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VUV Photoionization Study of the Allyl Radical from Premixed Gasoline/Oxygen Flame

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The allyl radical has been observed in a low-pressure premixed gasoline/oxygen/argon flame by using tunable vacuum ultraviolet photoionization mass spectrometry. The ionization potential of the allyl radical is derived to be (8.13 ± 0.02) eV from photoionization efficiency curve. In addition, a high level *ab initio* Gaussian-3 (G3) method was used to calculate the energies of the radical and its cation. The calculated adiabatic ionization potential is 8.18 eV, which is in excellent agreement with the experimental value. The result is helpful for identifying the allyl radical formed from other flames and for understanding the mechanism of soot formation.

Key words: Allyl radical, Photoionization efficiency curve, Flame

I. INTRODUCTION

Free radicals are important intermediates in many chemical reactions. Owing to the difficulty in producing these transient species, little information is available for free radicals. As a small conjugated π -electron hydrocarbon radical, the allyl radical (C_3H_5) is found to be worthy of study, in that it has the electronic structure similar to those in the fullerenes in interstellar space [1]. The allyl radical is also a key intermediate in tropospheric chemistry, and it plays important roles in the formation of polycyclic aromatic hydrocarbons (PAH) and soot in combustion processes [2]. The allyl radical exhibits several characteristic features that make it an ideal model system in understanding chemical dynamics in general. Therefore, its spectral properties and chemical behaviors have been extensively investigated experimentally and theoretically.

The ground state of the allyl radical has the Hartree-Fock configuration of $(core)(6a_1)^2(4b_2)^2(1b_1)^2(1a_2)^1X^2A_2$. The geometry of the 2A_2 electronic ground state of this radical is well known from IR laser diode spectroscopy [3–5] and the *ab initio* [6]. The ground state vibrational frequencies were observed by ultraviolet resonance Raman spectroscopy [7]. Recently numerous research groups have concentrated primarily on the excited states and Rydberg states of the neutral allyl radical using different experimental methods. The absorption spectrum and cross sections in the $A \leftarrow X$ bands of the allyl radical have been measured using cavity ring-down spectroscopy [8], Rydberg states of the allyl radical have been observed by two-photon resonant ionization spectroscopy [9], and primary photophysical processes upon UV excitation for the allyl radical have been elucidated using time-resolved pump-probe photo-

electron spectra [10, 11].

The allyl cation is poorly characterized experimentally to date. As an important thermochemical quantity, ionization energy (*IE*) values of 8.13 eV [12] and 8.15 eV [10] of the allyl radical derived from photoelectron spectra are well in agreement with that of 8.138 eV from the extrapolation of the discovered ns Rydberg series of the ally radical via REMPI spectroscopy [9]. And a more accurate value (8.153 eV) was determined from zero kinetic energy photoelectron (ZEKE) spectroscopy [13]. All the measurements described above are used to determination of the *IE* value indirectly by laser techniques, despite that one photon excitation using tunable vacuum ultraviolet (VUV) laser could be applied to detect free radicals, unfortunately because of limited tunable range of lasers, there are lots of difficulties in detecting radicals. However, VUV photoionization study is not found for the allyl radical.

Now many methods are available for the production of the clean and intense allyl radical suitable for the spectroscopic experiments: photolysis, electric discharges and flash pyrolysis. The allyl radical has been observed in several rich hydrocarbon flames, and may itself be involved in the chemistry of soot formation [2]. The tunable VUV near-threshold single-photon ionization with a high sensitivity molecular-beam sampling mass spectrometry is suitable for the detection and identification of free radicals formed in combustion.

In the present work, the photoionization efficiency curve (PIE) of the allyl radical, which was produced in a low-pressure premixed gasoline/oxygen/Ar flame, was measured with the tunable VUV photoionization mass spectrometry (PIMS).

