

# Combustion Research: A Leap Forward in the Diagnostics of Combustion

Combustion serves as a force to drive the development of modern society by providing over 85% of the primary supply of global energy, and also strongly challenges environmental security by being the greatest emission source of greenhouse gas CO<sub>2</sub> and air pollutants such as nitrogen oxides (NO<sub>x</sub>), sulfur oxides (SO<sub>x</sub>), soot, CO and unburned hydrocarbons. Combustion phenomena are basically chemical reactions with heat and light produced,<sup>1</sup> but the complicated intermediate pool and reaction channels in combustion remain challenging for researchers to understand fully and ultimately to control combustion. In particular, free radicals and reactive intermediates play crucial roles in combustion, but the comprehensive detection of these unstable species presents great challenges for combustion diagnostics.

Since its first application to combustion research in 2002, a synchrotron vacuum-ultraviolet photoionization mass spectrometer (SVUV-PIMS) has proved to serve as a diagnostic tool for combustion at the state of the art due to its ability to identify diverse combustion intermediates, such as many free radicals, isomers, enols, hydroperoxides, polycyclic aro-

matic hydrocarbons and so on. From September 2014, a research team of Fei Qi from University of Science and Technology of China (USTC), set up SVUV-PIMS combustion apparatus in two sets—a laminar flow reactor and a laminar premixed flame—at the TLS. The commissioning of the two combustion end stations connected to VUV beamline BL04C1 has been completed. Figure 1 shows the SVUV-PIMS premixed flame apparatus at the TLS, which consists of a flame chamber with a McKenna burner, a photoionization chamber, and a home-made reflectron time-of-flight mass spectrometer (RTOF-MS) with a mass resolving power ( $m/\Delta m$ ) approximately 3000. The McKenna burner generates laminar premixed

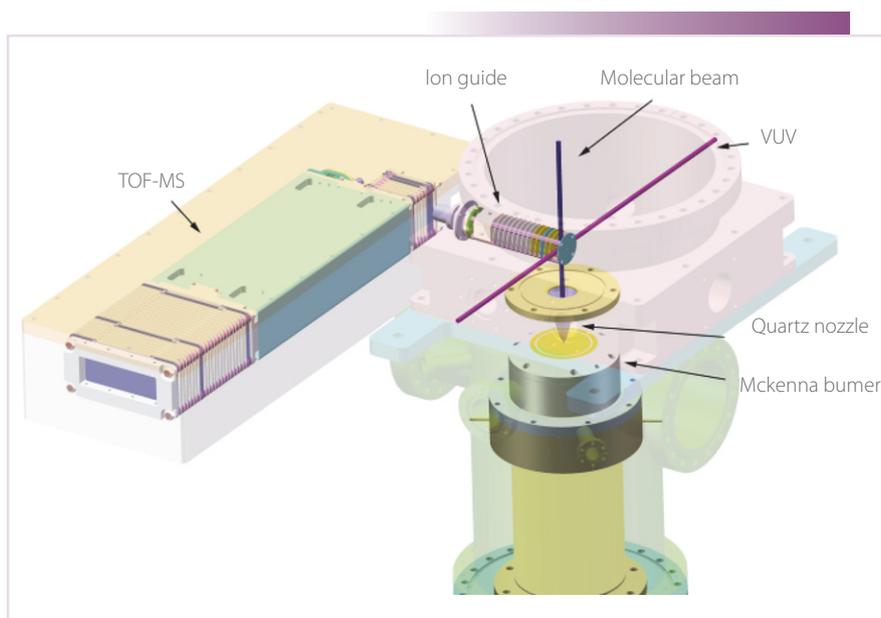


Fig. 1: Schematic drawing of the premixed flame apparatus at the TLS.

