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Abstract—Two-step laser desorption mass spectrometry is a well suited technique to the analysis of high priority classes of organics, such as poly cyclic aromatic hydrocarbons, present in complex samples. The use of decoupled desorption and ionization laser pulses allows for sensitive and selective detection of structurally intact organic species. We have recently demonstrated the implementation of this advancement in laser mass spectrometry in a compact, flight-compatible instrument that could feasibly be the centerpiece of an analytical science payload as part of a future spaceflight mission to a small body or icy moon.

Index Terms—Laser desorption, mass spectrometry, time-of-flight, L2MS, in situ

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1. INTRODUCTION

Future landed missions to diverse solar system bodies will demand advanced mass spectrometric techniques to characterize complex organic matter in situ. Understanding the origin, processing, and distribution of organic carbon in the solar system is of critical importance to fundamental planetary science as well as astrobiology. We will present recent work to develop a compact laser time-of-flight mass spectrometer that is optimized for detecting and analyzing the non-volatile organic composition of surface materials as part of a future in situ mission to an icy moon, comet, or carbonaceous asteroid. Two-step laser desorption/ionization mass spectrometry (L2MS) in particular has proven to be a useful tool in terrestrial studies to identify reduced carbon, particularly aromatic species, in meteoritic and returned primitive solar system materials [1-4]. We have recently demonstrated L2MS with a highly-compact time-of-flight mass analyzer that was previously developed for single-laser desorption and ionization studies on planetary analog materials [5-9].

L2MS employs two laser pulses to sequentially desorb (by an infrared pulse) and ionize (by a ultraviolet pulse) analyte from a solid surface. The delay between these two pulses is optimized for the geometry and dimensions of the instrument. In our system, the desorption laser wavelength is either 1064 nm or, more recently, in a tunable range between 2.7 μm and 3.1 μm. The ∼3μm wavelength is especially suitable for exploiting the strong vibrational features of many organic species as well as the water-ice matrix in this range. The ionization laser wavelength is currently 266 nm, which introduces instrument selectivity to aromatic species through a resonance-enhanced multiphoton ionization mechanism. Implications and plans for flight-qualifiable laser technology to meet these instrument needs will be discussed.

Additional features of the instrument have been developed to enable advanced mass spectrometric techniques in a small package. These include a precision pulsed ion gate that allows the selection of a narrow mass range of interest for improved sensitivity to mitigate adverse detector saturation effects when interrogating trace sample constituents in the presence of dominant species. Coupled with the ion gating capability, the recent implementation of induced dissociation techniques allows for molecular ion selection and targeted fragment analysis which can provide detailed structural information. Here, we describe these recent instrument developments, and present the performance of the instrument techniques as applied to relevant planetary analog samples.

2. MOTIVATION

It is known from remote spectroscopy that the Outer Solar System harbors a diverse population of macromolecular...
species that are likely to include aromatic and conjugated hydrocarbons with varying degrees of methylation and nitrile incorporation [10]. In situ exploration of Titan’s upper atmosphere via mass and plasma spectrometry has revealed a complex mixture of organics with a more distinctly aromatic character than predicted from chemical modeling and remote observation, strongly influenced by the production of benzene and higher order aromatic species [11, 12]. Similar material is expected to be produced on the Ice Giants, their moons, and other Outer Solar System bodies, where it may subsequently be deposited onto surface ices [13]. An in situ instrument that could decipher compositional contributions from major classes of molecules, either identifying individual species, could enable a thorough chemical investigation of a target of recent reconnaissance (Europa, Enceladus, Titan, or Mars) or an as-yet unexplored planetary body (Triton, KBO, comet, or Trojan). Determination of the organics inventory of each of these surfaces, compared to terrestrial investigations of meteorites and returned samples, can provide insight into the body’s formation and history of aqueous and thermal alteration.

Laser desorption/ionization mass spectrometry (LDMS) is a conceptually simple technique that can provide compositional information about the inorganic and organic species present in a solid material with relatively little need for sample preparation. A multi-pulse approach to MS, as described here, will allow resolution of spectral interferences by combining a selective two-step ionization technique with a tandem MS capability to isolate and correlate parent masses with their fragmentation fingerprints. Classes of molecule, and even single species, can be identified with high confidence within complex mixtures of organics. This technique targets a broad variety of astrochemically important classes of organics, including polycyclic aromatic hydrocarbons, amino acids, and nucleobases.

3. INSTRUMENT DESIGN

The development of a miniature time-of-flight mass spectrometer (TOF-MS) measuring less than 20 cm long has been previously reported [5-9]. In the simplest configuration, a UV laser (355 or 266 nm) is focused onto the surface of a solid sample to generate ions within a few-nanosecond pulse width, leading to unit mass resolution at several hundred Da.

