Dissociative Photoionization of 1,4-Dioxane with Tunable VUV Synchrotron Radiation

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The photoionization and photodissociation of 1,4-dioxane have been investigated with a reflectron time-of-flight photoionization mass spectrometry and a tunable vacuum ultraviolet synchrotron radiation in the energy region of 8.0–15.5 eV. Parent ion and fragment ions at m/z 88, 87, 58, 57, 45, 44, 43, 41, 31, 30, 29, 28 and 15 are detected under supersonic conditions. The ionization energy of DX as well as the appearance energies of its fragment ions C4H7O2+*, C5H6O+, C6H5O+, C6H4O+, C2H4O+, C2H3O+, C3H5+, CH3O+, C2H6+, C2H5+/CHO+, C2H4+ and CH3+ was determined from their photoionization efficiency curves. The optimized structures for the neutrals, cations, transition states and intermediates related to photodissociation of DX are characterized at the B3LYP/6-31+G(d,p) level and their energies are obtained by G3B3 method. Possible dissociative channels of the DX are proposed based on comparison of experimental AE values and theoretical predicted ones. Intramolecular hydrogen migrations are found to be the dominant processes in most of the fragmentation pathways of 1,4-dioxane.

Key words: 1,4-Dioxane, VUV photoionization mass spectra, Appearance energy, Dissociation channel, G3B3

I. INTRODUCTION

1,4-Dioxane (DX) can be easily found in nature as an intermediate in many chemical pathways [1–3]. It has a wide range of applications in paints [1, 2], textile and dye industries [2]. On the other hand, DX is also well known to induce kidney failure, liver damage [4, 5] and even human carcinogen. Recently, DX, a significant representative of cyclic ethers, has also been confirmed hard to degrade [6, 7], which will contribute to the concentration of DX in the atmosphere [8, 9]. DX can undergo further transformation or degradation with OH radicals and halogen atoms (such as Br, Cl) [9], then transform into low-volatility oxygenated organic compounds, which may contribute to secondary organic aerosol formation under atmospheric conditions. Hence, a better understanding of the unimolecular chemistry of DX is clearly desirable.

Up to now, a lot of methods [10–19] have been devoted to the unimolecular chemistry of DX. As an important physical property, the ionization energy (IE) of DX was determined to be in the range of 9.058–9.39 eV by photoionization (PI) spectroscopy [19], photoelectron-photoion-coincidence (PEPICO) spectroscopy [12], mass analyzed threshold ionization (MATI) spectrum [18] and photoionization mass spectrometry (PIMS) [15]. The appearance energy (AE) values of fragment ions investigated by different techniques also show considerable discrepancies. These large deviations may be enough to remind researchers to re-investigate the details of fragmentation patterns. In the case of dissociating channels, Fraser-Monteiro and co-workers [12] discussed the possible structures and the heats of formation for fragment ions from DX by using PEPICO. Then, they concluded that ionic DX trend to produce fragment ions and neutrals by simple bond cleavages. Zou et al. [15] discussed the possible fragmentation channels and structures of some fragment ions and argued that the rearrangement processes were involved in the dissociation of DX, not just involved breaking bonds. It should be noted that AE values derived from the previous PIMS suffered from poor signal to noise ratio. Apart from these experimental studies, there are a few theoretical reports describing the dissociative photoionization process of DX. Lam et al. [20] studied the detailed mechanism of C3H60+ isomers (m/z=58) fragmented from DX cation and Hudson et al. [21] explored the formation behaviors of C2H6+ (m/z=30) and C2H5+ (m/z=29) from CH3CH2OCH2+.

As mentioned above, despite considerable experime-
ntal studies performed on cationic DX, the IE, AE values as well as some formation pathways of the fragment ions, still have not been definitely confirmed. Thus, more evidences based on real-time analysis and isomeric selectivity are needed to fully understand the dissociative mechanism of DX. This may be obtained by using tunable VUV-PIMS technique [22–27]. This approach features several advantages. First, the molecular-beam reduces collision effects and allows unstable intermediates to be isolated. Furthermore, the high-energy resolution and tunability of the synchrotron radiation minimize fragmentation and allows different isomers to be distinguished [26, 27]. Indeed, the experimental method employed in this work was also successfully employed in the previous studies [22–25]. In this work, we report a quantitative study on the photoionization and dissociative photoionization of DX on the basis of VUV-PIMS experiments and theoretical calculations.

