sources and detectors with a limited dynamic range. These limitations have constrained the potential sensitivity, resolution, and/or economics of using this technique. Plus, their fairly narrow spectral range (only up to 3 to 6 THz) limits their ability to do complete and reliable chemical identification for many materials.

“THz-Raman” refers to a new technique that extends the range of Raman spectroscopy from the fingerprint region into the terahertz regime, adding important insight to molecular and intermolecular structure to the data about chemical composition (Figure 1). It has been shown that low-frequency Raman/THz-regime spectra can be used to greatly improve differentiation and analysis of both the structure and chemistry of materials, thereby improving accuracy, sensitivity, and scientific or forensic analysis². Detection, identification, and forensic analysis of many substances, including explosives, drugs, pharmaceuticals, biological tissues, polymers, and hazardous materials, can all benefit from this extended spectral information.

We report here on a new, compact, efficient and affordable way to *simultaneously* deliver both chemical and structural analysis to a wide range of Chemical, Biological, Radiological, Nuclear, and Explosives (CBRNE) materials. An integrated, compact THz-Raman system is demonstrated utilizing a single stage spectrometer to show both Stokes and anti-Stokes measurements down to $<10\text{cm}^{-1}$ on a wide variety of materials. These all are shown to exhibit characteristically different low frequency/THz peaks that can be exploited for chemical analysis, identification, monitoring, forensics, and contamination applications.

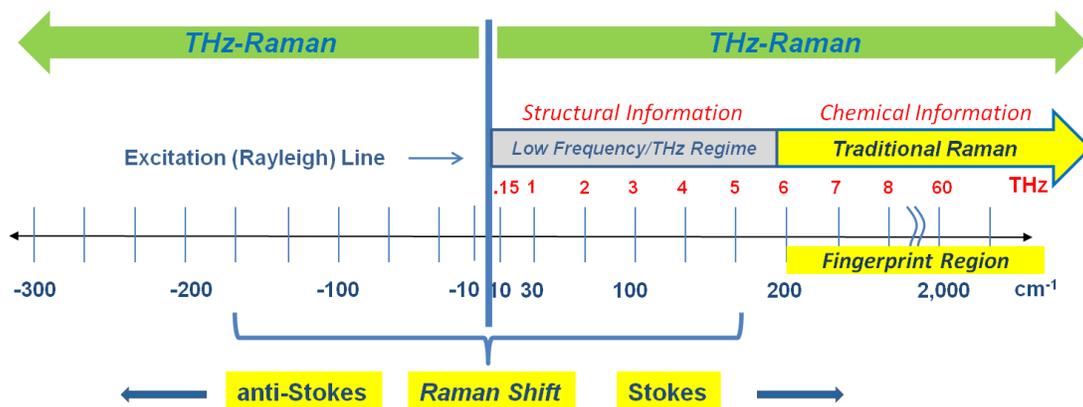


Figure 1. THz-Raman combines the entire low-frequency/THz regime, the traditional fingerprint region, and anti-Stokes spectral ranges, yielding additional structural information and improving chemical detection sensitivity.

2. THZ-RAMAN SPECTROSCOPY

As mentioned above, “THz-Raman” refers to the simultaneous capture of both Stokes and anti-Stokes shifts in the ultra-low frequency region (from $\pm 5\text{cm}^{-1}$ to 200cm^{-1}). (THz-Raman systems also capture the “fingerprint” region from 200cm^{-1} to $>2,000\text{cm}^{-1}$). The low-frequency regions (for both Stokes and anti-Stokes shifts) are particularly difficult to resolve, as they reside extremely close to the excitation wavelength. Most of the collected light is elastically scattered with no corresponding wavelength shift, producing a strong Rayleigh scattered line at the excitation wavelength. Only about 1 in

approximately every 10^8 photons exhibit a shift in energy due to interaction with the material so to observe any Raman signals, the Rayleigh scattered light needs to be attenuated by at least OD 8. Most traditional Raman systems currently utilize thin-film edge filters, which end up completely removing both the Rayleigh excitation *and* the entire anti-Stokes region, cutting off all signals below about 200cm^{-1} from the Rayleigh line. And most commercial notch filters, which will allow some of the anti-Stokes signal to come through, will still block all signals below about $\pm 150\text{cm}^{-1}$ or more. Getting *both* high Rayleigh attenuation *and* resolution close to the excitation line has only been possible by using a multi-stage spectrometer system, which (1) is large, bulky, and expensive, (2) requires very precise alignment and set-up that makes it difficult to operate and (3) significantly reduces the overall throughput of the already weak Raman signal.

