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Determination of absolute photoionization cross-sections of some aromatic hydrocarbons

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Abstract

Rationale: Aromatic hydrocarbons play an important role in the formation and growth of polycyclic aromatic hydrocarbon (PAH) and soot particles. Measurements of their absolute photoionization cross-sections (PICSs), that benefits the quantitative investigation of mass spectrometry, are still lacking, however.

Methods: PICSs of some aromatic hydrocarbons were measured with tunable synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS). Nitric oxide and benzene were chosen as standard references for PICS calibration, since their photoionization cross-sections are well-known in literature. Binary liquid mixtures of the investigated molecules and their specific solvents were used in the measurements.

Results: The investigated aromatics include naphthalene, phenanthrene, 1-methylnaphthalene, indene, 2-/3-/4-methylphenylacetylene, 2-methylindene, diphenylacetylene, 1-/2-ethynylnaphthalene and acenaphthylene. Photo-induced fragments from the molecules were also observed with increasing photon energy.

Conclusions: Based on our measurements and literature data, PICSs of most aromatic molecules have very similar values beyond their ionization energies. However, molecules that contain phenylacetylene structure have PICSs higher than other aromatics.

Keywords: *Photoionization cross-section; Synchrotron vacuum ultra-violet photoionization; Molecular beam mass spectrometry; Polycyclic aromatic hydrocarbons; Benzene.*

1. Introduction

Photoionization mass spectrometry (PIMS) has been used extensively for the analysis of organic molecules,^{1,2} and for combustion studies in recent years.³⁻⁷ In traditional electron ionization (EI) mass spectrometry of complex mixtures, typically carried out at an electron energy of 70 eV, a large number of peaks overlap including parent ion and fragment ion signals. It is usually quite difficult to deduce specific components from these fragments. Compared with this widely applied ionization source for mass spectrometry, photoionization reduces fragmentation during the detection process. Vacuum ultraviolet (VUV) light, produced by discharge lamps,⁸ lasers,⁹⁻¹¹ and tunable synchrotron radiation,³ is an elegant ionization source for mass spectrometry. As a soft ionization process, VUV photoionization can facilitate selective identifications of species to avoid interference from fragmentation.¹²⁻¹⁵ The photoionization cross-section (PICS) is thus the key parameter to quantify the concentration of organic compounds. Conventionally, the total absolute photoionization cross-sections were measured using single/double/multiple ion-collection plates in ionization chamber with discharge lamp or high-resolution synchrotron radiation.¹⁶⁻²¹ The partial cross-sections of dissociation fragments could be detected separately until quadrupole or time-of-flight mass spectrometers were applied.^{22,23} Later, Person and Nicole²⁴ developed a method to measure the PICSs for hydrocarbons by comparing reference and target molecules, and Cool et al²⁵ applied it in synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS). The PICSs of stable intermediates²⁶⁻³² as well as free radicals³³⁻⁴³ have been measured using this method.

Polycyclic aromatic hydrocarbons (PAHs) have been of great interest in many research areas, due to their importance in the interstellar medium,^{44,45} environment,⁴⁶ combustion,⁴⁷ and semiconductors.^{48,49} Compared with the extensive studies on simple aliphatic hydrocarbons,²⁵⁻

^{31,50,51} reliable measurements of photoionization cross-sections for aromatic hydrocarbons are still limited.⁵²⁻⁵⁷ DeWitt et al⁵³ determined the relative PICSs of some monocyclic aromatics using femtosecond laser ionization and time-of-flight mass spectrometry (TOF-MS). Walther et al⁵⁴ measured the PICS of toluene and xylene with a laser-based TOF mass spectrometer. More recently, the PICSs of benzene and a series of other aromatic hydrocarbons were measured exclusively at 10.5eV.^{55,56} Another study reported the relative photoionization curves of o-xylene, 2-methylstyrene, indene and five atmospheric degradation products in the photon energy range of 7–15eV.⁵⁷ However, PICSs of only a few aromatic compounds were obtained at 10.5 eV.⁵⁷ More recently, Zhou et al⁵² determined the PICSs of a series of aromatic species by SVUV-PIMS. Generally, PICSs of aromatic species, which are required for a better understanding of the aromatic chemistry in combustion, interstellar, and atmospheric environments, are still lacking.

