

# Laser desorption lamp ionization source for ion trap mass spectrometry

Qinghao Wu and Richard N. Zare\*

**A two-step laser desorption lamp ionization source coupled to an ion trap mass spectrometer (LDLI-ITMS) has been constructed and characterized. The pulsed infrared (IR) output of an Nd:YAG laser (1064 nm) is directed to a target inside a chamber evacuated to ~15 Pa causing desorption of molecules from the target's surface. The desorbed molecules are ionized by a vacuum ultraviolet (VUV) lamp (filled with xenon, major wavelength at 148 nm). The resulting ions are stored and detected in a three-dimensional quadrupole ion trap modified from a Finnigan Mat LCQ mass spectrometer operated at a pressure of  $\geq 0.004$  Pa. The limit of detection for desorbed coronene molecules is 1.5 pmol, which is about two orders of magnitude more sensitive than laser desorption laser ionization mass spectrometry using a fluorine excimer laser (157 nm) as the ionization source. The mass spectrum of four standard aromatic compounds (pyrene, coronene, rubrene and 1,4,8,11,15,18,22,25-octabutoxy-29H,31H-phthalocyanine (OPC)) shows that parent ions dominate. By increasing the infrared laser power, this instrument is capable of detecting inorganic compounds. Copyright © 2015 John Wiley & Sons, Ltd.**

**Keywords:** photoionization; VUV lamp; aromatic compounds; two-step mass spectrometry; CO<sub>2</sub> laser

## Introduction

Laser desorption laser ionization mass spectrometry (L<sup>2</sup>MS) has been widely used for studies of ancient terrestrial rocks,<sup>[1]</sup> sediments and soils,<sup>[2,3]</sup> meteorites,<sup>[4,5]</sup> interplanetary dust particles,<sup>[6,7]</sup> cometary particles,<sup>[8]</sup> atmospheric aerosols,<sup>[9]</sup> agricultural samples,<sup>[10]</sup> polymers,<sup>[11]</sup> asphaltenes<sup>[12–16]</sup> and natural water samples.<sup>[17]</sup> Compared to one-step laser ionization mass spectrometry, such as matrix-assisted laser desorption/ionization (MALDI) and surface-assisted laser desorption/ionization (SALDI), L<sup>2</sup>MS separates the desorption and ionization steps. In the first step of L<sup>2</sup>MS, analytes are desorbed by a pulsed infrared (IR) laser. The rapid heating in this step favors desorption over decomposition, minimizing fragmentation.<sup>[18]</sup> Ionization rarely happens in this step because of the low power and low photon energy of the IR laser pulse. In the second step of L<sup>2</sup>MS, analytes are ionized by an ultraviolet (UV) laser pulse through resonance enhanced multiphoton ionization (REMPI) or by means of single photon ionization (SPI). Both of these two ionization schemes produce little fragmentation so that parent ions dominate the mass spectrum.<sup>[19]</sup> The REMPI process at 266 nm (fourth harmonics of the Nd:YAG laser) selectively ionizes polycyclic aromatic hydrocarbons (PAHs), whereas the SPI process is a more universal ionization source that can ionize molecules with an ionization potential below the photon energy.<sup>[20–22]</sup> The second advantage of L<sup>2</sup>MS is that the *in situ* analysis can be easily performed with little sample preparation. In addition, L<sup>2</sup>MS has the capability of making a chemical map with high spatial resolution by using a moving stage to cause the desorption laser spot to move across the target surface.<sup>[4]</sup>

