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Deep Ultraviolet Single-Photon Ionization Mass Spectrometry

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Abstract

The requirement of accurate analysis for organic chemicals has stimulated uprising research interest of single-photon ionization mass spectrometry (SPI-MS). Considering that ~90% compounds bear absorption in the deep ultraviolet (DUV) region, it is crucial for SPI-MS applications to employ effective DUV light sources. Here, we summarize the advances of SPI-MS by utilizing deep ultraviolet lamps and lasers, including the combination with quadrupole mass spectrometer (QMS), ion-rap mass spectrometer (ITMS), and time-of-flight mass spectrometer (TOFMS) systems. We then emphasize on the newly developed SPI-MS instrument coupled with an all-solid-state deep ultraviolet (DUV) laser at 177.3-nm wavelength. The advantages of SPI-MS instruments have been illustrated on several organic compounds, where the capability of low fragmentation enables to identify chemicals from unknown mixtures.

Keywords: deep ultraviolet (DUV), single-photon ionization (SPI), time-of-flight mass spectrometry (TOFMS), all-solid-state DUV laser, low-fragmentation

1. Introduction

Simply by measuring the ions abundance relating to their mass-to-charge ratios, mass spectrometry is known as the most powerful tool for identifying the quantity and type of chemicals present in a sample. According to the ionization strategies, mass spectrometry can be classified into hard ionization techniques (typically by direct electron impact, i.e., EI method) [1] and soft ionization techniques which usually include photoionization (PI) [2–8], chemical ionization (CI) [9, 10], matrix-assisted laser desorption/ionization (MALDI) [11], and electrospray ionization

(ESI) [12]. Comparing with the EI technique which readily brings rigorous fragmentation for organic compounds, soft ionization techniques find their own advantages of maximal ionization efficiency without using high-energy electron impact. History keeps moving forward. The requirement for precise chemistry and fragmentation-free identification of mixed complexes has brought new opportunity and challenge to mass spectrometry.

Single-photon ionization mass spectrometry (SPI-MS) is known as an attractive soft-ionization technique resulting in simple mass identification neither utilizing matrix assistance nor rendering interference of multiple-charge ions [13–26]. Reasonable research interest has been attracted to SPI-MS due to the interference-free and fragmentation-free mass spectra, which is especially helpful for complex contaminant detection and mixed sample identification [7], for example, gasoline and diesel, cigarette smoke, and volatile organic compounds (VOCs) [27–48]. The accurate measurements of molecular weight also enable promising applications in conformational analysis [49, 50], real-time process monitoring [51], online characterization of aerosols [52, 53], and pyrolysis and combustion chemistry [54]. It is notable that ~90% of all organic compounds have absorption in the deep ultraviolet (DUV) region ($\lambda < 200$ nm), and thus, the development of better DUV light sources becomes crucial for SPI-MS applications.

In general, DUV sources are obtained using nonlinear frequency conversion of the radiation of DUV lamps [13, 55], gas discharges [56], lasers [57], and electron synchrotrons [54, 58]. **Table 1** lists the present typical DUV light sources for SPI-MS investigations, where a coverage of 117–200 nm illustrates the applicability of SPI-MS for a variety of molecule systems with different ionization energies. Among them, the newly developed technique of all-solid-state DUV laser (177.3-nm) by second harmonic generation of 355-nm laser, in help of a KBBF-CaF₂ prism-coupled device [57, 59], has shown several advantages in photon flux, bandwidth,

| Source of DUV | Generation | Medium | Center Wavelength (nm) |
|--------------------------|-------------------------------------|-----------------------|------------------------|
| Laser-based DUV light | SHG of 355 nm Nd:YAG laser [59, 60] | KBBF crystal | 177.3 |
| | THG of 355 nm Nd:YAG laser [64, 65] | Xe-Ar gas | 118 |
| | Four-wave mixing [53] | Xe gas | 122–168 |
| | F ₂ laser [66] | F ₂ gas | 157 |
| | H ₂ laser [67] | H ₂ gas | 160 |
| Gas discharged DUV lamps | Excimer DUV lamp [56] | dense rare gases | 120–200 |
| | Krypton discharge lamps [68] | Kr gas | 117 |
| | Microwave discharge lamps [51] | He/H ₂ gas | 121.5 |
| Synchrotron light | Monochromatizing the beam line [58] | Electromagnetic field | tunable |

Table 1. Typical DUV light sources for single-photon ionization mass spectrometry.

beam quality, and coherence [59–61], giving rise to largely improved sensitivity/resolution of SPI-TOFMS [62, 63]. Here, we summarize the advances of DUV-SPI mass spectrometry, emphasizing on the SPI-MS techniques based on two typical ionization strategies, that is, VUV lamps and radiation of lasers.

2. VUV Lamps for SPI-MS

2.1. VUV Lamps for SPI-ITMS

Regarding to typical DUV light sources available for SPI-MS investigations (as listed in **Table 1**), low-pressure discharge lamps filled with rare gases (e.g., Kr and Xe/Ar) have been widely utilized in previously published studies such as the online monitoring of organic compounds [69]. Combining with thermogravimetric (TG) device, evolved gas analysis was demonstrated as the most straightforward way for gas-phase reactions. A typical set up in Zimmermann group (**Figure 1**) [69] employs sample matrix of evolved-off gas coupled with a single-photon ionization (SPI) ion-rap mass spectrometer system (ITMS). This set up has been utilized to provide distinct substance identification for evolved gas from roast and ground coffee powder, etc.