In this work, molecular-beam sampling combined with SVUV-PIMS was used to measure the PICSs of some aromatic hydrocarbons with very low vapor pressures. Nitric oxide and benzene are taken as dual reference species due to their well-known PICSs. In total, 12 aromatic hydrocarbons were studied at suitable photon energy ranges, including naphthalene, phenanthrene, 1-methylnaphthalene, indene, 2-methylindene, 2-/3-/4-methylphenylacetylene, diphenylacetylene, 1-/2-ethynylnaphthalene and acenaphthylene.

2. Experimental approaches

2.1 Instrumentation

All experiments were carried out in a flow reactor at an undulator-based VUV beamline (BL03U) of the Hefei Light Source (HLS II; Hefei, China). This flow reactor facility and the experimental data evaluation process have been described in detail in previous work^{3,58}; only a

brief description will be given here. HLS II is operated at 800 MeV with a beam current of 360 mA in top-up mode. This beamline is equipped with a grating with a line density of 200 lines/mm, covering the photon energy range of 5–25 eV with the full width at half-maximum of 1.87 meV at 7.3 eV (energy resolution is 3900 at 7.3 eV). Gas filter and MgF₂ windows were used to eliminate high-order harmonic radiation from the grating. In general, the photon flux at the end-station is higher than 1.0×10^{13} photons/s.

The flow reactor is composed of a home-made furnace and an α -type alumina ceramic tube (inner diameter 7.0 mm, wall thickness 1.5 mm). Electric heating wire is uniformly twined in the inner layer of the furnace, and the outermost layer acts as a heat shield. The total length of the heating zone is ~ 220 mm. A tungsten–rhenium (W–Re) thermocouple is positioned at the middle region to monitor the reactor temperature. For the experiments reported here, a liquid chemical mixture is prepared by the procedure introduced in Section 2.2, and then injected into a heated vaporizer. The flow rate was regulated by a micro syringe pump (LSP01-2A, Baoding Longer Precision Pump Co., Ltd, Baoding, China). The gasified chemicals are fed to the flow reactor at the same high temperature. Reference gas (nitric oxide, 99.99%) and dilution gas (argon, purity 99.999%) are regulated by MKS (Andover, MA, USA) mass flow controllers at 10 and 990 SCCM, respectively. The pressure of the flow reactor is kept constant at 2 Torr (266 Pa), controlled by an MKS throttle valve. The gas mixture was sampled 10 mm downstream from the outlet of the ceramic tube by a quartz nozzle with an orifice of 1.1 mm. Due to the large pressure difference between the flow reactor (266 Pa) and differential chamber (0.05 Pa), a molecular beam is formed through the quartz nozzle. The molecular beam is collimated by a nickel skimmer, and ionized by an orthogonal tunable VUV light beam. Ions are detected by a home-made time-of-flight mass spectrometer *via* an ion introducer. A schematic diagram of the entire facility is shown in Figure 1.

Photons were propelled into the flight tube by a pulse extraction field triggered at a frequency of 30 kHz by a home-made pulse generator, and the ions were then reflected to a microchannel plate (MCP) detector. After amplification by a TA2000 preamplifier (FAST ComTec GmbH, Oberhaching, Germany), the ion counts were recorded by a P7888 multi-scaler (FAST Comtec). A silicon photodiode SXUV-100 (International Radiation Detectors Inc., Newbury Park, CA, USA) was used to monitor the photon flux for normalizing the ion signals after quantum efficiency corrections to the photodiode response.

