

# Dissociative photoionization of isoprene: experiments and calculations

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Vacuum ultraviolet (VUV) dissociative photoionization of isoprene in the energy region 8.5–18 eV was investigated with photoionization mass spectroscopy (PIMS) using synchrotron radiation (SR). The ionization energy (IE) of isoprene as well as the appearance energies (AEs) of its fragment ions  $C_5H_7^+$ ,  $C_5H_5^+$ ,  $C_4H_5^+$ ,  $C_3H_6^+$ ,  $C_3H_5^+$ ,  $C_3H_4^+$ ,  $C_3H_3^+$  and  $C_2H_3^+$  were determined with photoionization efficiency (PIE) curves. The dissociation energies of some possible dissociation channels to produce those fragment ions were also determined experimentally. The total energies of  $C_5H_8$  and its main fragments were calculated using the Gaussian 03 program and the Gaussian-2 method. The IE of  $C_5H_8$ , the AEs for its fragment ions, and the dissociation energies to produce them were predicted using the high-accuracy energy model. According to our results, the experimental dissociation energies were in reasonable agreement with the calculated values of the proposed photodissociation channels of  $C_5H_8$ . Copyright © 2009 John Wiley & Sons, Ltd.

**Keywords:** isoprene; photoionization; photodissociation; appearance energies of ions; synchrotron radiation

## Introduction

Biogenic volatile organic compounds (BVOCs), such as isoprene and monoterpenes, are emitted into the atmosphere in substantial amounts mainly from terrestrial vegetation. Total global biogenic organic emissions are estimated to range from 491 to 1150 Tg/year, which exceeds the estimated anthropogenic emissions by almost an order of magnitude.<sup>[1]</sup> They can be quite reactive under atmospheric conditions, and therefore the emission of BVOCs plays a central role in the photophysics and photochemistry of the atmosphere. After methane, and together with the terpenes, isoprene (2-methyl-1,3-butadiene) is the organic compound with the highest global emission, between 250 and 503 Tg/year.<sup>[1]</sup>

Isoprene is a harmful environmental pollutant and toxicant in atmosphere,<sup>[2]</sup> and it is more reactive towards the three atmospheric oxidants OH, NO<sub>3</sub>, and O<sub>3</sub> than most of the anthropogenic VOCs. The role of isoprene in photochemical ozone (O<sub>3</sub>) production has been examined extensively in laboratory, field and modeling studies in the past two decades. Its role in secondary organic aerosol (SOA) formation has recently been established on the basis of laboratory and field studies.<sup>[3]</sup>

Because of the reasons mentioned above, isoprene has been studied widely with various spectroscopic techniques, such as infrared (IR) spectroscopy,<sup>[4]</sup> Raman spectroscopy,<sup>[5–7]</sup> and vacuum ultraviolet (VUV) absorption spectroscopy.<sup>[8]</sup> The ionization energy (IE) of the isoprene molecule was determined in the range 8.84–9.04 eV using photoelectron spectroscopy, photoionization spectroscopy, electron impact mass spectroscopy and VUV absorption spectroscopy.<sup>[9]</sup> The appearance energies (AEs) of the fragment ions from isoprene molecular ions were also determined using electron impact mass spectroscopy, but not very precisely; for example, the AEs of the  $C_5H_7^+$  and  $C_4H_5^+$  ions were in the range 10.54–10.93 eV and 11.44–11.93 eV, respectively.<sup>[9]</sup> Recently, an experimental study of the electronic excitation

and ionic dissociation of the isoprene molecule was performed using electron and synchrotron radiation (SR).<sup>[10]</sup> Even so, the mechanism of VUV dissociative photoionization of isoprene above its IE is still not well understood experimentally and theoretically. In order to determine IE of isoprene and the AEs of its fragmental ions, and to explore the mechanism for its dissociative ionization, we undertook the present a study of VUV dissociative photoionization of isoprene in the energy range ~8.5–18 eV. Quantum chemical calculations were also performed using the Gaussian 03 program and the G2 method to obtain some photochemical parameters. The mechanisms of dissociative photoionization of isoprene will also be discussed in this paper.