2.2. VUV Lamps for SPI-QMS

A similar VUV lamp apparatus relates to quadrupole mass spectrometry (QMS) which was designed to study free radical-molecule kinetics of molecular beam from a Knudsen flow

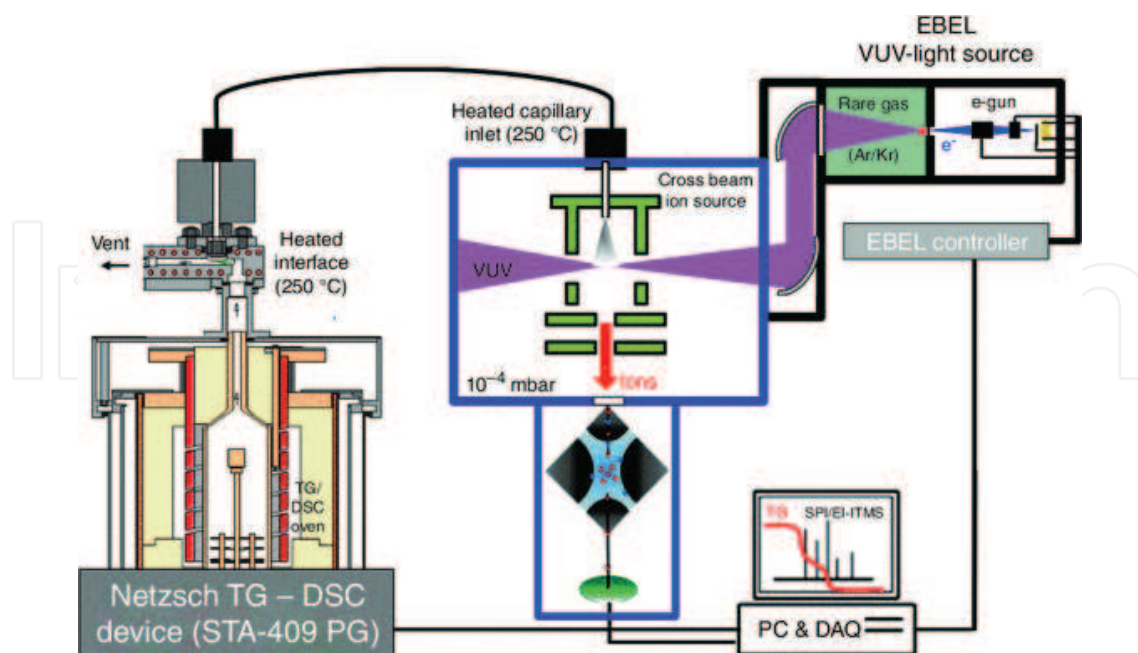


Figure 1. A scheme of the experimental TG–SPI–ITMS setup. The TG is depicted on the left side; the enlarged ionization manifold with ITMS is shown in the middle, and the electron beam pumped rare gas excimer light source (EBEL) for SPI with double parabolic mirror optics is sketched on the right side. Reproduced with permission from Ref. [69].

reactor (**Figure 2**) [70], where the propagating molecular beam and VUV photons meet in a crossed-beam ion source. From such a SPI-MS set up, an interesting study found steady-state exit flow of $\text{C}_2\text{H}_5^\bullet$ (ethyl) and $\text{t-C}_4\text{H}_9^\bullet$ (t-butyl) free radicals indicating the advantages of VUV-lamps for SPI-QMS analysis toward volatile organic compounds (VOCs).

2.3. VUV Lamps for SPI-TOFMS

The VUV lamp with SPI capability has also been developed for time-of-flight mass spectrometry (TOFMS). Utilizing a 10.6 eV krypton discharge lamp (a photon flux up to $\sim 10^{11}$ photons per second), the coupling of SPI with TOFMS (SPI-TOFMS) takes the advantages of rapid detection speed and also simple spectral analysis. SPI-TOFMS has been recognized as a powerful technique for monitoring various fast processes in gas phase, for instance, to real-time monitor the catalytic olefin synthetic reactions [71], to help assign the double bond position in linear olefins, and to verify rapid chemical derivatization such as ozonolysis. **Figure 3** shows a typical SPI-TOFMS instrument in H. Li group [13], where the ion source includes a commercial VUV krypton discharge lamp and an ionization cavity that is made of six steel electrodes. Oxygen gas flow (e.g., olefin and olefin ozonolysis products) can be introduced into the ionization cavity by a fused-silica capillary. They found that relatively high pressure (0.3 mbar) of the ion source is helpful to extend the photoionization length (e.g., ~ 36 mm) and hence to improve ionization efficiency. As a result, toluene, benzene, and *p*-xylene were found to attain

