

## Recent Applications of Synchrotron VUV Photoionization Mass Spectrometry: Insight into Combustion Chemistry

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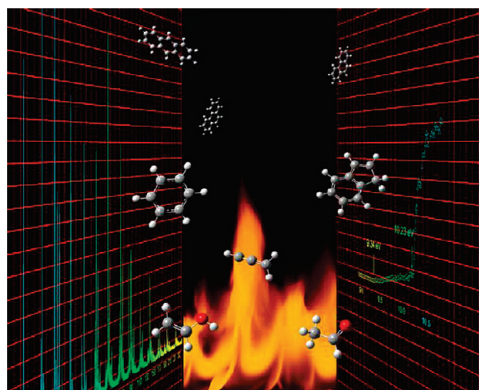
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### CON SPECTUS

Combustion is one of the earliest developed human technologies and remains our primary source of energy, yet it embodies a complex suite of physical and chemical processes that are inadequately understood. Combustion chemistry involves both chemical thermodynamics and chemical kinetics, and experimental advances mostly depend on the development of combustion diagnostics, which effectively serve as the foundation of theoretical progress. The major objective of combustion diagnostics is to provide comprehensive product identification and concentration information of a flame species, which can be used to develop kinetic models for the simulation of practical combustion. However, conventional combustion diagnostic methods face difficult challenges in distinguishing isomeric species, detecting reactive radicals, obtaining real-time measurements, and so forth. Therefore, for deeper insight into combustion chemistry, a diagnostic method with high detection sensitivity, isomeric selectivity, and radical detectability is required.

In this Account, we report recent applications of synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV–PIMS) in various areas of combustion chemistry research. The wide tunability of synchrotron photon energy can facilitate the selective identification of isomeric intermediates and the near-threshold detection of radicals (thus avoiding fragmentation interference). Moreover, the convenient combination of SVUV–PIMS with various laboratory-based combustion approaches demonstrates its universality in combustion studies. Recent experimental achievements have demonstrated the successful applications of this technique in premixed flames, pyrolysis in flow reactors, coflow diffusion flames, catalytic oxidation, plasma diagnostics, and analysis of polycyclic aromatic hydrocarbons (PAHs) and soot. More applications of SVUV–PIMS are expected in the near future, not only in combustion studies, but also in other research topics of chemistry such as analytical chemistry, photochemistry, biochemistry, and the like.

In all applications, combustion intermediates, including isomers and radicals, can be distinguished unambiguously, extending our knowledge of intermediate pools and providing more precise targets for quantum chemical calculations of significant reaction channels. The observed mass range covers both small and large combustion products, such as PAHs with two to five carbonic rings. Such analyses present clues toward understanding the molecular growth process from fuel to PAHs and, consequently, soot in fuel-rich hydrocarbon flames. Furthermore, quantitative analyses of chemical structure are available in most applications. For example, one can acquire concentration profiles of flame species versus position in premixed and diffusion flames or versus temperature in pyrolysis and catalytic oxidation. The objectives of validating current kinetic models and developing new kinetic models are thus well served with SVUV–PIMS as an analytical tool in combustion research.



### 1. Introduction

Combustion has been used by human beings for around one million years and provides about 90% of the worldwide energy supply in modern society.

Combustion chemistry is a general discipline embodying both chemical thermodynamics and chemical kinetics in combustion. It has many unresolved problems such as the formation mechanisms of combustion pollutants, for example, nitrogen oxides ( $\text{NO}_x$ ),

polycyclic aromatic hydrocarbons (PAHs), and soot.<sup>1</sup> Furthermore, combustion chemistry serves as the foundation of most combustion studies because combustion is a fluid system from which the chemistry cannot be decoupled. However, understanding combustion chemistry remains a great challenge, since combustion is a complex physicochemical process including numerous important isomeric structures of key species that may have widely differing reactivity, and important reactive but unstable radicals that may be present in low concentrations but have a large impact on the chemistry.

The identification of combustion products is achieved by combustion diagnostics. Conventional diagnostic techniques can be classified into two categories. One includes the “non-intrusive” optical spectroscopic techniques including laser-induced fluorescence,<sup>2</sup> cavity ring-down spectroscopy,<sup>3</sup> coherent anti-Stokes Raman spectroscopy,<sup>4</sup> etc. These in situ methods can be applied to detect simple combustion intermediates such as NO, OH, CH, etc. However, it is difficult for them to selectively and sensitively detect complex intermediates with weak featureless spectra, for example, PAHs, because these species have large partition functions and small rotational constants at typical combustion temperatures (500–2000 K).

The other category includes the extractive sampling methods combined with mass spectrometry (MS), gas chromatographs (GC), or the coupling of GC and MS (GC/MS). The major disadvantage of sampling techniques is the disturbance to flame structure caused by the insertion of the probe. But as the sole method to possess general sensitivity for combustion intermediates, it is more widely used in combustion studies than the optical methods.<sup>5</sup> Among the detection procedures, GC and GC/MS have been widely applied in analytical chemistry because of their good sensitivity and isomeric selectivity. However, they cannot directly detect radicals and may cause disturbance to the analytes by secondary (catalytic) reactions, condensation, and phase equilibria because of the long retention times.<sup>5</sup> Moreover, columns need to be changed for the detection of different groups of flame species, which complicates the measurements with GC and GC/MS.

Sampling methods directly combined with MS have been proven as powerful and universal diagnostic procedures in many research fields of chemistry, physics, and biology. Two sampling methods have been adopted in combustion studies. One is capillary sampling, which only causes minor distortion of the flame structure.<sup>6</sup> However, it cannot detect unstable intermediates such as radicals because of the enhanced effects on wall and gas collisions. The other approach is molecular-beam sampling with a cone-shaped

nozzle instead of the capillary probe.<sup>7</sup> Its combination with MS is called as molecular-beam mass spectrometry (MBMS). The big cone angle (40–70°) and high vacuum downstream can ensure free molecular flow of sampled gas and reduce collision effects,<sup>7</sup> making it possible to detect both stable and unstable combustion intermediates. Furthermore, 40° has proven to be the optimum cone angle which can both maintain the above advantages and minimize the disturbance to flame structure.<sup>8</sup>

A conventional MBMS apparatus utilizes electron-impact (EI) ionization or laser photoionization as the ionization procedures. However, the relatively high energy employed and unsatisfactory energy resolution of the electron beam can cause severe fragmentation that interferes with the detection of smaller intermediates, especially radicals, and limit the selectivity of EI ionization, excluding it from distinguishing isomeric structures. Laser photoionization, including vacuum ultraviolet (VUV) single-photon photoionization (SPPI) and resonance enhanced multiphoton ionization (REMPI), can minimize fragmentation of most hydrocarbons because the total absorbed photon energy barely exceeds the ionization energy (IE).<sup>5</sup> However, the tuning of VUV laser is very time-consuming to cover a wide energy range, which limits the practical application of laser SPPI in isomeric identification. REMPI is seldom used because it is quite time-consuming and awkward because the wavelength must be changed for each molecule of interest to obtain isomeric selectivity and the necessary spectroscopic data is often unavailable.<sup>5</sup> Furthermore, some combustion intermediates, e.g. large free radicals, have unknown photoionization cross sections. Using estimated cross section will result in greater uncertainties of the evaluated concentrations of these intermediates. Therefore relevant measurements of photoionization cross section are requisite.