## Experimental

Our experimental apparatus has been described previously.<sup>[11,12]</sup> In brief, we performed photoionization mass spectrometry (PIMS) measurements on the atomic and molecular physics beamline with the supersonic expansion molecular beam/a reflectron time-of-flight mass spectrometer (RTOFMS) system at the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. Photon energies in the region 7.5–22.5 eV with a resolving power of 5000 at 15.9 eV and a photon flux of  $10^{12}$  photons/s were selected with a grazing-incidence SGM monochromator employing a grating of

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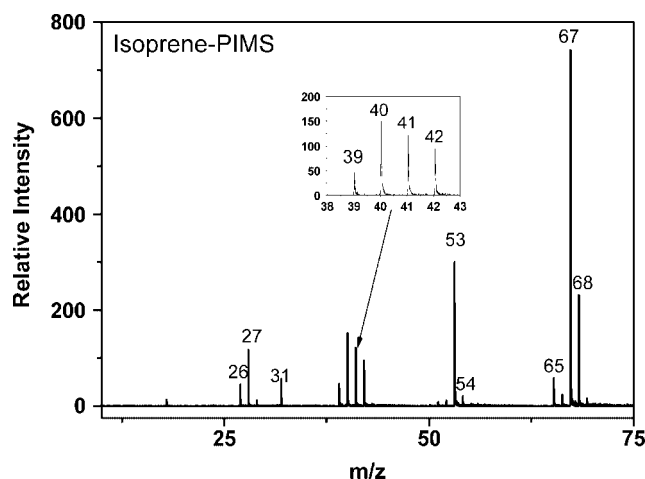
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1200 grooves/mm and a slit width of 80  $\mu\text{m}$ . For calibration of the photon energies, we used the photoionization spectrum of Ar with an accuracy better than 0.002 eV.

Isoprene (2-methyl-1,3-butadiene) (99%) (CAS #78-79-5) was obtained from Alfa Aesar, USA, and used without additional purification. Isoprene is a liquid with high vapor pressure under atmospheric conditions. Neither a heating procedure nor a carrier gas was necessary for introducing the sample into the beam source chamber. During experiments, the pressures in beam source chamber and the ionization chamber were kept in the range of  $2.5 \times 10^{-2}$  Pa and  $2.5 \times 10^{-4}$  Pa, respectively. Isoprene was expanded to form a molecular beam through a nozzle with a diameter of 70  $\mu\text{m}$  and two skimmers with diameters of 1 mm. The monochromatic VUV radiation intersected perpendicularly with molecular beam to ionize the supersonic, cooled isoprene molecular beam in the ionization chamber. The ions produced were mass-analyzed with the RTOFMS mounted in a direction perpendicular to the plane defined by molecular and photon beams; a microchannel plate (MCP) operated in pulse-counting mode served for the collection and detection of the ions. Signals from the detected ions were counted with a multiscaler P7888 counter (FAST Comtec, Germany) after they were amplified with preamplifier VT120C (EG & G, ORTEC) and before being transferred to a computer for further processing. The PIMS spectrum of isoprene can be obtained when it is excited using a fixed photon energy above its ionization threshold. The PIE curve was measured while the monochromator was scanned with an energy increment of 2–30 meV, and the data acquisition time for each point was 10–20 s depending on the ion abundance. To normalize the ion signals, we monitored the photon intensity simultaneously with a silicon photodiode (SXUV-100, International Radiation Detectors, Inc.). By the end of 2007, a rare-gas harmonic filter was inserted into the beamline to overcome higher-order harmonics contamination in the energy range from 7.5 to 21.5 eV. We used the rare-gas harmonic filter for this study, and the pressure of the argon gas was about 4 Torr.

## Quantum Chemical Calculations

The equilibrium geometry and vibrational frequencies of isoprene were calculated using the 6–31G\* and 6–311G\* basis sets at the Hartree–Fock (HF) and MP2 (full) levels of theory. The total energies of  $\text{C}_5\text{H}_8$  and its fragment products were calculated with the Gaussian 03 program<sup>[13]</sup> and the G2 method.<sup>[14,15]</sup> Briefly, the equilibrium structure of the molecule was optimized and its harmonic vibrational frequencies were calculated first by HF/6–31G(d), and its zero-point energy was scaled by a factor of 0.8929. Then, the equilibrium structure of each species was optimized again at the MP2 (Full)/6–31G\* level. To calculate the  $E(\text{G2})$  energy, single-point energy calculations were carried out at the levels of MP4/6–311G(d,p), MP4/6–311 + G(d,p), MP4/6–311G(2df,p), MP2/6–311 + G(3df,2p) and QSCISD (T)/6–311G(d,p) with a higher-level correction and a zero-point vibrational energy correction. After the calculation of the energy  $E(\text{G2})$ , the high-accuracy energy model was used to calculate the thermochemical parameters, such as IE of  $\text{C}_5\text{H}_8$ , AE for its fragment ions and the dissociation energies to produce them.



