MALDI TOF MS: An Exobiology Surface-Science Approach for Europa

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Abstract

If Europa is to be of primary exobiological interest, namely as a habitat for extant life, it is obvious that: (i) a hydrosphere must prevail beneath the cryosphere for a long time, (ii) internal energy sources must be present in a sufficient state of activity, and (iii) a reasonable technical means must be available for assessing if indeed life does exist in the hypothesized hydrosphere. This discussion focuses on technological issues, because the the compounding evidence about Europa indicates that the first two are highly likely to be true. We present a consideration of time-of-flight mass spectroscopy (TOF MS) conducted *in-situ* on the cryosphere surface of Europa during a landed robotic mission. We assert that this is a reasonable technical means not only for exploring the composition of the cryosphere itself, but also for locating any biomolecular indicators of extant life brought to the surface through cryosphere activity. We also describe a MALDI (MAtrix Laser Desorption and Ionization) TOF MS system that we are constructing as a proof-of-concept prototype for conducting TOF MS measurements on Europa.

1. Introduction

This paper is the summary of a poster contribution to NASA's Laboratory Astrophysics Workshop (held in 2002 May), which itself was based on a prior publication by Wdowiak *et al.* (2001). The reader is directed to that work for further details.

Observations of Jupiter's satellite Europa continue to compound the evidence that subtantial amounts of liquid water exist beneath its icy surface (as hypothesized by Squyres *et al.* 1983), as well as a possible ice-capped ocean or hydrosphere. Were that hydrosphere to be populated with living organisms, some chemical tracers may be available for detection on the Europan surface. Therefore future missions to the surface of Europa will serve as platforms for *in-situ* investigations relevant to exobiology as well as planetary science. The Jovian magnetosphere inflicts Europa with a proton flux of $1.9 \times 10^9\,\mathrm{m}^{-2}\,\mathrm{s}^{-1}$ for $E > 2.5\,\mathrm{MeV}$ (Vogt *et al.* 1979). Two consequences of this environment are (i) that radiation chemistry will play a significant role in the surface ices, and (ii) that deployed instruments must be radiation hardened. Thus, the challenge is to arrive at an instrument or instrument suite that is robust and yet still capable of high-quality results in the service of both planetary science and exobiology. The development of such devices should be of the highest priority. After consideration of all aspects of the issue, it is our assessment that time-of-flight mass spectroscopy (TOF MS) is the instrumental technique most suitable for deployment on the surface of Europa. It permits a definitive level of identification for small molecular species in the surface ices and any larger biomolecules brought to the surface from the hypothesized hydrosphere through ice-cap activity, were the hydrosphere populated by extant life. Moreover, this technique should be less susceptible to a high-radiation environment than optical devices.

2. Reconciliation of Measurements at Low and High Molecular Weight

Given the potential presence of biomolecules and the technical challenge of actually putting a lander on the surface of Europa, it makes good sense to give the instrument the capability of large biomolecule/biopolymer detection. Recent years have shown the usefulness of mass spectroscopy for such tasks, including the characterization of microorganisms (Fenselau 1994). In life-science laboratories, a method of choice for measurement of large biomolecules is matrix laser desorption and ionization mass spectroscopy (MALDI-MS). The key to MALDI-MS is to place the sample in close proximity to an agent that vaporizes and ionizes under the action of a UV laser pulse, and then transfers its charge to the sample molecules. The most significant benefit of this process is that delicate molecular species such as DNA, which fragment under other ionization techniques (compounding the task of identification), remain intact and are only singly charged.

While strikingly successful for identifying biomolecules, MALDI agents such as 2,5-dihydroxybenzoic acid produce such an intense mass distribution in the low molecular-weight region that they mask the signal of small molecules present in the sample. This is a significant issue for planetary science objectives on Europa. The key, then, to utilizing a TOF MS system on Europa will be to produce an instrument capable of detecting both small and large molecules.

MALDI agents that do not proliferate in the low molecular-weight range are therefore necessary for such an instrument. We propose the use of nanometer-sized metallic particles. By virtue of their size, these particles have very large optical absorption cross-sections, and efficiently vaporize and ionize under the action of a laser. The contribution of this type of MALDI agent to a mass spectrum is merely its atomic weight and can be readily separated from other species in the mass distribution. Cobalt particles 20 nm in diameter have been shown to be useful as MALDI agents (Tanaka *et al.* 1988; Kawabata *et al.* 1998), since their only contribution to the mass spectrum is the Co^+ ion at $m/z = 58.9332$.

Evaporating a metal onto a cryo-ice at 77 K results in, rather than a film, a deposit of small "islands" in the nm-size range (Wdowiak, unpublished result). Methods of dispensing metallic species, such as Co, and other potential MALDI agents mentioned previously onto cryo-ice, by vaporization and other means, are now being explored in our laboratory.

MALDI, as done in biomolecular laboratory measurements, involves mixing the agent and the sample prior to insertion into the instrument. On the other hand, a metal agent couples the laser energy to the material under interrogation through its optical absorption. Although applied to the surface the laser pulse vaporizes both the metal MALDI agent and the sample underneath, and these are mixed in an extremely rapid manner in the vapor phase. This simplifies sample preparation as compared to current laboratory MALDI methods.