2.2 Sample preparation

Binary liquid mixtures (**Table 1**) of the solvent and target molecules were prepared in molar ratios that enabled them to avoid condensation and reach full gasification of the mixture. The physical properties of the target molecule, such as molecular weight (M_i), boiling point (b.p.) and saturated vapor pressure at room temperature, were considered to determine the relative mole fractions. Benzene ($M_i = 78$, b.p. = 353 K), 1,3,5-trimethylbenzene ($M_i = 120$, b.p. = 438 K) and acetophenone ($M_i = 120$, b.p. = 475 K) were selected as suitable solvents for various target molecules. Since all the target molecules measured in this study have low vapor pressures, a very small amount was dissolved in the selected solvent. These solutions were then injected at a very slow flow rate (< 0.5 mL/hour), and diluted by a large amount of argon (480 SCCM). The concentration of the target molecule was typically hundreds of ppm, which limited its adsorption / condensation in the ionization area.

All chemicals were used without further purification: naphthalene (99%, Shanghai Macklin Biochemical Co., Ltd, Shanghai, China), phenanthrene (97%, Shanghai Bide Pharma Tech Co., Ltd, Shanghai, China), 1-methylnaphthalene (99%, J&K Scientific Ltd, Beijing, China), indene (97%, Shanghai Yuanye Bio-Technology Co., Ltd, Shanghai, China), 2-

methylphenylacetylene (Shanghai Boka Chem Co., Ltd., Jinshan, China), 3-methylphenylacetylene (98%, Zhengzhou Alfa Chemical Co., Ltd, Zhengzhou, China), 4-methylphenylacetylene (98%, Zhengzhou Alfa Chemical Co., Ltd), 2-methylindene (98%, Shanghai Bide Pharma Tech Co., Ltd), diphenylacetylene (99%, Shanghai Aladdin Biochem Inc., Shanghai, China), acenaphthylene (98%, Shanghai Bide Pharma Tech Co., Ltd), 1-ethynylnaphthalene (99.7%, Shanghai Haohong Pharma Tech Co., Ltd, Liaocheng, China), 2-ethynylnaphthalene (98%, Shanghai Bide Pharma Tech Co., Ltd), 1,3,5-trimethylbenzene (98% Shanghai Aladdin Biochem Inc.), acetophenone (99% Shanghai Aladdin Biochem Inc.), nitric oxide (99.99%, Nanjing Special Gases Inc., Nanjing, China) and argon (99.999%, Nanjing Special Gases Inc.).

2.3 Measurement method

The PICSs of target molecules can be evaluated from measurement of their photoionization efficiency spectra. Since the pressure remains constant at the sampling position, the variation of the signal between reference species and target molecules at different photon energies is caused by the mole fraction, mass discrimination factor and photoionization cross-section.⁶⁰ This procedure was introduced in previous publications,^{28,29,52,61} and only a brief description is presented herein.

For species i , the ion signal S_i can be written as:

$$S_i(E) = C \times X_i(E) \times \sigma_i(E) \times D_i \times \varphi_p(E) \quad (1)$$

Here C is a proportional constant, $X_i(E)$ is the mole fraction of species i at photon energy E , $\sigma_i(E)$ is the photoionization cross-section of the species i at photon energy E , D_i is the mass discrimination factor for species i ,^{62,63} and $\varphi_p(E)$ is the photon flux. By taking nitric oxide or benzene as the reference species, the PICS of species i can be calculated as:

$$\sigma_i = S_i(E) \times \frac{X_{ref}(E)}{X_i(E)} \times \frac{\sigma_{ref}}{S_{ref}(E)} \times \frac{D_{ref}}{D_i} \quad (2)$$

D_i was measured in this study for various species, and a fitted expression (Eq. 3) is plotted in Figure 2 (M_i is the molecular weight of species i).

$$D_i = (M_i/30)^{0.55 \pm 0.1} \quad (3)$$

2.4 Cross validation

Benzene is a good solvent for most aromatic compounds. It is also a good reference species as: i) it does not undergo dissociative ionization in the energy range from its ionization threshold (9.24 eV) to 12 eV;⁶⁴ and ii) its accurate PICS is available in the literature.^{25,27,65} Meanwhile, nitric oxide is also a good reference species due to its particular PICS curve shape in the energy range of 9–11 eV,⁶⁶ as shown in Figure 3B.

