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Time-resolved detection of aromatic compounds on planetary surfaces by ultraviolet laser induced fluorescence and Raman spectroscopy

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ABSTRACT

Raman spectroscopic instruments are highly capable in the search for organics on Mars due to the potential to perform rapid and nondestructive measurements on unprepared samples. Upcoming and future Raman instruments are likely to also incorporate laser-induced fluorescence (LIF) capabilities, which can be added for modest cost and complexity. We demonstrate that it is possible to obtain sub-ns fluorescence lifetime measurements of Mars-relevant organics and minerals if a fast time-gating capability is used with an intensified detector and a short ultraviolet laser pulse. This serves a primary purpose of discriminating mineral from short-lived (less than 10 ns) organic fluorescence, considered a potential biosignature. Additionally, lifetime measurements may assist in determining if more than one fluorescing species is present and provide information concerning the molecular structure as well as the local environment. Fast time-gating is also useful at longer visible or near-IR wavelengths, as this approach increases the sensitivity of the instrument to organic material by removing the majority of the fluorescence background from the Raman signal and reducing the effect of ambient light.
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1. Introduction

Recent discoveries of organic carbon (Freissinet et al., 2015) and methane (Webster et al., 2015) on Mars have continued to motivate the search for complex organics and signs of extant or past life on the Martian surface. Mars Science Laboratory (MSL) has located environments that could potentially have supported life (Carr, 2015), and the exploration strategy for future missions will advance from locating habitable environments with an aqueous past to entering those environments and directly searching for traces of organics (Johnson, 2010).

Instrumentation that directly identifies and characterizes organic carbon is a high priority for the Mars 2020 rover, the successor to MSL. A Raman instrument is ranked highly by NASA for both detecting organic carbon and observing fine-scale mineralogy (Mustard et al., 2013). Although no Raman instrument has been used in a planetary setting other than Earth, Mars 2020 will contain both SHERLOC, a 248 nm Raman instrument, and a 532 nm Raman system as part of the SuperCam instrument (Clegg and Wiens, 2015; Beegle et al., 2015; Hug et al., 2014). A 532 nm Raman instrument has also been selected for the 2018 ExoMars mission (Rull et al., 2010; Bost et al., 2015). Raman spectroscopy is an inelastic process where light scattered from an incoming laser pulse exchanges energy with the sample, and allows for fast, non-destructive fingerprinting of low concentrations of organics. Typically the molecules in a sample are in their vibrational ground state, and Raman scattered photons impart energy to the sample equal to the energy difference between the ground and first excited vibrational states. As different molecules have varied structures and bond strengths, a Raman spectrum offers a fingerprint of a molecule, with peaks indicating which molecular bonds and functional groups are present.

A large volume of recent work has established the ability of a Raman instrument to detect a wide range of astrobiological targets, from simple amino acids and PAHs to more complex biosignatures and microbial life. Raman instruments, including standoff prototypes and handheld units, have been able to detect organics in pure form (Misra et al., 2012; Sharma, 2007) and in trace quantities in mineral matrices representative of Martian environments (Vítek et al., 2014; Sharma et al., 2012; Vandenabeele and Jehlička, 2014), often employing techniques such as Raman mapping and database matching to locate and classify organic and mineral spectral signatures (Vandenabeele et al., 2012; Vandenabeele, 2011). A Raman instrument is capable of detecting a wide spectrum of organic material including PAHs and aromatics, geologically preserved organic material, and more

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complex biosignatures including active microbial colonies (Frank et al., 2007; Jehlička et al., 2006).

The choice of excitation wavelength for a Raman instrument is not straightforward. Visible and near-IR excitations, including 532 nm and 785 nm, allow for sensitive detection of organics, but the Raman signal can be overwhelmed if the sample exhibits fluorescence (Jehlička and Vandenabeele, 2015; Blacksberg et al., 2010). An ultraviolet excitation wavelength offers several advantages to longer visible or near-IR excitations, including reduction of fluorescence in the Raman window, increased scattering efficiency, and increased scattering due to resonance with some organics, but may result in increased absorption of the incoming and scattered radiation (Eshelman et al., 2014; Skulinova et al., 2014).

Upcoming and future ultraviolet Raman instruments are likely to incorporate laser-induced fluorescence (LIF) capabilities, as these capabilities can be added for modest cost and accommodation increases (Sharma et al., 2012; Hug et al., 2005). Fluorescence occurs when a photon incident on a molecule is energetic enough to excite an electron to some vibrational level in a higher electronic state. The electron will settle to the ground vibrational level of the first excited electronic state through internal conversion, but will emit a photon when relaxing to the ground electronic state (Holcombe and Farnsworth, 2010). The minimum photon energy needed to induce fluorescence in a compound is equivalent to the energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Energies in the ultraviolet are sufficient to meet this gap for a wide range of organic compounds, especially compounds with aromatic rings containing de-localized π electrons (Storrie-Lombardi et al., 2009). Many complex organics therefore exhibit strong fluorescence when excited with ultraviolet radiation. This laser induced fluorescence may be several magnitudes stronger than the Raman scattering, yet the emission spectrum is Stokes-shifted to longer wavelengths (Stokes, 1852), with generally all fluorescence occurring above 270 nm (Bhartia et al., 2008). Fluorescence will therefore be energetically separated from the Raman window if an excitation of 266 nm or lower is selected (Eshelman et al., 2014).

