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A combined single photon ionization and photoelectron ionization source for orthogonal acceleration time-of-flight mass spectrometer

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ABSTRACT

A novel ion source has been introduced in the present study, which combines the characteristics of single photon ionization (SPI) and photoelectron ionization (PEI). The VUV photons for SPI were generated by a commercial krypton discharge lamp (10.6 eV), and the photoelectrons for electron ionization (EI) were produced through photoemission from a stainless-steel skimmer. The energy of photoelectrons can be well controlled by adjusting the voltages applied on the skimmer. The ionization methods, SPI (SPI mode) and SPI combined photoelectron ionization (SPI–PEI mode), can be rapidly switched. Benefited from the higher working pressure in the ion source, the achieved detection limit of benzene and SO_2 were 0.1 ppmV and 20 ppmV, respectively. The experimental results show the combined ion source has the potential in chemical process and environmental monitoring.

1. Introduction

Single photon ionization (SPI) has been widely used in on-line monitoring volatile organic compounds (VOCs) [1–11]. In contrast to hard ionization methods (e.g., electron ionization (EI), fast atom bombardment (FAB)), this technique is characterized by high yield of parent ions and drastically reduced fragment ions [12,13]. By adopting this method, most VOCs can be easily monitored and discriminated according to their molecular ions [14–16]. However, there are some inherent drawbacks limiting its further applications. First of all, SPI cannot ionize molecules with the ionization energy (IE) higher than the photon energy. As known to us, the highest photon energy, produced by the commercially available window material of VUV lamp, is only 11.8 eV, therefore some compounds that play important roles in atmosphere environment (e.g., CO (IE 14.01 eV), CO_2 (IE 13.78 eV), CH_4 (IE 12.61 eV), SO_2 (IE 12.35 eV), N_2O (IE 12.89 eV), etc. [17]) are absent in most of SPI mass spectra. Secondly, due to lack of characteristic fragment ions and standard SPI mass spectra as a reference, the ability of SPI to deduce the chemical structure is quite weak in a non-tandem mass spectrometer. These disadvantages to a large extent limit the applications of SPI. Therefore, a combined ion source, which can allow the user to rapidly switch between SPI and EI, is desirable, especially in the analysis of compounds with a wide range of IEs.

Zimmermann and co-workers reported an SPI ion source coupling a traditional hot-filament EI ion source using an electron beam pumped rare gas excimer lamp (EBEL) as light source [18]. The ion source provided a convenient means of producing both EI mass spectra and SPI mass spectra with a good sensitivity. In fact, a better sensitivity could be achieved by increasing the pressure in the ion source, because the sensitivity to a certain degree is directly proportional to the pressure in SPI mass spectra. However, the working pressure in EI ion source must be kept less than 1×10^{-3} Pa due to the oxidization of heated filament, which limits the sensitivity of EI.

Another ion source called photoelectron ionization (PEI) ion source with wider working pressure may be better for such combined ion source. Similar to typical EI ion source, PEI source is capable to ionize a wide range of molecules and generate abundant diagnostic fragments when the energy of electrons is high enough. Several laser-based photoelectron ionization ion sources have been reported since 1991 [19–25], but these devices were not widely used in practice until now because of the complication and high cost of laser components. In addition, the pressure advantage of PEI was not fully utilized because the ionization mostly occurred in the extraction region of the time-of-flight analyzer, where the working pressure must be kept in a low pressure.

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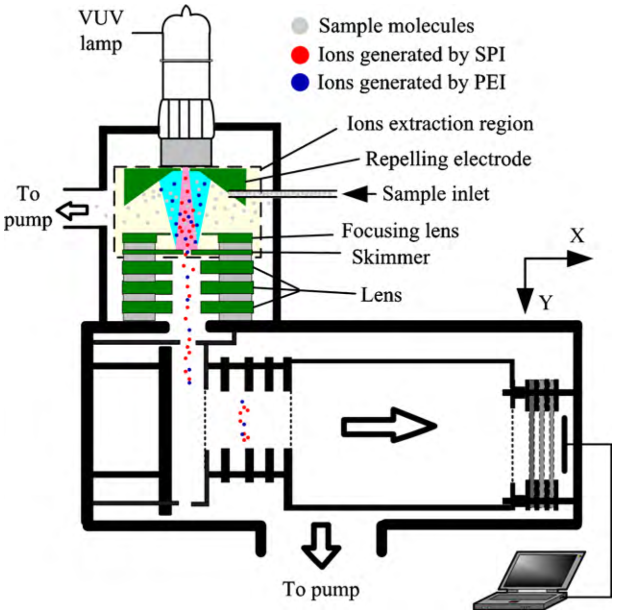

Fig. 1. Schematic diagram of the combined ion source for orthogonal acceleration time-of-flight mass spectrometer.