Recent advances in volume holographic grating (VHG) filter technology^{3,4,5} have enabled the manufacture of exceptionally narrow bandwidth notch filters with very high throughput (Figure 2). Each VHG filter has a notch profile that is designed to diffract only one specific wavelength matching the laser and transmit all other wavelengths. The ultra-narrow transition bandwidth of these filters enables extremely high attenuation of the laser wavelength ($>OD\ 4$ for each filter), while maintaining very high transmission of nearby Raman signals beyond $\sim 5\text{cm}^{-1}$ (Figure 2).

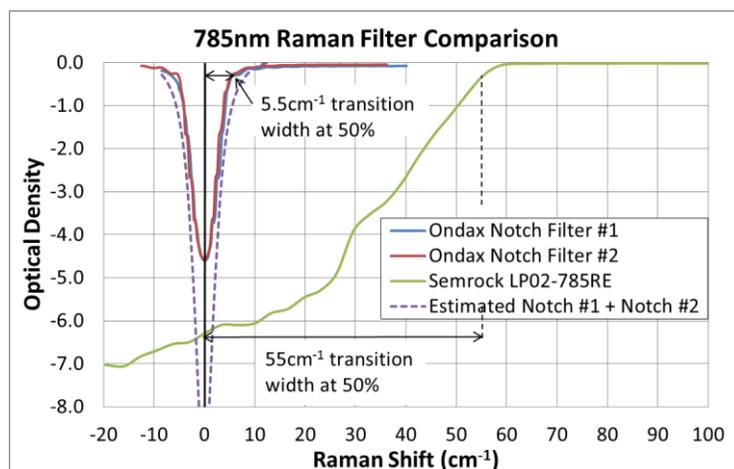


Figure 2. A VHG notch filter has an approximately 10x narrower transition width than a thin-film edge filter, enabling very high Rayleigh attenuation without blocking low-frequency or anti-Stokes Raman signals.

This has led to systems that are capable of rapid acquisition of high-quality, ultra-low frequency Raman spectra in the $5\text{--}200\text{cm}^{-1}$ region. These systems are based on a stable wavelength laser source, a series of VHG filters and a single stage spectrograph (Figure 3). This combination of strong Rayleigh attenuation and high broadband transmission enable the system to simultaneously capture both the intense low-frequency Stokes and anti-Stokes Raman bands and the “fingerprint region” transitions, greatly simplifying the overall system and reducing size and cost, while improving the sensitivity and reliability of using Raman for chemical identification and other applications.

