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Spatially resolved multimodal vibrational spectroscopy under high pressures

Sabine N. Neal, Dario Stacchiola, and Samuel A. Tenney

In this perspective, we discuss the potential impact on in-situ studies under controlled environments of a novel multimodal spectroscopic technique, optical photothermal infrared + Raman spectroscopy, which enables the simultaneous collection of infrared and Raman scattering spectra, along with hyperspectral imaging and chemical imaging with wavelength-independent sub-500 nm spatial resolution. A brief review of the current literature regarding the O-PTIR technique is presented along with recent work from our own lab on determining the crystallinity of soft and inorganic materials. The results highlight the possibility of resolving differences in the crystallinity of soft materials associated with changes in material processing. We also demonstrate the first reported use of a diamond anvil cell with simultaneous infrared and Raman measurements that showcases, using a high energy material as an example, the potential use of O-PTIR spectroscopy in diamond anvil cell techniques.

1 Introduction

Infrared and Raman spectroscopy are two complementary spectroscopic techniques that have the potential to examine a variety of material properties from qualitative and quantitative studies of molecules to information regarding atoms and their bonds in a system. Though these traditional spectroscopic techniques are useful in macroscale studies, their spatial resolution when applied for microscopy is naturally inadequate for micro (IR) and sub-micron (Raman) studies, because they are diffraction limited. [1,2] One approach to overcome this limitation is to combine either IR or Raman spectroscopy with a scanning probe to operate in the near-field regime. [3]

The ability to reach beyond the traditional far-field diffraction limit was initially accomplished through the use of near-field aperture-based microscopy. Here, the spatial resolution is not determined by the wavelength of the light, but rather the aperture size. [2–5] However, the sensitivity of aperture-based techniques is limited by the collection efficiency due to aperture transmission scaling. [5] Recently, technological advances in near-field spectroscopy (tip-based) have enabled a spatial resolution near 10 nm, exceeding the conventional (far-field) spectroscopy limit of $\approx$ 10 microns, and therefore overcoming the diffraction limit needed to study systems at the

at the nanoscale. [8] Other near-field microscopy work has enabled the hyperspectral imaging of single walked carbon nanotubes. [9] However, tip-based work is not always conducive to the sample, and therefore an alternative spatially resolved technique is necessary. Optical-photothermal infrared (O-PTIR) spectroscopy offers an alternative path to combine sub-micron spatial resolution for IR microscopy without the need of coupling to a nearby nano-structure.

Optical photothermal infrared and Raman spectroscopy bridges the gap between traditional infrared (far-field) spectroscopy and tip-based nano-IR spectroscopy, by providing a spatially resolved, and a non-contact method to probe infrared and Raman properties simultaneously, showing a broad range of applications in the areas of chemistry, biological and material sciences. [11-47] A schematic of this process (adapted from literature) is shown in Figure 1(a). [12,16,21,29,48,49] When a wavelength is reached that excites a vibration in the sample, absorption occurs, therefore yielding a photothermal response and subsequent expansion in the material. A 532 nm visible laser focused on the same area, measures this photothermal response via the scattered light, which is directly proportional to the coefficient of thermal expansion for the sample at said wavenumber. [11,12] As the infrared light is pulsed, the change in Raman shifted light can be detected, therefore yielding simultaneous infrared and Raman scattering responses (Fig. 1), at the same point, with the same spatial resolution. [49] There are a variety of other benefits of this O-PTIR and Raman combination in addition to the high spatial resolution ($\approx$ 500 nm). Among the advantages are, ease of sample preparation, and the ability to operate in either reflection or transmission mode. When operating in reflection mode the need for thin, cross-sectioned, or microtomed samples is eliminated. The O-PTIR method also overcomes the limited pathlengths of conventional IR spectroscopy in water. [25] Though the O-PTIR technique is relatively new, it has proven useful in the studies of microplastics, [12,18-20,41-43] polymer systems, [16,17] organic [18–21] and biological materials, [22–30,34-38] pharmaceuticals, [31,32] and even explosives. [33] Perhaps, most profoundly has been the influence of this spatially resolved system in the field of biology, where it has found success in everything from evaluating the biochemical structure of bone tissue [28] to studies of Alzheimer's Disease (AD), and even exploration at the single cell. [23,25,26,28] For example, through the use of the O-PTIR system, it has been shown that the structural polymorphism of amyloid proteins may actually trigger the progression of Alzheimer's Disease and that in AD-like neurons, iron
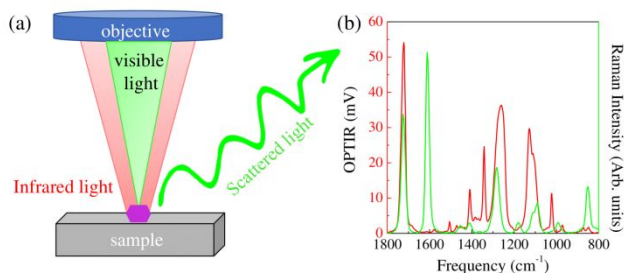

