

The Incorporation of Multi-dimensional Spectroscopic Techniques in the Future of Planetary Science. C. J. Bennett¹, ¹Department of Physics, University of Central Florida, Orlando FL 32816 (e-mail: christopher.bennett@ucf.edu)

Introduction: A high-priority for NASA as outlined in the decadal Visions and Voyages survey is the development of versatile future instrumentation that is capable of meeting the needs of future proposed missions [1]. However, the majority of traditional spectroscopy techniques (e.g., UV-VIS, Fluorescence, Infrared, or Raman) currently utilized on modern spacecraft (e.g., Mars 2020 [2]), typically take spectra in a single dimension. As such, these techniques become severely limited in real-world situations where complex mixtures of minerals or chemical species are present at the same time and can give rise to absorptions/transmissions within the same bandwidth resulting in what is known as spectral confusion, and therefore it is impossible to identify unambiguously materials that are being studied. Typically laboratory measurements of analog samples are prepared to suggest likely candidates that resemble the original spectra. Though perhaps the idea of the StarTrek Tricorder seems a little bit far-fetched for the moment, there do currently exist multi-dimensional spectroscopy techniques capable of essentially asking the question: “Are any molecules that absorb at this frequency present here?”; the response of the molecules in question can either be a simple “yes/no” or *their entire spectral signature - leading to their unambiguous characterization*. Multi-dimensional spectroscopy holds many advantages over traditional techniques and will likely be widely utilized in future planetary science missions over the next few decades. Here, we will showcase one promising example, 3D-IR Raman spectroscopy [3,4], and briefly describe how it works, as well as some of the ways this could be beneficial with the context of planetary science.

How does 3D-IR Raman work: The principle of the technique builds upon that of traditional Raman spectroscopy. Here, a visible laser is typically used which excites a molecule into a virtual state. Though the majority of laser light is simply (Rayleigh) scattered, a small percentage (ppm – ppb) return at a slightly different frequency. Normal (or Stokes) Raman spectroscopy is where a molecule is initially in its ground state and then returns to a vibrationally excited state – the returning photon is red-shifted by an amount equivalent to the vibrational quanta involved (of note, fluorescence typically competes with normal Raman). Conversely, anti-stokes Raman spectroscopy requires for the molecule to be initially in an excited state and then upon interaction with the visible laser

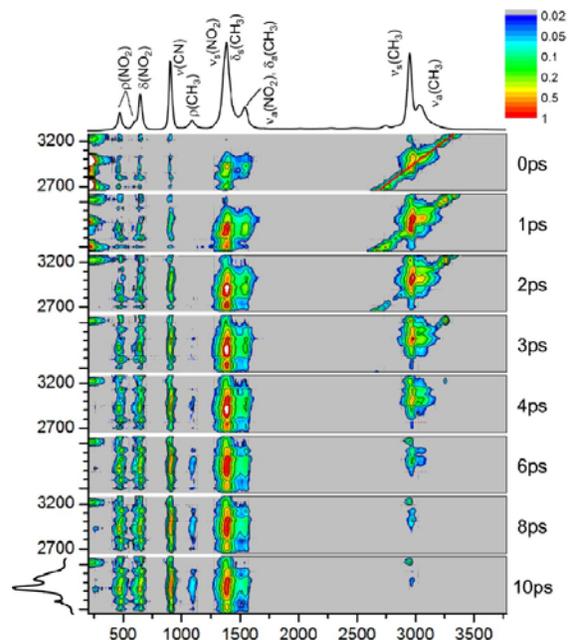


Figure 1: 3D-IR Raman spectrum of nitromethane with reference Raman (top) and IR (bottom left) spectra, taken from [4].