flames with satisfactory radial homogeneity. Controlled with a step motor, the burner can move along the axial direction of the flame. The flame species can be sampled at varied axial positions with a quartz nozzle (included angle  $30^\circ$ ) and an orifice ( $\sim 350 \mu\text{m}$ ) at the tip, forming a molecular beam in the photoionization chamber. The molecular beam is crossed by the synchrotron VUV light; the ions formed are detected with the RTOF-MS. Details of the premixed flame apparatus are available elsewhere.<sup>2</sup>

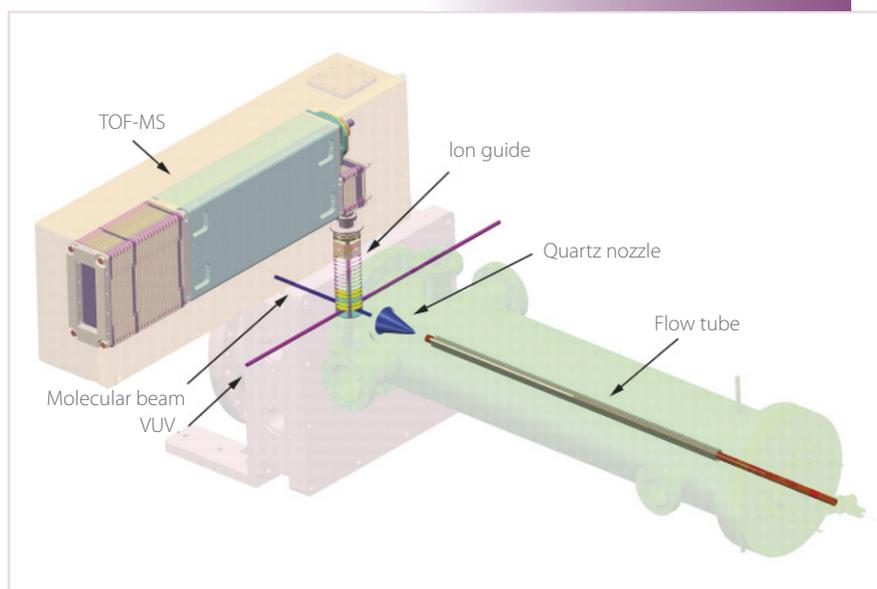


Fig. 2: Schematic drawing of the flow-reactor pyrolysis apparatus at the TLS.

Figure 2 shows the SVUV-PIMS pyrolysis apparatus at the TLS. The apparatus comprises a pyrolysis chamber, a photoionization chamber and a homemade RTOF-MS. A laminar flow reactor with an electrically heated flow tube ( $\alpha$ -alumina) was installed in the pyrolysis chamber to pyrolyze fuels of varied types, e.g. hydrocarbons, oxygenated fuels and nitrogenous fuels. The molecular-beam sampling system and photoionization chamber are the same as those in the premixed-flame apparatus.

A significant feature of the combustion chemistry end stations at the TLS compared with conventional SVUV-PIMS combustion apparatus<sup>3,4</sup> is the novel design of the sampling and ionization system. Relative to a conventional two-stage sampling system, the one-stage sampling system in both apparatus at the TLS has a smaller distance between the sampling position and the ionization position, enabling more free radicals and reactive molecules to survive for detection.