Figure 3 shows a cross validation of the PICS evaluation method introduced in this study. After a steady injection of nitric oxide and benzene to the flow reactor, a mass spectrum can be recorded at 10.5 eV. In addition to the strong peaks at m/z 30 (NO) and 78 (C_6H_6), the expected ^{13}C isotope peak of benzene is also observed at m/z 79 ($^{13}CC_5H_6$). As shown in Figure 3B, our measurement of the NO ionization profile agrees perfectly with the literature data reported by Watanabe et al.⁶⁶ The PICS of benzene calculated from the reference of nitric oxide also shows good agreement with the data of Rennie et al.⁶⁵ and Cool et al.²⁵ (<4%). However, the values reported in Yoshino et al.⁶⁷ are significantly lower than those in the other three datasets.

3. Experimental results

PICS measurements of all 12 aromatic hydrocarbons are presented here, and collected in the Supporting Information. Binary mixture compositions for each of the target molecules are given in **Table 1**, along with the temperature of vaporizer, gas transferring line and flow reactor. Uncertainty analysis was performed using root-sum-squared method to estimate errors in the measured PICSs, as shown by grey shadows in Figs. 4-15. The sources of errors considered here include: reference cross-sections ($\pm 4\%$), largest deviation of the mass signal ($\pm 5\%$, including the error of the photon energy), mass discrimination factor ($\pm 10\%$), and the impurity of chemicals ($< 3\%$). In general, the uncertainty of the measured cross-sections is $\sim \pm 12\%$ in this study.

3.1 Naphthalene, 1-methyl-naphthalene and phenanthrene

Figures 4 and 5 present the PICSs of naphthalene and phenanthrene, respectively. Here, 4.88% naphthalene and 1.51% phenanthrene are dissolved in benzene, which is also taken as the reference species. The inserted frames in Figures 4 and 5 are the mass spectra taken at 10.0 eV. We observe a strong benzene peak at m/z 78 and weaker peaks of naphthalene and phenanthrene at m/z 128 and 178, respectively. According to these PICS curves, the photoionization thresholds of naphthalene and phenanthrene measured in this study are 8.15 ± 0.03 and 7.90 ± 0.03 eV, respectively. The measurements agree well with the recommended values in the NIST database (8.144 eV for naphthalene and 7.891 eV for phenanthrene).⁶⁴ Although both naphthalene and phenanthrene are very important intermediates in the formation of PAHs,⁶⁸⁻⁷¹ their PICSs were not available in literature prior to this study. Similar to those of other peri-condensed aromatic species, the PICS curves of

naphthalene and phenanthrene display a smooth variation with photon energy⁵² because photo-induced fragmentation is not easy for these species.

1-Methyl-naphthalene is in the liquid phase at room temperature and is thus injected directly by a micro syringe pump. Nitric oxide is adopted as the reference species for its PICS evaluation. As shown in Figure 6B, its PICS dramatically rises at its ionization threshold (7.95 ± 0.03 eV). Our measured ionization energy agrees well with the literature reported values (7.96 eV in NIST database⁶⁴ and 7.97 eV from Zhou et al⁵²). From the mass spectrum recorded at a photon energy of 13.5 eV, shown in Figure 6a, we observe a peak at m/z 141 in addition to those of nitric oxide (m/z 30) and 1-methyl-naphthalene (m/z 142). With the increment of photon energy, a photo-dissociation fragment (m/z 141, $C_{11}H_9^+$) appears at 12.20 eV, which is 0.1 eV higher than that observed by time-resolved photodissociation.⁷² Zhou et al⁵² also measured the PICSs of 1-methyl-naphthalene up to a photon energy of 11.7 eV. Our measurements are in very good agreement with their data in respect of the curve shape, but have smaller absolute values. As emphasized in the sample preparation section (Section 2.2), this discrepancy may be because of the adsorption or condensation of 1-methyl-naphthalene in the ionization area. In the measurements of Zhou et al,⁵² a much higher concentration of 1-methyl-naphthalene was employed. Over time, adsorption or condensation of the chemicals provided a very strong background signal of the target molecule, thus leading to an over quantification of the PICSs in their measurements.