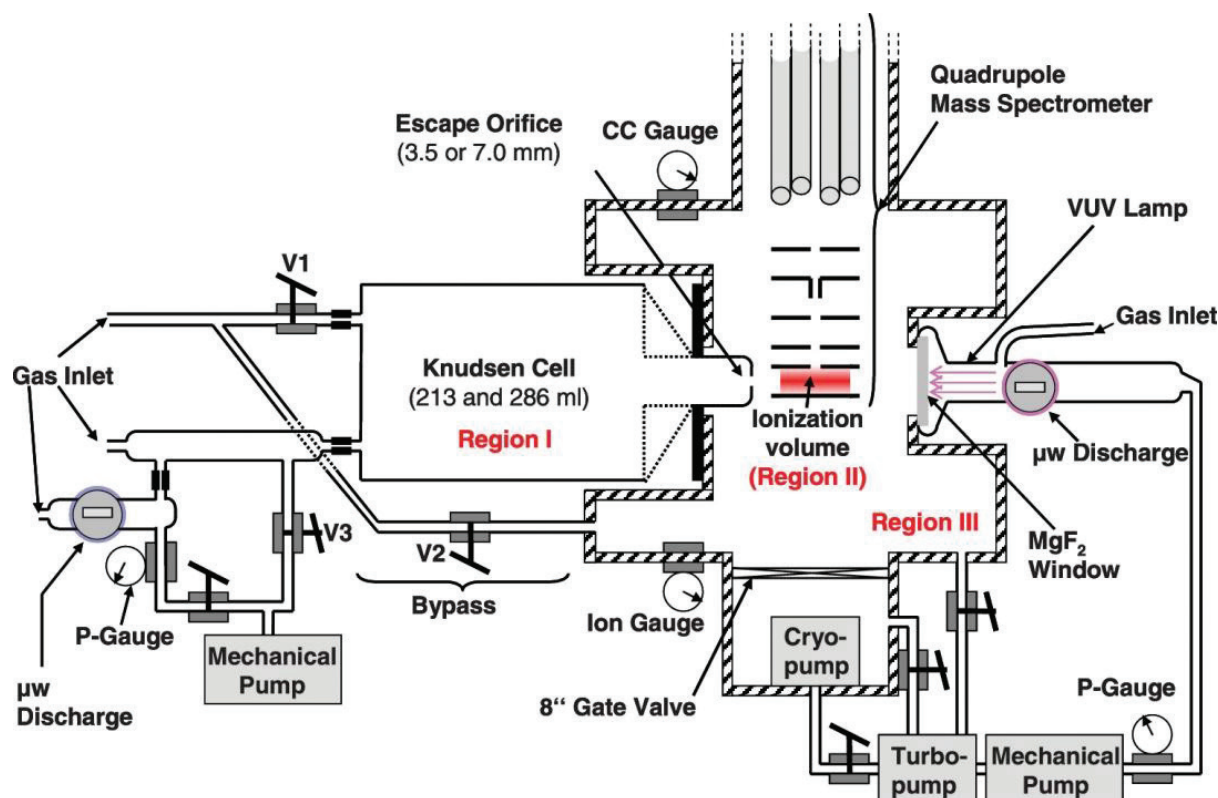


Figure 2. A schematic showing of the VUV-SPIMS for free radical detection by using an external free radical source based on microwave discharge (2.46 GHz) to create H or Cl atoms. Three PTFE capillary inserts of 1–2 mm diameter and 10–20 mm length are displayed on the free radical source (left). Reproduced with permission from Ref. [70].

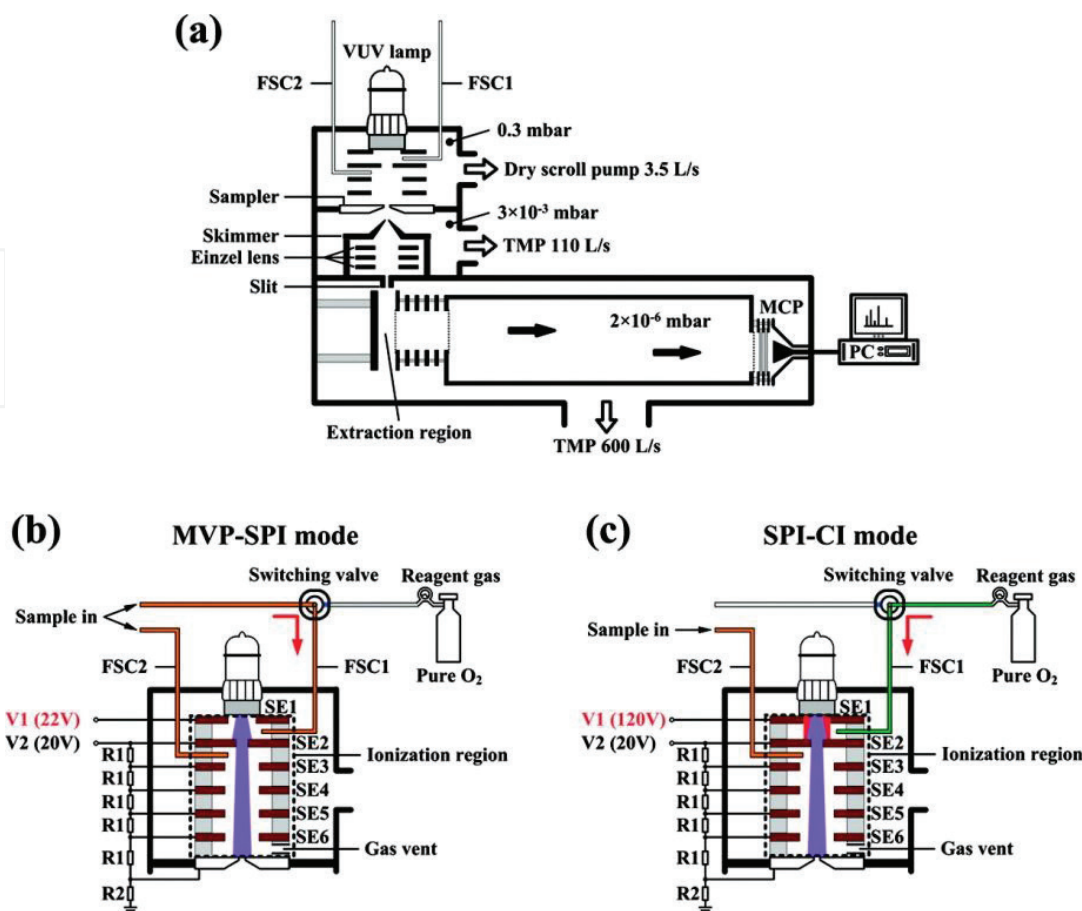


Figure 3. (a) Schematic diagram of a home-built mass spectrometer combining SPI and CI ion sources (a), and its operation in MVP-SPI mode (b), and in SPI-CI mode (c) respectively. Reproduced with permission from Ref. [13].

a limit of detection (LOD) down to 3, 4, and 6 ppbv. Within such SPI-TOFMS strategy, toluene and chloroform also showed LODs values of 8 and 10 ppbv [13]. The capability of SPI-TOFMS method with online ozonolysis has been found operative to quantitatively identify isomeric olefin mixtures [71]. Interestingly, the applicability of SPI-TOFMS for evolved gas analysis of coffee has also been demonstrated in the previously reported study, where kahweol was used as a tracer compound enabling to discriminate arabica coffee from robusta species [72].