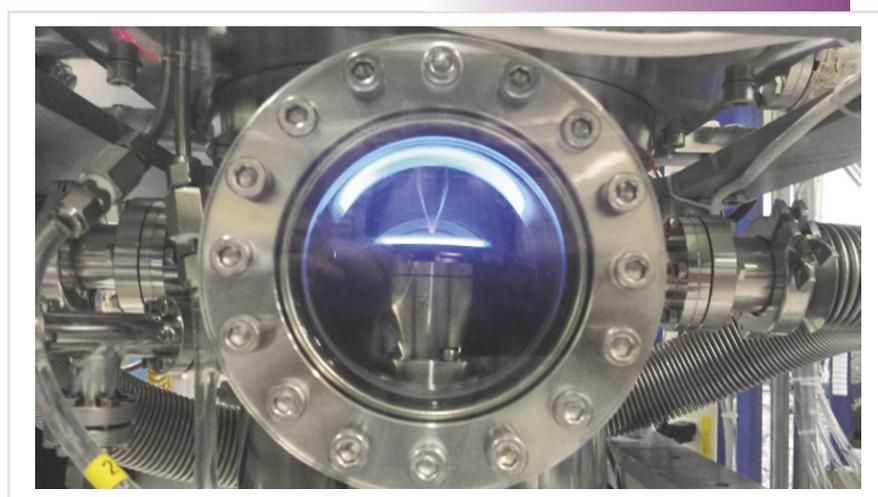


Fig. 3: A photograph of the new premixed flame apparatus at the TLS.

Some test experiments have been performed using the new SVUV-PIMS premixed flame apparatus. Figure 3 is a photograph of the new premixed-flame apparatus. The luminous region in the center of the photograph is the flame. Benefiting from the wide tunability, great energy resolution and large photon flux in the VUV region from the TLS, the secrets of combustion can be revealed to an unprecedented level. Dozens of combustion intermediates can be detected, even in the combustion of quite simple fuels. Figure 4 illustrates a mass spectrum taken from a rich ethene flame with equivalence ratio  $\phi = 2.0$  at 30 Torr. More than 10 free radicals were

detected and identified, including methyl, vinyl, formyl, ethyl, hydroxymethyl, propargylene, propargyl, allyl,  $C_4H_3$ ,  $C_4H_5$ ,  $C_5H_3$  and  $C_5H_5$  radicals, many of which were previously not reported in ethene flames. The great mass resolving power of the homemade RTOF-MS can, notably, distinguish unambiguously between intermediates with small differences of molecular masses, e.g. the reactive formyl and ethyl radicals.

Because ethene has a simple flame structure, the detection of larger intermediates in its flame experiment is limited. To test further the performance of the new SVUV-PIMS premixed flame apparatus, the *iso*-octane flame with  $\phi = 1.7$  has been conducted at 30 Torr. *iso*-octane is one of two dominant components of reference motor fuels and is widely used to index gasoline anti-knocking properties. Many free radicals were detected and identified. In particular, reactive and scarcely reported  $C_4$ - $C_8$  alkyl and  $C_4$ - $C_5$  alkenyl radicals in series were observed, such as *iso*-propyl, 1-buten-3yl, 2-methylallyl, *tert*-butyl, 3-methyl-1-buten-3-yl, *neo*-pentyl and  $C_8H_{17}$  radicals. Figure 5 illustrates several photoionization-efficiency (PIE) spectra of alkyl radicals in a rich *iso*-octane flame, which can be identified unambiguously by the accordance of the measured ionization thresholds with ionization energies in the literature. The detection of these radicals provides clear and direct experimental