3.2 Indene and 2-methyl-indene

Similar to 1-methyl-naphthalene, liquid-phase indene was injected directly by a micro syringe pump, and nitric oxide was adopted as the reference species for its PICS evaluation. Figure 7A shows the peaks of nitric oxide (m/z 30), indene (m/z 116) and a photo-induced

fragment (m/z 115) in the mass spectrum recorded at 13.0 eV. Figure 7B presents the comparison of PICSs of indene measured in this study and by Zhou et al.⁵² The measured photoionization threshold of indene is 8.15 ± 0.03 eV, which is in reasonable agreement with the reference data (8.14 in NIST database⁶⁴ and 8.17 eV in Zhou et al.⁵²). With increased photon energy, a photo-dissociation fragment (m/z 115, $C_9H_7^+$) appears at 11.90 eV, which is 0.7 eV smaller than that observed by electron ionization.⁷³ Our measured PICSs of indene coincide with the curve shape of Zhou et al.,⁵² but again appear to be smaller than their absolute PICS values. The reasons are similar to those for 1-methyl-naphthalene, and thus are not repeated here.

2-Methyl-indene has been observed to be a critical intermediates in the ring expansion process from indene to naphthalene,⁷⁴ but no previous publication has reported its PICSs. Different from indene, 2-methyl-indene is solid at room temperature. A solution containing 8.82% 2-methyl-indene in acetophenone was used for the measurements. As shown in the inserted frame of Figure 8, the mass spectrum recorded at 9.4 eV presents three strong peaks: the target molecule (2-methyl-indene, m/z 130), the solvent (acetophenone, m/z 120), and the reference species (nitric oxide, m/z 30). Figure 8 presents the PICSs of 2-methyl-indene measured in this study. The measured photoionization threshold for 2-methyl-indene is 7.79 ± 0.03 eV, which is slightly smaller than the value reported by Zhao et al.⁷⁴ (7.90 ± 0.05 eV). The curvature of the PICS of 2-methyl-indene is different from that of indene. It shows a sharp increment at a photon energy of ~ 9.1 eV, i.e., 1.3 eV higher than its ionization threshold.

3.3 Methyl-phenylacetylene

2-, 3- and 4-Methyl-phenylacetylene are the isomers of indene. In particular, 2-methyl-phenylacetylene is a dominant intermediate during the indene unimolecular decomposition

process.⁷⁵ However, the PICSs of these molecules have not been reported in previous publications. In this study, a 10.95% molar solution in 1,3,5-trimethyl-benzene was used for measurements. Figures 9-11 present the measured PICSs of 2-, 3- and 4-methyl-phenylacetylene, respectively. As shown in the inserted frames of these Figures, the mass spectra recorded at 11.0 eV present three strong peaks: the target molecule (methyl-phenylacetylene isomer, m/z 130), the solvent (1,3,5-trimethyl-benzene, m/z 120), and the reference species (nitric oxide, m/z 30). The measured photoionization thresholds of these three isomers are 8.51 ± 0.03 , 8.53 ± 0.03 and 8.42 ± 0.03 eV, respectively. Our values for 2- and 3-methyl-phenylacetylene are 0.1 eV smaller than those measured by photoelectron spectroscopy (8.61 ± 0.02 and 8.63 ± 0.02 eV).⁷⁶ No literature data are available for the ionization energy of 4-methyl-phenylacetylene. In general, these three isomers have very similar curvatures of their PICSs, but slight differences are seen in the absolute values.

3.4 Diphenylacetylene

Diphenylacetylene is an isomer of phenanthrene and anthracene, which is a favorable product in the reaction of a phenyl radical and phenylacetylene.⁷⁷ The PICSs of diphenylacetylene have not been reported in the literature. Here, we measured its PICSs using 1.04% molar solution in benzene. As shown in the inserted frame of Figure 12, three peaks are observed: m/z 178 (diphenylacetylene), m/z 30 (nitric oxide, reference species) and m/z 78 (benzene, solvent). The ionization energy of diphenylacetylene measured in this study is 7.95 ± 0.03 eV, which agrees perfectly with the recommended value in the NIST database.⁶⁴ The PICS of diphenylacetylene dramatically increases with the photon energy, showing plateaux near 9.0 and 10.0 eV. Due to its stable molecular structure, no photo-induced fragmentation peak is observed within the investigated photon energy range.