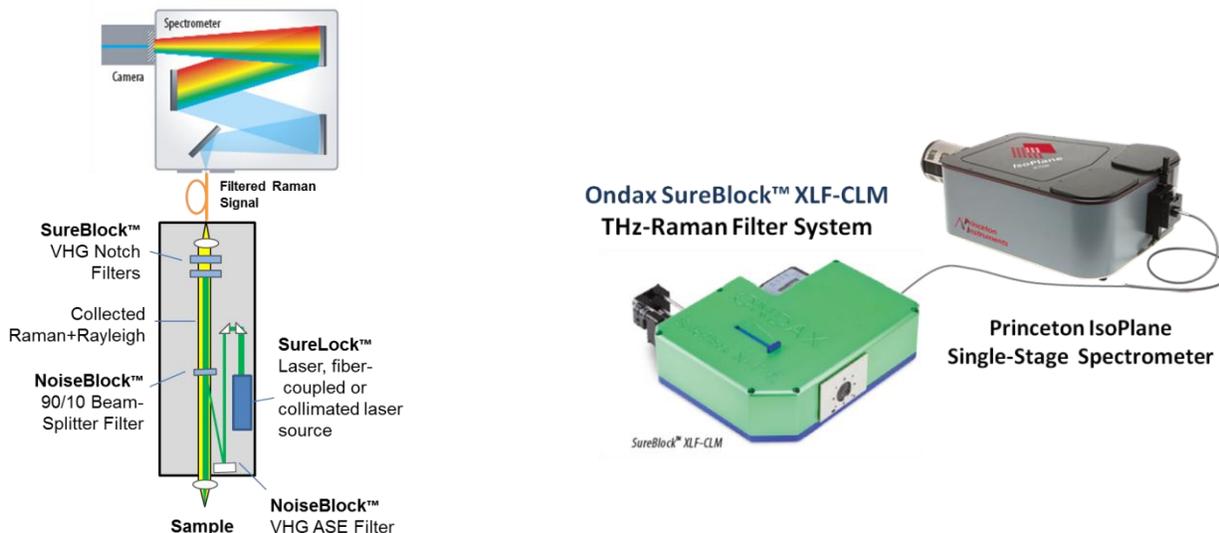


Figure 3. A THz-Raman system is comprised of a compact, confocal optical system that includes a single-frequency/wavelength stabilized laser source, ASE filters, a high-throughput beamsplitter, sample collection optics, and multiple cascaded VHG notch filters. The filtered Raman signal is fed into a single-stage spectrometer for readout. (A schematic of the system is depicted on the left, and a photograph of system is to the right).

3. THZ-RAMAN SYSTEM ARCHITECTURE

Experimental measurements were taken with the confocal THz-Raman system shown in Figure 3. The system was comprised of a single mode 785nm wavelength stabilized diode laser (SureLock™ LM series, Ondax, Inc.) and a series of ultra-narrowband VHG filters that were spectrally matched to the laser output wavelength. Two VHG ASE suppression filters (NoiseBlock™, Ondax, Inc.) were used to remove amplified spontaneous emission (ASE) from the laser. (ASE is often on the same order of magnitude or larger than the Raman signals, which can reduce SNR or swamp low frequency signals if it is not attenuated). A dichroic 90/10 VHG beamsplitter filter (NoiseBlock™, Ondax, Inc.) redirects the laser towards the sample, where a 10X objective lens focuses the laser onto the sample and collects the back-scattered light. The 90/10 beamsplitter then reflects 90% of the Rayleigh scatter back towards the laser while transmitting all of the Raman shifted signals. (The dichroic nature of the 90/10 beamsplitter results in an almost 4X improvement in collected Raman signal compared to a broadband 50/50 beamsplitter). Two ultra-narrowband VHG notch filters (SureBlock™, Ondax, Inc.), each having optical density >4.0, then further attenuate the collected Rayleigh scattered light while transmitting the Raman signals with an estimated system transmission efficiency of >80%. The filtered signal was focused into a 25µm core diameter, 0.1NA step index fiber (HPSC25, ThorLabs) and connected to a high-resolution, high-throughput single stage spectrometer (IsoPlane series, Princeton Instruments) 0.3m imaging spectrometer. It was equipped with a 1200 lines/mm grating and a 1340x400 imaging array (Pixis model 400BR with eXcelon, Princeton Instruments) with 20 x 20 µm pixel size and 98% peak quantum efficiency to ensure maximum signal collection and ~1.25cm⁻¹ resolution; appropriately matched for analysis of the 5-200cm⁻¹ frequency range. (Note: the range, resolution, and noise level of the overall system is ultimately determined by the specifications of the spectrometer, including grating, detector, and size).

The entire laser and filter assembly is extremely compact – approximately the size of a ream of notebook paper – and the fiber coupling allows for remote location of the spectrometer (we have demonstrated at least 15m separation without signal loss or interference from fluorescence). The low power requirements of the laser also enable the filter system to be battery operated if needed. Finally, it is important to note that the ultra-narrow bandwidth of the VHG filters (<0.1nm) require the use of either a wavelength-stabilized diode laser, narrow-band DPSS laser, or gas laser. Normal diode lasers tend to mode hop, shifting the laser wavelength outside the blocking range of the filters and resulting in either reduced Rayleigh suppression or a complete loss of signal in the described configuration.