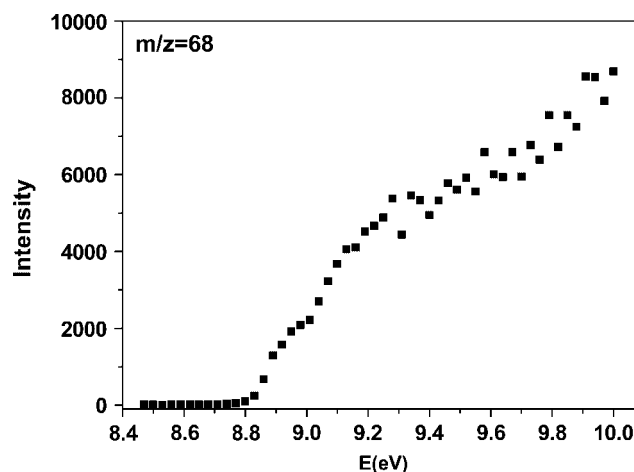
**Figure 1.** Photoionization mass spectrum of  $\text{C}_5\text{H}_8$  excited at 17 eV photon energy.

## Results and Discussion

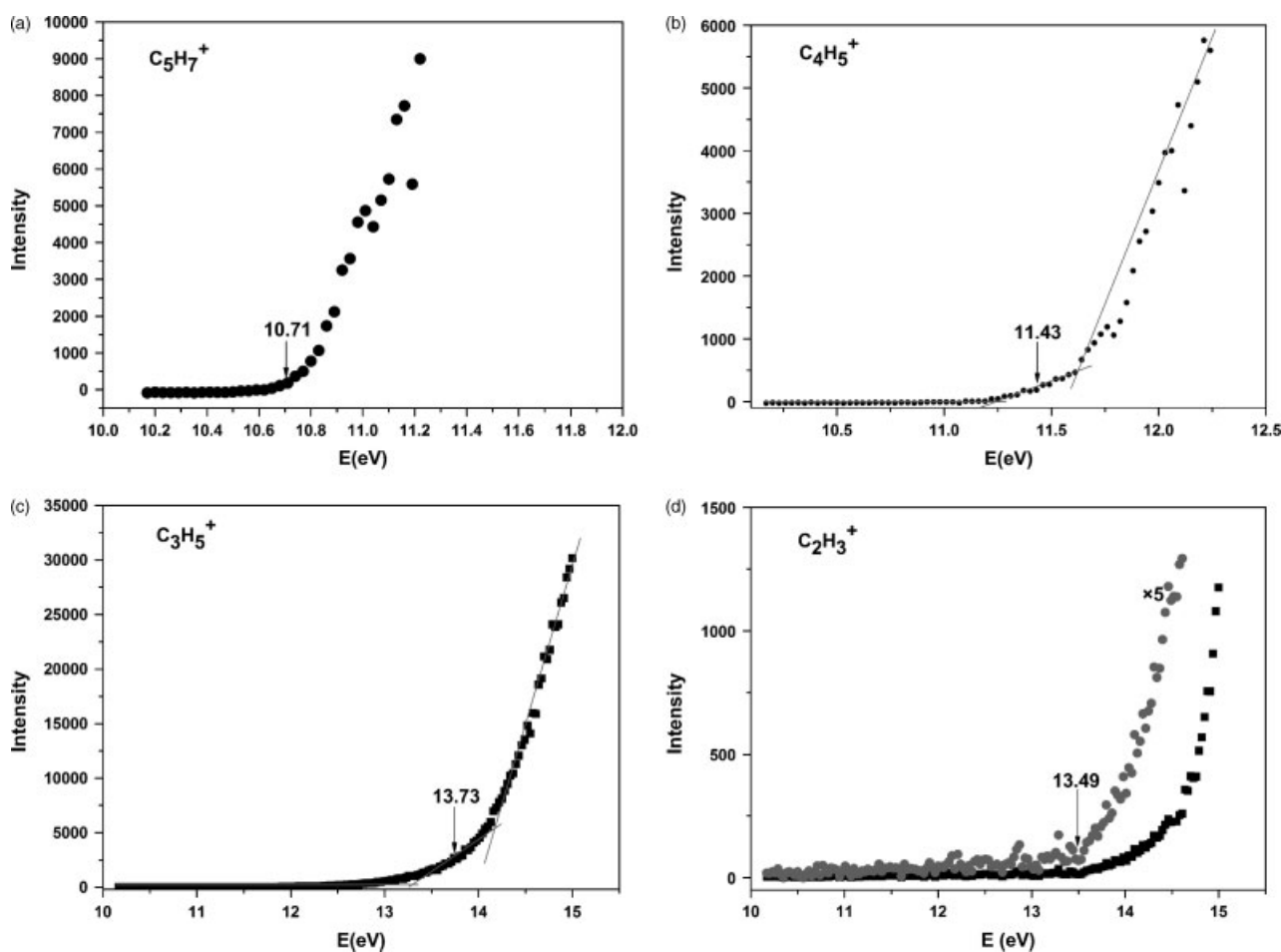
### Experimental results

The PIMS spectrum of isoprene was measured at the photon energy of 17.00 eV (Fig. 1). The signal from the parent ion  $\text{C}_5\text{H}_8^+$  is not very strong; however, the signal of the fragment ion  $\text{C}_5\text{H}_7^+$  is the strongest among those of all fragment ions. The ions  $\text{C}_4\text{H}_5^+$ ,  $\text{C}_3\text{H}_6^+$ ,  $\text{C}_3\text{H}_5^+$ ,  $\text{C}_3\text{H}_4^+$  and  $\text{C}_2\text{H}_3^+$  are observed as the major fragment ions, while  $\text{C}_5\text{H}_5^+$ ,  $\text{C}_3\text{H}_3^+$ ,  $\text{C}_2\text{H}_2^+$  and  $\text{CH}_3^+$  are the minor ones. As no signal at mass greater than that of  $\text{C}_5\text{H}_9^+$  was detected under our experimental conditions, all detected fragment ions were considered to originate from the dissociation of the parent ion.

The photoionization efficiency (PIE) curves of  $\text{C}_5\text{H}_8^+$  and those of the observed fragment ions, such as  $\text{C}_5\text{H}_7^+$ ,  $\text{C}_5\text{H}_5^+$ ,  $\text{C}_4\text{H}_5^+$ ,  $\text{C}_3\text{H}_6^+$ ,  $\text{C}_3\text{H}_5^+$ ,  $\text{C}_3\text{H}_4^+$ ,  $\text{C}_3\text{H}_3^+$  and  $\text{C}_2\text{H}_3^+$ , from their respective appearance onsets to 15 eV, were recorded at a scan step of 20 meV and normalized with respect to the photon flux. As an example, the PIE curves of the parent molecular ion  $\text{C}_5\text{H}_8^+$  and some of its daughter ions,  $\text{C}_5\text{H}_7^+$ ,  $\text{C}_4\text{H}_5^+$ ,  $\text{C}_3\text{H}_5^+$  and  $\text{C}_2\text{H}_3^+$ , are shown in Figs 2 and 3, respectively. In the study of VUV dissociative photoionization of