Laboratory-scale L2MS has been shown to be a sensitive and selective tool in determining the presence and composition of macromolecular aromatic material in meteorites [1-3], Titan haze simulants [14], and returned cometary samples from Stardust [15]. The adaptation of the L2MS technique will be a valuable capability for future in situ investigations of related planetary bodies.

In L2MS, the energy of an incident IR laser is set below the ionization threshold to gently produce neutral desorption from the sample. A transverse ultraviolet (UV) laser (157-266 nm) pulse, operated at a few-microsecond delay (depending on instrument geometry), is then used to selectively ionize constituents with a high degree of aromaticity in the neutral plume. This technique produces clearly identifiable parent peaks at low UV energy, with a bias against inorganic species that represents a considerable simplification to the mass spectrum of a mixture.

A miniature LD-TOF-MS instrument with curved field reflector [15] has been retrofitted to implement the two-laser ionization technique, as shown in Figure 1. In an initial proof-of-concept, the 1064 nm fundamental frequency of a pulsed Nd:YAG was used to desorb neutral analyte from the sample surface. After a delay of 300 ns – 3 μs, depending on sample position, an orthogonal 266 nm pulse (frequency-quadrupled from a second Nd:YAG) intersects the expanding neutral plume to ionize the analyte through resonance-enhanced multi photon ionization (REMPI). Most recently, the 1064 nm desorption laser has been replaced by a tunable optical parametric oscillator (OPO) producing pulsed IR in the range 2.7-3.1 μm.

![Figure 1](image-url)

Figure 1. (a) Proof-of-concept L2MS measurements have been demonstrated in a miniature time-of-flight mass spectrometer prototype. (b) The schematic shows the orthogonal relationship between the IR desorption pulse (shown in red) and the UV ionization pulse (shown in blue) and the reflected ion trajectories through the analyzer. The flight time of each molecular ion depends inversely on mass-to-charge ratio, such that recording pulses at the detector as a function of time is used to produce a mass spectrum.

Laboratory-scale measurements on a selected sample suite have also been performed using L2MS facilities at Stanford University to contribute to the assessment of miniature L2MS performance. In the L2MS at Stanford, a pulsed CO₂ laser (λ = 10.6 μm; Alltec GmbH, Model AL 882 APS) was used to generate the IR laser pulse. This beam was focused to a spot of 50 μm in diameter to desorb the sample from a copper platter. The neutral plume is then intersected perpendicularly by the UV output of the fourth harmonic (λ = 266 nm) of a Nd:YAG laser (Spectra Physics, DCR 11). The ions are then mass analyzed in a homebuilt TOF-MS employing a modified
Wiley–McLaren geometry [17]. A dual microchannel plate (MCP; 20 cm² active area; Burle Electro-Optics, Sturbridge, MA) in a chevron configuration is coupled to a large collector anode (Galileo TOF-4000) for ion detection. These facilities have been instrumental to the first demonstrations of two-step laser mass spectrometry for analysis of meteorites, interplanetary dust, and refractory Titan simulants. Corroborative analysis of the sample suite under study, in parallel with our instrument development efforts at GSFC, provides ground-truth for comparison of L2MS results.

Recent proof-of-concept demonstrations of L2MS [8] and precision ion gating [9] has shown the feasibility of implementing these techniques in a miniature mass spectrometer. Here we further describe characterization of the L2MS technique using a compact instrument prototype for a suite of standards relevant to the study of planetary organics.

4. EXPERIMENTAL METHODS

The PAH calibration mix (Sigma-Aldrich) contains 16 organic standards as listed in Table 1, where 10 μg/ml, each component is resolved in acetonitrile. The tryptophan and 2,6-diaminopurine samples are solid powder purchased from Sigma-Aldrich. For the experiments done by the miniaturized instrument, the liquid-phase PAH mixture was drop-cast onto a stainless steel sample probe that allows the sample to be held at the necessary voltage during TOF-MS analysis. The sample droplet is air-dried to form a film, and the sample probe is introduced into the vacuum chamber for pump-down and analysis. The powdered samples were directly pressed onto the sample probe for loose cohesive attachment without the use of a solvent and transferred into the chamber for pump-down and analysis.

The sample stub is mounted on a linear motion feedthrough, and the distance of the sample from the instrument inlet and the intersection of the ionization laser pulses can be easily adjusted. The delay between laser pulses was precisely controlled with delay generators (DG645; Stanford Research Systems, Sunnyvale, CA, USA) coupled to the external Q-switch triggers of each laser. During the experiment, the IR laser is first set to just below the prompt ionization threshold, in the absence of the UV laser ionization pulse. Then a delay between the two lasers is set at an average starting value, typically 1 μs, and the UV laser energy is gradually increased by increments of tens of μJ until a two-step laser mass spectrum is observed and recorded. Both the energy of the two lasers and the delay can be tuned during each experiment to maximize the ion intensity of the species of interest at detector.