4. EXPERIMENTAL RESULTS

4.1 Polymorph Identification

As noted above, one key application of chemical structural analysis is the identification of polymorphs (defined as solid materials that exist in more than one form or crystal structure). For example, in the pharmaceutical industry many compounds exhibit polymorphism, and each form may exhibit significantly different therapeutic efficacy and bio-availability. Therefore only one form of the compound is normally approved for medical use. In the petrochemical industry, the form of the polymer chain can strongly affect the physical properties of the material. Some explosives exhibit polymorphism as well, so it is often critical that the polymorphic form can be clearly and reliably identified during formulation, quality assurance, or analysis.

One good example is Carbamazepine (CBZ), an anticonvulsant and mood-stabilizing drug commonly prescribed for treatment of epilepsy and bipolar disorder. It has four different polymorphic forms that have been well characterized in the literature^{6,7,8,9,10} with form 3 being the active pharmaceutical ingredient (API) approved for medical use. We obtained pure samples of form 2 and form 3 as well as the hydrated form, and measured the entire Raman spectra (Figures 4a and 4b). As expected, since the molecules have the same chemical composition, the fingerprint region signals are quite similar. However, the different structural forms of the polymorphs are clearly evident in the low frequency/THz regime, and are actually much stronger than those in the fingerprint region. Figure 4b shows expanded details of the various polymorphs and Hydrate in this region. Note that the anti-Stokes signals (which are symmetrical to the Stokes signals but lower in intensity) can also be used to clearly validate the low-frequency measurements, as well as providing additional information that can be used to boost the detection capabilities of the system.

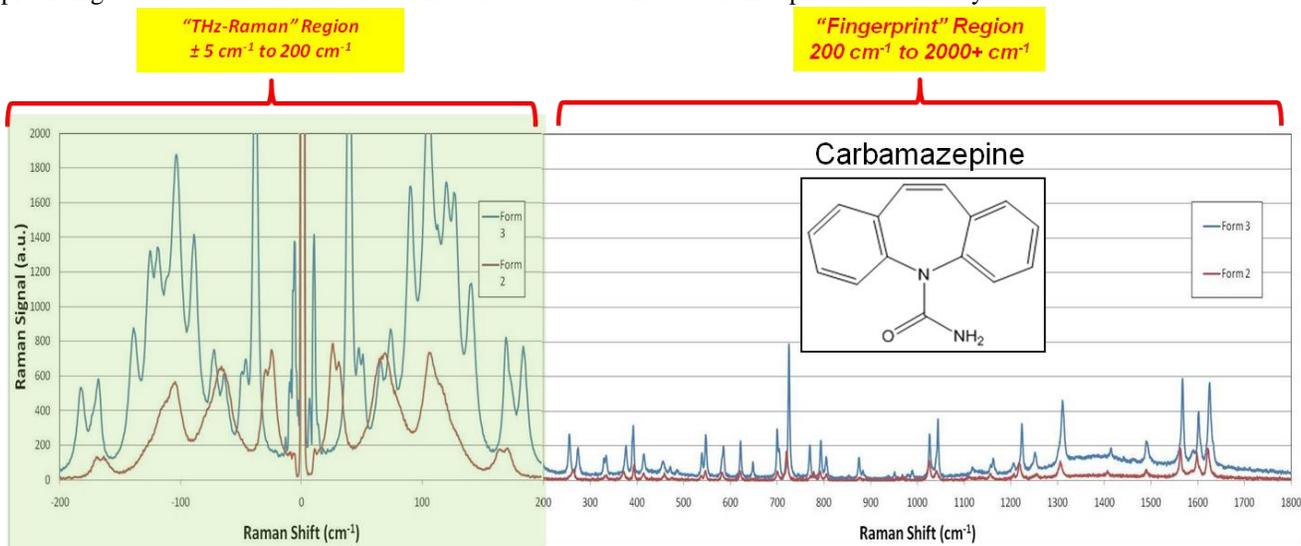


Figure 4a. The THz-Raman spectra of two polymorphs of CBZ, form 2 (red) and form 3 (blue with larger peaks), showing extremely strong and differentiated low-frequency signals when compared to the fingerprint region.

