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Time-Domain Raman Spectroscopy: An Emerging Technique in Space Exploration?

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ABSTRACT

The potential of time-domain Raman spectroscopy in space exploration is discussed. This work is motivated by the emergence of robust, space-qualified femtosecond lasers and by the fact that time-domain detection allows the design of very compact instruments. As is shown, time-domain Raman spectroscopy gives access to the same fingerprint spectrum of minerals as conventional Raman spectroscopy, while avoiding problems such as fluorescence or ambient light backgrounds.

1 | Introduction

Since its discovery in 1928 [1], Raman scattering has evolved into one of the most powerful techniques to study the vibrational spectrum of matter (e.g., [2]). The applications have evolved from studying simple gases, liquids, and solids to analyzing biological tissue and planetary materials. Photonic advancements have led to ever more performant and robust instruments. Stand-off Raman instruments are since 2021 operational on rovers on Mars and are under development for operation on moons (e.g., [3, 4]). In this communication, we propose that the emergence of compact, space-qualified femtosecond lasers [5] may enable the detection of Raman-active fingerprints in space research with particularly compact and better-suited instruments based on time-domain Raman spectroscopy (TDRS) (for more details, see Section S6).

In contrast to conventional frequency-domain Raman spectroscopy (FDRS), TDRS detects the modulation of the polarizability directly by transient, stroboscopic measurements of changes in the linear or nonlinear optical properties (see, e.g., [6]). Prerequisite is that a coherent ensemble of the molecular vibrations is prepared, or in other words, that the excited vibrational modes are phase-locked. This can be achieved if appropriately short laser pulses are utilized. The pulse duration limits the detectable spectral bandwidth in time-domain detection as well as the signal strength towards higher frequencies via the time-bandwidth product (TBP) [7]. Non phase-locked photons, such as from fluorescence or ambient light, are not detected.

Meanwhile, the rapid progress of femtosecond lasers provides pulse durations down to sub-10 fs. This enables broadband TDRS over a large part of the spectral range typically utilized for fingerprinting minerals (see Figure 1). Of special interest for space exploration are fiber lasers, as they can be designed to be quite compact and have already been shown to be robust enough to operate in space (e.g., [9]).

TDRS studies have been performed on gases, liquids, and solids, in transmission, reflection, or emission geometries, and exceptional sensitivities to surface or interface properties have been demonstrated [6]. In contrast, TDRS studies on planetary materials are scarce, and there exists no published work on rock-forming minerals, to our knowledge. Here, we show

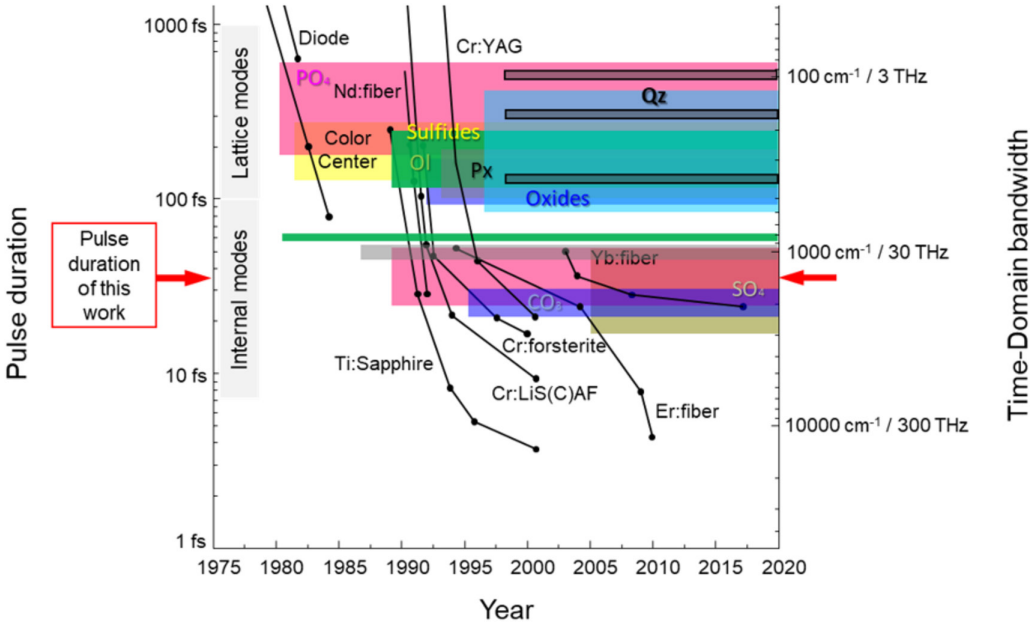

FIGURE 1 | Evolution of pulse durations of solid-state laser systems since 1975 (adapted from [8]). The corresponding spectral bandwidth [7] in time-domain detection is also shown. Ranges of selected relevant vibrational eigenfrequency classes in planetary materials are also displayed (Qz, quartz; PO_4, phosphates; SO_4, sulfates; CO_3, carbonates; Px, pyroxenes; Ol, olivine).

measurements of the vibrational fingerprints of two relevant minerals (for details, see Section S7): quartz (the second-most common Si-bearing mineral) and calcite (the most common carbonate) of the Earth's crust.