Unlike Raman scattering, which occurs on a femtosecond timescale, fluorescence emission occurs on the nanosecond timescale, or greater. Many organic compounds exhibit strong short-lived fluorescence when excited with ultraviolet radiation, while some minerals exhibit longer lived fluorescence (Blacksberg et al., 2010), which can be due to the presence of transition metals or rare earth impurities (Gaft and Panczer, 2013). Fast fluorescence (a lifetime less than <10 ns) is considered a potential biosignature due to its probable organic origin. We demonstrate that if a fast time-gating (FTG) capability is used with an intensified detector and a short laser pulse, it is possible to obtain sub-ns fluorescence lifetime measurements of Mars-relevant organics and minerals. While not achieving the time resolution of time correlated single photon counting (TCSPC) (Wahl et al., 2002) or other traditional lifetime measurement techniques (Vetromile and Jameson, 2014), the method presented here may be performed in situ on a planetary surface without greatly adding to the complexity of a combined Raman and fluorescence instrument. This serves a primary purpose of discriminating mineral from organic fluorescence. Additionally, this may assist in determining if more than one fluorescing species is present and provide information concerning the molecular structure as well as the context of the sample. The nanosecond timescale of fluorescence emission is sufficient to allow chemical reaction of the excited molecules with the local environment, which can affect both the emission wavelength and lifetime through quenching mechanisms (Joseph, 2006). FTG also improves the system capabilities and operational utility by allowing the removal of the majority of the fluorescence background from the Raman signal and reducing the effect of ambient light. Combining fluorescence and Raman measurements results in an instrument with the discriminating power provided by Raman spectra and increased sensitivity to organic material due to the high cross section of fluorescence, potentially allowing detection of organic material to ppb scales (Storrie-Lombardi et al., 2001).

2. Materials and methods

2.1. Sample preparation

Three aromatic amino acids, L-phenylalanine (Sigma-Aldrich P2126), L-tyrosine (Sigma-Aldrich T3754), and L-tryptophan (Sigma-Aldrich T0254) were obtained in pure form from Sigma-Aldrich. The lifetimes of these compounds are well defined in the literature (Joseph, 2006), and therefore they serve as good lifetime standards to calibrate and verify the measurement methodology. Time-resolved spectra of the aromatic amino acids were obtained by first dissolving the compounds in distilled water at a concentration of 0.001% by mass, as lifetime values are typically reported in the literature for aqueous solutions. The resulting solutions were placed in fused-silica quartz cuvettes, which do not exhibit fluorescence when excited with 266 nm radiation. Minimal Raman scattering from Si–O–Si stretching modes is present in the quartz (Robert, 1958), but it is several magnitudes weaker than the fluorescence scattering and is restricted to below 500 cm^{-1} (269.5 nm) and does not overlap with the fluorescence emission. Four Mars-relevant polycyclic aromatic hydrocarbons (PAH) 9-nitroanthracene (Sigma-Aldrich N1020-9), dibenzothiophene sulfone (Sigma-Aldrich D3240-7), phenoxathiin (Sigma-Aldrich 21882-0), and phenoxazine (Sigma-Aldrich P1485-8) were also obtained from Sigma-Aldrich in pure powdered form with a sub-45 μm grain size. The PAHs were placed in powdered form into disposable UV cuvettes for testing. The disposable cuvettes used are highly transparent to UV light, and do not exhibit significant fluorescence. As the cuvettes are constructed from an organic polymer, a C–H Raman stretching mode is visible around 3000 cm^{-1} (Daimay Lin-Vien and Colthup, 1991), but does not interfere with fluorescence lifetime measurements. Research grade calcite was obtained from Ward's Science to investigate mineral fluorescence described in Section 3.3. Microbial mat from Probe Lake in the Cariboo Plateau, British Columbia was mixed with the calcite to generate a sample displaying both mineral and organic fluorescence. The microbial mat was composed of 60–65% carbonate inorganic phases, with the remaining organic content dominated by cyanobacteria (Brady et al., 2013). The mixed sample contained 1% microbial mat by dry mass, resulting in an organic concentration of 0.35 ± 0.05%.

2.2. Raman and fluorescence instrumentation

The instrumentation used to collect fluorescence spectra is a laboratory-bench prototype for a stand-off ultraviolet Raman spectrometer intended to search for Martian organics. The instrument specifications are designed with a spaceflight instrument in mind, primarily considering the laser power, spot size, and angular resolution when operating in a mapping mode. Excitation is provided by a diode pumped solid state 266 nm laser with a pulse width of 700 ps and a pulse energy of 1.6 μJ. The repetition rate of the laser is variable between 100 Hz and 5 kHz and its adjustment depends on the fluorescence quantum yield of the compound under observation. The laser is focused onto the sample with a spot size of 1 mm^2, and emitted light is collected in a near-180 degree backscatter geometry and focused into an optical fiber. Rayleigh scattering is rejected using an edge filter, and the spectrum passes through a Czerny–Turner spectrometer before being imaged by an intensified CCD. In order to coordinate the nanosecond scale timing required to observe fluorescence decay the detector gate is triggered by a photodiode placed

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