**Figure 2.** PIE spectra of  $\text{C}_5\text{H}_8^+$ .



**Figure 3.** PIE Spectra for (a)  $C_5H_7^+$ , (b)  $C_4H_5^+$ , (c)  $C_3H_5^+$  and (d)  $C_2H_3^+$ .

$C_5H_8$  in the energy region 8.5–15 eV, the IE of  $C_5H_8$  and the AEs of its fragment ions can be reached directly by scanning the photon energy of the monochromatized SR. It should be pointed out that we ignored the thermal energy distribution of the parent molecule in our data processing, considering the presence of the supersonic nozzle expansion condition mentioned above. In addition, no correction was made for possible kinetic shifts in determining the AEs.

In the PIE curve of  $C_5H_8$ , the onset of ionization of  $C_5H_8$  is  $8.83 \pm 0.02$  eV. The AE of the fragment ion was determined by the onset in each PIE curve, such as the AE of  $C_5H_7^+$ ,  $C_5H_5^+$ ,  $C_4H_5^+$ ,  $C_3H_6^+$ ,  $C_3H_5^+$ ,  $C_3H_4^+$ ,  $C_3H_3^+$  and  $C_2H_3^+$ , which are  $10.71 \pm 0.02$ ,  $13.67 \pm 0.02$ ,  $11.43 \pm 0.02$ ,  $11.50 \pm 0.02$ ,  $13.73 \pm 0.02$ ,  $12.00 \pm 0.02$ ,  $13.48 \pm 0.02$  and  $13.49 \pm 0.02$  eV, respectively. It should be noted that for the fragment ions we used two approaches to determine their AEs from their PIE curves. When the ion signals rise abruptly but with a gradual, slow slope near the threshold, such as in the case of  $C_4H_5^+$  and  $C_3H_5^+$ , the AE was determined as the midpoint of the two intersects among the baseline, the slowly rising line and the rapidly rising line. For ion signals that increase linearly with IE, the AE was determined from the intersection of the baseline and the gradually rising line, as shown in Fig. 2(a) for  $C_5H_7^+$  and Fig. 2(d) for  $C_2H_3^+$ .<sup>[16]</sup>