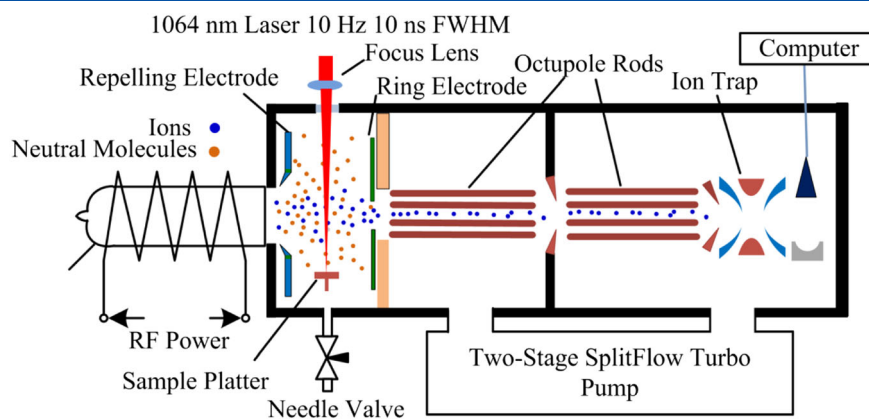
Compared to the ambient ionization method, such as ambient pressure chemical ionization (APCI)<sup>[23,24]</sup> and ambient pressure photon ionization (APPI),<sup>[25–27]</sup> SPI takes place inside the vacuum chamber and avoids reactions between ions and neutrals. By this means the SPI mass spectrum is dominated by parent ions rather than the hydrogen-attached or metal-attached parent ions. In

addition, in APCI and APPI the ionization efficiency largely depends on the proton affinity energy of the analytes and neutral molecules, which may result in a sensitivity variation of several orders in magnitude. In contrast, the difference of ionization cross section between classes in SPI is less than one order of magnitude,<sup>[21]</sup> which greatly aids approximate quantification of compounds.

As the ionization laser is relatively expensive, vacuum ultraviolet (VUV) lamp could be an alternative way to ionize the molecules. VUV lamps have been successfully used in mass spectrometry with the merits of low cost and robustness.<sup>[28–31]</sup> Due to the different photon energies that are available with different kinds of VUV lamps, such as 8.4 eV, 10 eV, 10.6 eV and 11.8 eV, the VUV light source can ionize most organic compounds.<sup>[20]</sup> Although the photon intensity in a continuously working VUV lamp is much lower than that in a pulsed fluorine excimer laser beam, the typical output power is higher, 0.6 W from the VUV lamp (model PXR 084, Heraeus Noblelight GmbH, Hanau, Germany) and 0.4 W from the fluorine excimer laser (model ExciStar XS, Coherent, Inc., Santa Clara, CA). This comparison suggests the possibility that an ionization source using a VUV lamp might provide a superior sensitivity to that of L<sup>2</sup>MS. In addition, the duration of the pulse in the ionization laser is 10 ns to achieve good resolution, which results in a duty cycle of  $10^{-7}$  (ionization time divided by the period of 0.1 s). However, the duration of the desorbed molecules in the ionization chamber is estimated to be on the order of several microseconds. Benefitting from the longer duration of the desorbed molecules exposed to the ionizing radiation, the continuously working VUV lamp increases the duty cycle by more than two orders of magnitude.

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**Figure 1.** Schematic diagram of the LDLI-ITMS. The actual dimensions (excluding the computer and laser) are 1 m long, 1 m wide and 0.8 m high.

Johnson *et al.*<sup>[31]</sup> have reported an alternative two-step form of mass spectrometry in which the ionization laser was replaced by VUV lamps (Ophos instruments, Inc, Rockville, MD, USA) and the ion source are kept at Martian conditions ( $\sim 2.5$  Torr  $\text{CO}_2$ ) for the purpose of detecting organic compounds on Mars. They used a time-of-flight detection system. However, because the VUV lamp must work continuously, an ion trap should be a better mass analyzer for it, owing to the superior detection efficiency when coupled to a continuous ion source. In addition, ion trap mass spectrometry can obtain structural information of compounds through MS/MS experiments. This study illustrates some of the advantages of combining laser desorption lamp ionization with an ion trap mass spectrometer which we call an LDLI-ITMS instrument.

## Experimental

### Construction of the LDLI-ITMS

Figure 1 shows a schematic diagram of the LDLI-ITMS apparatus including the data acquisition system. The ion trap was modified from a commercial instrument (Finnigan Mat LCQ, Thermo Electron Corporation, Waltham, MA). An IR pulse (O.D. = 2 mm) from a Nd:YAG laser (Quanta-Ray, Santa Clara, CA, USA; model DCR-11,  $\lambda = 1064$  nm) is used to desorb analytes on the brass sample platter in a vacuum chamber whose pressure can be adjusted from 1 Pa to 20 Pa by turning a needle valve. The desorbed neutral molecules form a plume in the upper region of the sample platter. This plume is irradiated perpendicularly by the light from a VUV lamp (Heraeus, Hanau, Germany; model PXR084, main photon energy at 8.4 eV). During this process, single photon ionization (SPI) occurs. The created ions are pushed by the repelling electrode (9 V) and focused by the ring electrode in the ionization region and then transmitted into a 3D quadrupole ion trap mass spectrometer through a pair of octupole rods. The mass resolution is approximately unit resolution from 50 to 2000 amu.