II. EXPERIMENTAL AND THEORETICAL METHODS

A. Experimental methods

The whole experiments were performed at the atomic and molecular physics beamline (BL09U) at the National Synchrotron Radiation Laboratory (NSRL) Hefei, China. The synchrotron radiation beam from an undulator of the 800 MeV electron storage ring of the NSRL was monochromatized with a 6-m length monochromator equipped with a grating (370 lines/mm), which covers the photon energy range from 7.5 eV to 22.5 eV. The absolute photon of monochromator is precisely calibrated with the known IEs of inert gases. The energy resolution ($E/\Delta E$) of photons at 15.9 eV is measured to be 9 meV (full width at half maximum) [28], with an average photon flux $\sim 10^{12}$ photons/s. The monochromatic VUV radiation, the supersonic molecular beam and the PIMS are mutually perpendicular. The setup consists of seven electrostatic lenses that focus and accelerate the ions from the region of interaction to the home-made TOF-MS and allow the ions to travel in a straight path. The beam consisting of neutral monomeric DX then passes through a skimmer with diameter of 1 mm to form a continuous supersonic molecular beam before it reaches the photoionization region. The skimmed molecular beam is detected by the VUV radiation in the ionization region of a TOF-MS. In view of the supersonic jet expansion conditions, the thermal energy distribution of parent molecule is not taken into account in data processing. During the experiment, Ar is used as the filter gas with an operating pressure of 6 Torr to effectively suppress higher harmonics of the undulator [32].

B. Theoretical calculation

In the process of photoionization and dissociative photoionization of a molecule M by monochromatic radiation of energy $h\nu$, the ionic fragment $m_0^+$, and several neutral fragments $m_i$ are produced as the following equation.

$$M + h\nu \rightarrow M^+ + e \rightarrow m_0^+ + \sum m_i + e \quad (1)$$

The adiabatic IE of M is determined by using Eq.(2) and the adiabatic AE of $m_0^+$ is calculated by Eq.(3):

$$IE (M) = E (M^+) - E (M) \quad (2)$$
$$AE (m_0^+) = E_{\text{max}} - E (M) \quad (3)$$
$$\Delta E = AE (m_0^+) - IE (M) \quad (4)$$

where $E_{\text{max}}$ refers to the highest energy barrier involved in the formation pathway of corresponding ionic fragment $m_0^+$. $E(M^+)$ and $E(M)$ represent the absolute energy of ionic and neutral precursor, respectively. The energies to form related products are calculated by subtracting adiabatic IE of the parent molecule from its adiabatic AE, namely Eq.(4).

To obtain IE for M and AE values for various fragment ions, we performed calculations of single-point energies for reactants, products, intermediates and transition states at G3B3 level and the calculated results are given in Table S1 in supplementary materials. In this theory, prior to energetic calculations, the geometry of a species is optimized at the B3LYP/6-31+G(d,p) level with the Gaussian 09 programs [35]. The calculated values of the IE, AE, and $\Delta E$ for possible formation pathways in the dissociative photoionization of DX are summarized in Table I as well as our experimental values.

III. RESULTS AND DISCUSSION

A. Experimental measurements

The VUV photoionization mass spectra of DX at photon energies of 15.50, 11.51, and 9.50 eV are
C3+ ions at 58, 87 and 88 can be recognized as CH channels in the dissociative photoionization of 1,4-dioxane. The background of setup. With photon energy decreasing to 15.50 eV, ions at m/z=15, 28, 29, 30, 31, 41, 43, 44, 45, 57, 58, 87 and 88 can be recognized as CH3+, C2H5+, C2H4O+CHO+, C2H6+, CH3O+, C3H5+, C2H2O5+, C2H2O+, C2H5O+, C2H5O+, C4H7O2+ and molecular ion C4H8O2+, respectively. This is well consistent with the data from the NIST database [36]. The signal at m/z=18 is neglected because it is water from the background of setup. With photon energy decreasing to 11.51 eV, a few ion signals C2H5O+, C2H3O+, C2H3O+, C2H5O+, C2H2O2+, and C4H6O2+ can be distinguished clearly. When the photon energy is further reduced to 9.50 eV, only parent ion can be detected.

