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IR resonance-enhanced organic detection with two-step laser desorption time-of-flight mass spectrometry

K. Uckert[a], A. Grubisic[c], X. Li[d], W.B. Brinckerhoff[b], T. Cornish[e], B. Farcy[c], S.A. Getty[b,*]

[a] *Department of Astronomy, New Mexico State University, Las Cruces, NM 88003, Mexico*
[b] *NASA/GSFC, Greenbelt, MD 20771, USA*
[c] *Department of Astronomy, University of Maryland, College Park, MD 20742, USA*
[d] *Center for Space Science and Technology, University of Maryland, Baltimore County, Baltimore, MD 21250, USA*
[e] *C & E Research, Inc., Columbia, MD 21045, USA*

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ABSTRACT

We explore resonance-enhanced sample analysis with a prototype two-step laser desorption time-of-flight mass spectrometer (L2MS) to characterize the dependence of resonant desorption on the L2MS detection sensitivity. In L2MS, desorption and ionization of analyte is separated into two distinct steps: an IR laser desorbs surface material and a UV laser ionizes analyte from the resulting neutral plume. Desorption of analyte, including trace organic species, may be increased by coupling the wavelength of the desorption laser to IR absorption features associated with vibration transitions of minerals or organic functional groups. We demonstrate this effect on minerals relevant to icy bodies, doped with the aromatic amino acid tryptophan, and find a correlation between the optimal L2MS desorption laser wavelength for organic detection and the presence of vibrational transitions in the mineral substrate. We present the unique organic detection capabilities of the L2MS, and demonstrate the value of exploiting this resonant-enhanced desorption effect to optimize the detection of organics on other planetary bodies.

1. Introduction

The detection of organics on other planetary surfaces provides insight into the chemical and geologic evolution of a solar system body, and can inform our understanding of its potential habitability. Mass spectrometry offers *in situ* analysis of the elemental and mineralogical composition of a planetary environment as part of a landed or roving payload. In this study, we explore the use of an advanced compact two-step laser desorption/ionization time-of-flight mass spectrometer (L2MS), compatible with a future *in situ* science payload, which uses an infrared (IR) desorption laser pulse, followed at a delay by an ultraviolet (UV) ionization pulse to target certain classes of organic molecules of high astrobiological interest in planetary surface materials, such as polycyclic aromatic hydrocarbons, organic acids, amino acids, and nucleobases (Getty et al., 2013; 2014a).

In single-laser positive-ion laser desorption/ionization (LDI) mass spectrometry, low-mass salts frequently overwhelm the mass spectrum and could reduce the detection sensitivity of complex organic molecules; conversely, L2MS is insensitive to salt and other dominant inorganic cations and allows for the selective analysis of the organic content of a complex sample. The use of two separate and optimized laser wavelengths allows efficient coupling to the vibrational and electronic spectra of the analyte or mineral substrate in independent desorption and ionization steps, allowing for the mitigation of excess energy that can lead to fragmentation during the ionization process in more conventional LDI mass spectrometry (Han et al., 1988; Zenobi et al., 1989). L2MS therefore has the potential to preserve high-molecular weight biosignatures against excessive fragmentation, and offers selectivity to certain high-priority classes of organics in a complex mass spectrum. Single laser LDI could complement L2MS by operating in a survey mode as part of an instrument package.

In addition to the selectivity of the 266 nm ionization laser to aromatic compounds demonstrated by Zenobi et al. (1989), the use of a tunable IR desorption laser wavelength provides further specificity to certain compounds by exploiting resonances with vibrational modes associated with structurally bound water and organic moieties. Desorption of analyte is strongly dependent on the ability of the IR laser to couple with the molecular vibration and rotation modes (Mihesan et al., 2006), which we infer from IR spectra.

We present L2MS measurements of organically-doped minerals representative of solar system analogs. Specifically, we consider

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[*] Corresponding author.
E-mail address: stephanie.a.getty@nasa.gov (S.A. Getty).

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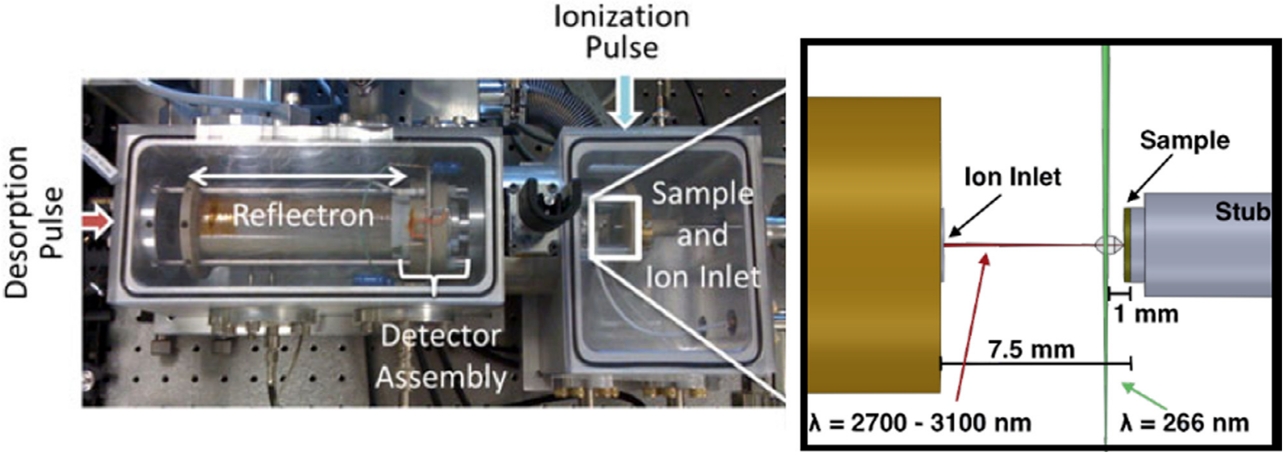