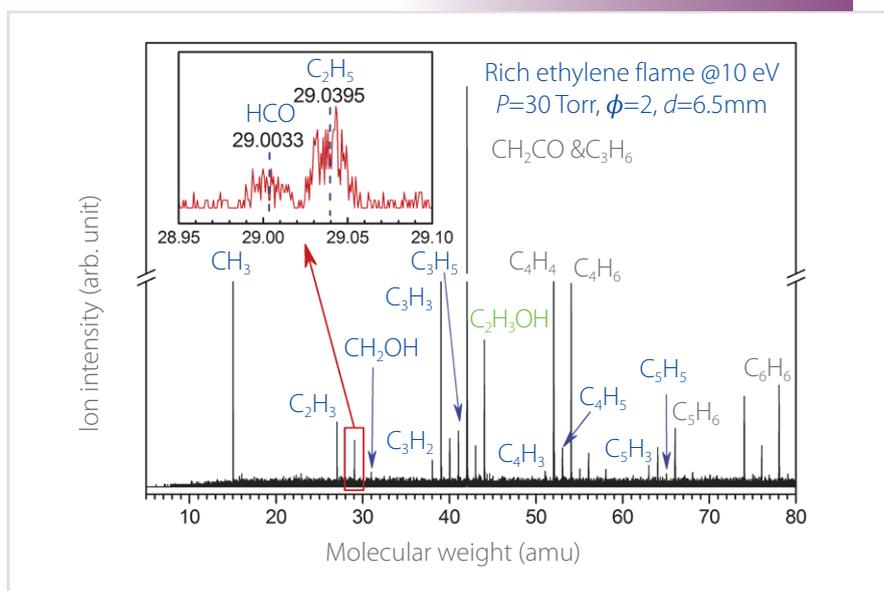


Fig. 4: Mass spectrum taken at 6.5 mm and 10 eV in a rich ethene flame ( $\phi = 2.0$ ) at 30 Torr. Black denotes stable intermediates, blue for free radicals and green unstable molecules.

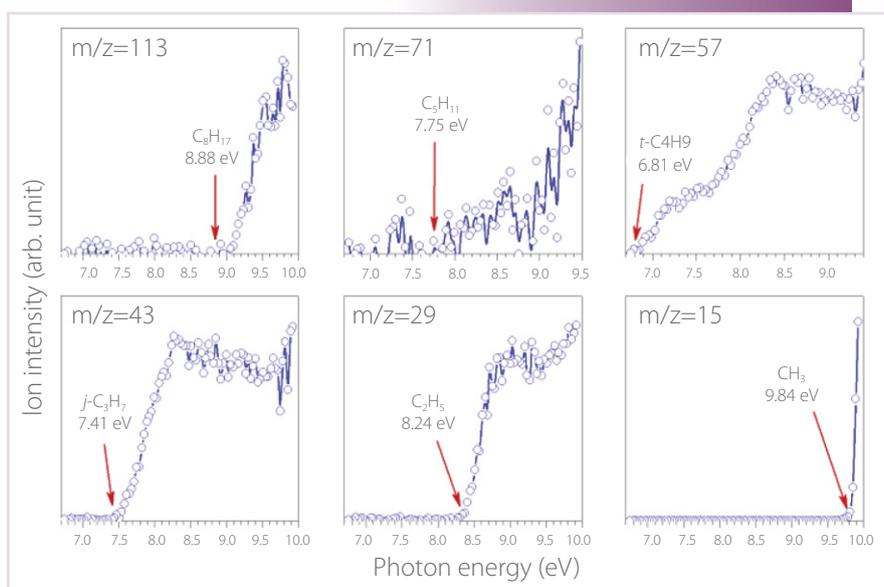


Fig. 5: PIE spectra of alkyl radicals in an *iso*-octane flame ( $\phi = 1.7$ ) at 30 Torr.

evidence for the scheme of decomposition of this important fuel for the first time.

In summary, the commissioning of combustion chemistry end stations at the TLS proceeds smoothly under the collaboration of USTC and NSRRC teams. The new apparatus present powerful abilities to detect free radicals and to distinguish intermediates with small dif-

ferences of molecular masses based on a novel design of sampling system and great mass-resolving power of the RTOF-MS. The detailed information on chemical structures can provide more direct information for the development and validation of models of combustion kinetics, merging the gap between the present knowledge and the mystery of the combustion phenomena. (Reported by Fei Qi, Yuyang Li, and Yin-Yu Lee)

## References

1. H. W. Emmons, *Proc. Combust. Inst.* **13**, 1 (1971).
2. Z. Y. Zhou, Y. Wang, X. F. Tang, W. H. Wu, and F. Qi, *Rev. Sci. Instrum.* **84**, 014101 (2013).
3. F. Qi, *Proc. Combust. Inst.* **34**, 33 (2013).
4. N. Hansen, T. A. Cool, P. R. Westmoreland, and K. Kohse-Höinghaus, *Prog. Energy Combust. Sci.* **35**, 168 (2009).