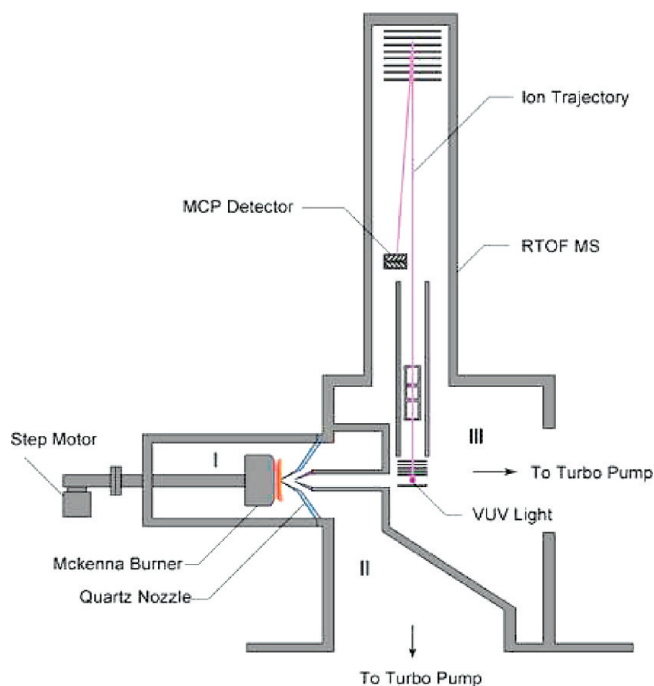
Recently synchrotron VUV photoionization combined with MBMS, also referred to as synchrotron VUV photoionization mass spectrometry (SVUV-PIMS), was applied in studies of low-pressure premixed laminar flames.<sup>9</sup> Benefiting from the wide tunability and high energy resolution, synchrotron VUV photoionization can minimize fragmentation interference, distinguish isomers, and detect radicals. Therefore, it is a selective and sensitive ionization method and can overcome the drawbacks of other ionization techniques. The application of SVUV-PIMS has achieved great success in this area, presenting amazing detection of combustion intermediates and comprehensive measurement of flame structure for combustion studies.<sup>10–21</sup>

There are two SVUV-PIMS combustion facilities developed to date around the world. One is located at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory and is focusing exclusively on the premixed flame studies.<sup>21</sup> The other one is located at National Synchrotron Radiation Laboratory (NSRL), Hefei, China. This Account reports the recent efforts of NSRL group to apply SVUV-PIMS in several research topics of combustion chemistry, from premixed flames to diffusion flames, from pyrolysis in flow reactor to catalytic oxidation, and from plasma diagnostics to PAH and soot analysis. These achievements exhibit the power of SVUV-PIMS in current applications, as well as its potential contribution to other research topics.

## 2. Synchrotron VUV Photoionization Mass Spectrometry

**2.1. Beamline.** A SVUV-PIMS combustion facility consists of three major instruments, that is, the beamline, MBMS system, and combustion instrument. Two beamlines in NSRL are used to study combustion chemistry. One utilizes the bending magnet radiation from a 800 MeV electron storage ring as reported elsewhere.<sup>22</sup> In brief, a 1 m Seya-Namioka monochromator equipped with a 1200 grooves/mm grating is used to disperse the radiation with an energy resolving power ( $E/\Delta E$ ) of 500. The available photon energy ranges from 6.2 to 11.8 eV with average photon flux of  $5 \times 10^{10}$  photons/s. A LiF window is used to eliminate the high-order harmonic radiation. The other beamline utilizes the undulator radiation, which is dispersed by a 1m Seya-Namioka monochromator equipped with a 1500 grooves/mm grating, covering the photon energies from 7.8 to 24.0 eV. A gas filter with Ne or Ar filled in the gas cell is used to eliminate high-order harmonic radiation. Its energy resolving power is around 1000 with average photon flux reaching  $1 \times 10^{13}$  photons/s. The difference between the lowest photon energies available from two beamlines (6.2–7.8 eV) is significant, since IEs of most PAHs locate in this region.

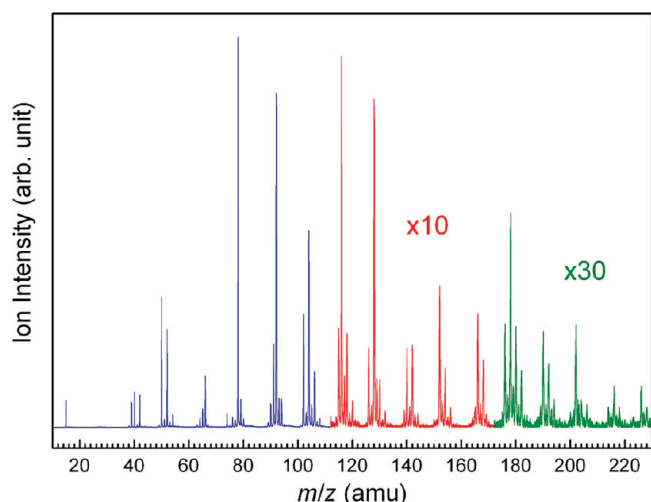
**2.2. MBMS System.** Description of our MBMS system can be found in our previous publications.<sup>14,15,22</sup> Here, we take the premixed flame system as an example to concisely introduce the detection procedure. Figure 1 shows the combination of premixed flame system and MBMS system. The flame chamber (I) with a 6.0-cm-diameter McKenna burner is coupled to the MBMS system which consists of a differentially pumped chamber (II) with a molecular-beam sampling system and a photoionization chamber (III) with a homemade reflectron time-of-flight mass spectrometer (RTOF-MS).<sup>23</sup> The



**FIGURE 1.** Scheme of the MBMS system coupled to the premixed flame apparatus in NSRL.

flat premixed flame stabilized on the burner surface is sampled by a quartz cone-shaped nozzle with a 40° included angle and a  $\sim 500 \mu\text{m}$  orifice at the tip. The sampled flame species can form a molecular beam in the differentially pumped chamber and pass into the photoionization chamber through a nickel skimmer. The molecular beam intersects the synchrotron VUV light perpendicularly in the ionization region. The produced photoions are collected and analyzed by the RTOF-MS with a mass resolving power ( $m/\Delta m$ ) of 1400.