3.5 Acenaphthylene and ethynylnaphthalene

Acenaphthylene and ethynylnaphthalene are $C_{12}H_8$ isomers commonly detected in rich combustion and pyrolysis of hydrocarbons.^{5,68,70,78,79} Their PICSs have not been reported in the literature. Here, we present our measurements of the PICSs of acenaphthylene, 1-ethynylnaphthalene and 2-ethynylnaphthalene using the low concentration solutions in acetophenone. As shown in the inserted frames of Figures 13-15, four peaks are observed: m/z 152 (acenaphthylene or ethynylnaphthalene), m/z 30 (nitric oxide, reference species) and m/z 120 and 105 (acetophenone and its fragment, solvent). The ionization energies of acenaphthylene, 1-ethynylnaphthalene and 2-ethynylnaphthalene measured in this study are 8.00, 8.05 and 8.15 ± 0.03 eV, respectively. Our measurements agree very well with the literature data of Dewar et al⁸⁰ (8.02 eV for acenaphthylene) and Gleiter et al⁸¹ (8.03 eV for 1-ethynylnaphthalene and 8.11 eV for 2-ethynylnaphthalene). The PICSs of these $C_{12}H_8$ isomers are close to each other, with that of 2-ethynylnaphthalene being slightly higher. However, the curvature of the PICS of acenaphthylene is obviously different from those of the ethynylnaphthalene isomers, which show a sharp rise near 11.0 eV. No photo-induced fragmentation peak is observed within the investigated photon energy range for all three isomers.

4. Discussion

The PICSs of a variety of aromatic hydrocarbons are compared in Figure 16, including toluene, ethylbenzene, n-propylbenzene, o-/m-/p-xylene, phenylacetylene and all the species measured in this study.⁵² We divide aromatics into different groups, namely monocyclic aromatics (Monocyclic), bicyclic aromatics (Bicyclic) and tricyclic aromatics (Tricyclic). Since these aromatic compounds have different ionization energies, each PICS curve is shifted

to zero as its ionization threshold. As shown by the horizontal axis of Figure 16, PICS $\sigma_i(E)$ can be expressed as $\sigma_i(\Delta E)$, in which $\Delta E = E - E_i$ (E and E_i are the photon energy and ionization energy of species i , respectively).

Some specific trends can be observed in Figure 16 among the PICSs of different aromatics. Species with similar molecular structures have similar behavior in terms of $\sigma_i(\Delta E)$. Most of the species are located in the grey shaded area, regardless of their benzene ring number and sidechain type/length/number. With the increment in the number of benzene rings, the PICSs of peri-condensed aromatics decrease, as seen by comparing benzene, naphthalene and phenanthrene in Figure 16. Therefore, the gray shaded area in Figure 16 indicates the most probable values of the PICSs of aromatics. We also observe some special aromatic species having PICSs higher than this shaded area; these are phenylacetylene, 2-/3-/4-methylphenylacetylene, 2-ethynylnaphthalene, diphenylacetylene, indicated by the green circles in Figure 16. All these species have the phenylacetylene structure in their molecules, and they have larger PICSs than other common aromatics but their PICSs agree well with that of phenylacetylene.

5. Conclusions

Experimental determinations of the absolute photoionization cross-sections (PICSs) of 12 aromatic hydrocarbons were carried out using tunable SVUV-PIMS. All these data are very helpful in the future quantitative analysis of organic compounds, especially in the area of environmental and combustion chemistry. PICSs are critical parameters in determining the absolute concentrations of these key intermediates, which are essential in understanding the underlying chemistry of polycyclic aromatic hydrocarbon (PAH) and soot formation. The binary liquid mixture method used in this study is a feasible and reliable strategy for organic

compounds which have high boiling points. PICSs of most aromatics have very similar values beyond their ionization energies, with the exception of molecules that contain the phenylacetylene structure which show higher PICSs than other aromatics.