The cryogenic conditions on Europa provide a unique opportunity to implement this technique, one that would not be normally used in a room-temperature laboratory. On Europa, the lack of a significant atmosphere and the low ($\sim$ 125 K) temperature make it possible to manufacture nanophase MALDI metal agent deposits directly onto the sample simply by va-

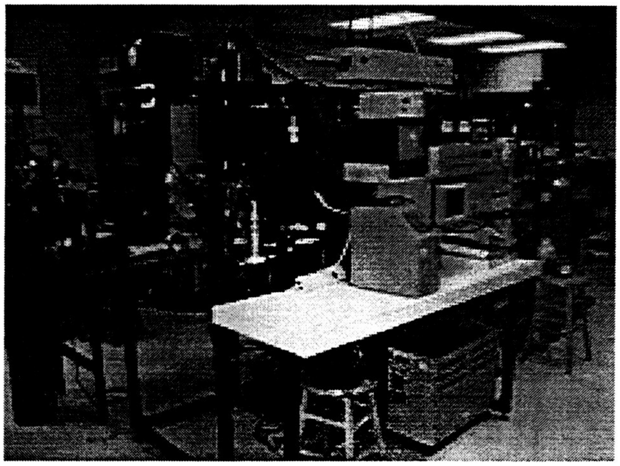

Fig. 1.— Operational system of the test bed. The 266 nm laser is seen horizontal at top, fronted on the left end with the fiber-optic interface/attenuator assembly out of which comes the silica fiber optic cable terminating in the UV optical bench that directs the radiation to a focus in the vacuum chamber. The large box adjacent to the stool under the console table is the 266 nm laser power system. The assemblies at the left end of the test bed are shown in detail in Fig. 2.

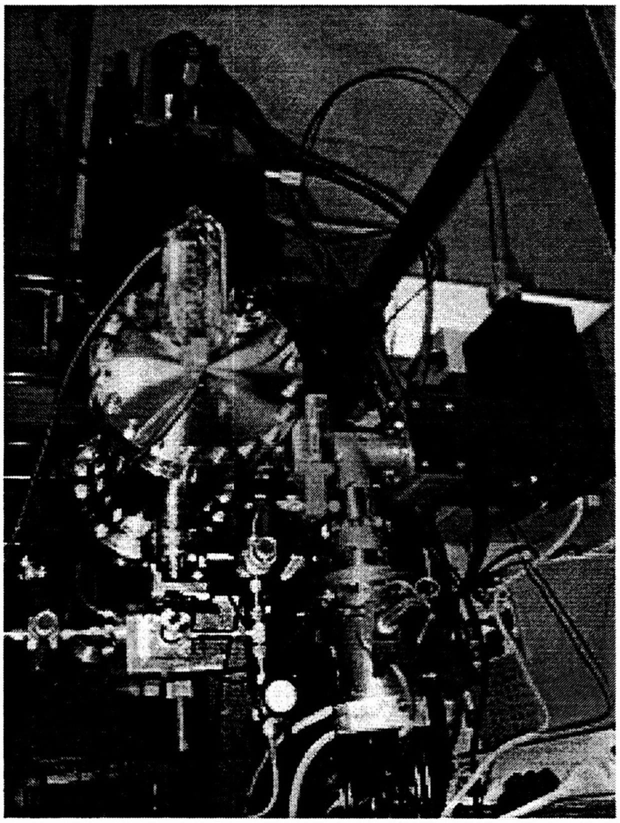

Fig. 2.— The bulkhead plate of the ionization chamber region of the TOF MS (left of center) accomodates the vacuum ionization and thermocouple gauge tubes. Below it is the airlock assembly utilizaed for introducing solid samples during the shakedown stage of the test-bed's development. This will be the position of the cryogenic target assembly. To the right of the chamber, is an airlock LED pressure-status gauge and vacuum tee, below which is a turbomolecular pump and to which the L-shaped UV optics bench is mated. The fibeer-optic UV link from the 266-nm lader can be seen terminating at the top of the UV optical bench. At the upper left, the 1064-nm deosrption laser head can be seen.

porizing the metal onto the cold surface. This permits the use of easily evaporated metals such as aluminum, magnesium, sodium, or potassium as MALDI agents (other metals are of interest as well).

3. Conclusions and Future Work to be Done

Figures 1 and 2 contain photographs of our current TOF MS system at the University of Alabama at Birmingham. At this time, our work has only included room-temperature samples, but this year a cryo-ice system will be attached to the test bed in order to simulate the low temperatures on Europa (and elsewhere in the outer Solar System). Our instrument will be able to simulate surfaces with temperatures ranging from 6 to 300 K. It will be interfaced at the current position of the room-temperature airlock that is presently being utilized to introduce solid samples. The metal MALDI agent dispenser is also to be added to the system in the coming year.

Acknowledgments

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