Figure 4 presents the SPI mass spectra of linear 1-, 2-, 3- octenes, 1-, 2-, 5- decenes, and their corresponding ozonolysis products. It is notable that some ions which are absent in the SPI mass spectra become dominant in the spectra of corresponding ozonolysis products, such as m/z 96/97 and 113/114 ions for 1-octene, assigned to deprotonation (or protonation) of aldehyde dehydrated ions and aldehyde molecular ions. This was proven to result from ion-molecule reactions between aldehyde products and olefins. Also found from the SPI-MS was the appearance of two new ions corresponding to $[M + 12]^+$ due to “ $-H_2O + CH_2O$ ” and $[M + 18]^+$ due to “ $-C_2H_4 + O_3$ ”, seen at m/z 126 and 132 for 1-octene, also at m/z 154 and 160 for 1-decene, which were found to be only formed for the terminal olefins. At this point, such SPI-TOFMS identification along with corresponding ozonolysis products could be used to distinguish isomers of linear terminal olefins.

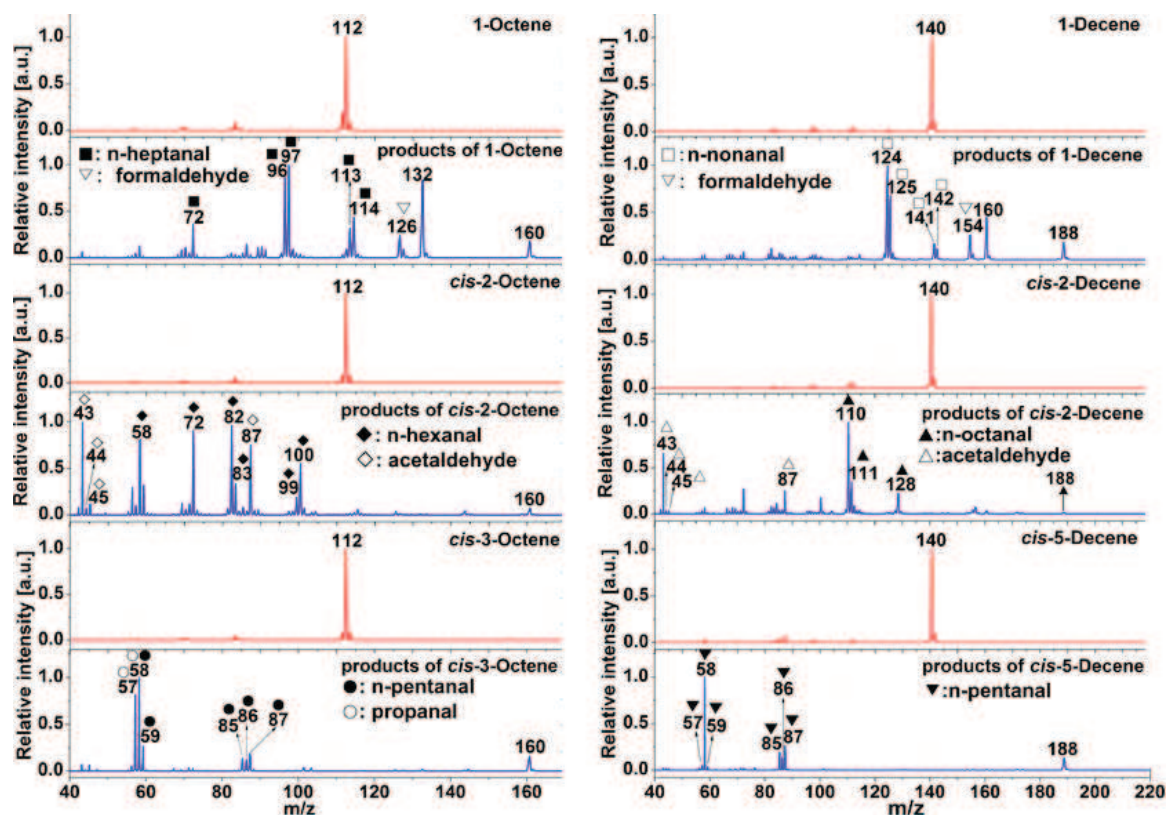


Figure 4. SPI mass spectra of linear octenes, decenes, and corresponding ozonolysis products. Reproduced with permission from Ref. [13].

Figure 5 presents an application of SPI-MS combined with a custom-made smoking machine system. Analogous to the above, the innovative EBEL source filled with argon provides ~ 9.8 eV single-photon energy of the VUV light. The investigated analytes include carbon nitride, acetone, acetaldehyde, acrolein, butadiene, propanal, butanal, 2-butanone, isoprene,

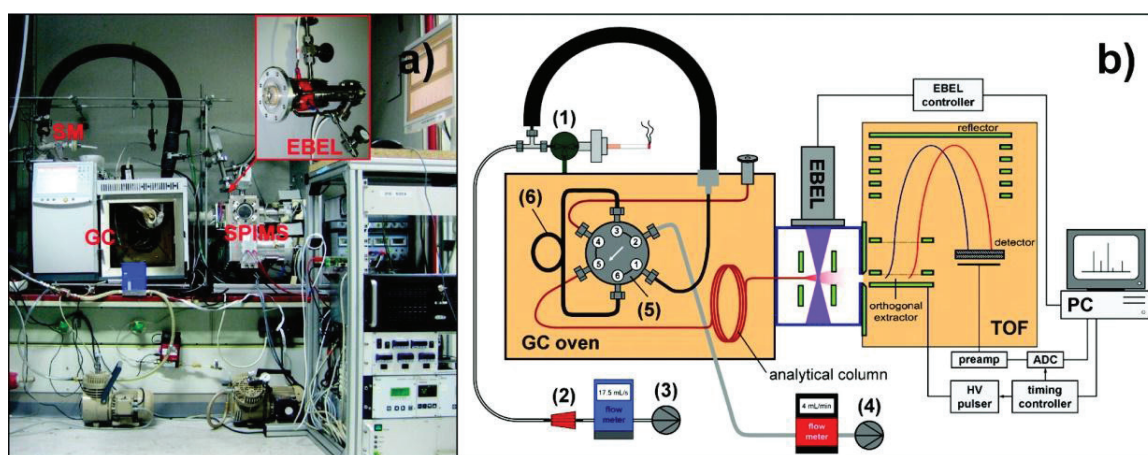


Figure 5. (a) A photo of the two-dimensional smoke analysis system consisting of a home-built smoking machine, a gas chromatograph, and a single-photon ionization mass spectrometer (SPI-MS). (b) Schematic representation of the smoke analyzer: (1) Borgwaldt smoking valve; (2) particle filter; (3) smoking pump; (4) sampling pump; (5) six-port, two-position valve; (6) sample loop. Reproduced with permission from Ref. [73].

furan, isobutanal, crotonaldehyde, benzene, toluene, etc [73]. From such SPI-MS analysis, the determined amounts of these compounds find well consistence with the empirical values. This is another important application of SPI-MS.