### Sample preparation

All compounds in the experiment are purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification. A mixture of pyrene (202.25 g/mol), coronene (300.35 g/mol), rubrene (532.7 g/mol) and 1,4,8,11,15,18,22,25-octabutoxy-29H, 31H-phthalocyanine (OPC, 1091.4 g/mol) was made to test the characteristics of the instrument. To test the sensitivity, a surface concentration of coronene at  $8.8 \text{ pmol/mm}^2$  was prepared by

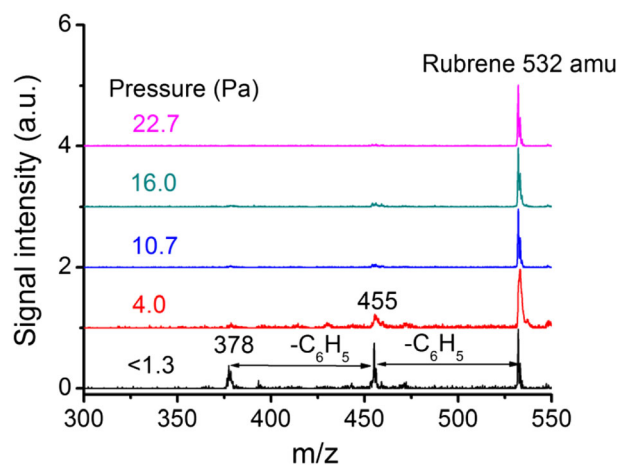
applying 5- $\mu\text{l}$  coronene solution ( $0.05 \text{ }\mu\text{mol/ml}$ ) onto the sample platter (O.D. 11.3 mm).

## Results and discussion

### Pressure effect

Collisions are inevitable in the ion trap mass spectrometer, and they are more important in the photon ionization ion source because the ions may be in a highly excited state after ionization. In such a state, strong collisions will easily cause fragmentation, but weak collisions may release excess energy, making the ions more stable. The energy of collision can be controlled by the pressure. Higher pressure reduces the mean free path, which results in a higher collision frequency. The energy lost in collisions is also increased, and at the same time, the energy gained from electric field between collisions is reduced. This effect reduces collision-induced fragmentation.

In our instrument, the pressure in the ionization chamber is controlled by a needle valve and monitored by a thermal conductivity gauge. Figure 2 shows rubrene mass spectra under different pressures in the ionization chamber. Under low pressure (less than 1.3 Pa), the rubrene mass spectrum shows strong fragmentation signals at 455 and 378 amu, caused by losing phenyl groups. With increasing pressure, the fragment signals are reduced. For a pressure higher than 16 Pa, negligible fragmentation occurs.