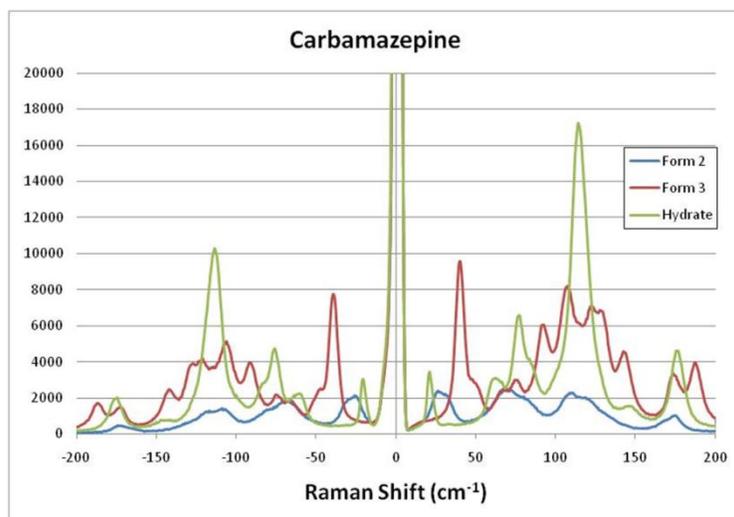


Figure 4b. A close-up of the low-frequency Stokes and anti-Stokes spectra of Form 2, Form 3 and the Hydrate form of CBZ.

4.2 Explosives and Drug Detection

Raman has been increasingly used for identification of explosives and illicit drugs in the security and defense field¹¹. Portable, hand-held systems have now made this a ubiquitous tool for first-responders and military personnel around the world. However, there still remain some limitations to sensitivity and/or occasional false positives. THz-Raman offers the promise of improving overall sensitivity and also providing insight into the structure that could yield forensically valuable information on the preparatory methods or sources of origin of the substances.

Ammonium Nitrate (NH₄NO₃) is a common material used in homemade explosives (HME), specifically the Oklahoma City bombing in 1995 and also cited as the source material in the West, Texas blast in April, 2013. It also exists in five stable polymorphic forms^{12,13}. Figure 5 shows the Raman spectra of Ammonium Nitrate powder (99.5%, Sigma Aldrich). Once again, notice the very strong, broad signals in the low frequency/THz-Raman region. Importantly, these signals will be even more pronounced (compared to the sharp spectra at higher frequencies) when observed with a lower-resolution system, since the signal is proportional to the total integrated area under the spectrum. Sharp, high peaks represent only a relatively small amount of photons, and while easily detectable in a high-resolution scan, they can nearly disappear when measured with a lower-resolution system, such as those commonly used in handheld systems. The broad peaks in the low frequencies will remain apparent under all conditions.