Among others, magnetic-field enhanced sources have also been coupled with SPI-MS instruments. Typically, a radio-frequency powered VUV lamp could be used, and the photoelectrons (generated by photoelectric effect) were accelerated to induce ionization, strengthened by a strong magnetic field (~ 800 G) with a permanent annular magnet. Compared to a nonmagnetic field SPI source, the signal could be enlarged two orders with photoelectron energy of ~ 20 eV, with soft-ionization characteristics remained. The advantages of this source are ascribed to the increased electron moving path and the improved electron transmission under magnetic field [74].

3. Laser radiation for SPI-TOF MS

3.1. THG of 355 nm laser in Xe-Ar gas cell

It is well known that a synchrotron source and four-wave mixing techniques have the ability to generate tunable DUV light, but the bulky and complicated devices confine their applications for SPI-MS [2]. Alternatively, there is an important finding that 118-nm laser can be generated through high harmonic generation (HHG) of 355-nm laser in a few noble gases such as a Xe-Ar mixture (e.g., 1:10) [64, 65]. By allowing the 355-nm laser penetrating through a convenient noble gas cell, the 118-nm DUV lasers have been widely applied for SPI-MS investigations. **Figure 6** shows such a method for analyzing organoselenium

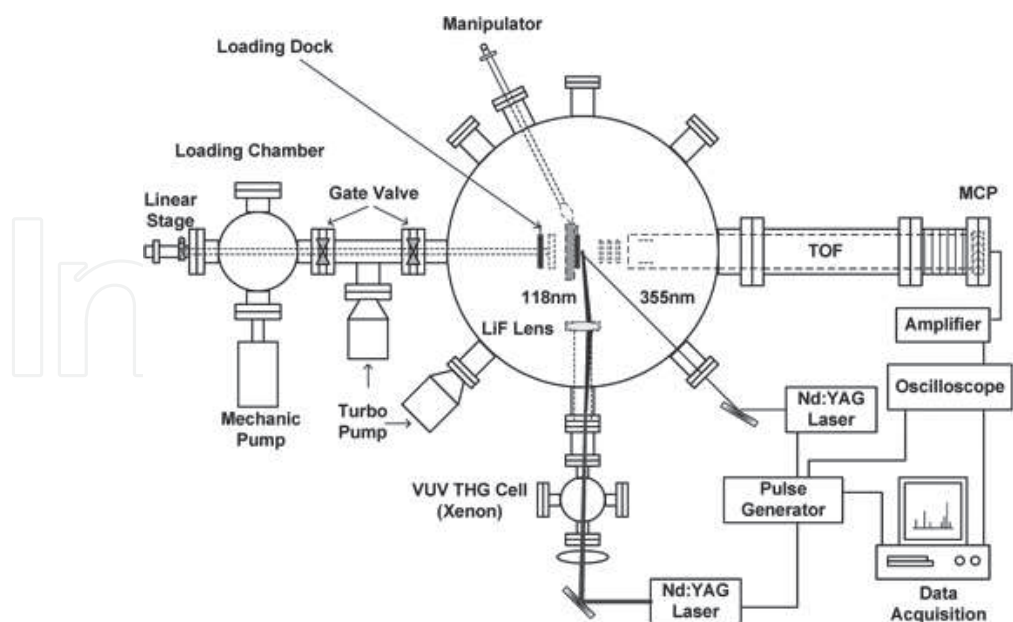


Figure 6. A sketch drawing of the laser desorption single-photon-ionization mass spectrometer consisting of an ultrahigh vacuum chamber equipped with a linear transfer antechamber, where a sample holder with an XYZ controller mounted on a 360° rotation stage, a THG cell, and a home-built linear TOF mass spectrometer. The neutrals were photoionized by a vacuum ultraviolet (118 nm) laser. Reproduced with permission from Ref. [32].

and organic acid metabolites [32], where the laser desorption was included from graphite surfaces coupled with a typical SPI-MS system. High sensitivity (up to fmol) allows quantitative detection of chemicals in complex biological samples such as from human/animal urine, where the accurate detection of biological metabolites is very helpful for medical diagnosis [32].

The application of such laser beam for SPI-TOFMS has also been demonstrated to be highly effective for the rapid detection of the nitro-containing explosives and the related compounds, such as nitrobenzene, *o*-nitrotoluene, 1,3-dinitrobenzene, 2,4-dinitrotoluene, and 2,4,6-trinitrotoluene, as shown in **Figure 7**. In addition to the direct identification capability, the limits of detection using such SPI-MS were found to be as low as ~40 ppb [75]. It is worth mentioning that, although ion mobility-based detection [3–5] is widely used for nitro-containing explosives, as known of a screening tool at airports, the conventional technology is not applicable to all explosive-related chemicals; also, any false negative and positive detection rates may be problematic. In this point, SPI-MS could be one of the most promising techniques for trace detection and identification of explosives.