The dissociation channels producing fragment ions can be deduced in Table 1, and two possible cases should be considered during the calculation of dissociation energy:<sup>[17]</sup> (1) The fragment

ion is formed from one neutral fragment of the parent molecule, and the dissociation energy to produce it is calculated by subtracting IE of the neutral fragment from its AE; (2) The fragment ion is formed by ionization of the parent molecule followed by the spontaneous dissociation of the primary parent ion. The latter is generally referred to as *dissociation ionization* and the emphasis in this paper is on it. The dissociation energy  $E_d$  to produce it is calculated empirically by subtracting IE of the parent molecule from its AE  $E_d = AE - IE$ , where  $E_d$  is the dissociation energy, AE is the appearance energy for fragment ion and IE is the ionization energy of parent molecule. As an example, the IE of  $C_5H_8$  is  $8.83 \pm 0.02$  eV, the AE of  $C_5H_7^+$  is  $10.71 \pm 0.02$  eV, and therefore the  $E_d$  ( $C_5H_7^+ - H$ ) is  $1.88 \pm 0.04$  eV. The IE of  $C_5H_8$  and AEs for its fragment ions  $C_5H_7^+$ ,  $C_5H_5^+$ ,  $C_4H_5^+$ ,  $C_3H_6^+$ ,  $C_3H_5^+$ ,  $C_3H_4^+$ ,  $C_3H_3^+$  and  $C_2H_3^+$  are listed in Table 1, along with some dissociation energies and possible dissociation channels of  $C_5H_8$ .

## Quantum Chemical Calculations

### The geometries and vibrational frequencies

It is known that the stable form of neutral isoprene is calculated to be planar *s-trans* and *gauche*, with a torional angle of  $33^\circ$ . In our quantum chemical calculations, the *s-trans* structure of isoprene was selected. The fully optimized structures (MP2(full)/6–31G(d))

**Table 1.** Experimental, theoretical and literature values of the ionization energy (IE), appearance energy (AE) and dissociation energy ( $E_d$ )

Ions	IE or AE (experimental) (eV)	IE or AE (theory) (eV)	IE or AE (literature) (eV)	References no.	Dissociation energy (experimental) (eV)	Dissociation energy (theory) (eV)	Possible dissociation channels
$C_5H_8^+$	$8.83 \pm 0.02$	8.91	$8.85 \pm 0.02$ (PE)	18	–	–	$C_5H_8^+$
–	–	–	8.85(EI)	19	–	–	–
–	–	–	$8.90 \pm 0.10$ (EI)	20	–	–	–
–	–	–	8.89(PE)	21	–	–	–
–	–	–	$8.845 \pm 0.005$ (PI)	22	–	–	–
–	–	–	$8.84 \pm 0.01$ (S)	20	–	–	–
–	–	–	8.85(PE)	23,24	–	–	–
–	–	–	8.87(PE)	25	–	–	–
–	–	–	9.04(PE)	26	–	–	–
$C_5H_7^+$	$10.71 \pm 0.02$	10.94	$10.93 \pm 0.10$ (EI)	8	$1.88 \pm 0.04$	2.03	$C_5H_7^+ + H$
			10.54(EI)	19,27			
$C_5H_5^+$	$13.67 \pm 0.02$	13.76	13.9(EI)	28	$4.84 \pm 0.04$	4.85	$C_5H_5^+ + H_2 + H$
$C_4H_5^+$	$11.43 \pm 0.02$	11.50	$11.93 \pm 0.10$ (EI)	20	$2.60 \pm 0.04$	2.59	$C_4H_5^+ + CH_3$
			11.44(EI)	29			
$C_3H_6^+$	$11.50 \pm 0.02$	11.56	$12.76 \pm 0.10$ (EI)	20	$2.67 \pm 0.04$	2.65	$C_3H_6^+ + C_2H_2$
$C_3H_5^+$	$13.73 \pm 0.02$	13.95	$14.04 \pm 0.10$ (EI)	20	$4.90 \pm 0.04$	5.04	$C_3H_5^+ + C_2H_2 + H$
$C_3H_4^+$	$12.00 \pm 0.02$	12.01	$12.39 \pm 0.12$ (EI)	20	$3.17 \pm 0.04$	3.10	$C_3H_4^+ + C_2H_4$
$C_3H_3^+$	$13.48 \pm 0.02$	14.21	$14.55 \pm 0.15$ (EI)	20	$4.56 \pm 0.04$	5.30	$C_3H_3^+ + C_2H_4 + H$
$C_2H_3^+$	$13.49 \pm 0.02$	13.54	–	–	$4.66 \pm 0.04$	4.63	$C_2H_3^+ + C_3H_5$