The relative branching ratio curves of various charged fragment are shown in FIG. 2. For the sake of

### TABLE I

<table>
<thead>
<tr>
<th>m/z</th>
<th>Species</th>
<th>IE or AE /eV</th>
<th>Possible dissociation channels</th>
<th>∆E/eV</th>
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<tr>
<td>88</td>
<td>C4H4O2+</td>
<td>9.10±0.04</td>
<td>9.10</td>
<td>9.058 (MATI) [18]</td>
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<td>9.39 (PIMS) [15]</td>
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<td>9.19±0.04 (PEPICO) [12]</td>
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<td></td>
<td></td>
<td></td>
<td>9.13 (PIS) [19]</td>
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<td>87</td>
<td>C4H2O2+</td>
<td>10.60±0.08</td>
<td>11.72</td>
<td>10.95 (EIMS) [10]</td>
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<td></td>
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<td>58</td>
<td>C3H3O+</td>
<td>10.58±0.05</td>
<td>10.77</td>
<td>10.56±0.10 (PEPICO) [12]</td>
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<td>11.12 (EIMS) [10]</td>
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<td>11.4 (PIMS) [15]</td>
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<td>11.0±0.10 (CEMS) [16]</td>
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<td>10.65</td>
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<td>10.30±0.10 (FT-ICRMS) [13]</td>
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<td>44</td>
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<td>10.99</td>
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<td>11.7±0.3 (CEMS) [16]</td>
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<td>12.20</td>
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<td>13.16 (EIMS) [10]</td>
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<td>11.8 (PIMS) [15]</td>
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<td>28</td>
<td>C2H4+</td>
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<td>12.02</td>
<td>11.90±0.10 (PEPICO) [12]</td>
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<td></td>
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<td>11.8 (PIMS) [15]</td>
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FIG. 1 Photoionization mass spectra of 1,4-dioxane at (a) 15.50, (b) 11.51, and (c) 9.50 eV. The insert shows expanded mass spectra between the m/z range from 41 to 45.
analysis can also be used for fragment ions $C_2H_2O^+$ predominates above 12.6 eV. As for area (V), all the dissociation channel to produce $C_2H_2O^+$ may indicate a common intermediate. When it comes to area (III), $C_2H_2O^+$ dominates the ion population until 12.6 eV, corresponding to a major dissociation channels. The similar AE values and shape of branching ratio curves of $C_2H_2O^+$ and $C_2H_2O^+$ may indicate a common intermediate. When it comes to area (III), $C_2H_2O^+$ decreases slowly along with the significant reduction of $C_2H_2O^+$. Meanwhile, the ionic species $C_2H_2O^+$ and $C_2H_2O^+$ begin to increase, indicating that these species may originate from $C_2H_2O^+$ or $C_2H_2O^+$ or even both. Analogous analysis can also be used for fragment ions $C_2H_2O^+$, $CHO^+/C_2H_2^+$ and $C_2H_2^+$ in area (IV). In the energy range of 12.4–14.0 eV, $C_2H_2O^+$ and $C_2H_2O^+$ decrease rapidly, as other fragment ions, such as $C_2H_2O^+$, $CHO^+/C_2H_2^+$ and $C_2H_2^+$ are produced more quickly. Moreover, the dissociation channel to produce $C_2H_2^+$ predominates above 12.6 eV. As for area (V), all the relative branching ratio values seem to remain stable.

The PIE curves of the parent ion and its main fragment ions are shown in FIG. 3 and FIG. 4, respectively. For the parent ion, our measured IE value of 9.10±0.04 eV is consistent with the experimental determination of 9.058 eV obtained from MATI measurement [18] and calculated value of 9.10 eV at G3B3 level. The geometries of parent ion and neutral DX at B3LYP/6-31+G(d,p) level are very similar because of symmetry restrictions that the oxygen lone pairs are primarily p-type orbitals and are essentially nonbonding. This is the reason why the PIE curve of $C_2H_2O^+$ exhibits a relatively sharp onset to some extent.