Zenobi and co-workers recently used a low cost commercial VUV lamp to produce photoelectron for EI source in an ion trap mass spectrometer [26]. The photoelectrons generated from repeller/end-cap were accelerated by the radio frequencies potentials. The resultant mass spectra had more EI characters than SPI. Because of the incapability of controlling the energy of electrons as traditional EI source, the ion source to a certain extent lost the advantage of identifying unknowns according EI reference spectra.

In the present study, a new ion source has been designed, which combines SPI and PEI using a commercial 10.6 eV VUV lamp as the light source. VUV lamp can be applied to a wide range of pressure with favorite features of robustness, low cost and low power consumption [27]. It is an ideal light source for SPI ion source except relatively low photon flux, which leads to a low sensitivity. Fortunately, the sensitivity in our setup can be increased up to a satisfactory level through increasing the pressure and designing proper electric field. The energy of photoelectrons can be well controlled to 70 eV to achieve mass spectra same as traditional EI mass spectra. A series of experiments were carried out to demonstrate the features of this new combined ion source. In addition, some proof-in-principle applications, such as fast monitoring the thermal desorption process of mixtures and rapidly analyzing of a puff of natural gas seeded in Helium stream, were performed.

2. Experimental

2.1. The combined ion source and oaTOFMS

A home-made mass spectrometer consists of an ionization chamber and an orthogonal acceleration time-of-flight mass spectrometry (oaTOFMS) analyzer as shown in Fig. 1. Gas sample was introduced into the ionization region through a fused silica capillary (150 μm i.d., 30 cm long) at ambient pressure. The oaTOFMS analyzer is the same as reported in our recent study [28]. An 11 L s^{-1} rotary pump (Leybold, Koln, Germany) was used to support two 110 L s^{-1} turbo-molecular pumps (KYKY Technology Development Ltd., Beijing, China). One of the turbo-molecular pumps was used to provide pressure below 1×10^{-3} Pa for the analyzer, and the other pump was employed to achieve a pressure about 0.2 Pa in the ionization chamber.

The ion source consists of three parts: VUV lamp, ion extraction region and lens. A commercial low-pressure krypton discharge lamp (10.6 eV, Cathodeon Ltd., Cambridge, UK) with a flux of about 1×10^{11} photons s^{-1} was installed on the top of ionization chamber. The ion extraction region is comprised of three stainless-steel electrodes as shown in Fig. 1. The voltage applied on the repelling electrode was 8 V. The focusing lens, used for controlling the field grads, was 1 mm-thick ring and a voltage of 6 V was applied on it. The skimmer was used to maintain pressure of 0.2 Pa in the ionization chamber. In addition, the switch between SPI mode and SPI–PEI mode is controlled by the voltages on this electrode, typically −4 V for the SPI mode and −60 V for the SPI–PEI mode. A three-electrode lens is used to transmit ions from skimmer to a 1.6 mm × 8 mm slit in the ion extract region of the oaTOFMS. The mass spectrum was recorded by a 1 GHz multiple event time-to-digital converter (TDC) (FAST ComTec GmbH, Oberhaching Germany) at a repetition rate of 25 kHz. The mass resolution of the oaTOFMS is about 300.

2.2. The differences in SPI and SPI–EI modes

In the SPI mode, due to the low voltages on skimmer (−4 V), the energy of electrons obtained from electronic field is about 10 eV when passing through the focusing lens. At such energy of electrons, the impact ionization cross section is close to zero, thus only few molecules can be ionized by electron ionization. The dominant ions in SPI mode are molecule ions. Whereas in SPI–PEI mode, the voltages on skimmer are −60 V, and the energy of photoelectrons is reached to 70 eV after passing through the focusing lens, therefore, typical EI fragment ions should be observed.