2 | Experimental

Both z-cut samples calcite and α-quartz were purchased from Korth Crystals GmbH.

TDRS measurements were performed in transmission with 800-nm femtosecond pump and probe pulses with a duration of 34.4 ± 1.3 fs incident at normal (pump) and near normal (probe) incidence, at a repetition rate of 80 MHz. Pump and probe beams were linearly polarized, in parallel to each other. The pump and probe foci had diameters of 90 and 50 μm (FWHM), respectively. The pump pulse energy of 800 pJ ensured that the fluence stayed orders of magnitude below the damage thresholds of quartz and calcite. The pump pulse-trains were modulated at a frequency of 407 Hz. The detected probe laser signal was then denoised via a lock-in amplifier set to this reference frequency. For calcite, the transient changes of polarization were detected, while for α-quartz, the transient changes in transmission were measured (see insets of Figure 2). For more details on the experimental set-ups, see Section S1.

FDRS measurements were performed utilizing a commercial WITEC alpha-300 confocal microscope (for more details, see Section S2). The wavelength of the Raman laser was 532.2 nm, intensity 3 mW, and probe spot ~1.5 μm. The Stokes intensity was detected in the backscattering geometry with polarization filtering and with intensity calibration.

3 | Results and Discussion

Figure 2 shows a comparison of TDRS and FDRS measurements on calcite and α-quartz. While there is an overall fair agreement, the relative amplitudes of detected modes differ significantly in the as-measured data. In the following, the current understandings for the observed discrepancies shall be discussed (for more details, see Section S4).

The TDRS signal (ΔS) is fundamentally proportional to the first-order Raman tensor $\left(\frac{\partial \chi}{\partial Q}\right)$ [12]:

$$\Delta S \sim \left(\frac{\partial \chi}{\partial Q}\right).$$

The observed intensity of phonons in TDRS is furthermore governed by the TBP, which for a Gaussian intensity profile with frequencies ω and a pulse duration of τ_p takes the following form [7]:

$$\Delta S \sim e^{-\left(4 \ln 2\, t/\tau_p\right)^2}.$$

For calcite, a fair agreement between FDRS and TDRS is found, and the relative amplitudes in the Stokes intensity are well reproduced when including the influence of the TBP (for more details, see Section S3).

The agreement between TDRS and FDRS of α-quartz with the Stokes intensity is also fair. However, only five of the seven modes observed in FDRS are detected. While the missing high frequency E mode at 35 THz/1167 cm^{-1} can be explained by the noise in the measurement, the absence of the E modes at 11.9 THz/397 cm^{-1} and 21 THz/700 cm^{-1} cannot be explained by the TBP alone. The relative amplitudes of the E and A_1 modes at