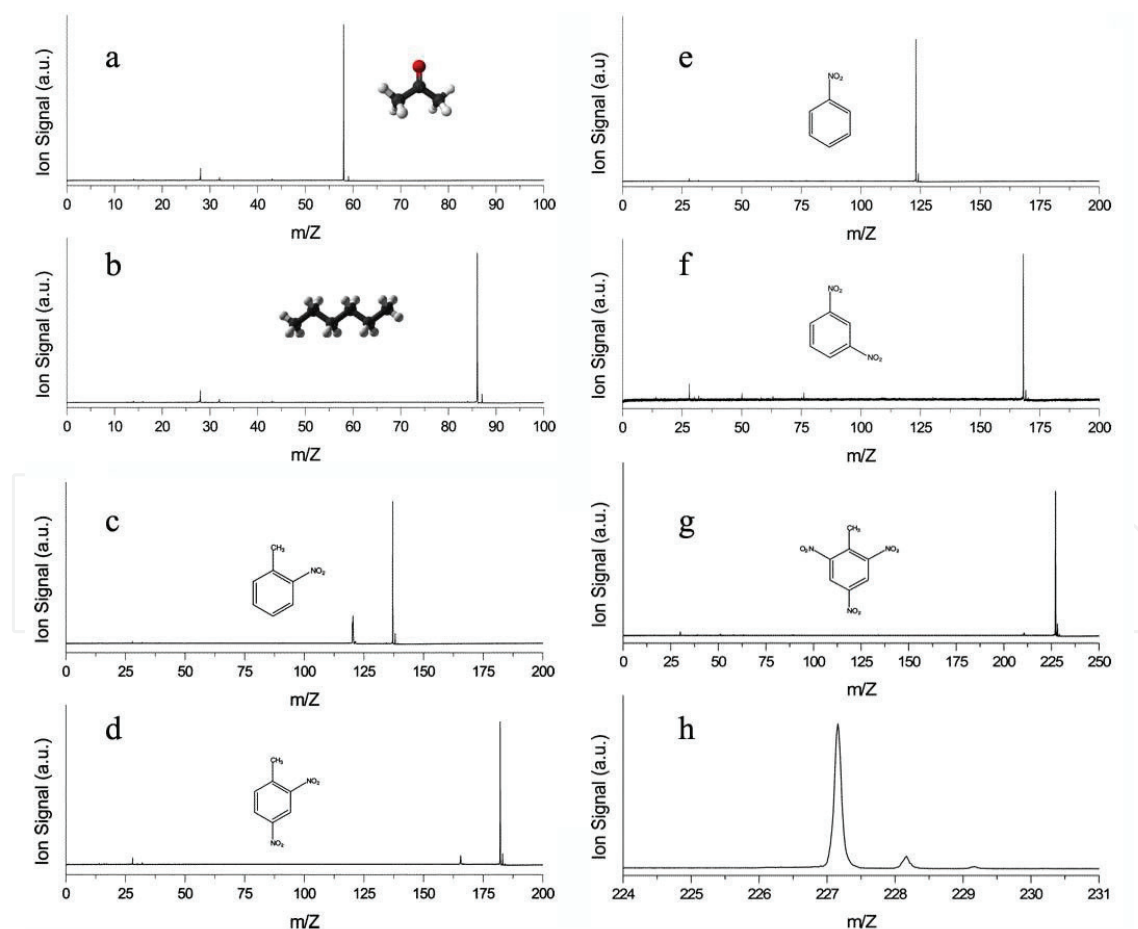


Figure 7. (a) Single-photon ionization mass spectrum of acetone (a), hexane (b), nitrobenzene (c), 1,3-dinitrobenzene (d), *o*-nitrotoluene (e), 2,4-dinitrotoluene (f), and 2,4,6-Trinitrotoluene (g/h). Reproduced with permission from Ref. [75].

3.2. All-solid-state DUV laser for SPI-MS: SHG of 355 nm

Figure 8 shows a sketch of the all-solid-state 177.3-nm DUV laser system for SPI-MS in Luo's group [76], where a picosecond 355-nm laser was chosen as the pump. The 355-nm laser comes from the third harmonic generation of 1064-nm Nd:YAG laser with a pulse duration of ~ 16 ps (a repetition rate of 10 Hz). The 355-nm pump laser was then well modulated at proper height and incident direction prior to the KBBF-PCT device for frequency doubling. The KBBF-PCT device was set on a mobile optics stage allowing rotation and XYZ translation in order to adjust the phase-matching angle and laser beam position. All the reflection mirrors (M4, M5, M6) are motor controlled from outside the chamber. A coated CaF_2 lens (800-mm focus length) was used to focus the DUV laser beam before it was introduced into the vacuum-connected TOFMS chamber. The power of the DUV laser source can be measured by two power meters with plug-in probes via ultrahigh vacuum feedthroughs to evaluate the transfer efficiency in the DUV laser chamber. The DUV optical chamber and the TOFMS chamber were separated by a CaF_2 window which maintains 95% transmittance of the 177 nm DUV laser.

Figure 9 sketches the customized Re-TOFMS system which is made up of two vacuum chambers along with relating pumping system, respectively. Two sampling systems were designed allowing different samples to be analyzed, that is, a pulsed buffer gas contained source and a thermal evaporation molecular beam source. The two sources share a same sampling chamber, and the thermal evaporation source is located downstream crossing the ionization region, allowing the sample vapor to expand upward entering the half-cylinder section through a nozzle and then a skimmer until arriving the ionization zone of Re-TOF chamber. Photo-