2.3. Methods used for gas preparation

The standard gas mixture of benzene, toluene and *p*-xylene diluted with N_2 (99.9993% purity) at calibrated concentrations of 100 ppmV was purchased from Dalian Special Gas Company (Dalian, China). The samples of SO_2, *n*-heptane, 2-butanone and furan were prepared by diluting pure samples with pure helium (Dalian Special Gas Company, Dalian, China). The dilution process was as follows: a measured amount of helium was blown into a PTFE sampling bag from a high-pressure gas bottle, and then a desired amount of sample was added into the bag. The amount of helium was measured by a calibrated gas mass flow controller (Seven Star Electronics Co., Ltd., Beijing, China). The samples of benzene with different concentrations were obtained by diluting 100 ppmV standard gas with pure N_2 in a mixing chamber. The flow rates of the calibrated gas and pure N_2 were controlled by mass flow controllers at calculated flux proportion.

3. Results

3.1. Characters of the combined ion source

SO_2 is one of the common air pollutants, but its IE (12.35 eV) is larger than the energy of photon (10.6 eV), therefore difficult to be ionized in SPI mode (Fig. 2a). Note that Helium (IE 24.6 eV) was also absent from the spectra although it served as carrier gas (Fig. 2a). The observed SPI mass spectrum indicates that molecules with higher IE cannot be ionized in SPI mode. However, in SPI–PEI mode, the peaks at $m/z = 64$, 48 and 32 (Fig. 2b) are observed, which correspond with SO_2^+, SO^+ and S^+, according to the EI mass spectrum from NIST. The peaks at $m/z = 18, 28, 32$ can be assigned to H_2O (IE 12.62 eV), N_2 (15.58 eV) and O_2 (12.07 eV) due to the existence of trace air in the sample. These results suggest that the VUV-based ion source can work as a typical EI ion source to ionize high IE compounds and generate diagnostic fragments.

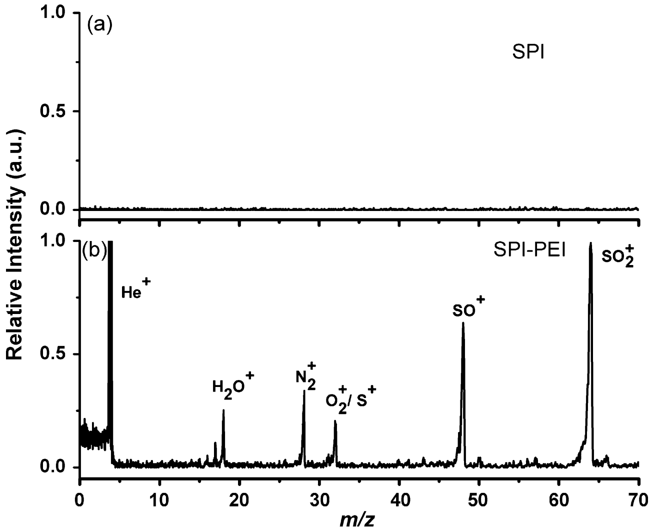

Fig. 2. Mass spectra of SO_2 in helium. (a) SPI mass spectrum; (b) SPI–PEI mass spectrum.

The mass spectra of *n*-heptane molecule obtained in SPI and SPI–PEI modes are shown in Fig. 3. In SPI mode, the intensive parent ions at $m/z = 100$ and little fragments at $m/z = 71$ were observed (Fig. 3a), which indicate SPI is an almost fragment-free ionization method. In SPI–PEI mode, the fragment peaks at $m/z = 27, 29, 39, 41, 43, 55, 56, 57, 70, 71$ (Fig. 3b) were observed, similar to the EI mass spectrum from NIST. The major difference between SPI–PEI mass spectrum and standard EI mass spectrum is that the intensity of parent ion at $m/z = 100$ in the SPI–PEI mass spectrum is more intensive than that in EI mass spectrum, which is resulted by mixing molecular ions generated by SPI and PEI.