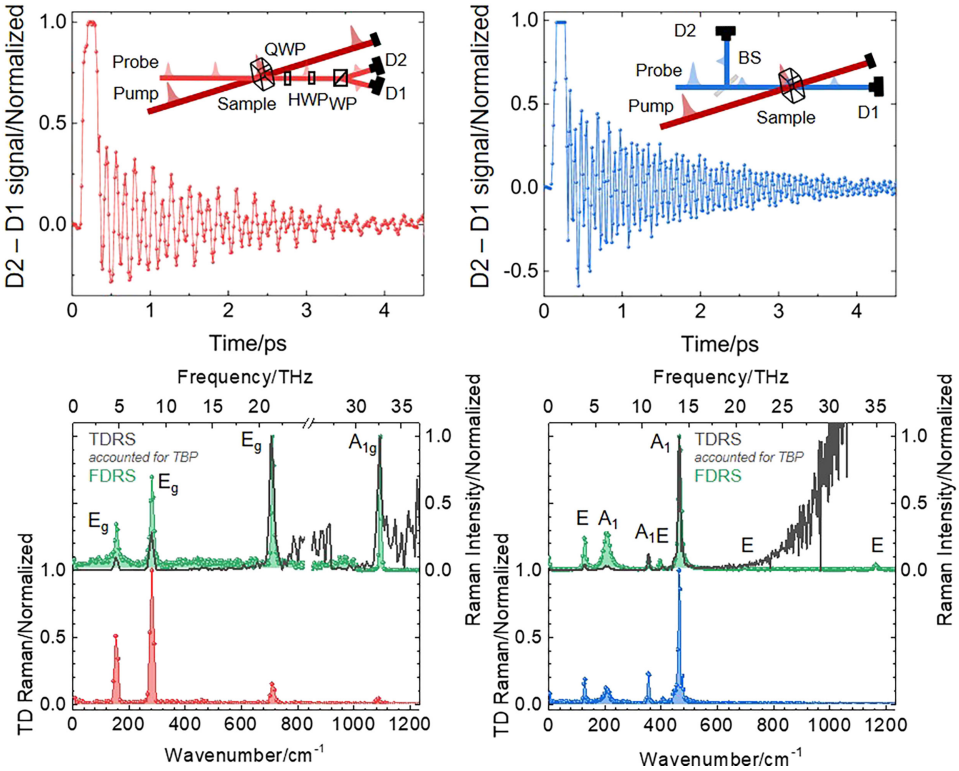

FIGURE 2 | TDRS measurements of changes in birefringence in calcite (left) and changes in transmitted intensity in α-quartz (right). The TDRS signal and the respective measurement geometries are shown in the top panels. The Fourier transform (FT) of the time-domain signals is shown in the bottom panels (red and blue). Note that the so-called coherent artefact [10] in the first 300 fs is omitted and the signal was apodized by the Hamming window [11] function before the FT. The Stokes intensities measured with a conventional FDRS instrument are also shown and the TDRS signal corrected for the convolved TBP of pump and probe pulses is overlaid as a black line. Note that the incident and detected light in all measurements were polarized in parallel (for more details see Sections S1, S2, S3, and S5).

3.8 THz/127 cm^{-1} and 6.2 THz/207 cm^{-1} with respect to the dominant A_1 mode at 13.9 THz/464 cm^{-1} are also underestimated. Future work will focus on gaining a deeper understanding of these discrepancies. It is interesting to note that the TDRS measurements are in better agreement with FDRS measurements on the α-cristobalite phase of quartz [13].

4 | Conclusions and Outlook

TDRS on minerals can be performed with comparatively weak (sub-nJ) near-infrared femtosecond pulses. TDRS and FDRS give comparable results. Differences of relative amplitudes between TDRS and FDRS are not fully understood. Development of a breadboard-level instrument optimized for stand-off detection is in progress, as is research on photonic chip integration of time-domain detection building blocks.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

1. C. V. Raman and K. S. Krishnan, "A New Type of Secondary Radiation," *Nature* 21 (1928): 501–502.

2. L. A. Nafie, "Recent Advances in Linear and Nonlinear Raman Spectroscopy. Part XIV," *Journal of Raman Specroscopy* 51 (2020): 2354–2376.

3. R. Bhartia, L. W. Beegle, L. DeFlores, et al., "Perseverance's Scanning Habitable Environments With Raman and Luminescence for Organics and Chemicals (SHERLOC) Investigation," *Space Science Reviews* 217, no. 4 (2021): 58, https://doi.org/10.1007/s11214-021-00812-z.

4. Y. Cho, U. Böttger, F. Rull, et al., "In Situ Science on Phobos With the Raman Spectrometer for MMX (RAX): Preliminary Design and Feasibility of Raman Measurements," *Earth, Planets and Space* 73 (2021): 232.

5. M. E. Fermann and A. Rolland, "The Impact of Femtosecond Fiber Lasers in Technology and Science," *Optics Communication* 574 (2025): 131197.

6. K. Ishioka and O. Misochko, *Progress in Ultrafast Intense Laser Science*, Vol. 5, ed. K. Yamanouchi, A. Giulietti, and K. Ledingham (Springer, 2010): 23–46.

7. J. C. Diels and W. Rudolph, *Ultrashort Laser Phenomena: Fundamentals, Techniques, and Applications on a Femtosecond Time Scale*, vol. 10, 2nd ed., (Academic Press, 2006).

8. F. X. Kärtner, E. P. Ippen, and S. T. Cundiff, *Femtosecond Optical Frequency Comb: Principle, Operation, and Applications*, eds. J. Ye and S. T. Cundiff (Springer, 2006): 54–77.

9. J. Lee, K. Lee, Y. S. Jang, et al., "Testing of a Femtosecond Pulse Laser in Outer Space," *Scientific Reports* 4 (2014): 5134.

10. F. J. Harris, "On the Use of Windows for Harmonic Analysis With the Discrete Fourier Transform," *Proceedings of the IEEE* 66 (1978): 51–83.

11. M. V. Lebedev, O. V. Misochko, T. Dekorsy, and N. Georgiev, "On the Nature of "Coherent Artifact"," *Journal of Experimental and Theoretical Physics* 100 (2005): 272–282.

12. T. Dekorsy, G. C. Cho, and H. Kurz, *Light Scattering in Solids VIII. Topics in Applied Physics*, vol. 76, eds. M. Cardona and G. Güntherodt (Springer, 2000): 169209.

13. J. Etchepare, M. Merian, and P. Kaplan, "Vibrational Normal Modes of SiO_2. II. Cristobalite and Tridymite," *Journal of Chemical Physics* 68 (1978): 1531–1537.

Supporting Information

Additional supporting information can be found online in the Supporting Information section.