Fig. 1 (a) displays a schematic of O-PTIR spectroscopy (adapted from literature) showing both infrared and visible light (532 nm) focused onto the sample surface by means of a 40X objective. Panel 1(b) Displays the O-PTIR (red) and Raman scattering (green) spectra that were gathered simultaneously on polyethylene terephthalate sample.

nanoscale. [1,2,5–9] For example, lens-free tip-enhanced Raman, with 1 nm spatial resolution, has been demonstrated to be a highly efficient spectroscopic technique, paving the way for the ability to provide both complementary, as well as spatially correlated information of a system

clusters co-localize with β sheet structures and lead to lipid oxidation. [27,29] Fluorescence guided O-PTIR has recently enabled analysis of such amyloid structures at the subcellular level. [38] Gustavsson et al. provided proof of concept for single cell imaging in

their studies of AD.[27] This became essential for exploring the uptake of isotope-labeled compounds by *E. coli*,[26] exploring antimicrobial resistance at the cellular level via isotope labeling,[34] revealing the complete vibrational profile of living pancreatic and breast cancer cells in an aqueous environment,[25] determining the spectroscopic differences in the outer and center parts of healthy cells (biochemical variability),[23] and has also demonstrated the effectiveness of IR spectroscopy as a tool in clinical application pathology.[28]

Aside from advancement in the field of biology, O-PTIR has found use in the qualitative analysis and detection of microplastics, where microplastics were found in sediment on the ocean floor, in aquatic organisms, corn flour, in wastewater at treatment plants, and intermingled with biological matrices.[13-15,39,41] Other environmental concerns that have been explored involve the occurrence of antibiotics in the water supply, along with the adsorption of antibiotics on different sized particles,[50] as well as in atmospheric chemistry, revealing the presence of both inorganic and organic modes in sub- and super-micrometer atmospheric particles.[21] Recent work has made use of this system to explore the solid-electrolyte formations in batteries,[46] analyzing antifouling coatings for industrial and medical useage,[47] and enabled the study of the release of metallic nanoparticles from silicon baby products.[43] Another area of interest that has shown potential for growth because of this technique has been in the analysis of historical art and decorative items, yielding information regarding the complete chemical characterization of paint and materials in a non-invasive manner, being of utmost importance in the field of art conservation.[18–20] Furthermore, O-PTIR spectroscopy has made it possible to map the drug distribution in aerosol particles, showing the location of the drugs of interest is directly dependent on the formulation type.[31] This system also has potential as a forensics tool,[44] with the ability to detect highly explosive materials on finger prints.[33] The current literature shows just how multifaceted and advantageous the O-PTIR system has been to many scientific problems. In particular, recent progress has shown surface-enhanced Raman scattering (SERS) and surface enhanced infrared absorption spectroscopy (SEIRA) capabilities with single molecule sensitivity.[42] Further versatility may be offered by extending the capabilities of the technique via the addition of a specialized cell that enables the study of samples under controlled environmental conditions or even extreme pressures by coupling diamond anvil cells.