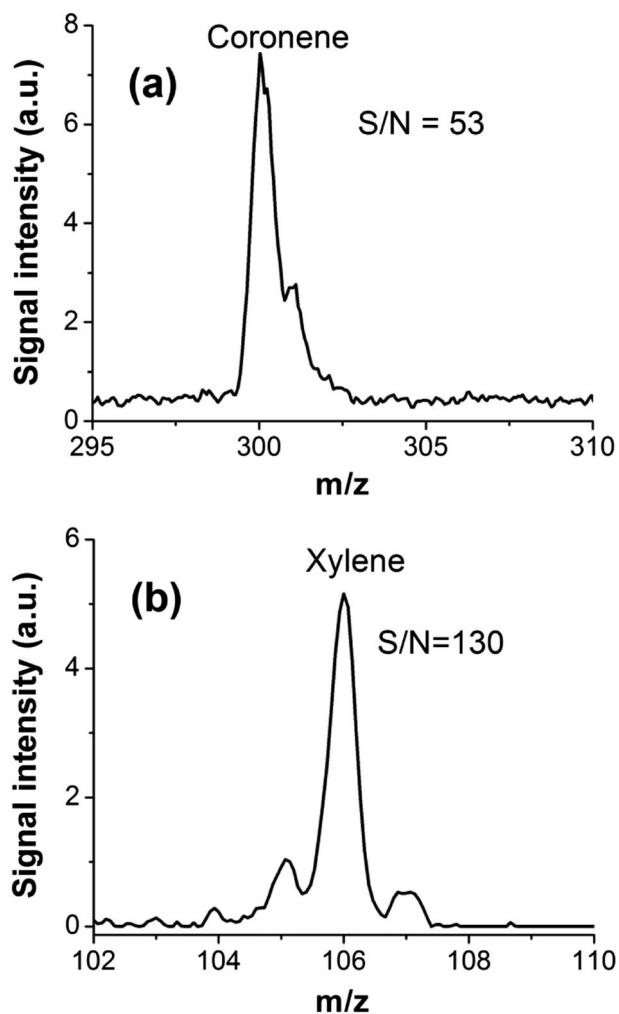
**Figure 2.** Mass spectra of rubrene at different pressures in the ionization chamber. The signal intensity is normalized to unity for the largest peak in each trace.

### Limits of detection (LODs)

The LODs in this instrument are one of the most important issues because of the low photon intensity produced by the VUV lamp. Figure 3(a) shows the peak of coronene at surface concentration of  $8.8 \text{ pmol/mm}^2$ . The calculated LOD is  $0.5 \text{ pmol/mm}^2$  based on  $S/N=3$ . Taking into account the laser spot area, the amount of molecules desorbed at the detection limit is  $1.5 \text{ pmol}$ .

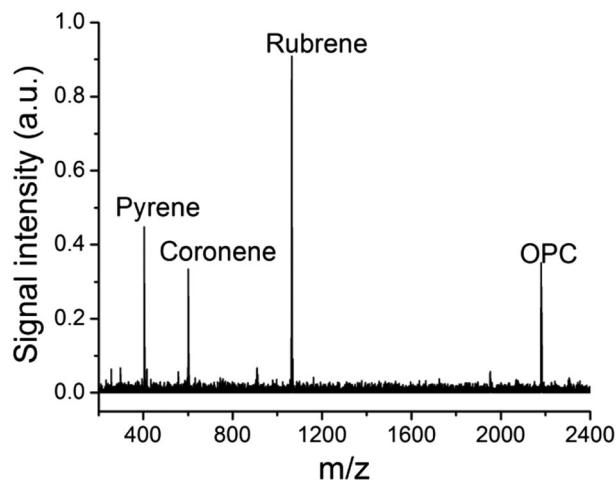
The good sensitivity in LDLI-ITMS can be attributed to several factors. First, the high transmission efficiency of ions in ITMS reduces the ion loss. Second, the VUV light can go through the ionization region and through the octupole rods. This prolonged light path increases the ionization efficiency. Moreover, the pumping of the buffer gas (usually air) from the ionization chamber through the chamber in which the octupole pair is located causes many of the desorbed molecules to stay longer in the VUV light path, which is also helpful for increasing the ionization efficiency. Experiments show that the signal intensity increases when pressure in the ionization chamber is increased.

As gas can be easily introduced into the ionization chamber through the needle valve, the LOD of xylene diluted in nitrogen was also tested. In the experiment, a VUV lamp with a photon energy of  $10 \text{ eV}$  (filled with krypton, major wavelength at  $124 \text{ nm}$ )