**Table 2.** The calculated (MP2 (Full)/6–31G (d)) bond lengths (Å), bond angles (degrees) and vibrational frequencies ( $cm^{-1}$ ) for the *s*-trans neutral isoprene and isoprene radical cation

	Neutral	Radical cation
$C_1C_2$	1.35	1.40
$C_2C_3$	1.46	1.42
$C_3C_4$	1.34	1.37
$C_2C_5$	1.50	1.50
$C_1C_2C_3$	$120^\circ$	$116^\circ$
$C_2C_3C_4$	$125^\circ$	$123^\circ$
$C_5C_2C_3$	$119^\circ$	$123^\circ$
$C_1C_2C_3C_4$	$180^\circ$	$180^\circ$
$C_4C_3C_2C_5$	$0^\circ$	$0^\circ$
Vibrational frequencies	147.7, 214.6, 286.4, 394.1, 429, 539.4, 645.6, 787.7, 814.4, 903, 915.2, 994.4, 1024.7, 1037, 1100.8, 1117.1, 1355.3, 1374.2, 1460.1, 1478.9, 1508.8, 1542.6, 1564.4, 1685.2, 1737.2, 3099.7, 3177.3, 3198.3, 3202.5, 3208, 3224.5, 3298.5, 3312.6	73.5, 157.3, 290.8, 401.6, 431.5, 491.6, 551.9, 602.1, 835.7, 986.2, 1016.4, 1045.4, 1046.4, 1088.7, 1124.8, 1128.1, 1281.8, 1373.3, 1443, 1475.5, 1527.2, 1535, 1559, 1569.3, 1693.8, 3112.9, 3193.2, 3226.4, 3230.6, 3238.5, 3247.4, 3341, 3349.3

of  $C_5H_8$ ,  $C_5H_7$ ,  $C_5H_5$ ,  $C_4H_5$ ,  $C_3H_6$ ,  $C_3H_5$ ,  $C_3H_4$ ,  $C_3H_3$ ,  $C_2H_4$ ,  $C_2H_3$ ,  $C_2H_2$ ,  $CH_3$  and their corresponding ions were obtained in this work. The optimized geometries of  $C_5H_8$  and  $C_5H_8^+$  with MP2 (full)/6–31G (d) method are given in Fig. 4. As shown in Fig. 4, the bond length C2–C5 is the longest, and so the C2–C5 bond is the easiest to break into fragments  $C_4H_5^+ + CH_3$ , which can explain why we could obtain the relatively high  $m/z = 53$  ( $C_4H_5^+$ ) peak in PIMS of  $C_5H_8$ . The equilibrium properties of  $C_5H_8$  was investigated using MP2 (full)/6–31G (d) based on HF/6–31G\*. The optimized parameters, such as the main bond length, bond angle and the dihedral angle, are given in Table 2. The vibrational frequencies of  $C_5H_8$  were calculated by the geometry optimizations as described above. Twenty-seven frequencies were calculated for the *s*-trans structure of isoprene, indicating a true minimum on the potential energy surface. In the similar way, the equilibrium properties and

vibrational frequencies of  $C_5H_8^+$  were also calculated using MP2 (full)/6–31G (d).