Fig. 1. An annotated photograph of the L2MS (left) with a schematic (right) depicting the geometry of the sample and ion inlet region where the IR desorption and UV ionization occurs.

sulfates with variable quantities of waters of hydration, including epsomite ($MgSO_4 \cdot 7H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$), and anhydrite ($CaSO_4$) to characterize an enhanced desorption of analyte at IR laser wavelengths coincident with O-H stretching vibrational transitions. Mg sulfates match the spectral characteristics of Europa's surface (Brown and Hand, 2013), and are expected to retain structurally bound water over geologic time periods under Europa surface conditions (McCord et al., 2001), making epsomite an ideal icy body analog for these laboratory studies. We also investigate calcium sulfate minerals (gypsum and anhydrite), which have recently been discovered on the Martian surface by the Sample Analysis at Mars (SAM) and Chemistry and Mineralogy (ChemMin) instruments on Curiosity (Nachon et al., 2014), suggesting the presence of aqueous environments during formation (Gendrin et al., 2005; Ackiss and Wray, 2014). When measured by the L2MS, we expect more significantly hydrated minerals to couple with a resonant IR laser more effectively at wavelengths corresponding to O-H stretching vibration modes, leading to an enhanced desorption of surface material, and increasing the detection of embedded organics. We also measured organically doped enstatite due to its relevance to small solar system bodies, particularly E-type asteroids (Gaffey et al., 1992), and organically-doped water ice. To characterize the resonance-enhanced desorption effect, we measure the aforementioned laboratory samples with the L2MS using an IR desorption laser tunable from 2.7–3.1 µm - a wavelength range that includes vibrational modes of mineral hydration and organic functional groups. By coupling the IR desorption laser wavelength to mineral or organic vibrational modes, the analyte signal may be amplified to better identify the organics within a mixture, while minimizing power requirements.

2. Experimental methodology

We investigate the organic detection capabilities of an L2MS, which separates the desorption and ionization functions into two distinct laser pulses to provide selectivity to key subclasses of organic species, such as aromatic hydrocarbons (Zenobi et al., 1989). In L2MS, the surface of a target is first irradiated by a soft IR laser pulse, which heats the sample below the thermal ionization potential of the target, resulting in desorption of neutral molecules. Thermally induced neutral desorption of analyte, including trace organic species, may be increased by coupling the wavelength of the IR desorption laser to IR absorption features associated with vibration transitions of minerals or organic functional groups. Absorption of IR photons with a wavelength matching vibrational modes in the mineral substrate or analyte leads to further heating; IR photons are absorbed at these transitions, vibrating the compound and leading to additional photodesorption from the surface (Focsa et al., 2006). After a tunable delay (with an empirical, optimal value of 2–3 µs for analyte detection with the prototype L2MS (Getty et al., 2012)), the neutral plume of desorbed analyte is then irradiated by a UV laser directed orthogonal to the IR desorption laser. Shortening the delay between the desorption and ionization laser pulses results in the preferential ionization of low-mass fragments associated with the inorganic mineral matrix, which is not of interest to this study. The resulting ions are accelerated into the miniaturized time-of-flight mass analyzer with a curved-field reflectron and a microchannel plate detector (Brinckerhoff et al., 2000; Cornish et al., 2000).

A photograph of the TOF-MS and sample chambers is presented in Fig. 1, along with a schematic depicting the geometry of the desorption and ionization laser pulses. The instrument measures approximately 30 cm in length (from the end of the curved-field reflectron to the sample plane) and approximately 5 cm in diameter. A detailed description of the development, specifications, and sensitivity of this instrument is provided elsewhere (Getty et al., 2012; 2013; 2014a; 2014b). We use an Opotek Opolette 2731 pulsed tunable OPO (optical parametric oscillator) IR laser (2.7–3.1 µm, pulsed with repetition rate up to 20 Hz, and pulse width as short as 4 ns) for desorption, and an orthogonally positioned pulsed UV laser (Nd:YAG, 266 nm, pulse width 5 ns) for ionization of the desorbed neutral species. The UV ionization laser intersects the plume of neutrals approximately 1 mm above the sample surface.

Several minerals including epsomite (Sigma-Aldrich Co.), gypsum (Wards Science), anhydrite (Sigma-Aldrich Co.), and enstatite (field sample from Bamble, Norway) doped with the aromatic amino acid tryptophan (Sigma-Aldrich Co.) were measured with the L2MS to demonstrate the detection enhancement of analyte due to resonant IR desorption. Samples were prepared by adding a solution of tryptophan dissolved in a nonaqueous solvent (methanol in this case) to a mineral matrix powdered to a $< 150\,\mu m$ grain size. We measured a quantity of the tryptophan solution to achieve a 1000 ppm (0.1 wt%) tryptophan in mineral concentration. The powdered mixture was dried, pressed onto a stainless steel stub, and mounted into the vacuum chamber of the instrument. The limit of detection of organic acids mixed with sulfate mineral matrices for the GSFC prototype L2MS is approximately 20 ppm (Uckert et al., 2016); we measure a higher concentration here to demonstrate the signal enhancement effect. For measurements of organically doped water ice, a mixture of