Furan and 2-butanone are isomers, and their mass spectra obtained in SPI mode are almost the same, only the parent ion appeared in their mass spectra, as shown in Fig. 4a and b. However, in SPI–PEI mode, as shown in Fig. 4c and d, the two isomers can be easily distinguished according to the pattern of fragment ions. The results show that the VUV-based ion source operated in the SPI–PEI mode may be helpful in identifying some isomeric compounds.

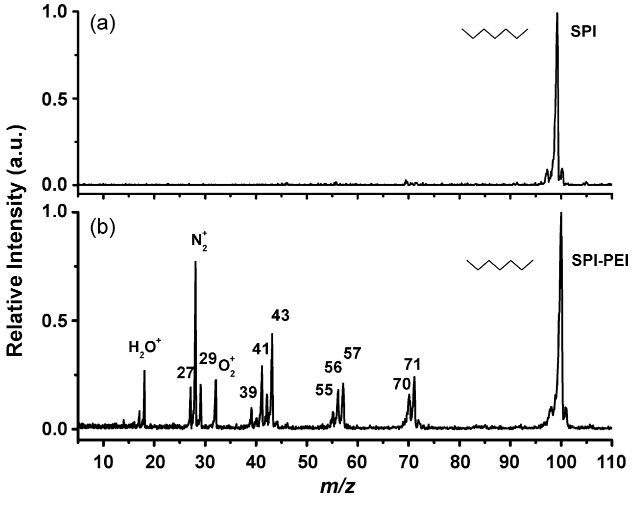

Fig. 3. Mass spectra of *n*-heptane obtained in SPI and SPI–PEI modes. (a) SPI mode; (b) SPI–PEI mode.

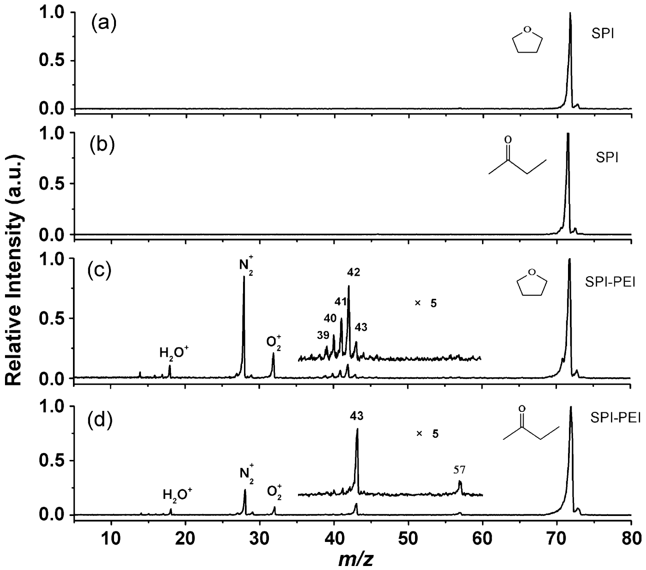

Fig. 4. Mass spectra of 2-butanone and furan in helium obtained in SPI and SPI–PEI modes. (a) SPI mass spectrum of furan; (b) SPI mass spectrum of 2-butanone; (c) SPI–PEI mass spectrum of furan; (d) SPI–PEI mass spectrum of 2-butanone.

3.2. Limits of detection (LODs)

The sensitivity of the combined ion source was also investigated. The measured LODs (S/N = 3) were based on spectrum obtained from 100,000 consecutive oaTOFMS extractions at 25 kHz. The noise was obtained by calculating the standard deviation from a section of spectrum that contains no signal peak [29,30]. After calculation, the LOD of SO_2 in SPI–PEI mode was about 20 ppmV, and the LODs of benzene were 0.1 ppmV and 1 ppmV in SPI and SPI–PEI modes, respectively. The poorer LODs in SPI–PEI mode is due to the higher level of noise which may result from the scattered ions of intensive nitrogen peak.

In Ref. [16], the light source used for SPI was pumped by a rare gas excimer lamp (EBEL) with photons flux about 1.5×10^{13} photons s^{-1}, and the LOD for toluene based on $S/N = 2$ was 35 ppb at SPI mode (65,000 consecutive oaTOF extractions at 100 kHz). Compared with present study, although the photons flux in EBEL was about two orders of magnitude higher than that in VUV lamps (1×10^{11} photons s^{-1} in VUV lamp), the differences of LODs in the two different oaTOFMSs in SPI modes are not significant. This may be ascribed to the difference of pressure in the ion source, because the gas pressure in current study was about 20-fold higher than that in Ref. [16].