B. Dissociation mechanisms

1. Formation pathway of $C_4H_7O_2^+$

DX has a chair conformation with a center of symmetry in the gas phase and possesses the point group of $D_{2h}$ [37]. That is to say there are two types of C–H bonds (for example: C6–H14 point to the plane and C6–H13 point out of the plane) in DX. The fragmentation channel attributable to the loss of an H atom in DX may occur via two distinguishable fragmentation pathways. In one case, the process involves the rupture of the C6–H13 bond with an energy barrier of 1.62 eV (TS1-1), resulting in a six-membered ring with double bond structure (P2). The calculated AE of $C_4H_7O_2^+$ in this channel (named channel 1a in the following) is 10.72 eV, consistent well with our experimental value of (10.60±0.08) eV. The other case, named channel 1b, involves the cleavage of C6–H14 bond overcoming an energy barrier of 2.53 eV, forming the final products P2 and H atom. These measurements of AE values and energy barriers show that channel 1a is favored.

2. Formation pathway of $C_3H_6O^+$

As the dominant fragment product of $C_4H_7O_2^+$ between 10.9–12.5 eV, the fragment ion $C_3H_6O^+$ has been
confirmed to be a mixture of CH$_2$CH$_2$OCH$_2^+$ as major component (90%–95%) and CH$_3$OCHCH$_2^+$ as a minor component (5%–10%) of the C$_3$H$_5$O$^+$ ions [14, 20]. Lam and co-workers [20] proposed three formation pathways for CH$_2$CH$_2$OCH$_2^+$ (involves AE values of 10.78 eV for channel 2a, 11.07 eV for channel 2b and 11.19 eV for channel 2c) and two for CH$_3$OCHCH$_3^+$ (involves large AE values of 11.91 eV for channel 3a and 11.78 eV for channel 3b) in their detailed G3 (MP2) study of the C$_3$H$_6$O$^+$ isomers fragmented from DX. Furthermore channel 2b and 2c are suggested to be more efficient in producing CH$_2$CH$_2$OCH$_2^+$ in their theoretical studies.

From the point of AE value, our experimental AE value of (10.58±0.05) eV suggests perhaps that the channel 2a with a calculated AE value 10.78 eV (also showing good agreement with our theoretical value 10.77 eV) is more favored. Taking into account the facts that C$_3$H$_5$O$^+$ involves a number of re-dissociation processes [17, 21, 38], we believe that the three channels mentioned above are possible and may even compete with each other. Particularly, the channel 2a plays a major role in low energies, while the other two channels dominate at high energies. In our study, the $\beta$-distonic ion CH$_2$CH$_2$O$^+$→CH$_2^+$ (P3) is assumed to be the only component of the C$_3$H$_6$O$^+$ fragment for its decisive abundance.

C. Formation pathway of C$_3$H$_5$O$^+$

As noted by Dunbar and co-workers [38], C$_3$H$_5$O$^+$ can be generated in a sequential way (C$_3$H$_6$O$_2^+$→C$_3$H$_5$O$^+$+CH$_2$O→C$_3$H$_5$O$^+$+H+CH$_2$O) or a simultaneous way that competes with C$_3$H$_6$O$^+$, C$_2$H$_5$O$^+$ and C$_2$H$_4$O$^+$ from parent ion. This matches well with our analysis results of relative branching ratios, which suggests that C$_3$H$_5$O$^+$ originates from C$_4$H$_8$O$_2^+$ or C$_3$H$_6$O$^+$ or even both. Additionally, the loss of H form C$_3$H$_6$O$^+$ must be accompanied by complicated rearrangements and does not produce CH$_2$OCH=CH$_2^+$ or the oxetanyl cation but dissociates largely via complicated rearrangements yielding CH$_3$CH$_2$CO$^+$+H at threshold [17]. We thus suppose the sequential channel (CH$_3$CH$_2$CO$^+$+CH$_2$O+H) to be the formation pathway of C$_3$H$_5$O$^+$. In the case of CH$_3$CH$_2$CO$^+$ (P4a), the first step is 1,4-H shifting to form a relatively stable intermediate INT1 via a five-membered ring transition state TS2 overcoming an energy barrier of 0.97 eV, which is the highest energy step along the entire pathway. The second step is formation of the mentioned important intermediate CH$_3$CH$_2$CHO$^+$ via transition state TS3 by prolongation and rotation about the C–O bond. However, the structure of TS3 is not found at B3LYP/6-31+G(d,p) level, but can be found at QCISD/6-31G(d) theory.
FIG. 5 Formation pathway of C\textsubscript{4}H\textsubscript{7}O\textsubscript{2}+ calculated at the G3B3//B3LYP/6-31+G(d,p) level.

and MP2 theory [21]. The last step is the H atom loss from aldehyde group to form P4a through TS4 by overcoming an energy barrier of 0.75 eV.