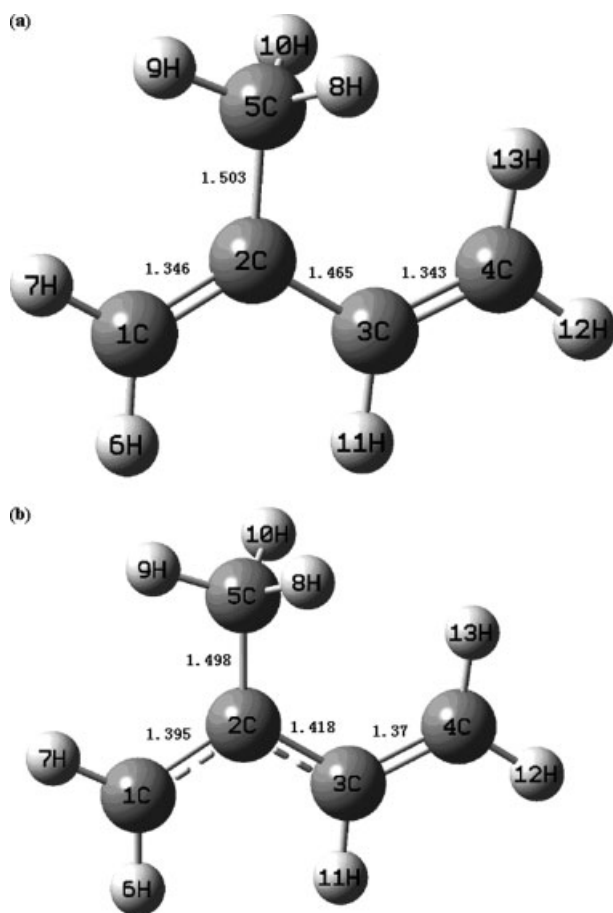
### Ionization energy, appearance energies and dissociation energies

In this study, total energy  $E_0$  (G2) of  $C_5H_8$  and its fragment radicals was calculated at first with the Gaussian 03 program and G2 method. The total energy of the related species is given in Table 3.

In high-accuracy energy model of Gaussian 03,<sup>[14]</sup> the IE of each molecule is taken as the amount of energy required to remove an electron from a molecule, computed as the energy difference between the cation and the neutral molecule. For example, the IE of  $C_5H_8$  is calculated as follows:

$$IE(C_5H_8) = E_0(G2)(C_5H_8^+) - E_0(G2)(C_5H_8) = 8.91 \text{ eV} \quad (1)$$





**Figure 4.** Geometries of (a)  $C_5H_8$ , (b)  $C_5H_8^+$  optimized at MP2 (full)/6-31G (d) level of theory.

**Table 3.** Total G2 energies of species involved in dissociative photoionization of  $C_5H_8$

Species	$E_0(G2)(\text{Hartree})$	Species	$E_0(G2)(\text{Hartree})$
$C_5H_8$	-194.894751	$C_5H_8^+$	-194.567266
$C_5H_7$	-194.231729	$C_5H_7^+$	-193.992231
$H(^2S)$	-0.500000	$H_2$	-1.166358
$C_5H_5$	-193.021360	$C_5H_5^+$	-192.722770
$C_4H_5$	-155.002965	$C_4H_5^+$	-154.726993
$CH_3$	-39.745085	$CH_3^+$	-39.385589
$C_3H_6$	-117.645086	$C_3H_6^+$	-117.284311
$C_2H_2$	-77.185732	$C_2H_2^+$	-76.765987
$C_3H_5$	-116.973564	$C_3H_5^+$	-116.696216
$C_2H_3$	-77.739830	$C_2H_3^+$	-77.423489
$C_3H_3$	-115.773298	$C_3H_3^+$	-115.456553
$C_3H_4$	-116.417838	$C_3H_4^+$	-116.037493
$C_2H_4$	-78.415935	$C_2H_4^+$	-78.027240

This theoretical value of adiabatic IE of  $C_5H_8$  is close to our experimental value of  $8.83 \pm 0.02$  eV.

For possible dissociation channel  $C_5H_8 \rightarrow C_4H_5^+ + CH_3$ , the AE of  $C_4H_5^+$  is calculated as

$$AE(C_4H_5^+) = E_0(G2)(C_4H_5^+) + E_0(G2)(CH_3) - E_0(G2)(C_5H_8) = 11.50 \text{ eV} \quad (2)$$

In the dissociation channel  $C_5H_8^+ \rightarrow C_4H_5^+ + CH_3$ , its dissociation energy is calculated as

$$E_d = E_0(G2)(C_4H_5^+) + E_0(G2)(CH_3) - E_0(G2)(C_5H_8^+) = 2.59 \text{ eV} \quad (3)$$

The AEs of other fragment ions and some dissociation energies of other possible dissociation channels can also be calculated in similar ways. The IE of  $C_5H_8$ , AE for the fragmental ions  $C_5H_7^+$ ,  $C_5H_5^+$ ,  $C_4H_5^+$ ,  $C_3H_6^+$ ,  $C_3H_5^+$ ,  $C_3H_4^+$ ,  $C_3H_3^+$  and  $C_2H_3^+$  as well as the  $E_d$  of some possible dissociation channels predicted by the G2 method are also given in Table 1.