**2.3. Photoionization Efficiency Spectrum.** The most important feature of combustion studies using SVUV-PIMS is the measurement of the photoionization efficiency (PIE) spectrum, which facilitates the unambiguous identification of combustion intermediates. With variation of photon energy, a series of mass spectra are measured, for example, in the middle of the luminous flame region of a premixed flame, where most combustion intermediates have high concentrations. The integrated ion signals of each mass peak weighted by photon flux are plotted versus the photon energy, yielding a PIE spectrum containing precise information of the ionization thresholds (deflections on the PIE spectrum). Because of the cooling effect in molecular beam sampling,<sup>24</sup> the discrepancies of measured ionization thresholds caused by the hot band ionization are typically less than 30 meV.<sup>25</sup> Knowing the molecular weight and ionization thresholds can identify the dominant intermediates in combustion through the accordance of ionization thresholds and obtained literature IEs, for



**FIGURE 2.** Photoionization mass spectrum taken at 8 mm in a near-sooting ethylbenzene flame.

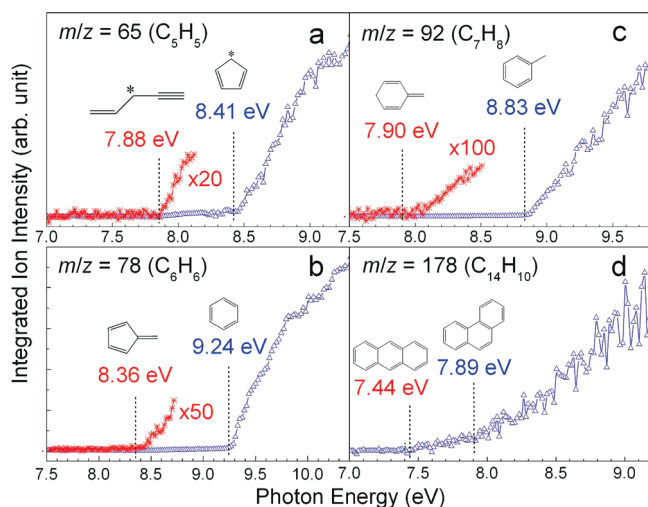
example, from NIST online database<sup>26</sup> and many previous calculations.<sup>11,12,14,19</sup> For the candidates of combustion intermediates with unknown IEs, high-level ab initio theoretical methods can be used for IE prediction, especially for the free radicals whose IEs are difficult to be experimentally determined.<sup>27</sup>

### 3. Applications in Combustion Study

**3.1. Laminar Premixed Flame.** Because of the relatively simple structure, excellent stability, and almost invariable stoichiometry within a particular flame, the laminar premixed flame is used widely in combustion studies. Among various premixed flames, the premixed flat flame, usually operated at low pressure to reduce three-body termination reactions of radicals, is ideal for studies of combustion chemistry using sampling methods. Three major categories of fuels have been studied with SVUV-PIMS, including hydrocarbons, oxygenated hydrocarbons, and nitrogenous hydrocarbons.

**Hydrocarbon Flames.** Being the dominant components in most practical fuels, hydrocarbons usually combust incompletely in practical combustors and generate PAHs, soot, CO, and unburned hydrocarbons (UHC). To understand formation mechanisms of PAHs and soot in combustion, especially the gas-phase molecular growth process including aromatics formation and subsequent PAH growth, requires promoted PAH concentrations that can be achieved by using fuels with benzenoid ring structure. Therefore, we investigated fuel-rich premixed flames of aromatic hydrocarbons including benzene, toluene, and ethylbenzene.<sup>14,17,19</sup>

Figure 2 shows a mass spectrum taken at 8.0 cm from the burner surface and the photon energy of 10.50 eV in the ethylbenzene flame,<sup>17</sup> which includes mass peaks from  $m/z = 15$

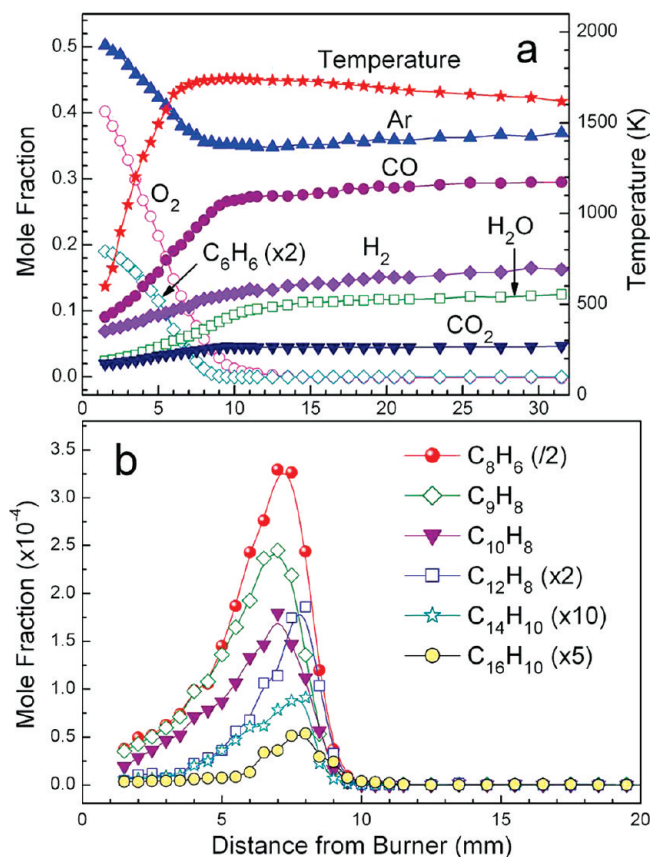


**FIGURE 3.** PIE spectra of  $m/z = 65, 78, 92,$  and  $178$  in a near-sooting toluene flame.

to 240. Identification from the PIE spectra exhibits that more than 100 intermediates are formed in these flames, including numerous isomers, radicals, and PAHs. Figure 3 illustrates the PIE spectra of  $m/z = 65, 78, 92,$  and  $178$  in the toluene flame.<sup>19</sup> Mole fraction profiles of observed flame species can be obtained from the scan of burner position, and temperature profiles are recorded by a Pt/Pt-13% Rh thermocouple. For example, Figure 4 shows the mole fraction profiles of major flame species and typical PAHs in the benzene flame.<sup>14</sup> The comprehensive identification of aromatics from monocyclic aromatics to pentacyclic PAHs in these flames can be used to qualitatively verify current aromatic formation and growth mechanisms, for example, the hydrogen-abstraction-carbon-addition (HACA) mechanism,<sup>28</sup> the five-member ring recombination mechanism,<sup>29</sup> and the propargyl recombination mechanism.<sup>30</sup>