Obviously, FIG. 6(a) shows the sequential fragmentation pathway, while the competitive formation pathway has been shown in FIG. 6(b). Considering the facts that the product set CH\textsubscript{2}OCH\textsubscript{2}+ requires 3.0 eV of excitation, while C\textsubscript{3}H\textsubscript{5}O+ is observed abundantly at 2.2 eV, the formation of CH\textsubscript{2}OCH\textsubscript{2}+ through this pathway has been precluded. We then find a competitive formation pathway to produce CH\textsubscript{2}OCH\textsubscript{2}+ (P4b) according to C\textsubscript{4}H\textsubscript{8}O\textsubscript{2}+!CH\textsubscript{2}OCH\textsubscript{2}+ (P4b)+CH\textsubscript{2}OH, giving a calculated AE value of 11.22 eV closer to experimental one (11.24±0.04) eV. Such plausible mechanism starts from the molecular ion P1 followed by ring-opening and a successive H-shifts to form INT3 via TS5 with an energy barrier of 1.55 eV. CH\textsubscript{2}OCH\textsubscript{2}+ can be formed simply by breaking C2–C3 bond directly from INT3, which can be further confirmed by scanning the C2–C3 bond length from 1.5 Å to 4.5 Å with a finding that no possible transition state exists. Additionally, the calculated reaction barrier of 2.12 eV is in good agreement with our experimental value of 2.14 eV. We then suppose the latter channel to be the more likely one.

D. Formation pathway of C\textsubscript{2}H\textsubscript{5}O+

According to the results of FIG. 1 and FIG. 2, C\textsubscript{2}H\textsubscript{5}O+ appears to be one of the dominant as well as the lowest energy fragment ions in the energy region we studied. As for the possible structure of C\textsubscript{2}H\textsubscript{2}O\textsuperscript{+}, the first one is CH\textsubscript{3}CH\textsubscript{2}O\textsuperscript{+} which is energetic accessible but has been excluded due to its failure to transfer a methyl cation rapidly onto acetone as CH\textsubscript{3}OCH\textsubscript{2}+ does [13]. We also eliminate the structure of protonated oxirane as m/z 45 fragment ion because of a significantly high revised value of the proton affinity while confirm CH\textsubscript{3}CHOH\textsuperscript{+} as the possible structure of C\textsubscript{2}H\textsubscript{2}O\textsuperscript{+} due to its similar enthalpy of formation and specific H+ transfer rate. The calculated AE of CH\textsubscript{3}CHOH\textsuperscript{+} is 10.64 eV, agrees reasonably well with our experimental results of (10.52±0.06) eV.

Thissen and co-workers [13] proposed an interesting mechanism that the CH\textsubscript{3}CHOH\textsuperscript{+} can be formed via a H\textsuperscript{+} transfer from the hydroxyl group of CH\textsubscript{2}CHOH\textsuperscript{+} (a detailed discussion of this charged fragment can be found in the next section) to the aldehyde group of CH\textsubscript{2}CHO, which gives a rational explanation for the formation of a CH\textsubscript{2}CHOH\textsuperscript{+} fragment ion, whose AE value is identical to that of the C\textsubscript{2}H\textsubscript{4}O\textsuperscript{+}, which is also in good agreement with our experimental results. However, this mechanism cannot be confirmed under the present study. Instead, another formation pathway (P1!TS5!INT3!TS6!INT4) is found. For the purpose of brevity, only the remaining intermediate INT3 and its subsequent steps are discussed. Besides breaking C–C bond to form P4b directly, INT3 can also transform into INT4 via 2,3-H-shift with a transition state TS6 located at 10.23 eV, which is 0.42 eV lower than the highest energy step of TS5. Afterward, a cleavage of C2–O4 bond of INT4 can further dissociate to CH\textsubscript{3}CHOH\textsuperscript{+}(P5)+CH\textsubscript{2}CHO. Moreover, if we assume CH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2} to be the neutral species, the rel-

FIG. 6 Formation pathways of CH\textsubscript{2}CH\textsubscript{2}CO\textsuperscript{+}(P4a) and CH\textsubscript{2}OCHCH\textsubscript{2}+ (P4b) calculated at the G3B3//B3LYP/6-31+G(d,p) level.
ative energy of \( \text{COOH}^+ + \text{CH}_3\text{C}_2\text{H}_2 \) is calculated to be 10.50 eV, which is remarkable close to our experimental AE of (10.52±0.06) eV, but the likelihood of the complex rearrangement as well as the energy barrier required to reach these structures seem uncertain.