### Dissociation mechanism

On the basis of PIMS spectrum and PIE curves of isoprene, the IE of isoprene and AE for its fragment ions were determined, and then the dissociation energy to produce the fragment ions was calculated empirically. Some dissociation channels are also proposed. The molecular ion  $C_5H_8^+$  can be formed directly by a single-photon ionization of the VUV Sr.  $C_5H_7^+$  is produced by H elimination from the molecular ion  $C_5H_8^+$  ( $C_5H_8^+ \rightarrow C_5H_7^+ + H$ ). There are four possible dissociation channels to get  $C_5H_7^+$  from  $C_5H_8^+$ , which likely result from the H elimination from C1-H, C3-H, C4-H or C5-H bonds within  $C_5H_8^+$ . It is likely that H abstraction from isoprene by radicals such as  $CH_3$  and  $C_4H_5$  could also produce  $C_5H_7^+$ .<sup>[30]</sup> Of course, an understanding of the mechanism of formation and dissociation of  $C_5H_7^+$  is clearly of importance, and it is proposed that a secondary dissociation of some interest is the process  $C_5H_7^+ \rightarrow C_5H_5^+ + H_2$ . Direct molecular elimination resulting in the cleavage of the C2-C5 bond was considered to form  $C_4H_5^+$  or  $CH_3^+$  ( $C_5H_8^+ \rightarrow C_4H_5^+ + CH_3$  or  $C_5H_8^+ \rightarrow C_4H_5 + CH_3^+$ ). By the way, the likely mechanism for the methyl loss in isoprene is isomerization via C3-C1 1,3 hydrogen shift to dimethylallene and the subsequent dissociation to the  $CH_3$  and methylallenyl radicals. Perhaps, the 1,3 hydrogen shift isomerization to dimethylallene becomes the more favorable isomerization pathway and leads to  $CH_3$  loss.<sup>[30]</sup> Some ions in the cluster  $m/z$  39 to 42 could arise from bond cleavages (or minimal rearrangements) of the molecular ions. It would appear that losses of ethylene and acetylene take place from the molecular ions ( $C_5H_8^+ \rightarrow C_3H_4^+ + C_2H_4$  and  $C_5H_8^+ \rightarrow C_3H_6^+ + C_2H_2$ ) and the predominant process is the loss of acetylene from  $m/z$  67 ( $C_5H_7^+ \rightarrow C_3H_3^+ + C_2H_4$  and  $C_5H_7^+ \rightarrow C_3H_5^+ + C_2H_2$ ). These processes may necessitate considerable rearrangement before fragmentation,<sup>[27]</sup> while  $C_3H_5^+$  or  $C_2H_3^+$  may be formed through the cleavage of the C2-C3 bond ( $C_5H_8^+ \rightarrow C_3H_5^+ + C_2H_3$  or  $C_5H_8^+ \rightarrow C_3H_5 + C_2H_3^+$ ). The radical ion  $C_3H_4^+$  could also decompose to  $C_3H_3^+ + H$ , and the dissociation channel to form  $C_3H_3^+$  should be  $C_5H_8^+ \rightarrow C_3H_3^+ + C_2H_4 + H$ .

According to the high-accuracy energy model, the IE of  $C_5H_8$ , AEs for its fragment ions  $C_5H_7^+$ ,  $C_5H_5^+$ ,  $C_4H_5^+$ ,  $C_3H_6^+$ ,  $C_3H_5^+$ ,  $C_3H_4^+$ ,  $C_3H_3^+$  and  $C_2H_3^+$  as well as the dissociation energies to produce them were predicted with the Gaussian 03 program and G2 method. On the basis of comparison of the experimental and calculated dissociation energies mentioned above, most of them are in agreement with each other, but some of are different, for example, the dissociation energies to produce  $C_5H_7^+$  and  $C_3H_3^+$ , indicating that in future studies on the dissociation mechanism of isoprene molecule we should consider not only the thermochemistry parameters predicted using the high-accuracy energy model but also some different transition states with specific barriers.

## Conclusions

IE of the isoprene molecule, AEs for its fragment ions, and dissociation energies to produce these fragment ions were obtained from experimental studies on photoionization and fragmentation of the molecule, and were also calculated using the Gaussian 03 program and G2 method. The dissociation energies of some possible dissociation channels to produce them were then estimated using these total energies. On the basis of comparison between the experimental results and those of the theoretical calculations, the mechanism of photoionization and dissociative photoionization of isoprene was discussed. Generally speaking, for a possible dissociative photoionization channel of isoprene, most of the experimental dissociation energies are in agreement with the theoretical dissociation energies predicted from the G2 calculation.

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