Comparison among these flames demonstrates that the PAH concentrations increase with increasing complexity of fuel side chain structure,<sup>17</sup> which obeys the same order of sooting tendency. It is concluded that the HACA mechanism can connect observed PAHs from monocyclic aromatics to tetracyclic PAHs. For example, the major HACA reaction sequence can start from benzene to pyrene via phenylacetylene, naphthalene/1,4-diethynylbenzene, 2-ethynyl-naphthalene, and anthracene. Modeling studies based on the obtained mole fraction information can validate current kinetic models of PAH and soot formation and reveal the contributions of different mechanisms in the aromatics growth process.

Furthermore, many previously undetected intermediates, most of which contain isomeric structures, have been identified in hydrocarbon flames using SVUV-PIMS, for example, the enol family ( $C_nH_{2n-1}OH, 2 \leq n \leq 4$ ),<sup>10</sup> the  $C_4H_3$  and  $C_4H_5$  rad-

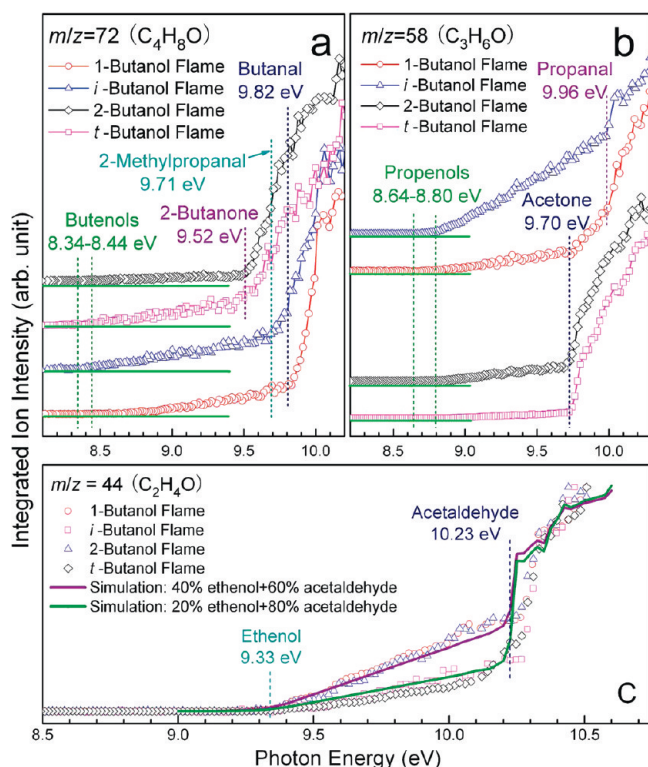


**FIGURE 4.** Mole fraction profiles of (a) major flame species and (b) several typical aromatic intermediates in a fuel-rich benzene flame.

icals,<sup>11</sup> the  $C_5H_3$  and  $C_5H_5$  radicals,<sup>12</sup> and large polyynes ( $C_{12}H_2$ ) and polyynic  $C_7H_4$  molecules ( $C_9H_4$  and  $C_{10}H_4$ ).<sup>18</sup> A lot of other radicals, from  $CH_3$  to  $C_9H_7$ , were also detected. The finding of enols exhibited the salient advantages of SVUV-PIMS, and may extend our knowledge of the formation of aldehydes, which are a category of air toxics and attract more and more concern because of the use of ethanol as gasoline additives.

**Oxygenated Hydrocarbon Flames.** Oxygenated hydrocarbons are major components in biofuels such as alcohols and biodiesels, which are potential substituents for fossil fuels. Oxygenated fuels are also expected for low soot emission levels in view of existing oxygen atoms in fuel molecule. Therefore, we studied the premixed flames of butanol isomers and  $C_3$ -oxygenated hydrocarbons including acetone, *n*- and *i*-propanols.<sup>15,16</sup> The intermediate identification indicates the existence of many oxygenated intermediates, such as aldehydes, ketones, enols, etc.

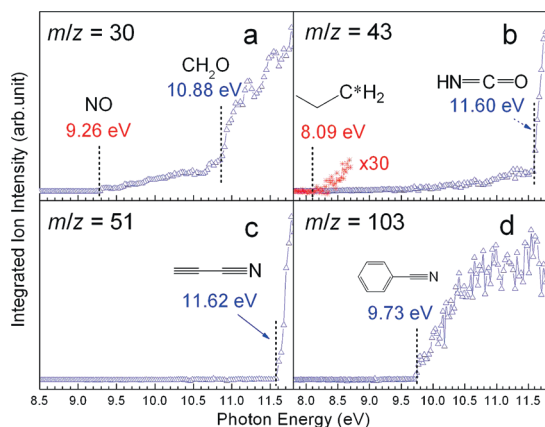
It was found that specific features of fuel molecules are conserved in the primary fuel decomposition process and are lost gradually as the decomposition progresses.<sup>15,16</sup> Figure 5 shows the PIE spectra of  $m/z = 72$ , 58, and 44 in the four butanol flames,<sup>15</sup> which belong to molecules with formula of



**FIGURE 5.** PIE spectra of  $m/z = 72$ , 58, and 44 in fuel-rich premixed flames of four butanol isomers.

$C_4H_8O$ ,  $C_3H_6O$ , and  $C_2H_4O$ , respectively. Different thresholds on the PIE spectra represent various decomposition products, and different compositions of identical isomeric structures can be inferred from the different slopes of the PIE spectra. These phenomena indicate the influence of original fuel structures on the primary and secondary decomposition products. However, the influence of fuel structure becomes negligible after the loss of oxygenated functional groups. Moreover, because of the existence of oxygenated functional groups in the fuel molecule, aldehydes, and ketones have obviously elevated concentrations in oxygenated hydrocarbon flames compared with hydrocarbon flames, while benzene formation is reduced.<sup>16</sup> Analysis of the concentration relation of benzene and its precursors demonstrates the reduced proportion of benzene formation in the consumption of its precursors in oxygenated hydrocarbon flames.<sup>16</sup>