E. Formation pathway of \( \text{C}_2\text{H}_4\text{O}^+ \)

The fragment ions of \( \text{C}_2\text{H}_4\text{O}^+ \) generated from ionized DX has been reported to possess the enol structure \( \text{CH}_2\text{CHOH}^+ \) but not \( \text{CH}_2\text{OCH}_2^+ \) by means of ion-molecule reactions coupling with AE measurements [13]. However, the detailed mechanism of this feasible route are still unknown. According to our calculated results in Fig. 7 and Fig. 8, whether INT3 transforms into TS6 or TS7-2 via 2,3-hydrogen or 2,4-hydrogen shift can lead to different products of similar AE values, indicating that a mechanism via the common intermediate INT3 may account for the same AE values for \( \text{CH}_2\text{CHOH}^+ \) and \( \text{CH}_2\text{COOH}^+ \), which has been predicted in the previous discussion section of relative branching ratios. As depicted in Fig. 8, the rate-limiting step in \( \text{CH}_2\text{CHOH} \) loss is the transfer of the proton, coupled with the cleavage of C2–O5 single bond via the TS7-2 (10.76 eV, Table I), the final structure of \( \text{CH}_2\text{CHOH}^+ + \text{CH}_3\text{CHO} \) can be formed, subsequently.

Besides the pathway described above, we have also investigated the possibility of 3,6-hydrogen shift in INT3. On the basis of G3B3 calculation, a channel of little higher AE values (10.99 eV) is found. Staring from INT3, the 3,6-H shift in INT3 leads to the formation of INT5 via TS7-1 with an energy barrier of 1.33 eV. Then, 2,3-hydrogen shift and a simple cleavage of C3–O4 bond can transform INT5 into dissociating products \( \text{CH}_2\text{CHOH}^+ + \text{CH}_3\text{CHO} \), overcoming a barrier of 1.57 eV via transition state TS8. The calculated AE 10.76 eV of \( \text{CH}_2\text{CHOH}^+ \) is more close to our experimental AE value (10.52±0.03) eV, suggesting that the dissociative channel \( \text{CH}_2\text{CHOH}^+ + \text{CH}_3\text{CHOH} \) is more favored.

F. Formation pathway of \( \text{C}_2\text{H}_3\text{O}^+ \)

In the case of \( \text{C}_2\text{H}_3\text{O}^+ \), from the analysis of metastable ion spectra of the distonic radical cation \( \text{CH}_3\text{CHOCH}_2^+ \) obtained by neutralization-reionization mass spectrometry (NRMS), Polce et al. [17] have drawn the following three conclusion. Firstly, elimination of \( \text{CH}_3 \) to yield \( \text{C}_2\text{H}_3\text{O}^+ \) can be observed from \( \text{CH}_3\text{CHOCH}_2^+ \). Secondly, the elimination \( \text{CH}_3 \) is exothermic and must, therefore, be associated with sizable activation energies, according to the presence of large kinetic energy releases. Thirdly, the structure of \( \text{C}_2\text{H}_3\text{O}^+ \) is attributed to be the lowest energy structure of \( \text{CH}_3\text{CO}^+ \) with a calculated standard formation enthalpy value of 799 kJ/mol, which stands much closer to that of \( \text{C}_2\text{H}_2\text{O}^+ \) (874 kJ/mol) than \( \text{CH}_2=\text{C}–\text{OH}^+ \) (784 kJ/mol) favored by Fraser-Monteiro et al. [12]. As shown in Table I, for the \( \text{CH}_3\text{CO}^+ \), the measured AE value of (12.06±0.10) eV is reasonable consistent with the calculated value of 12.37 eV and is ~0.10 eV lower than the experimental value of (11.96±0.10) eV [12]. In the present case, a pathway for the formation of \( \text{CH}_3\text{CO}^+ \) is found and the corresponding energy profile is shown in Fig. 9. The distonic radical cation \( \text{CH}_3\text{CHOCH}_2^+ \) can undergo a hydrogen transfer from the middle C atom to the terminal C atom to generate INT6 via transition state TS9 with an energy barrier of 1.6 eV. It should be noted that INT6 possess the structure of \( \text{CH}_3\text{OCH}_2^+ \), which is exactly the mentioned minor component of \( \text{C}_2\text{H}_6^+ \). This may imply that the two structures of \( \text{C}_2\text{H}_6^+ \) are actually interchangeable. Subsequently, another hydrogen shift between the adjacent C atoms by passing through structure TS10 located at 11.89 eV can explain the formation of INT7 with an elongated C–O bond. Finally, the further cleavage of a weak C–O bond in INT7 can yield \( \text{CH}_3 \) and \( \text{CH}_3\text{CO}^+ \) (P7).

