

# The Incorporation of Multi-Dimensional Spectroscopic Techniques in the Future of Planetary Science

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## The Issue with Traditional Spectroscopy – Spectral Confusion

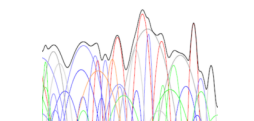


Figure 1: Spectral Confusion arises when several potential species may be contributing to an emission, absorption, or reflection feature.

Planetary Science seeks to help understand the compositions of Solar System bodies so we may learn more about their origins, or their potential for present or extant life. One of the power powerful tools that is used in present-day missions is spectroscopy where the interaction of light with matter is dependent upon the nature of the material.

In most planetary environments, we are dealing with mixtures of many similar chemical components can be contributing to the signal. The result is often termed 'spectral confusion' – see Figure 1.

The mid-infrared region is a favorite among analytical chemists because many molecular species have incredibly unique fingerprints (see Figure 2). Here, even when spectral confusion arises, it is still possible to determine functional groups such as O-H stretches, C=O stretches, etc. However, since we are still limiting ourselves to asking 'does anything interact at a single wavelength', then we cannot uniquely determine the composition of complex mixtures. We need something that can provide us more information on their interaction with light spectrally. Like in Figure 3?

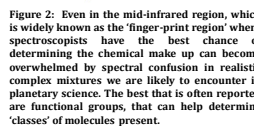


Figure 2: Even in the mid-infrared region, which is widely known as the 'finger-print region' where spectroscopists have the best chance of determining the chemical make up can become overwhelmed by spectral confusion in realistic complex mixtures we are likely to encounter in planetary science. The best that is often reported are functional groups, that can help determine 'classes' of molecules present.

Figure 3: In such instances, we find ourselves wishing for Star Trek style tricorders that can instantly tell us what is there. Well, with the technique described here, we are reaching the point of asking questions like "Hey is there an alcohol here?" and each alcohol responds back "Yes, I'm here ... and here is my (spectral) ID to prove it!"

## Our Solution – The 3D-IR Raman Technique

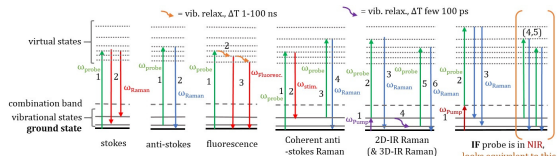


Figure 4: Raman Schemes discussed: basic Raman processes leading to Stokes and anti-Stokes bands are depicted along with the competing time-delayed fluorescence process. A scheme for the commonly employed coherent anti-Stokes Raman spectroscopy (CARS) technique is shown alongside the schemes for 2D-IR Raman spectroscopy if a fundamental band is pumped in the mid-IR, or a combination band in the Near-IR (far right). Note that 3D-IR Raman is equivalent to 2D-IR Raman, except the pump is tunable in addition. CARS achieves a similar result, but requires high peak powers.

In traditional Raman spectroscopy (Stokes-Raman), molecules begin in their ground state. When they are excited (typically by a laser light when performing these experiments, such as at green 532 nm wavelengths, for example here), they are excited to a virtual state for a brief period, before re-emitted the light. In the majority of cases, the molecule returns to the ground state, Rayleigh scattering has occurred, and chemically this is not particularly interesting. However, about one in a million times, the molecule will instead be returned to a vibrationally excited level, which means the photon emitted is red-shifted by an amount coinciding with that vibrational level (mid-IR). Alternatively, if molecules are promoted to a vibrationally excited state (by thermal excitation, or a tunable mid-IR laser), we can perform the reverse (anti-Stokes) Raman spectroscopy where the molecule starts in a vibrationally excited level and then returns to the ground state. Here, the photon is blue shifted by the same amount. In anti-Stokes Raman however, there is no competition from fluorescence which is a major problem for many instruments used today. The technique of 3D-IR Raman basically uses a tunable IR laser to selectively excite molecular compounds into vibrationally excited states and record the resulting anti-Stokes Raman signal.

## Acknowledgements

This work is partially supported with the help of the Center for Lunar and Asteroid Surface Science (CLASS, NNA14AB05A). We are currently seeking funding for this project and have a PICASSO submitted to investigate what benefit could realistically be expected from using this technique in the field of planetary science.

## Molecular Fingerprinting with 3D-IR Raman System

The 3D-IR Raman technique has been used to investigate intermolecular and intramolecular vibrational transfer processes. However, its potential benefits for planetary science have yet to be realized. There are two main ways that the technique can be used to uniquely identify species. The first requires femtosecond lasers to be able to trace the resulting 3D-IR Raman signal over time when a specific pump frequency is used. As shown in Figure 5 (below), the intramolecular transfer occurs within a few picoseconds into lower energy vibrational states. The re-distribution of energy via those intramolecular transfer processes can be very diagnostic in itself, and the later intermolecular transfer can provide additional information on the surrounding medium. **What happens if instead of pumping a fundamental band, we move to the near-IR and excite combination or overtone bands?** Per the literature, "a populated combination state appears as a vibration of the corresponding fundamental and an overtone as a fundamental with doubled population", as shown to the right of figure 4. 1-3

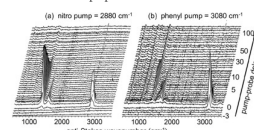


Figure 5: 3D-IR Raman spectrum of nitrobenzene with selective pumping to (a) the nitro group, and (b) the phenyl group (Ref. 1)