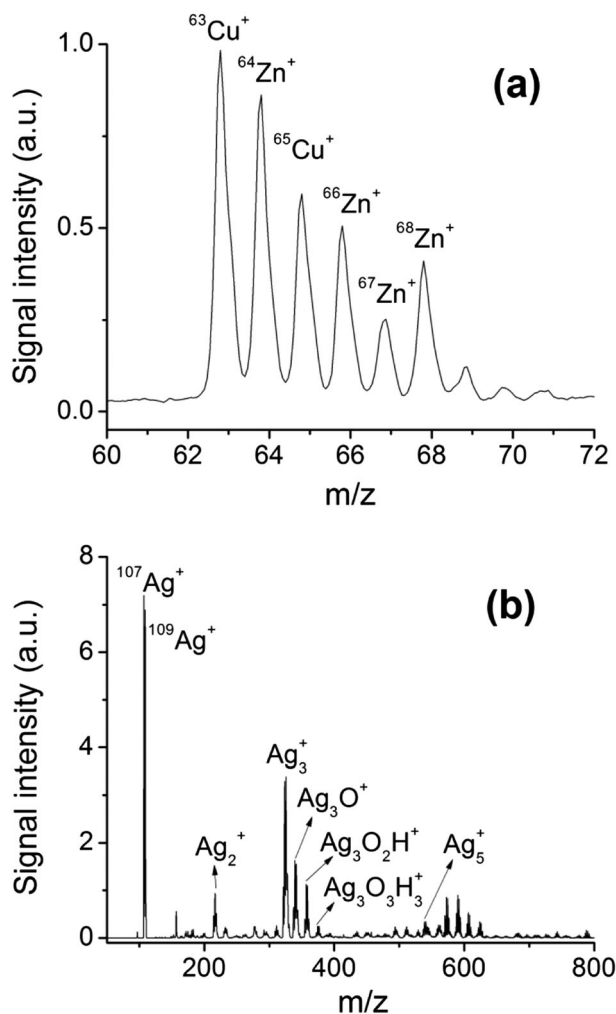


**Figure 3.** Sensitivity test: (a) the mass spectrum of coronene at a surface concentration of  $8.8 \text{ pmol/mm}^2$ ; and (b) the mass spectrum of xylene at a concentration of  $36 \text{ ppbv}$ .

was used to ionize xylene. Figure 3(b) shows that the LOD for xylene is lower than  $1 \text{ ppbv}$  based on the  $S/N=3$  and an accumulation time of  $20 \text{ s}$ .



**Figure 4.** Mass spectra of a mixture of pyrene, coronene, rubrene and OPC in LDLI-ITMS.



**Figure 5.** The mass spectra of (a) brass and (b)  $\text{AgNO}_3$  recorded in LDLI-ITMS with VUV lamp off.

### Detection of a mixture of aromatic compounds

A mixture of four organic compounds (pyrene, coronene, rubrene and OPC) is tested in LDLI-ITMS under a pressure of 15 Pa. Figure 4 shows that parent ions dominate in the mass spectrum. Weak signals from fragments are observed, which should be caused by the collisions that are unavoidable in the LDLI-ITMS as previously discussed.

### Detection of inorganic compounds

In the experiments, when the IR laser power was increased to a very high level, mass spectra of copper and zinc were observed (Fig. 5(a)). These atoms come from the brass sample platter. The signals from brass are very strong even when the VUV lamp is turned off. Therefore, these ions should come from the desorption step. In this mode, the high power of the laser induces a small plasma on the target. The plasma will ionize a portion of molecules desorbed by the IR laser, and the ions are transmitted into the ion trap mass analyzer due to the low voltages on the repelling electrode (9 V). To further demonstrate the ability for detecting inorganic compounds, silver nitrate was tested. In the mass spectrum from silver nitrate in Fig. 5 (b), silver ions, aggregated silver ions and silver oxides are observed. This mass spectrum is in a good agreement with a previous study using laser desorption/ionization mass spectrometry.<sup>[32]</sup> For organic compounds, the high laser power desorption mode will result in complex mass spectra which are difficult to interpret. However, for inorganic compounds, the signals from elements are very helpful.

### Conclusions

In this study, a LDLI-ITMS instrument was constructed and characterized. The mass spectra in LDLI-ITMS are dominated by parent ions under optimized pressure. The clean mass spectra are very helpful for making assignments. The LODs in LDLI-ITMS are 1.5 pmol for desorbed coronene and less than 1 ppbv for xylene. The ability of detecting inorganic compounds in high IR laser power is very useful when elemental analysis of the sample is needed. In addition, other merits in the instrument, such as the ability to ionize most of organic compounds, MS/MS ability and the low cost of construction, suggest that this system may have many possible applications.

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