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TABLE I The specifications for the gasoline

Boiling point/ $^{\circ}\text{C}$				Compose/vol%			Density /(kg/L)
10%	50%	90%	100%	Alkanes	Alkanes	Aromatics	
59	105	159	184	47	29	24	0.737

II. EXPERIMENTAL AND THEORETICAL

A. Experimental

The experiment was carried out on the combustion and flame endstation at the National Synchrotron Radiation Laboratory in Hefei, China. A detailed description of the instrument will be published elsewhere. And it is outlined here: the apparatus consists of a low-pressure flame chamber, a differentially pumped flame-sampling chamber and a main photoionization chamber with a reflectron time-of-flight mass spectrometer (RTOF-MS). The premixed laminar flame was stabilized on a 6.0 cm diameter flat flame burner (McKenna, USA). Movement of the burner towards or away from the quartz sampling cone allows mass spectra to be taken at different positions in the flame. Flame sampling molecular-beam was accomplished with a quartz sampling cone of ~ 0.400 mm diameter orifice, and it was skimmed and passed into a differentially pumped ionization region where it was crossed by the tunable vacuum ultraviolet (VUV) light from a bending magnet of the 800 MeV electron storage ring. A 1 m Seya-Namioka monochromator with a 1200 lines/mm grating was used to disperse synchrotron radiation. The photon flux is about 10^{10} photons/s under usual operational conditions in the 7–11 eV photon energy range, and the energy resolution ($E/\Delta E$) is about 500. A lithium fluoride (LiF) window (1 mm in thickness) was used to eliminate second- or higher-order radiation when the experiments were performed at the wavelength longer than 105.0 nm, and a silicon photodiode (SXUV-100, International Radiation Detectors, Inc., USA) was used to correct the variation of the light intensity. The photon energy was calibrated against known *IEs* of inert gases.

The molecular beam was intersected perpendicularly with the synchrotron radiation light beam, and then molecules and free radicals were ionized. A SRS DG 535 with 18000 repetition ratio was used to feed the start of the multiscaler (FAST Comtec P7888, Germany) and trig the pulsed power supply. The pulse width of 1500 ns is sufficient to draw out most of the available ions. Ions were collected with a RTOF-MS. The multiscaler P7888 was used to record mass spectra signals in 5×10^4 channels with 1 ns bin width.

In this work, the allyl radical was formed in a low-pressure premixed gasoline/oxygen/Ar flame [14]. The gasoline flame in the present experiments is fueled by 90[#] Standard Unblended Gasoline for analysis, provided by Fangyuan Inc, Liaoning, China, and the specifications for the gasoline are given in Table I. Flow rates for oxygen, diluent argon and shroud argon were 0.80 standard liter per minute (SLM), 0.40 and 2.00 SLM, respectively. Liquid gasoline was controlled by a syringe

pump (ISCO 1000D, USA), and fed to a vaporizer with the flow rate of 0.45 mL/min. Pressure of the flame chamber was 3.33 kPa.

B. Computational

In this work, the *ab initio* calculations of the neutral and ionic allyl were carried out using the GAUSSIAN 03 suite of programs [16]. In general, the geometric structures and harmonic vibrational frequencies for the neutral and cationic allyl considered here were obtained via MP2 method using the 6-31G(d) basis set with all electrons included, and the energies in this work were calculated using the Gaussian-3 (G3) method of theory. It involved single-point calculations at the MP4/6-31G(d), MP4/6-31+G(d), MP4/6-31G(2df,p), and MP2(Full)/G3 large levels, all carried out with the structures optimized at the MP2(Full)/6-31G(d) level. The MP2 (Full)/6-31G(d) harmonic frequencies, scaled by 0.945, were used for correction of zero-point vibrational energies (ZPVE). A small semi-empirical correction was also applied to account for the high-level correlation effect. The adiabatic ionization energy was calculated as the difference in energy between the neutral molecule and the ion in the ground state for the allyl radical.

III. RESULTS AND DISCUSSION

Figure 1 shows a partial photoionization mass spectrum, recorded at the photon energy of 8.85 eV and at the position of 4.0 mm away from the surface of the burner. The peaks at $m/e=39$, 41 and 43 correspond to C_3H_3 , C_3H_5 and C_3H_7 , respectively. Some stable combustion intermediates like C_3H_2 , C_3H_4 and C_3H_6 were not detected at the photon energy of 8.85 eV, because the *IEs* of these species are higher than 8.85 eV. According to their m/e , a series of mass spectra of these compounds are recorded as a function of the height above burner (HAB), and the relative species concentration profiles are derived via integrating each mass peak and plotted as a function of HAB. The relative concentration profile for the allyl radical is shown in Figure 2. Thus, the highest ion intensity of the allyl radical is obtained at about 4.0 mm.