3.3. Applications

In order to further evaluate the new ion source, a series of compounds with different IEs, including benzene, toluene, O_2, N_2, SO_2, SO_2, CO_2 and H_2O, were simultaneously monitored during the thermal desorption process of a gas mixture from 13X molecular sieve. By controlling the temperature during the desorption process, those compounds were well detected through the SPI–PEI mode, as shown in Fig. 5. The accumulated time for each point in the profiles is 4 s, however, shorter accumulated time with higher LODs and longer accumulated time with lower LODs in TOFMS could be adjusted according to practical needs.

The advantage of rapid switch between SPI and SPI–PEI modes was also demonstrated by an experiment, in which a puff of natural gas was injected into a pipeline with flowing helium, and as shown in Fig. 6, the concentrations of different species in the pipeline were monitored through two modes switching within 0.4 s (this can be

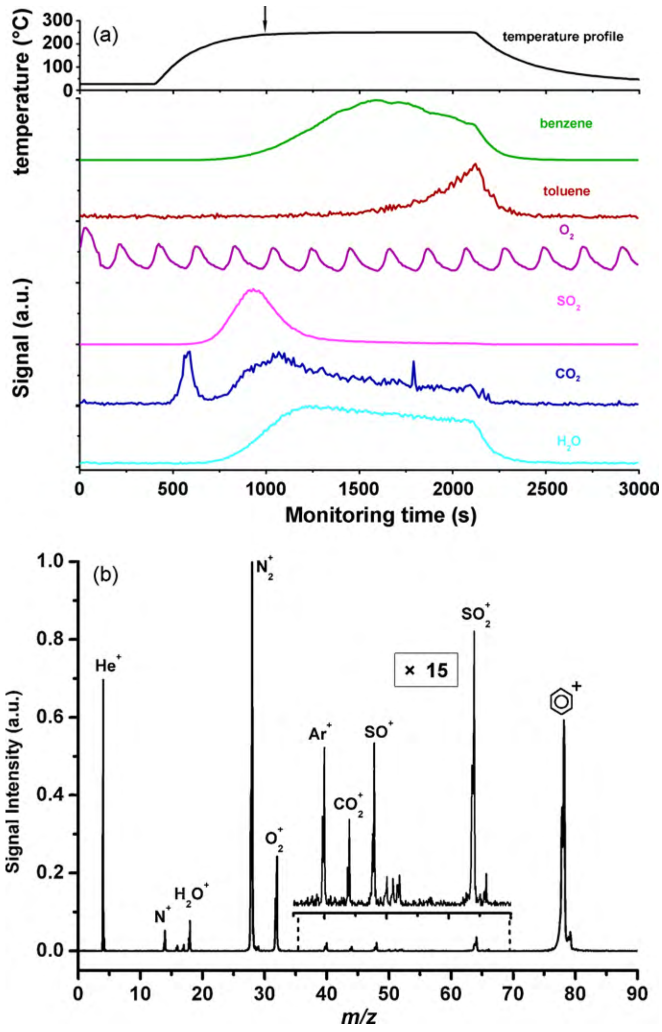

Fig. 5. (a) Rapid multi-species monitoring of thermal desorption of a mixture from 13X molecular sieve; (b) Mass spectrum obtained at monitoring time of 1000s.

greatly reduced by improving the electronics). Each mass spectrum was accumulated for 4 s. In the SPI spectra at 68 s and 78 s, samples in natural gas of ethylene (IE 10.51 eV), propylene (IE 9.73 eV), C_4H_8 (IE 9.6 eV) and C_5H_{12} (IE 10.4 eV) were well detected. It should be noted that ethylene, propylene and C_4H_8 are difficult to be monitored in SPI–PEI mode because of the overlap with the fragments of ethane, propane and C_4H_{10}. By contrast, in the SPI–PEI spectra at 54 s, 64 s and 73 s, the background gas of He (IE 24.59 eV), H_2O (IE 12.62 eV), N_2 (IE 15.58 eV) and O_2 (IE 12.07 eV) and species in natural gas of methane (IE 12.6 eV), ethane (IE 11.5 eV), propane (IE 10.94 eV), C_4H_{10} (IE 10.6 eV) and C_5H_{12} (IE 10.4 eV) can be well monitored. The experiment shows that the monitored species were increased by combining the information from the two modes. The above two proof-in-principle experiments show that the combined ion source has excellent capability for monitoring mixture gas with a wide range of IEs.