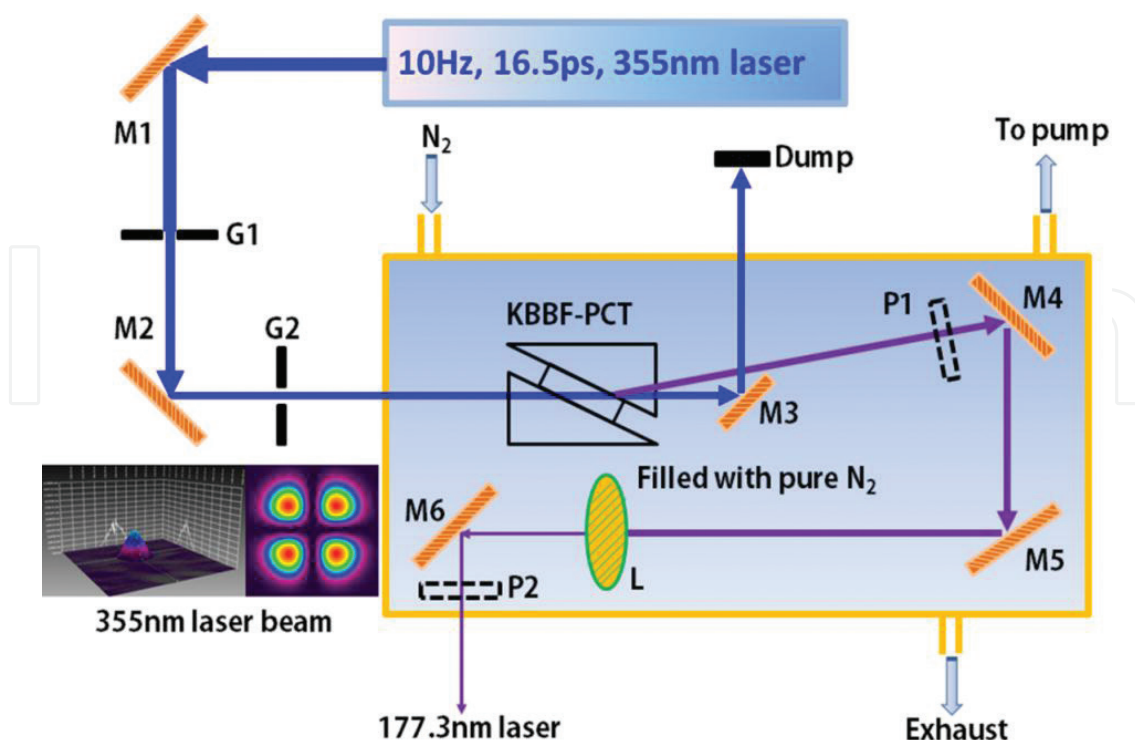


Figure 8. A schematic layout of the all-solid-state 177.3nm DUV laser optical system.

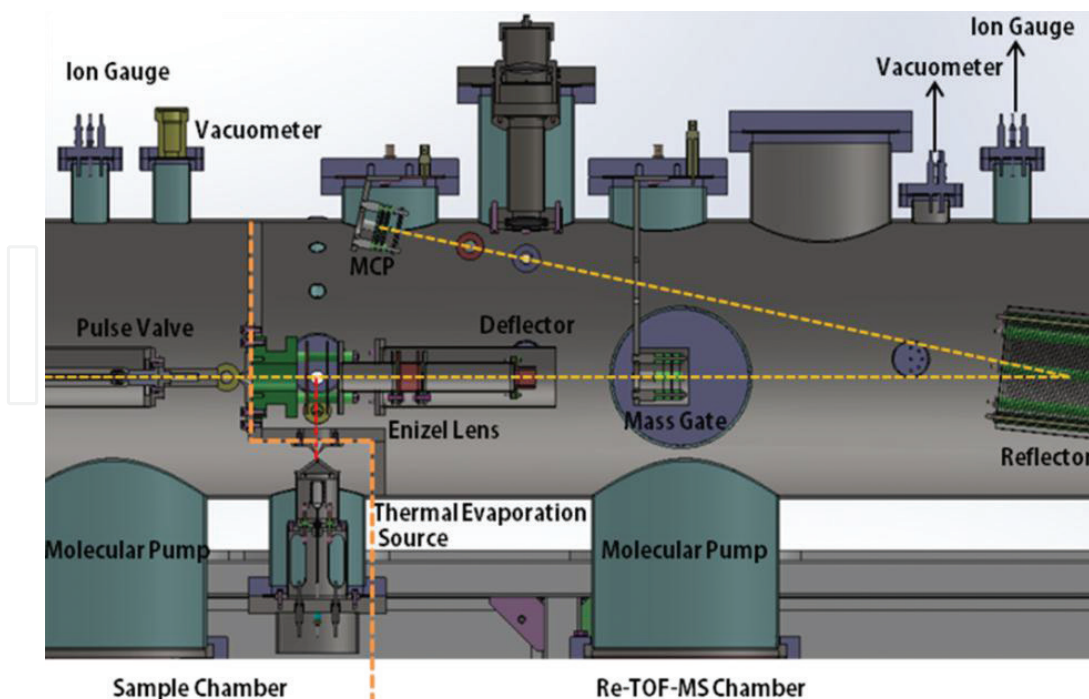


Figure 9. Schematic diagram of the customized mass spectrometer with two DUV-SPI sources.

ionized molecule beam will then horizontally or vertically go into the ionization region and accelerate along the electric field. An einzel lens was designed to focus the ions thus convert the initial energy dispersion of ions enabling to improve the ions collection and mass resolution capability of the TOF mass analyzer. Four electrostatic deflectors were designed to direct ions on the way to the reflector and finally MCP detector. For a maximum transmission efficiency of ions, typical voltages (U_1 and U_2) on the acceleration pole plates were set at 1.6 KV and 1.2 KV, respectively. The pulse valve and laser are synchronized using a DG 535 digital delay generator. A digital storage oscilloscope was employed to record the signal collected by MCP for which a voltage at -2100 V was used.

Based on this DUV-SPI-TOFMS system, several typical molecules have been tested, such as *N,N*-dimethyl-*p*-toluidine (DPT, $C_9H_{13}N$), *p*-phenylenediamine (PPD, $C_6H_8N_2$), 1,5-diaminonaphthalene (DAN, $C_{10}H_{10}N_2$), and porphyrins, as partly shown in **Figure 10**. From the mass spectra of them ionized with a 177.3-nm laser respectively, there are rare fragmentation peaks, which is in sharp contrast to that obtained by 355-nm laser ionization. Specifically for DPT sample, a predominant peak at $m/z=135$ points to DPT molecular ion, where a brother peak at $m/z=134$ is due to a hydrogen atom loss indicating the activation of C–H bond. Also a comparison of the ionization of PPD by 355-nm and 177.3-nm laser reveals that the mass spectrum obtained from DUV ionization shows a dominant peak at $m/z = 108$ identical to the molecular weight of PPD, verifying that the 177.3-nm DUV laser undergoes an excellent SPI process. In sharp contrast, the mass spectrum acquired from 355-nm laser ionization shows a weak parent peak but numerous fragments corresponding to the aromatic amines fragmentation. Several other unpublished DUV-SPI results have also been attained suggesting that the picosecond DUV laser is really an ideal choice for effective SPI-MS. Note that, the mass spectra obtained