In the L2MS experiments at Stanford, a 20-μl drop of the sample solution was spotted onto a glass plate and dried under ambient conditions. Then the glass plate was transferred into the vacuum chamber through an interlock. Each recorded spectrum is averaged over 50 laser shots.

For the GSFC prototype results given below, the 1064 nm IR laser energies ranged from 75 to 190 μJ, corresponding to a range of peak power density between 18 and 81 MW/cm². UV laser energies ranged from 40 to 140 μJ, corresponding to a range of peak power density between 77 and 450 MW/cm². OPO laser energies ranged from 10 to 290 μJ, corresponding to a range of peak power density between 2 and 59 MW/cm². For a laser spot size estimated to be ~300μm diameter. Each spectrum represents an average of 10-20 laser shots.

The UV laser energy in Stanford L2MS is tuned to 10 μJ, for a beam spot of 6 mm in diameter without focusing, corresponding to peak power density of approximately 3.5 MW/cm². The energy of the CO₂ laser is not well known, but is operated below the threshold for IR ionization.

5. RESULTS

Here we report results of L2MS measurements of three organic classes relevant to planetary astrochemistry: polycyclic aromatic hydrocarbons, amino acids, and nucleobases. Figures 2 and 3 show a comparison of results using different three different IR laser wavelengths: (Fig. 2) 10 μm at Stanford. (Fig. 3 top) 1064 nm at GSFC with the miniature prototype, and (Fig. 3 bottom) 2.9 μm at GSFC, also with the miniature prototype.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Class</th>
<th>m.w.</th>
<th>Structure</th>
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<tr>
<td>16-PAH Mixture</td>
<td>PAH</td>
<td></td>
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</tr>
<tr>
<td>47940-1, Sigma-Aldrich</td>
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<tr>
<td>Naphthalene</td>
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<tr>
<td>Aacenaphthalene</td>
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<tr>
<td>Aacenaphthene</td>
<td>154</td>
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<tr>
<td>Fluorene</td>
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<tr>
<td>Phenanthrene</td>
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<tr>
<td>Anthracene</td>
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<td>Fluoranthenne</td>
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<td>Pyrene</td>
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<tr>
<td>Benzo(b)fluoranthenne</td>
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<td>Benzo(k)fluoranthenne</td>
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<td>Benzo(a)pyrene</td>
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<tr>
<td>Indeno(1,2,3-cd)pyrene</td>
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<td>Dibenz(a,h)anthracene</td>
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<td>Benzo(g,h,i)pyrene</td>
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<tr>
<td>2.6 Diaminopurine</td>
<td>Nucleo-base</td>
<td>150.14</td>
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</table>

Table 1. A suite of organic standards has been analyzed with the compact L2MS prototype and the laboratory-scale L2MS instrumentation.
In all three measurements, multiple peaks are seen corresponding to a subset of the PAHs contained within the mixture. The Stanford results shown in Figure 2 (top), were obtained using a 10 μm desorption laser, and mass peaks are seen at \( m/z \) 166, 178, 202, 228, 252, 276, and 278. Comparing to Table 1, we can assign these peaks to the component PAHs contained within the mixture, with the exception of naphthalene (m.w. = 128 Da), acenaphthylene (m.w. = 152 Da), and acenaphthene (m.w. = 154 Da).

![Figure 2](image)

Figure 2. A commercially available mixture of polycyclic aromatic hydrocarbons has been analyzed using the laboratory L2MS instrument at Stanford University, with a 10 μm desorption laser pulse and an ionization pulse at 266 nm.

![Figure 3](image)

Figure 3. A commercially available mixture of polycyclic aromatic hydrocarbons has been analyzed (top) using the compact L2MS prototype at GSFC with a 1064 nm desorption pulse, and (bottom) using the same prototype at GSFC with the desorption pulse at 2.9 μm. In both cases, the ionization step used a 266 nm laser pulse.

Results from the miniature prototype, shown in Figure 2 (center), were obtained using a 1064 nm IR desorption laser and with the same ionization wavelength of 266 nm. Here, the lowest molecular weight PAHs detected are isomers fluorene and pyrene (m.w. = 202 Da). In further contrast, Figure 2 (bottom) shows the same prototype instrument configured to use the IR OPO output, tuned in this case to 2.9 μm wavelength. The same 266 nm ionization wavelength was used. A broader range of PAHs is seen for the 2.9 μm desorption laser, including isomers phenanthrene and anthracene at \( m/z \) 178 and through the high molecular weight species in the mixture. We provide plausible mechanisms for these biases seen between instruments and configurations in the discussion section below.