Pressure is a unique tuning parameter in that it directly changes bond lengths and angles, which in turn can alter the intrinsic properties of a material leading to structural transitions,[17,51] changes in polarization,[52] spin crossovers,[53] and even metallization.[51,54,55] The coupling of pressure measurements with the O-PTIR + Raman system is an interesting and unexplored avenue, allowing for spatially resolved simultaneous IR and Raman studies. These correlated measurements will ensure the same conditions for both measurements including applied pressure, the same crystal, and the exact same measurement area, something that has not been necessarily achievable to date.

In this work we present early work on O-PTIR + Raman spectroscopy and its application in examining a pressure-sensitive organic and inorganic system, revealing that the manufacturing process not only leaves striations on the sample surface, but that these striations in fact are due to variation in applied pressure by the process, leading to spectroscopic changes on the sample surface, namely a change in crystallinity. We also show preliminary pressure results obtained from the O-PTIR spectrometer and diamond anvil cell techniques. The Raman spectra presented matches with prior literature results on this crystalline system, as well as offering infrared data, which has not yet been studied. This paves the way for future pressure studies with the combined O-PTIR and Raman spectrometer.

2   Results and Discussion

Figure 2 displays data collected by the mIRage + Raman microscope on the pressure-sensitive semi-crystalline organic material composed of 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX), 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20), and a fluorinated organic binder. Figure 2 (a) and (b) display the infrared and Raman hyperspectral response, respectively, taken at 1300 cm^{-1}. The inset in Panel(a) shows the optical image (40x) of the pellet surface with noticeable striations due to the variation of
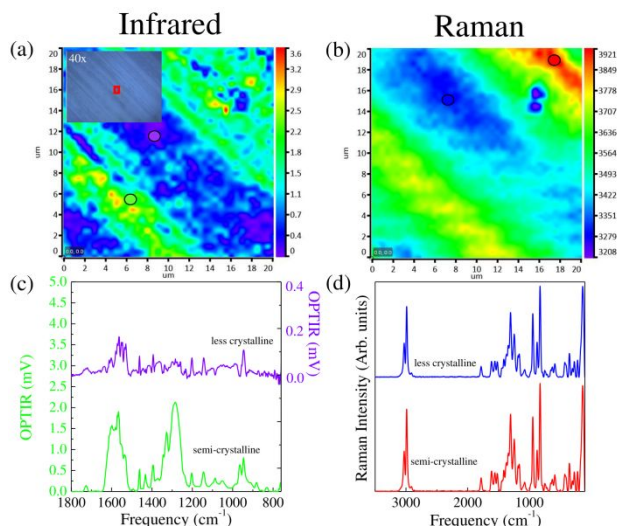

Fig. 2 Panels (a and b) display the infrared and Raman hyperspectral images, respectively. The hyperspectral IR and Raman slices were taken at 1300 cm^{-1}. The inset in (a) is the optical image (40x magnification) of a pressure-sensitive organic material, with the box defining the area in which chemical mapping [Panels (a, b)] was performed. Panels (c) and (d) show the correlating infrared and Raman spectra extracted from the red box in the inset in Panel (a).

pressure applied by the pellet press. Here, the red box defines the area in which hyperspectral O-PTIR [Fig. 2(a)] and Raman [Fig. 2(b)] maps were taken. Here, the striations are also visible, illustrating the chemical difference between areas exposed to lower pressure (red/yellow/green) and greater pressure (dark blue/violet) due to the manufacturing process. From this same area, simultaneous infrared and Raman scattering studies were performed correlating to the spectra in Panel (c) and Panel (d), respectively. Note the sharpness of the features in the green infrared spectra [Fig. 2(c)] indicate that the areas exposed to lower pressure (red/green/yellow) remain in a semi-crystalline state, whereas spectra that is extracted from areas exposed to higher pressure (violet spectra) from the manufacturing process tend to be less sharp, showing lower intensity (dark blue/violet in hyperspectral image), and are therefore less crystalline in nature. Interestingly, the Raman data [Fig. 2(d)] tends to show almost no spectral differentiation between the areas of less crystallinity (blue) and the areas that are of higher crystallinity (red), affirming that it is in fact essential to perform both O-PTIR and Raman spectroscopy to fully explore crystallinity in these organic materials. Experimental parameters may be found in the Supporting Information.