The photon energy can be precisely tuned near the ionization thresholds of the flame species with the synchrotron radiation light source. The energy resolution is far superior to that of the conventional electron impact ionization mass spectrometry (EIMS). VUV photoionization facilitates the identification of species by observations of apparent ionization thresholds. To obtain the PIE curves, the TOF spectrum is recorded at

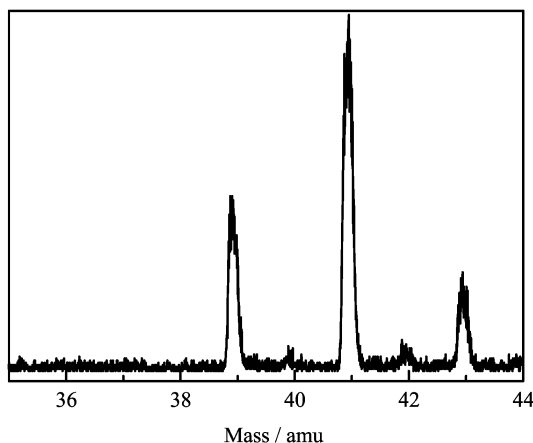


FIG. 1 A partial photoionization mass spectrum of the premixed gasoline/oxygen flame, taken at the sampling position of 4.0 mm from the burner surface and at the wavelength of 140 nm.

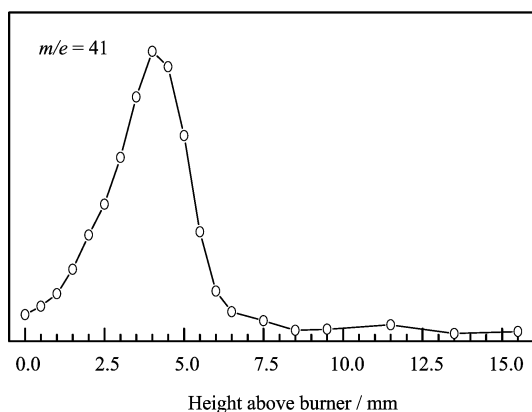


FIG. 2 A relative intensity profile for the allyl radical formed from the premixed gasoline/oxygen/Ar flame, measured at the wavelength of 136 nm

the different photon energies. The peak at $m/e = 41$ is integrated and the baseline contribution is subtracted at each photon energy. The flux-normalized integrated ion signal is measured as a function of photon energy. The PIE curve of C_3H_5 is shown in Fig.3. There is a sharp onset at (8.13 ± 0.02) eV in the PIE curve, and the photon energy at the onset corresponds to the ionization threshold of the species of $m/e = 41$ (C_3H_5). Thus the IE of (8.13 ± 0.02) eV is obtained for the allyl radical, and this value is in good agreement with the ionization energy of 8.13 eV for the allyl radical determined by conventional photoelectron spectroscopy [12], by an extrapolation of s-Rydberg series recently [15], and the value of 8.153 eV by $[1+1']$ ZEKE-spectroscopy through various intermediate states [13].

In the calculation, both the optimized geometrical parameters of the neutral and ionic allyl are obtained as planar structure with point group of C_{2v} at MP2(full)/6-31G(d) level, and the ground states of the neutral and ionic allyl radical correspond to 2A_2 and 1A_1 respectively. The detailed geometrical parameters

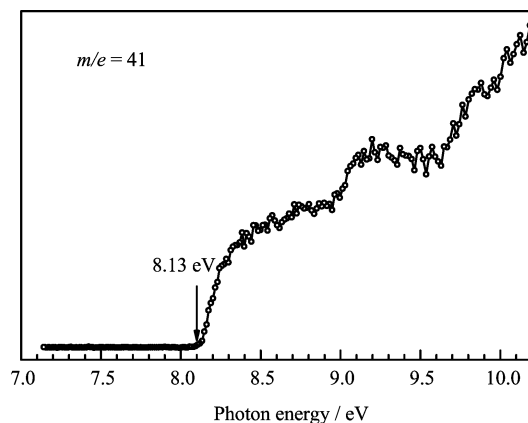


FIG. 3 The PIE curve of the allyl radical from 7.20 eV to 10.20 eV at a distance of 4.0 mm from the burner, recorded for the premixed gasoline/oxygen/Ar flame.