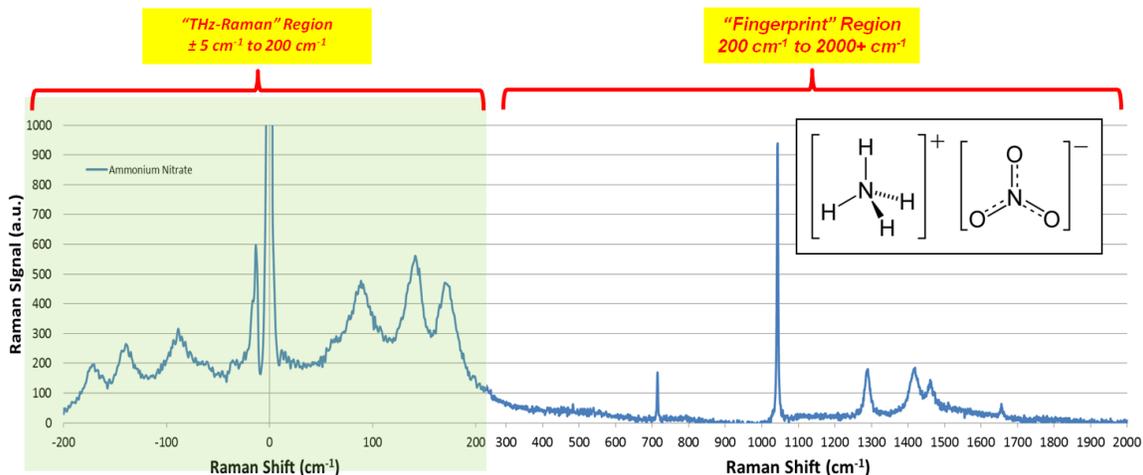


Figure 5. Ammonium Nitrate. The strong, broad peaks in the low-frequency/THz-Raman significantly boost overall signal and will remain observable even with a low-resolution scan. (Taken at 532nm).

HMTD (Hexamethylene Triperoxide Diamine) is another HME that has been cited in many terrorist IED and suicide bombing attacks. Figure 6 shows the clear, strong signals in the THz-Raman region for HMTD¹³, which can significantly boost sensitivity. It is also possible that a “forensic signature” associated with the preparatory method or source of origin (including identification of additional ingredients and contaminants), could be captured by the information in this region.

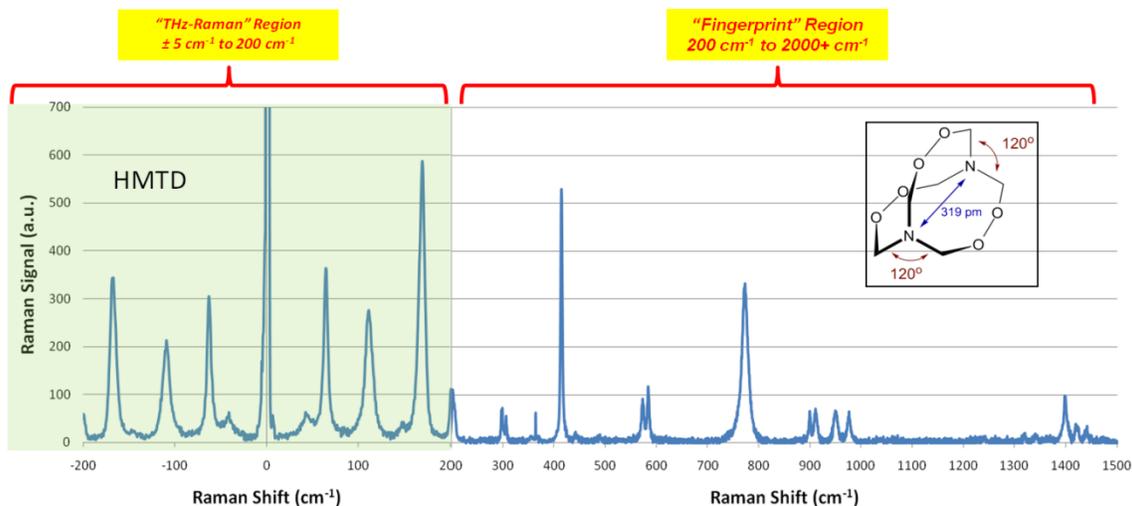


Figure 6. HMTD¹⁴ also shows strong peaks in the low-frequency/THz-Raman region. (Taken at 785nm).

5. CONCLUSIONS

The addition of low-frequency/THz-Raman signals to traditional Raman spectra can boost the sensitivity and significantly enhance the forensic value of Raman spectroscopy for a wide range of applications, including polymorph identification; explosives trace detection, polymer and industrial chemical development and manufacture, material science, and forensics analysis. Given the number of CBRNE materials that can exist in multiple stable polymorphic forms, accurate detection and identification of these different polymorphs can yield a tremendous amount of information about the origin and processing of these materials. VHG-enabled THz-Raman systems are compact, efficient, and add a wealth of information regarding the physical structure of the molecule in addition to chemical composition. These new platforms greatly simplify the use and lower the cost of exploiting the many benefits of low-frequency Raman spectroscopy.

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