light it returns to a ground state, along with a corresponding blue-shifted photon (higher energy; no fluorescence competes). Because anti-stokes Raman requires populated vibrational states it is typically less commonly employed. However, modern tunable near- and mid-infrared lasers can be used to selectively ‘pump’ specific vibrational frequencies, or even overtones of fundamental frequencies and combination bands of several fundamental frequencies. The intramolecular, followed by intermolecular redistribution of vibrational states occurs in the following femto-pico-nanosecond timescales after the initial ‘pump’ excitation. However, an anti-stokes Raman ‘probe’ can be used to monitor these processes as they evolve. In addition, it is worth noting that by probing overtone or combination bands in the femto-pico second timeframes, the resulting spectra signature corresponds to the resulting population of fundamentals leading to unique unambiguous characterization [3,5]. The intra- and inter-molecular timescales provide additional information on the nature of the species being probed, and the surrounding environment, respectively [4]. Therefore, anti-stokes Raman spectra can be obtained as a function of the IR pump wavelength as a function of the temporal evolution after the initial pump. Figure

1 shows an example of a typical 3D-IR Raman spectrum of nitromethane [4].

Application to Planetary Science: This technique is currently state-of-the-art and as such, no funding towards development of this technique to planetary science has been awarded thus-far, hence the benefits of this technique that will be presented are somewhat speculative.

A 3D-IR Raman instrument could potentially answer many of the high-priority questions across the entire range of missions and cross-cutting themes noted in the decadal survey [1]. We note that this is a non-destructive technique capable of identifying trace-species unambiguously at parts per million (ppm) and is equally well-suited to probing liquids or solids, as well as minerals, resources, biomolecules (e.g., amino acids, lipids, sugars, nucleobases, etc.), volatiles, and even hypervolatile species such as O₂, N₂, and CO which may be incorporated in comets; see [6]. Therefore, such an instrument would represent an excellent choice for surveying sites for sample collection or resource utilization. In particular we note that for the proposed New Frontiers Cryogenic Cometary Sample Return (CSSR) mission, a required technology advancement stated was "developing a reliable *in situ* method of determining that the sample contains at least 20% by volume of volatile ices and some fraction of organic matter". The 3D-IR Raman technique is capable of performing this task but in addition, it could search for biomarkers *in situ* as well as determine isotopic ratios of H/D ¹³C/¹²C, ¹⁵N/¹⁴N and ¹⁸O/¹⁶O. We note that determination of these isotopic ratios (besides H/D, and some instances of ¹³C/¹²C) is typically beyond the resolution of traditional spectroscopic methods (differing by perhaps ~10 cm⁻¹), however, since the 3D-IR Raman can target highly excited hot-bands the frequencies of species become sufficiently separated (>30 cm⁻¹) that a near-IR laser can selectively excite one over the other (near-IR bandwidth ~ 25 cm⁻¹) [7]. Such additional isotopic information would be incredibly helpful in determining the origin of primitive bodies in the Solar System [8].

In addition, a high-priority for NASA over the next decades will be to search for evidence for life throughout the solar system. Therefore, it is desirable to utilize a non-destructive technique which is capable of detecting molecular species on each rung of the "life detection ladder" which includes chemical species such as amino acids, lipids, and indicators of metabolism. A commonly sought after biomarker is the detection of chirality within, for example, amino acids which is thought to be a strong indicator of life based on the "Lego Principle" [9]. The 3D-IR Raman is compatible with emerging microfluidic devices which are capable

of separating molecular species based on chirality. Alternatively, this technique could additionally take advantage of the phenomenon known as Surface Enhanced Raman Spectroscopy (SERS) or SERs tagging techniques [10,11]. Here, enhancements up to 10¹¹ or 10¹² have been demonstrated which would enable detection limits down to better than parts per quadrillion (ppq; 10⁻¹⁵). However, enhancements of a more modest 10⁶-fold enhancement are regularly achievable simply by the addition of gold/silver nanoparticles allowing for routine detection down to parts per billion (ppb) to parts per trillion (ppt) levels (10⁻⁹ to 10⁻¹²). SERs tagging has been utilized to selectively enhance species based on their chirality [12], so it is very likely such tags will be developed for amino acids in the near future. The implications of these advancements suggest that 3D-IR Raman incorporated alongside a microfluidic detection scheme and/or equipped with SERS or SERs tags would enable life detection systems on missions searching for life on icy or ocean worlds, such as the Europa Multiple Flyby Mission (EMFM; a.k.a Europa Clipper) [1].

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