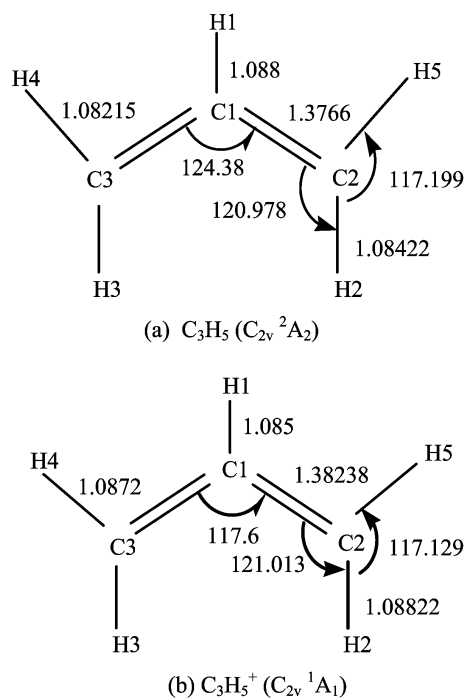


FIG. 4 The optimized geometries at MP2(full)/6-31G (d) level for the allyl radical (a), the cation (b).

are shown in Figure 4. Based on the calculation, the relatively pronounced change is the $\angle CCC$ value, changing from 124.4° in the allyl radical to 117.6° in the allyl cation. There are unnoticeable changes of other geometrical parameters between the neutral and ionic allyl.

The calculated energies of the neutral and ionic radical are list in Table II at G3 and CBS-QB3 level. And the derived adiabatic ionization potentials at 0 K of the allyl radical are also shown in Table II. By comparing the onset of the PIE of the allyl radical with the calculated ionization potentials, the experimental ionization energy (8.13 ± 0.02) eV is in excellent agreement with the calculated adiabatic ionization potential value of 8.175 eV (the CBS-QB3 method) and 8.18 eV (the

TABLE II The calculated energies of the neutral and ionic radical at G3 and CBS-QB3 level at 0 K, based on the optimized geometry of the neutral and ionic radical.

	Symmetry point groups	Electronic states	CBS-QB3 /Hartree	G3 energy/Hartree
C_3H_5	C_{2v}	2A_2	-117.009511	-117.144897
$C_3H_5^+$	C_{2v}	1A_1	-116.709076	-116.844105
IE/eV			8.175	8.18

G3 method) for allyl radical. At higher photon energies above the ionization energy threshold a series of vibrational progression should be seen from the PIE curve, but here the progression can not be seen clearly, due to present photon energy resolution, the vibronic fundamentals are overlapped with each other, broadening the peaks in the spectrum. As we can see, photon energies for the PIE curve are lower than the energy for the first excitation state of the allyl cation, so the undulating spectrum in the PIE curve can be rationalized as Rydberg states which converge to the first excited state of the allyl cation. The PIE curve measurement of the allyl radical formed from flame suggests that the allyl radical can be detected at the photon energy range of the ionization threshold to about 10 eV, in order to avoid the interference of fragment formed from larger hydrocarbons at higher photon energies.

IV. CONCLUSION

The ally radical has been observed in the low-pressure premixed rich gasoline/oxygen/argon flame by photoionization mass spectrometry with the tunable vacuum-ultraviolet synchrotron radiation. The photoionization efficiency curve of C_3H_5 has been measured at the energy range of 7.20–10.20 eV. The ionization energy derived from the PIE curve is in an excellent agreement with the theoretical computation. The experimental result will help in identifying the allyl radical from other flames.

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