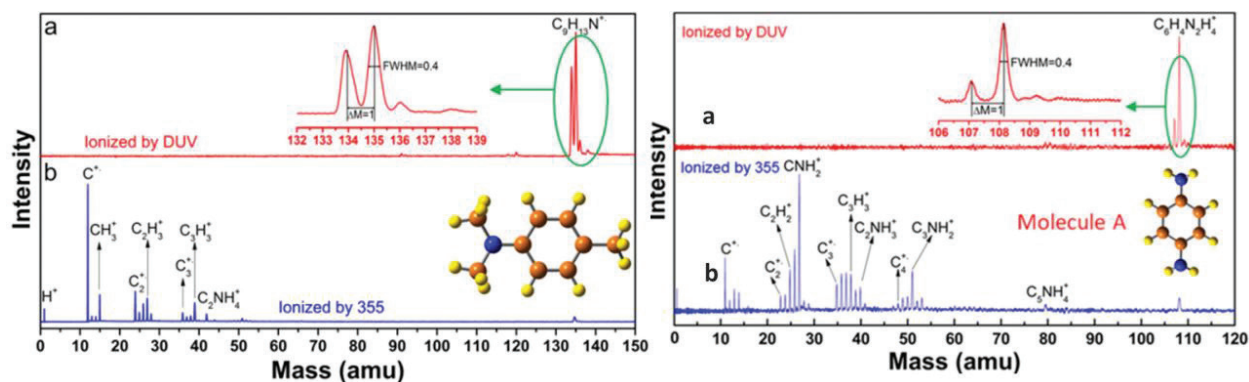


Figure 10. (Left) Mass spectra of N, N-dimethyl-p-toluidine ionized by 177.3 nm (a) and 355 nm laser (b). (Right) Mass spectra of p-phenylenediamine ionized by 177.3 nm (a) and 355 nm laser (b).

by the 177-nm DUV-SPI ionization display smaller full width at half maximum (FWHM) than that by 355-nm laser, indicating improved overall resolution associated with the all-solid-state DUV laser and ionization source.

To further reveal the DUV-SPI-MS ability to identify multicomponents, a sample by mixing the two solid samples PPD and DAN together has been tested, as shown in **Figure 11**. The mixture sample was prepared with a mass ratio of 1:1 of PPD and DAN by grinding method. As results, the parent peaks of PPD and DAN are solely observed in the 177.3-nm SPI-MS spectrum, which is in sharp contrast to the unjustifiable fruitful fragment peaks when ionized with 355-nm laser. The overlapped fragment peaks of organic chemicals make the 355-nm multiphoton ionization difficult to identify molecules from an unknown complex; however, the interference-free and fragmentation-free mass spectra by DUV-SPI-MS bear important

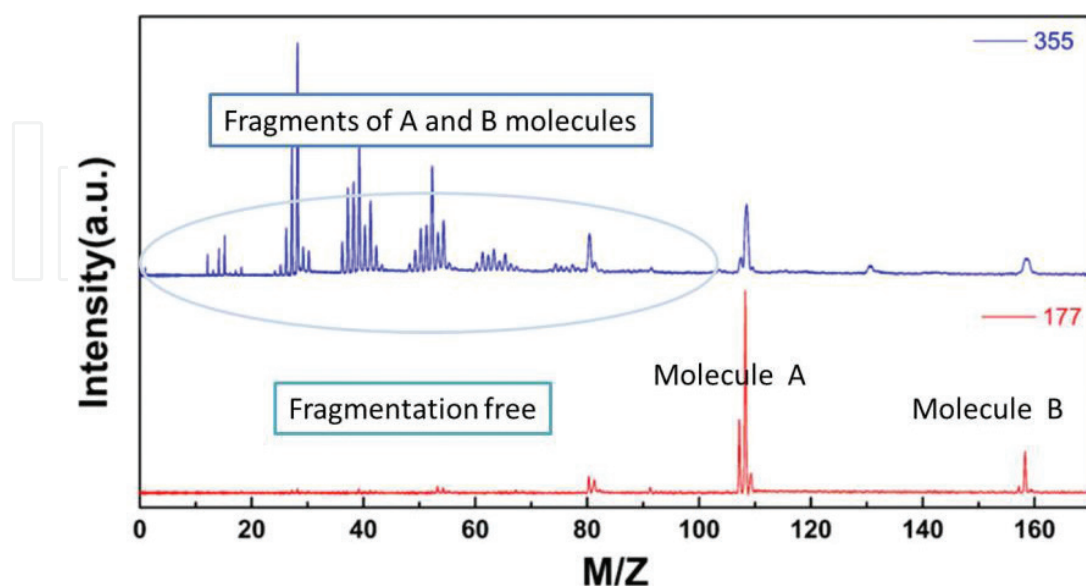


Figure 11. Mass spectra of the mixture of p-phenylenediamine (as named Molecule A) and 1,5-diaminonaphthalene (as named Molecule B) ionized by 355 and 177.3-nm DUV laser.

advantages to identify molecules from an unknown mixture. Further development of SPI-MS is desirable so as to identify intact atomic/molecular clusters & aggregates of strong/weak interactions, as involved in many chemical and biochemical processes [77, 78].

4. Conclusion

Single-photon ionization mass spectrometry (SPI-MS) is recognized a powerful technique for accurate molecular weight measurements with promising applications in a wide range of research fields, including conformational analysis, contaminant detection, real-time process monitoring, pyrolysis, combustion chemistry studies, and online characterization of aerosols. Considering that 90% compounds have light absorption in the DUV region, convenient DUV light sources are crucial for SPI-MS applications. The instrument development and technical research relating to DUV-SPI-MS demonstrate fragmentation-free and matrix-free advantages of over other mass spectrometers. DUV-SPI-MS is favorable for real-time and online detection of volatile organic compounds involved in environmental air and industrial waste.

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