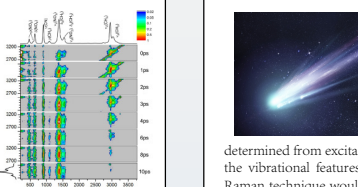


Figure 6: 3D-IR Raman spectrum of nitromethane with reference Raman (top) and IR (bottom left) spectra taken from Ref. 1

This in itself can be used to uniquely identify molecular species, however, when using a tunable laser it is additionally possible to scan over the pumping wavelengths resulting in a different kind of 3D-IR spectrum that can additionally be sampled over time additionally, as shown in Figure 6. **Therefore, utilizing different probe frequencies we can tell the corresponding fundamental frequencies from the same molecular species.**

## Example Set-up of our Proposed 3D-IR Raman System

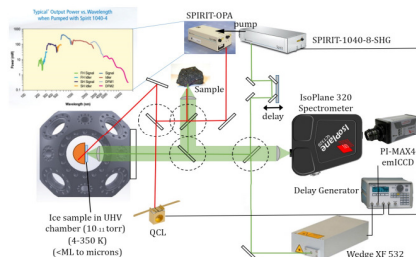


Figure 7: Simplified schematic of the experimental set-up (Not to scale). The set-up is based on refinements to the design of Bennett et al. (2013)12. Rotation, removal, or replacement of the four mirrors circled enable selection of sample (UHV or benchtop), IR pump laser (SPIRIT-OPA or QCL), and choice of Raman probe laser (Spirit or Wedge). Note that the SPIRIT and SPIRIT-OPA are one unit (SPIRIT pumps SPIRIT-OPA). The wedge pump is similar to that used by Blacksberg. 4

Although this technique has been demonstrated in the field of studying intramolecular vibrational transfer within liquid jets of pure compounds, 1-3,5,6 the potential benefits for Planetary Science have yet to be investigated. We therefore submitted a PICASSO to build a state-of-the-art set-up investigating these effects.

There have been many advances with laser and detector technology and more widely tunable lasers that are capable of providing sufficient power to easily detect ppm-quantities of material using this technique. We have previously integrated a pulsed Raman spectrometer into an ultra-high vacuum chamber in order to study Raman spectroscopy of icy material subject to radiation. Figure 7 shows the proposed experimental set-up to investigate the benefits of 3D-IR Raman to planetary science.

As an initial study, we would use this technique on a range of materials to demonstrate its benefit to planetary science ranging from those that can be prepared on a benchtop (e.g., meteorites, lunar and Martian analogs, or solutions cooled to liquid nitrogen temperatures that may be representative of Europa or Titan), or that require preparation within an ultra-high vacuum chamber (e.g., cometary, Titan, or Europa).

## References

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2 - Iwaki, L. K., Dirott, D. D., "Three-dimensional spectroscopy of vibrational energy relaxation in liquid methanol", Journal of Physical Chemistry A (2000), 104, 9101.  
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## Capabilities & Expected Mission Capabilities



The 3D-IR Raman technique would be an excellent choice as an instrument for the Cryogenic Surface Sample Return (CSSR) mission to a comet. Raman is capable of characterizing the pristine state (i.e. composition, including characterization of hypervolatiles (O<sub>2</sub>, N<sub>2</sub>, CO) and isotopically labeled species (levels of H/D in water, ammonia, methane, and others) down to the ppb level (ppt required). In addition, isotopic ratios of <sup>13</sup>C/<sup>12</sup>C, <sup>15</sup>N/<sup>14</sup>N and <sup>18</sup>O/<sup>16</sup>O can be

determined from excitation of combination and overtone bands where the vibrational features are resolvable (30 – 50 cm<sup>-1</sup>). The 3D-IR Raman technique would also be an excellent choice for Ocean World missions such as Europa, Enceladus and Titan. Not only is the technique capable of analyzing hydrocarbons, organics, minerals, etc. in a remote sensing capability (which also would make it invaluable as a prospecting tool for in-situ resource utilization (ISRU)), but it can be combined with other technologies to further increase its capabilities. For example, since Raman shares a lot of common apparatus as fluorescence spectroscopy, Co-I Stockton works with microfluidic devices that are capable of separating chiral compounds and detecting them using fluorescence spectroscopy. The 3D-IR Raman technique could easily be integrated into such a device. This is also compatible with the introduction of 40 nm gold nanoparticles which would enhance the 3D-IR Raman signal by factors of more than 10<sup>6</sup>. **Therefore, It is conceivable that 3D-IR Raman could be utilized in such a scheme to uniquely identify chiral biomarkers down to ppb or even ppt detection levels.**



## A Practical Technique for Space Flight?

Of course, the large tunable femtosecond laser system is not practical for space flight. However, Blacksberg et al. 4 are already working on picosecond pulsed Raman systems for space flight, and there are commercially available IR tunable Quantum Cascade Lasers (QCLs) which can be utilized for this purpose.

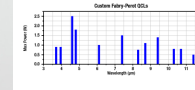


Figure 8: Example of the size of a QCL, along with Thorlabs wavelength options.

Although using a picosecond laser removes some of the temporal information learned, it can still be used to uniquely identify species based on the response at different wavelengths. Similarly, the QCLs have reduced temporal capabilities with pulses typically on the order of 100 ns and only ~ 100 cm<sup>-1</sup> tunability. We therefore propose to investigate such effects also (Figure 7).

## Summary

Hopefully, we will get the chance to demonstrate how valuable 3D-IR Raman, or indeed multi-dimensional spectroscopy will be for the field of Planetary Science, and in particular for the study of bodies in the outer solar system, but also could be a useful tool for prospecting missions closer to the Earth.

## The Incorporation of Multi-Dimensional Spectroscopic Techniques is the Future of Planetary Science