**Nitrogenous Hydrocarbon Flames.** Natural nitrogenous hydrocarbons widely exist in coal and low-rank fossil fuels. Some synthetic nitrogenous hydrocarbons such as nitroethane can be used as gasoline additives and propellants. Combustion of nitrogenous components in coal and certain oils is an important emission source of  $NO_x$  and other nitrogenous toxics. Therefore, premixed flames of many nitrogenous fuels such as pyrrole ( $C_4H_5N$ ) and nitromethane ( $CH_3NO_2$ ) were studied with SVUV-PIMS to understand the combustion chemis-

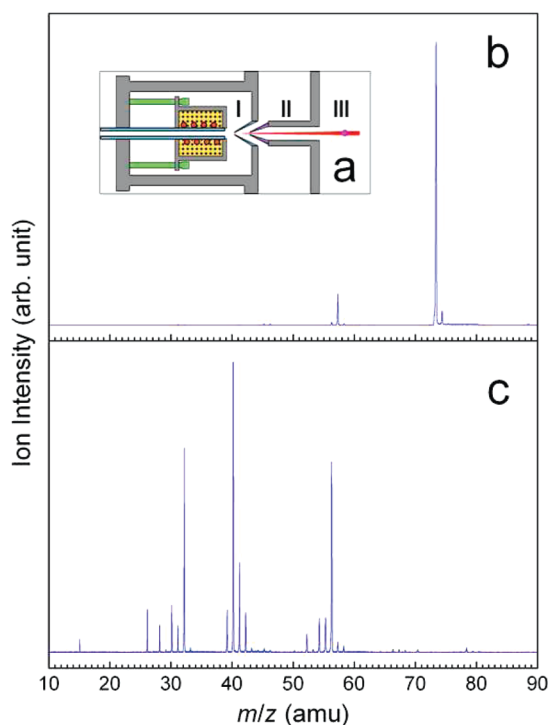


**FIGURE 6.** PIE spectra of  $m/z = 30$ , 43, 51, and 103 in a fuel-rich pyrrole flame.

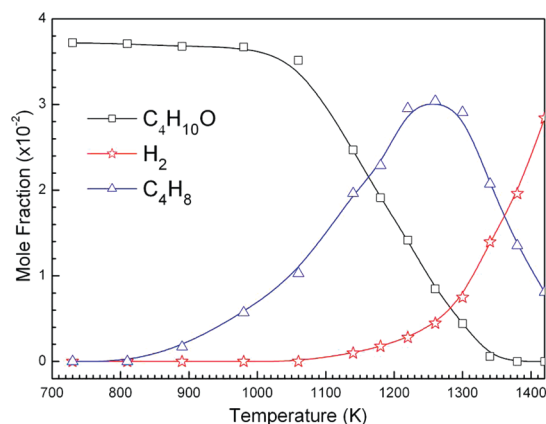
try of nitrogenous fuels.<sup>13,20</sup> More than 30 nitrogenous intermediates were identified in the pyrrole flames, including a lot of isomeric structures.<sup>13</sup> Figure 6 illustrates the intermediate identification in the fuel-rich pyrrole flame. The extended intermediate pool facilitates insight into the pyrrole decomposition process, which is useful for the modeling studies. On the basis of the experimental investigation of a fuel-rich nitromethane flame, a detailed oxidation mechanism including 69 species and 314 reactions was developed from previous models, which well predicted the experimental results compared with previous nitromethane models.<sup>20</sup>

**3.2. Pyrolysis in a Flow Reactor.** The concept of combustion contains two interactive processes, that is, pyrolysis and oxidation. Pyrolysis studies can exclude the influence of oxygen and demonstrate the fuel destruction and molecular growth processes. Most previous studies were performed in various instruments, such as a flow reactor, shock tube, jet stirred reactor, and Knudsen cell, using EI ionization mass spectrometry or GC to detect pyrolysis products. Recently, SVUV-PIMS was applied in pyrolysis studies in flow reactor to obtain unambiguous identification of pyrolysis products.<sup>31,32</sup> The apparatus is inserted in Figure 7a. The flow reactor is electrically heated with temperature controlled by a temperature controller. Pyrolysis products can be detected by the MBMS system with the nozzle located close to the outlet of the flow reactor and identified by the measurement of PIE spectrum. The variation of pyrolysis temperature can generate the mole fraction profiles of observed products versus pyrolysis temperature, providing information on the formation temperatures and concentrations of pyrolysis products.

Figure 7b shows the photoionization mass spectrum taken at 11.8 eV and the temperature of 820 K in the pyrolysis of methyl *tert*-butyl ether (MTBE).<sup>31</sup> Because of the low MTBE molecular ion, its concentration is represented by the signals

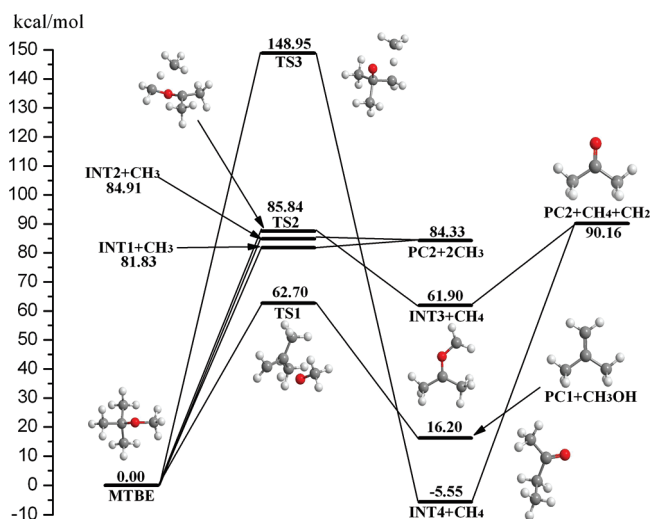


**FIGURE 7.** (a) Scheme of the pyrolysis apparatus. Photoionization mass spectra taken at (b) 820 K and (c) 1380 K in a MTBE pyrolysis.