FIG. 7 Formation pathways of \( \text{CH}_3\text{CHOH}^+ \) (P5) calculated at the G3B3//B3LYP/6-31+G(d,p) level.

FIG. 8 Formation pathways of \( \text{CH}_3\text{COOH}^+ \) (P6) calculated at the G3B3//B3LYP/6-31+G(d,p) level.
H. Formation pathway of $\text{C}_2\text{H}_5^+$ and CHO

A selectively-labelled derivatives study of $\text{CH}_2\text{CH}_2\text{OCH}_2^+$ [17] as well as the high-resolution mass spectra study [12] clearly show that both $\text{CHO}^+$ and $\text{C}_2\text{H}_5^+$ can be formed competitively. Our calculations indicate that both $\text{CHO}^+$ and $\text{C}_2\text{H}_5^+$ are energetically possible under G3B3/B3LYP/6-31+G(d,p) level. Then two energetic channels of $\text{C}_4\text{H}_6\text{O}_2^+\rightarrow\text{CHO}^+\text{C}_2\text{H}_5^+$ and $\text{C}_4\text{H}_6\text{O}_2^+\rightarrow\text{C}_2\text{H}_5^+\text{CHO}^+\text{CH}_2\text{O}_2$ are proposed. The AEs value of $\text{C}_2\text{H}_5^+$ is calculated to be 11.91 eV, showing reasonable agreement with our experimental value of (11.74±0.10) eV. While the calculated AE of $\text{CHO}^+$ are 12.33 and 12.20 eV, a bit higher than the experimental one, due to the following two formation pathways (shown in FIG. 11), respectively. This suggests that $\text{C}_2\text{H}_5^+$ dominates at lower photon energies, while $\text{CHO}^+$ appears at higher photon energies.

In the case of $\text{CHO}^+$, only the remaining part of pathway proceeding from INT1 is discussed. INT1 undergoes a $\text{C}^--\text{O}$ elongation via transition state TS11 with an energy barrier of 1.17 eV to form the final products $\text{CHO}^+(\text{P9b})+\text{C}_2\text{H}_5^+$. Additionally, analogous to the formation of $\text{C}_3\text{H}_2\text{CO}^+(\text{P4a})$, $\text{CHO}^+(\text{P9b})$ can also be formed through INT2 in which the $\text{CH}_3\text{CH}_2^--\text{CHO}$ bond is elongated with a relative high energy barrier of 2.13 eV. Subsequently, dissociation of TS12 yields $\text{C}_2\text{H}_5^+\text{CHO}^+$ as products.