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Table 1 Binary mixture compositions and properties

Target molecules	Solvents	p_i	X_i^T	b.p. ^T	b.p. ^S	$T_{vap.}$	Q
Naphthalene	Benzene	1.09×10^{-2}	4.88%	218	80	100	0.1
Phenanthrene	Benzene	3.37×10^{-3}	1.51%	336	80	100	0.1
1-Methyl-naphthalene	--	2.80×10^{-1}	--	241	--	245	0.2
Indene	--	3.56×10^{-1}	--	182	--	185	0.2
2-Methyl-indene	Acetophenone	1.18×10^{-2}	8.82%	208	202	205	0.1
2-Methyl-phenylacetylene	1,3,5-Trimethyl-benzene	1.57×10^{-2}	10.95%	197	165	180	0.1
3-Methyl-phenylacetylene	1,3,5-Trimethyl-benzene	1.57×10^{-2}	10.95%	207	165	180	0.1
4-Methyl-phenylacetylene	1,3,5-Trimethyl-benzene	1.57×10^{-2}	10.95%	195	165	180	0.1
Diphenylacetylene	Benzene	2.32×10^{-3}	1.04%	296*	80	100	0.1
Acenaphthylene	Acetophenone	2.83×10^{-2}	5.31%	280	202	240	0.4
1-Ethynyl-naphthalene	Acetophenone	1.01×10^{-2}	1.90%	272	202	240	0.4
2-Ethynyl-naphthalene	Acetophenone	1.70×10^{-2}	3.19%	272	202	240	0.4

p_i , partial pressure of target molecule in reactor, in Pa;

X_i^T , mole fraction of target molecule in solution;

b.p.^T and b.p.^S, boiling point of target molecule and solvent, in °C;

$T_{vap.}$, heating temperature of vaporizer, transfer pipeline and flow reactor, in °C;

Q, liquid injecting flow rate (accuracy $\pm 0.5\%$), in mL/hour;

*Boiling point calculated by adapted Stein & Brown method.

Figure 1 Schematic diagram of the experimental facility with SVUV-PIMS.⁵⁹

Figure 2 Measurements and fittings for mass discrimination factor, D_i .

Figure 3 (A) Mass spectrum recorded at 10.5 eV. (B) and (C) Photoionization cross-sections of nitric oxide and benzene, respectively.

Figure 4 Photoionization cross-sections of naphthalene. Inserted frame presents the mass spectrum at 10.0 eV, respectively.

Figure 5 Photoionization cross-sections of phenanthrene. Inserted frame: mass spectrum recorded at 10.0 eV.

Figure 6 (A) Mass spectrum recorded at 13.5 eV. (B) Photoionization cross-sections of 1-methyl-naphthalene.

Figure 7 (A) Mass spectrum recorded at 13.0 eV. (B) Photoionization cross-sections of indene.

Figure 8 Photoionization cross-sections of 2-methyl-indene. Inserted frame: mass spectrum recorded at 9.4 eV.

Figure 9 Photoionization cross-sections of 2-methylphenylacetylene. Inserted frame: mass spectrum recorded at 11.0 eV.

Figure 10 Photoionization cross-sections of 3-methylphenylacetylene. Inserted frame: mass spectrum recorded at 11.0 eV.

Figure 11 Photoionization cross-sections of 4-methylphenylacetylene. Inserted frame: mass spectrum recorded at 11.0 eV.

Figure 12 Photoionization cross-sections of diphenylacetylene. Inserted frame: mass spectrum recorded at 11.0 eV.

Figure 13 Photoionization cross-sections of acenaphthylene. Inserted frame: mass spectrum recorded at 12.0 eV.

Figure 14 Photoionization cross-sections of 1-ethynyl-naphthalene. Inserted frame: mass spectrum recorded at 12.0 eV.

Figure 15 Photoionization cross-sections of 2-ethynyl-naphthalene. Inserted frame: mass spectrum recorded at 12.0 eV.

Figure 16 Comparison of the PICs of aromatic hydrocarbons. ΔE : photon energy above ionization energy. Black solid line: benzene; orange solid line: phenylacetylene; red solid line: naphthalene.