**FIGURE 8.** Mole fraction profiles of MTBE,  $C_4H_8$ , and  $H_2$  in a MTBE pyrolysis with increasing pyrolysis temperature.

of its most abundant photodissociation products, that is,  $(CH_3)_3C^+$  at  $m/z = 57$  and  $(CH_3)_3CO^+$  at  $m/z = 73$ . Only these two peaks can be observed from the mass spectrum, indicating that MTBE does not decompose at this temperature. Figure 7c shows the effects of increasing pyrolysis temperature. Many pyrolysis products are detected, while the fuel fragment signals disappear at 11.8 eV, indicating the complete consumption of MTBE at 1380 K. About thirty pyrolysis products including many radicals and isomeric structures were identified, and their mole fraction profiles were evaluated as well. Figure 8 illustrates the mole fraction profiles of MTBE,  $H_2$ , and  $C_4H_8$ . The different tendencies of these profiles demonstrate



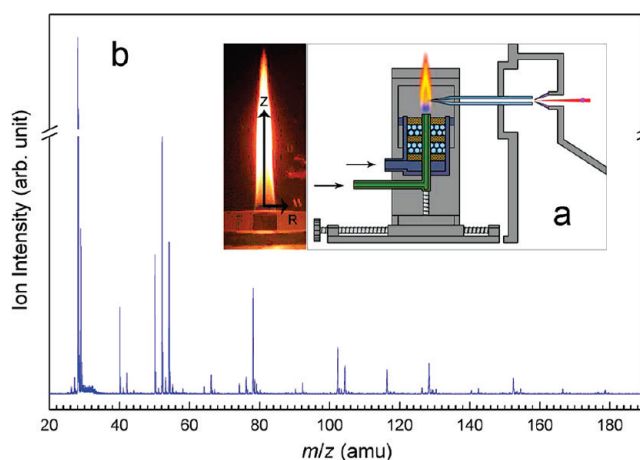
**FIGURE 9.** Relative energies of some primary products in a MTBE pyrolysis calculated at the G3B3 level of theory.

their different roles, that is, MTBE as fuel,  $H_2$  as final product, and  $C_4H_8$  as intermediate.

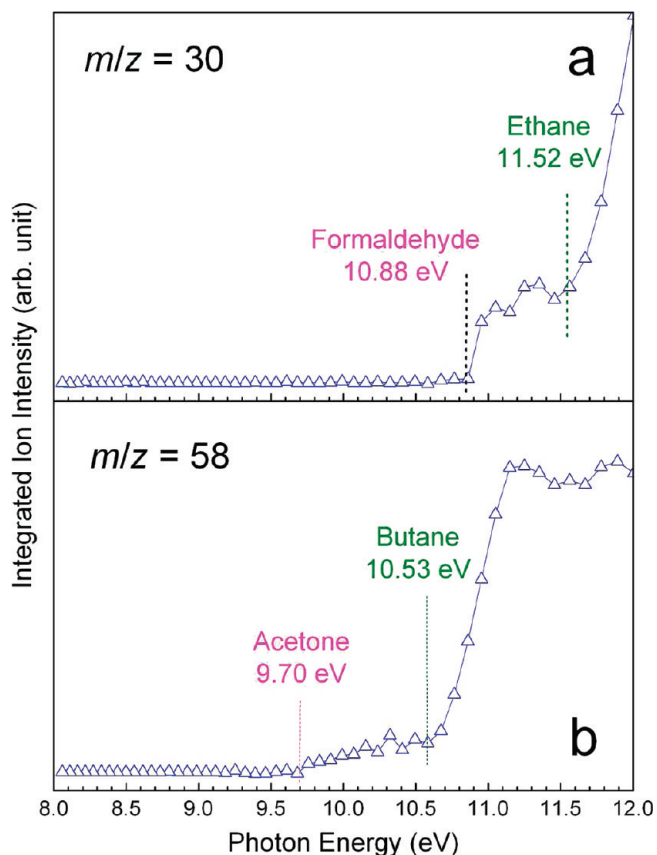
Furthermore, the formation temperatures of pyrolysis products measured from mole fraction profiles represent the activation energies of their formation channels. Therefore these formation channels can be theoretically studied using the high-level ab initio calculation.<sup>32,33</sup> Relative energies of the primary pyrolysis products and corresponding transition states in the pyrolysis of MTBE are illustrated in Figure 9, which elucidates the decomposition channels of MTBE. Among these channels, the one with the lowest energy barrier is the decomposition to methanol and isobutene via a four-member-ring transition state, which is in good accordance with the lowest formation temperatures of methanol and isobutene.<sup>31</sup>

**3.3. Coflow Diffusion Flame.** Most practical flames are nonpremixed diffusion flames. Diffusion flames can promote soot production because of the deficiency of oxygen in the fuel side, making them ideal systems to study soot chemistry. Most previous investigations used laser SPPI to detect the gas-phase products.<sup>5,34</sup> Here the SVUV-PIMS is applied to study coflow diffusion flames at atmospheric pressure. Figure 10a shows the scheme and a photograph of the atmospheric pressure coflow diffusion flame system. The burner is composed of two coaxial tubes, i.e. a 10-mm-diameter inner tube to supply fuel and a 110-mm-diameter outer tube to supply air. A quartz probe with a  $\sim 50\text{-}\mu\text{m}$ -diameter orifice on the tip is used to sample flame species; and the burner can be accurately moved in both axial and radial directions to change the sampling positions. The sampling system downstream the quartz probe is identical to that used in above applications.

Figure 10b shows a photoionization mass spectrum taken at 30 mm axially above the burner in a nonpremixed ethyl-

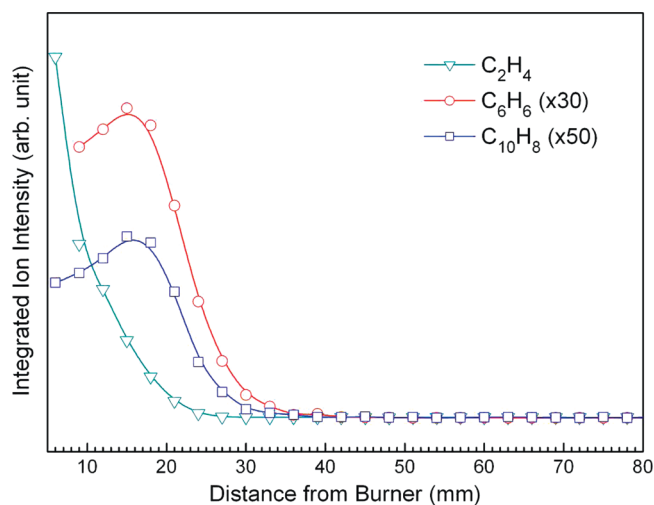


**FIGURE 10.** (a) Scheme and photograph of the coflow diffusion flame apparatus. (b) Photoionization mass spectrum taken at 30 mm in a coflow ethylene/air diffusion flame.