Preliminary pressure studies have been completed using traditional diamond anvil cell techniques. Figure 3 (a) shows a picture and schematic of the diamond anvil cell, while Figure 3 (b) and (c) display the O-PTIR and Raman pressures studies, taken simultaneously, of CL-20, a well-known high energy material. Note, the overall blueshift of features present in both the O-PTIR and Raman spectra, as pressure increases from 0 to .11 GPa, followed by a redshift when pressure is released. Also, notice evidence of clear structural changes, most evident in Panel (b), with an increase in pressure. The Raman studies, however,

in this instance show no clear spectral changes (aside from slight frequency shifts), showing the importance of obtaining both infrared and Raman spectra when investigating phase or structural changes. A complete pressure study, along with a detailed discussion is shown in the Supporting Information.
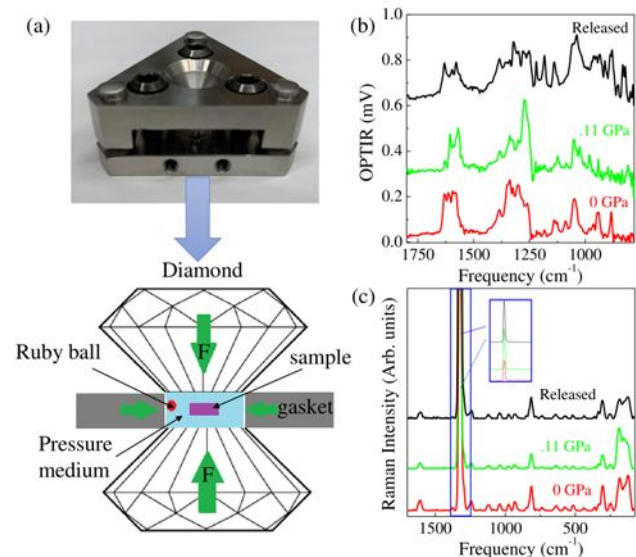

Fig. 3 Panel (a) depicts a diamond anvil cell (upper panel) and a close-up schematic of the diamonds and sample. Panels (b) and (c) show the O-PTIR and Raman pressures studies of CL-20, a high energy material.

4   Conclusions

Sub-micron multimodal vibrational spectroscopy is a promising and expanding technique in the scientific community with a large range of applications from biologics to organic and inorganic materials. Characterizing chemical systems with only IR or Raman separately can provide valuable information but may paint an incomplete picture as the conditions may not be exactly the same, not to mention the difference in spatial resolution. Only by combining simultaneous IR and Raman measurements at the same spot, the same time and with the same spatial resolution can a complete picture of the system in either static or dynamic conditions be determined. In this work we've highlighted the potential of the combined O-PTIR and Raman system towards analyzing the crystalline structure of both organic and inorganic samples either after the manufacturing process or in-situ through the use of a custom diamond anvil cell. The technique was able to clearly identify microscale heterogeneity in the organic sample as a result of the pellet pressing process. This paper also presents the first reported high pressure study of the highly energetic system, CL-20, in a diamond anvil cell with simultaneous IR and Raman measurements on the same spot with sub-500 nm spatial resolution.

The preliminary pressure findings from this paper allow for further proposed work with diamond anvil cell techniques. This includes pressure studies as a function of temperature. Aside from these, another interesting area of future work involves the addition of an environmental control chamber, which allows for the exploration of effects of external variants, such as temperature, on a sample. Additional multimodal capabilities such as fluorescence have likewise been added to existing O-PTIR systems.

Author Contributions

The authors confirm contribution to the paper as follows: O-PTIR and Raman measurements were conducted by SNN with data analyzed by SNN and SAT. All authors discussed data. The manuscript was written by SNN, DS, and ST. All authors read and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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