Representative species from the amino acid and nucleobase classes of molecule been analyzed using L2MS to illustrate the detection capabilities for classes of molecule beyond polycyclic aromatic hydrocarbons. As shown in Figure 4, the laboratory L2MS instrument at Stanford can readily detect the molecular ion of 2,6-diaminopurine at \( m/z \) 150 using a desorption laser pulse at 10 μm and ionization at 266 nm. Likewise, tryptophan can be detected using the same laser configuration. The strongest peak in the tryptophan spectrum, however, is the major fragment at \( m/z \) 130.

![Figure 4](image)

Figure 4. Organic standards been analyzed using the laboratory L2MS instrument at Stanford University, with a 10 μm desorption laser pulse. (top) The 2,6-diaminopurine molecular ion is seen at \( m/z \) 150 (top) and that of tryptophan is seen at \( m/z \) 204 (bottom).

For comparison, we show analysis of these standard organic with the GSFC prototype in the mid-IR desorption configuration, with desorption at 2.9 μm and ionization at 266 nm. The molecular ion of 2,6-diaminopurine, a nucleobase, is readily seen at \( m/z \) 150 (Fig 5 (top)). The major fragment at \( m/z \) 130 is the dominant mass feature in the mass spectrum of tryptophan (Fig 5 bottom). Also seen in these spectra is the molecular ion of coronene at \( m/z \) 300. Coronene was added to these samples as a mass calibrant.

6. Discussion

The results shown above allow us to compare the instrument performance using a range of desorption wavelengths from 1064 nm to ~ 3 μm to 10 μm. All analyses were performed using 266 nm for ionization. If we compare the mass spectra of the 16-PAH mixture, we observe that the 2.9 μm desorption wavelength produces a more representative mass spectrum of the PAHs contained within the mixture. The
mass spectrum obtained for the case of a 1064 nm desorption laser shows an apparent bias towards higher molecular weight compounds. In comparison, the mass spectrum obtained with the laboratory instrument using 10 μm desorption shows the broadest range of PAHs from the known mixture.

Further, we can postulate that instrument differences or details of the measurement between the laboratory L2MS analyzer and the compact prototype could lead to variations in results. For example, we have previously described a mass-dependent effect in the optimization of the delay time between the desorption and ionization pulses [8]. We cannot therefore rule out that small shifts in the delay timing could also give rise to mass biases in the resulting spectra.

While these experimental factors can all play a contributing role to the observed differences in spectra, we suggest that the particular vibrational energetics of the species under study are also important to the desorption wavelength dependence presented here. The fine wavelength dependence experiments are currently in progress, and our detailed findings will be the topic of a future report.

Whereas the nucleobase 2.6 dianinopurine is easily seen using desorption at both 10 μm and 2.9 μm, tryptophan does appear to exhibit a wavelength dependence that is qualitatively in agreement with the PAH results; that is, the molecular ion is more readily detected for the longer wavelength configuration. It is important to note that tryptophan is less subject to volatilization effects than the PAH mixture, given its stability in solid form under ambient conditions. The case of tryptophan also supports the conclusion that longer desorption wavelengths is important to the detection of certain species with the L2MS technique.

7. CONCLUSION

We have demonstrated two-step laser mass spectrometric analyses with compact instrumentation that would be compatible with future in situ planetary mission opportunities. The two-step mass spectra of a suite of organic standards reported here illustrate the sensitivity of L2MS to key aromatic species, including polycyclic hydrocarbons, nucleobases, and amino acids. Detecting and characterizing these species will be important as part of future exploration missions to understanding the astrochemical and prebiotic inventory of high priority solar system targets. Whereas our investigations suggest that longer desorption wavelengths provide the most efficient detection of certain organic species, a 3μm laser pulse can produce meaningful analysis of a broad variety of organics relevant to planetary chemistry in an instrument package that could feasibly be a core analytical capability of a future in situ science payload designed for studying an icy or primitive body.

REFERENCES


StephanieGetty is a Research Planetary Scientist at the Planetary Laboratory at NASA's Goddard Space Flight Center with interests in the development of advanced instrumentation for the compositional analysis of planetary environments. She currently serves as Principal Investigator of the PIDD-funded development of a two-step laser-tandem time-of-flight mass spectrometer for targeted elucidation of organics in non-volatile planetary surface chemistry. She also serves as Principal Investigator of the ASTID-funded development of OASIS, a liquid chromatography-mass spectrometer for in situ analysis of prebiotic compounds. She is a member of the ExoMars MOMA-MS team and a Mars Science Laboratory Collaborator.

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