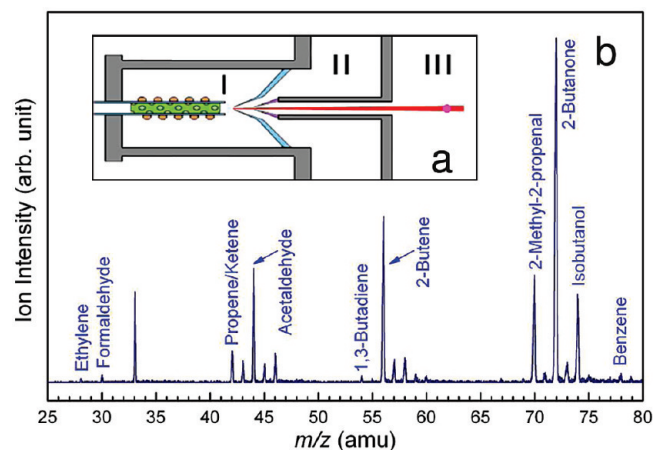


**FIGURE 11.** PIE spectra of  $m/z = 30$  and  $58$  in a coflow propane/air diffusion flame.

ene/air diffusion flame. Many peaks can be observed from the mass spectrum, covering  $C_1$ - to  $C_{12}$ -intermediates. Isomeric identification of flame species can be obtained from the measurement of PIE spectrum, as illustrated in Figure 11 from which ethane and formaldehyde were distinguished for  $m/z = 30$  in a propane/air flame, and acetone and butane for  $m/z = 58$ . More isomeric intermediates such as  $m/z = 42, 44, 52,$



**FIGURE 12.** Axial signal profiles of  $m/z = 28, 78,$  and  $128$  in a coflow ethylene/air diffusion flame.



**FIGURE 13.** (a) Scheme of the catalytic oxidation apparatus. (b) Photoionization mass spectrum of a catalytic oxidation of *i*-butanol taken at 603 K.

54, and 78 were also distinguished. Furthermore, mole fraction profiles of the flame species can be generated from the scan of axial or radial position from the burner. For instance, Figure 12 illustrates the axial signal distribution profiles of  $C_2H_4$ ,  $C_6H_6$ , and  $C_{10}H_8$  in the ethylene/air flame.

**3.4. Catalytic Oxidation.** Catalytic combustion techniques can be applied in control of  $NO_x$  and UHC emissions in heat and power generation plants and removal of volatile organic compounds and automobile exhaust. Most previous investigations of catalytic oxidation analyzed products through GC or MS with conventional ionization methods.<sup>35,36</sup> Recently the SVUV-PIMS was applied in product analysis of catalytic oxidation.<sup>37</sup> Figure 13a shows the low-pressure catalytic oxidation apparatus connected to the MBMS system. In brief, the catalyst bed locates inside a quartz tube, which is outwardly heated. The quartz nozzle of the MBMS system is put closely to the quartz tube to sample oxidation products. Normal-pres-

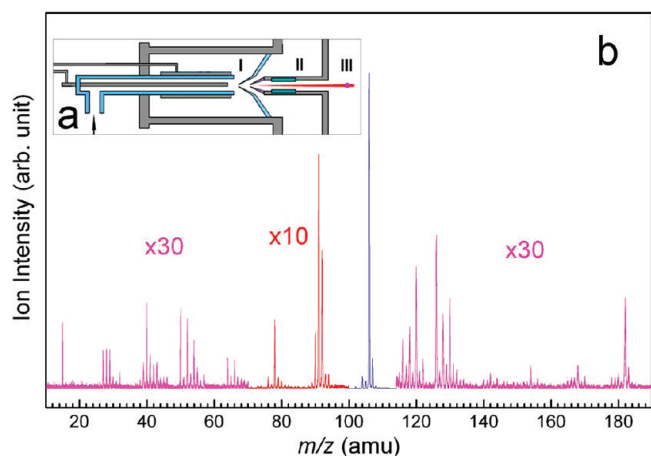
sure catalytic oxidation was also studied using the MBMS system, and the sampling system is similar to that of coflow diffusion flame.

Figure 13b presents the photoionization mass spectrum taken at 11.0 eV in the partial oxidation of *i*-butanol catalyzed by the  $Ag/Al_2O_3$  catalyst. The pressure is 6 Torr and the oxidation temperature is 603 K. More than 10 products were identified as labeled on the figure. Detailed illustration of PIE spectra can be found in the recent study of catalytic oxidation of ethanol and propanols,<sup>37</sup> which reported the detection of reactive products such as ethenol ( $C_2H_3OH$ ), ketene ( $C_2H_2O$ ), and propenal ( $C_2H_3CHO$ ). The detection of ethenol can verify the surface destruction channel of  $(CH_2-CH-O)^+$  generated from the dehydrogenation of ethanol on the surface of  $Ag/Al_2O_3$ .<sup>38</sup>

**3.5. Plasma Diagnostics.** Plasma-assisted ignition and combustion are of special interest at moderate gas densities and high-velocity gas flows, including ignition in supersonic flows, combustion support or enhancement by plasma at atmospheric pressure, stimulation of fuel-lean combustion, etc. Plasmas are extremely complicated systems with abundant ions, electrons, photons, and neutral reactive species, resulting in the incomplete understanding of its basic chemical composition, especially the transient or stable neutral reaction products which include many isomeric structures and radicals.<sup>39</sup> Furthermore, understanding plasma chemistry can be significant for other disciplines, such as astrochemistry and semiconductor manufacturing.

Mass spectrometric methods are preponderant in plasma diagnostics because they can be operated in a relatively convenient manner and detect both ionic and neutral products of plasma discharge. Therefore SVUV-PIMS has been applied as a plasma diagnostic procedure lately.<sup>40,41</sup> The plasma circumstance used in current studies is generated by the dielectric barrier discharge. Figure 14a shows the apparatus which has been reported elsewhere.<sup>40</sup> In brief, the plasma discharge is generated inside a quartz tube with a 2-mm-diameter tungsten rod located axially as the anode electrode and a stainless steel mesh wrapping outwardly as the ground electrode. A deflection field after the nickel skimmer can switch the experimental mode between ionic product detection and neutral product detection. Figure 14b shows the photoionization mass spectrum taken in an ethylbenzene discharge at 5 Torr, indicating the existence of numerous neutral products, many of which have greater molecular weights than the fuel. Therefore plasma discharge can not only decompose the fuel molecule but also lead to further combination of decomposition