4. Discussion

One distinguish merit of this combination ion source is its wide range of working pressure in compared with the typical EI ion source. This ion source can work under the pressure of 1×10^{-4} to 1 Pa, while typical EI ion source works under pressure less than 1×10^{-3} Pa [31,32]. Wider pressure range also gives great flexibility on assembling the ion source into different mass analyzers, and easily to be coupled to GC or HPLC. In addition, thermal fragments may be generated in the hot-filament EI source especially for the thermal labile compounds, whereas there is no heating device in our VUV–PEI ion source, thus can avoid such problems.

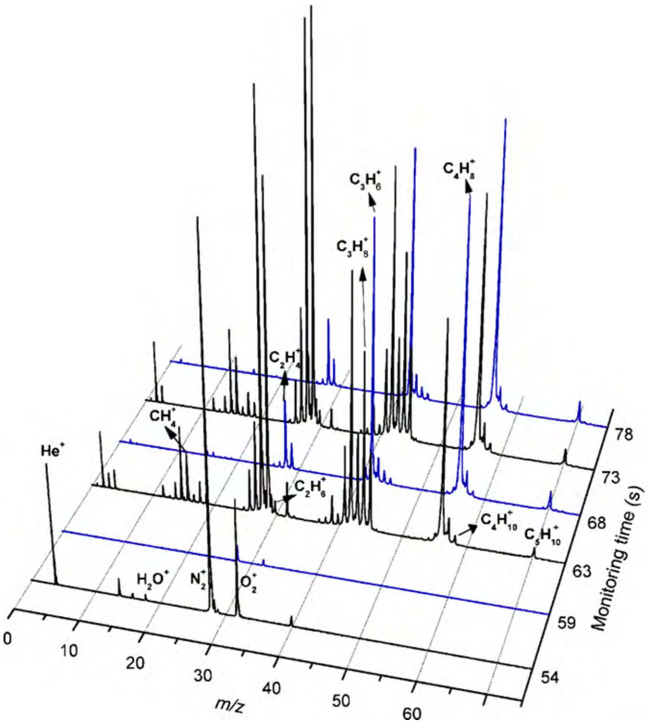

Fig. 6. Part of the monitoring results for a puff of natural gas in Helium stream. The curves corresponding to the monitoring time at 59, 68, 78 are the spectra in SPI mode and others are spectra in SPI-PEI mode, respectively.

The new ion source also demonstrates some other merits. First of all, the ion source can be used to monitor oxidant gases due to free of hot-filaments in the ionization chamber. Second, the power consumption of the ion source is less than 1.5 W, much less than typical EI ion source. The low power consumption is desirable especially in portable mass spectrometer [33].

A distinguish feature of the mass spectra in the combined ion source is the EI fragments and enhanced parent ions for most organic compounds in SPI–PEI mode. As well known, it is very difficult to identify the molecular ions for fragile molecule as the intensity of molecular ions is weak or disappeared in the EI mass spectrum. Therefore, the enhanced parent ions spectra in the combined ion source will greatly improve the reliability of identifying fragile compounds.

The ability to identify unknown by combining the information of two modes is better than that in single mode, however, it may be not good enough for complex organic mixtures because of the severe overlaps of fragments or isomers. Therefore, combination of SPI/SPI–PEI ionization method and some pre-separation or tandem mass spectrometry is needed.

5. Conclusions

The novel ion source with characters of SPI and PEI has been described and its capability of monitoring gas mixtures has been demonstrated experimentally. Benefiting from the rapid switching modes, the ion source has the ability of generating both fragments and molecular ions in SPI–PEI mode and dominative molecule ions in SPI mode. With the features of wide working pressure range, anti-oxidation, low power consumption and rapid switch between the two modes, the combined ion source has the potential in chemical process and environmental monitoring.

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