I. Formation pathway of $\text{C}_2\text{H}_4^+$

A typical structure of $\text{CO}^+$, with the same $m/z=28$ as $\text{C}_2\text{H}_4^+$, has been excluded by previous high-resolution mass spectra study [12] and a metastable ion mass spectra study [17] of deuterated $\text{C}_3\text{D}_6\text{O}^+$, where the original mass peak of $m/z=28$ shifts to 32. Therefore, the $m/z=28$ species is assigned to $\text{C}_2\text{H}_4^+$. The formation of $\text{C}_2\text{H}_4^+$ from that one step dissociation channels $\text{C}_2\text{H}_4^++\text{OCH}_3\text{CH}_2\text{O}$ and $\text{C}_2\text{H}_4^++\text{C}_2\text{H}_5\text{CH}_2\text{O}$ (four-membered-ring) would require energy of at least 15.47 and 14.47 eV, respectively, which are much higher than our experimental result (11.78±0.10) eV as well as the literature values.
C3H5O+ is referred to be CH3CH2CO+ and CH3CHOCH2+ respectively. They can be generated by further elimination of H from the CHO group of CH3CH2CHO+ and elimination of CH2OH from the molecular ion. Fragment ions with m/z=29 are attributed to C2H5+ and CHO+ which can be produced via CH2CH2O=CH2+→CH3CH2O=CHH+→CH3CH2CHO+→CH3CH2⋅⋅⋅H+⋅⋅⋅CO+→C2H5+ +HCO and by elimination of C2H3 through CH3CH2OCH+ or CH3CH2CHO+ or even both respectively. The present study is of great significance for understanding the photoionization and dissociation processes of DX in the photon energy region of 8.00–15.50 eV.

V. ACKNOWLEDGMENTS

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Dissociative photoionization of DX was investigated with VUV-TOF-PIMS in conjunction with supersonic expansion molecular beam. IE of parent molecule, AE values of twelve observed fragment ions, and relative branching ratios of major ions (m/z=88, 87, 58, 57, 45, 44, 43, 31, 30, 29, and 28) were derived from their PIE curves. A few of the determined values are revised with respect to previous publications. Based on comparison of the experimental and theoretical AE values, detailed dissociative photoionization channels of R1–R11 are identified R1: C2H2O2+ (P2, m/z=87)+H, R2: CH3CH2CO+ (P4a, m/z=57)+H+CH2O, R3: CH2CHOCH2+ (P4b, m/z=57)+H+CH2O, R4: CH2CHOH+ (P5, m/z=45)+CH2CHO, R5: CH2CHOH+ (P6, m/z=44)+CH2CHO, R6: CH2CHOH+ (P6, m/z=44)+CH2CHOH, R7: CH3CO+ (P7, m/z=43)+CH3+CH2O, R8: C2H3+ (P8, m/z=30)+CO+CH2O, R9: C2H5+ (P8a, m/z=29)+CHO+CH2O, R10: CHO+ (P8b, m/z=29)+C2H3+CH2O, R11: C2H4+ (P9, m/z=28)+CH2O+CH2O.

IV. CONCLUSION

Dissociative photoionization of DX was investigated with VUV-TOF-PIMS in conjunction with supersonic expansion molecular beam. IE of parent molecule, AE values of twelve observed fragment ions, and relative branching ratios of major ions (m/z=88, 87, 58, 57, 45, 44, 43, 31, 30, 29, and 28) were derived from their PIE curves. A few of the determined values are revised with respect to previous publications. Based on comparison of the experimental and theoretical AE values, detailed dissociative photoionization channels of R1–R11 are identified R1: C2H2O2+ (P2, m/z=87)+H, R2: CH3CH2CO+ (P4a, m/z=57)+H+CH2O, R3: CH2CHOCH2+ (P4b, m/z=57)+H+CH2O, R4: CH2CHOH+ (P5, m/z=45)+CH2CHO, R5: CH2CHOH+ (P6, m/z=44)+CH2CHO, R6: CH2CHOH+ (P6, m/z=44)+CH2CHOH, R7: CH3CO+ (P7, m/z=43)+CH3+CH2O, R8: C2H3+ (P8, m/z=30)+CO+CH2O, R9: C2H5+ (P8a, m/z=29)+CHO+CH2O, R10: CHO+ (P8b, m/z=29)+C2H3+CH2O, R11: C2H4+ (P9, m/z=28)+CH2O+CH2O.

of (11.90±0.10) eV [12] and 11.8 eV [15]. Whereas, the formation process simply by breaking bond can be clearly eliminated. From FIG. 2, the branching ratio of C2H4+ increases with the decreasing of the branching ratio of C3H6O+ with energy increasing, suggesting that C2H4+ is formed by C3H6O+. Then a higher energy consecutive dissociation path C2H5O2+→C2H4O+ +CH2O→C2H4H+ +2CH2O is proposed. As shown in FIG. 11, the calculated AE value of this consecutive dissociation path is 12.02 eV, showing reasonable agreement with experimental result of (11.78±0.10) eV.