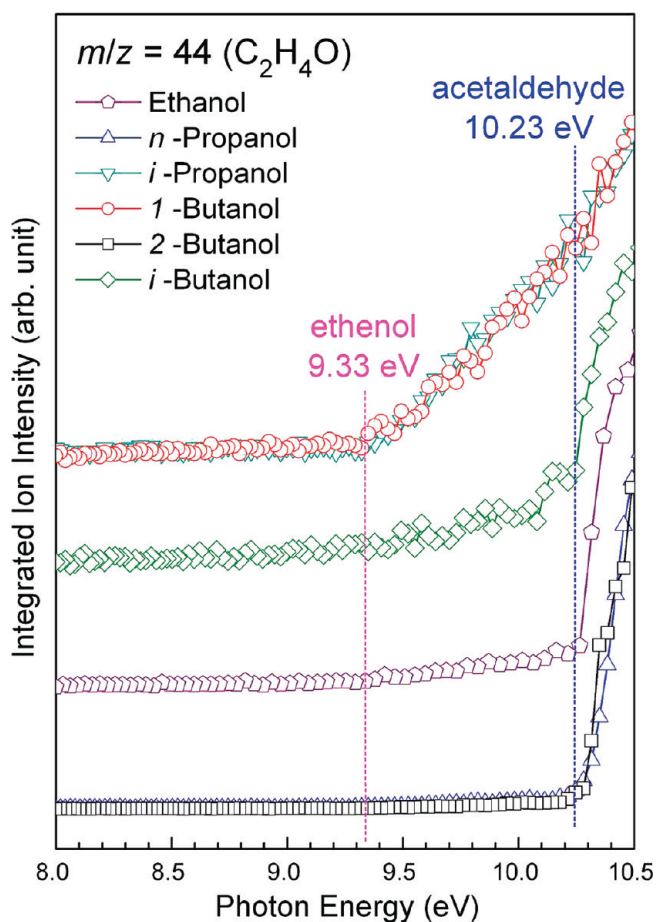


**FIGURE 14.** (a) Scheme of the plasma discharge apparatus. (b) Photoionization mass spectrum of an ethylbenzene discharge taken at 10.8 eV.

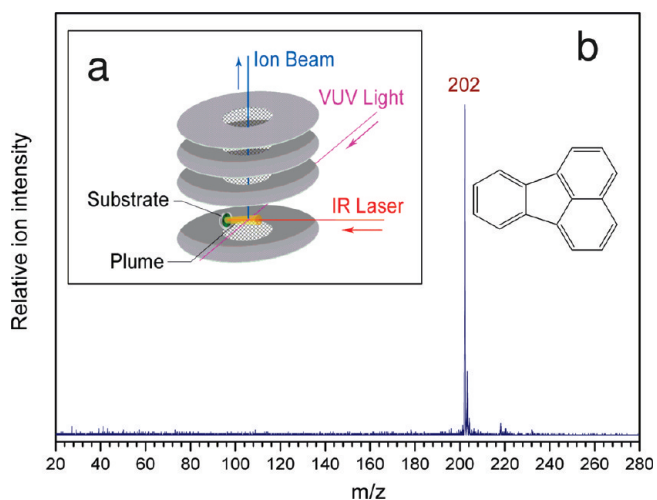
products. Radicals and isomers in plasma discharges are clearly identified from the PIE spectra as reported in our recent work.<sup>40</sup>

Moreover, plasma discharges of fuels with isomeric structures or similar structural features have been studied.<sup>41</sup> The fuels include seven alcohols, that is, ethanol, propanols, and butanols. It was noticed that the decomposition of these fuels in plasma discharge can lead to the formation of enols, ketones, aldehydes, and alkenes, which is quite similar to the observation in the premixed flames of propanols and butanols.<sup>15,16</sup> Further comparison among the thresholds and slopes of the PIE spectra can reveal the influence of special features of fuel molecules on the isomeric structures and/or isomeric compositions of primary decomposition products. For example, Figure 15 presents the PIE spectra of  $m/z = 44$  ( $C_2H_4O$ ) taken in the plasma discharges of six alcohols, indicating different isomeric compositions of acetaldehyde and ethenol.

**3.6. PAH and Soot Analysis.** Combustion generated PAHs, most of which are carcinogenic and mutagenic, are the major precursors of soot, and can be absorbed on the surface of fine soot particles ( $PM_{10}$ ) and enter human body through respiratory system. However, the analysis of soot and PAHs is one of the most challenging studies for conventional analysis procedures due to the high boiling points and large molecular structures. Therefore a novel method combining infrared laser desorption and SVUV-PIMS (IR-LD/VUV-PIMS) was applied to analyze PAHs and other organic compounds.<sup>42</sup> The detection procedure is illustrated in Figure 16a. Samples deposited on a stainless steel substrate without any matrix are put into the vacuum chamber by a feedthrough. To ensure effective desorption and avoid thermal dissociation of analytes, the desorption source utilizes the 1064 nm output from a pulsed Nd:YAG laser at the frequency of



**FIGURE 15.** PIE spectra of  $m/z = 44$  in plasma discharges of  $C_2$ – $C_4$  alcohols.



**FIGURE 16.** (a) Scheme of the IR-LD/VUV-PIMS apparatus. (b) Photoionization mass spectrum of fluoranthene taken at 9.0 eV.

10 Hz. A plume of intact neutral molecules formed in the quick desorption process can be detected by SVUV-PIMS.

Figure 16b demonstrates the photoionization mass spectrum of fluoranthene ( $C_{16}H_{10}$ ) at 9.0 eV. Benefited from the “soft” ion-

ization manner at relatively low photon energy, no fragmentation is produced. This manner makes it possible to distinguish different PAHs in a relatively complex mixture through the measurements of PIE spectrum.<sup>42</sup> Furthermore, fragmentations at different positions of the PAH molecules can be gradually generated and observed with increasing photon energy. On the basis of the fragmentation information and relative energy calculation, the structural features of analyzed molecules can be gained to understand their molecular structures. Therefore IR-LD/VUV-PIMS is a promising analysis procedure of gas-phase soot compositions.

## 4. Conclusions

The successful application of SVUV-PIMS in premixed flame studies promotes its applications in other research topics of combustion chemistry. The wide and easy tunability of synchrotron photon energy facilitates the selective detection of most combustion intermediates. Our recent efforts extended the coverage of SVUV-PIMS in various laboratory-based combustion systems, highlighting its universality in combustion studies. This Account summarized most of our recent achievements in combustion studies benefitted from these salient advantages.

The applications of SVUV-PIMS in premixed flame, pyrolysis in flow reactor, coflow diffusion flame, catalytic oxidation, plasma diagnostics, and analysis of PAHs and soot can improve our knowledge of intermediate pools in combustion. Combustion intermediates including isomeric structures and radicals have been distinguished unambiguously, many of which were unreported in previous studies. The comprehensive detection of combustion intermediates presents more precise targets for studies of reaction channels via quantum chemical calculation. Furthermore, quantitative analyses of chemical structure are available in most applications, for example, concentration profiles of flame species versus position in premixed and diffusion flames, or versus temperature in pyrolysis and catalytic oxidation, with aims to modify current kinetic models. In view of the convenient combination of SVUV-PIMS with low-pressure or normal-pressure experimental apparatus, more applications are expected in the near future, not only in combustion chemistry, but also in other research topics of chemistry such as analytical chemistry, photochemistry, biochemistry, etc.

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## FOOTNOTES

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