

# The structures, conversions and fragmentations of $C_2H_6O^{2+}$ isomers: An ab initio study

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## Abstract

The fragmentations of a  $C_2H_6O$  dication in both singlet and triplet states are investigated in the present study. We propose several probable reaction channels to explain the source of the peaks which are found in the mass spectrum of ethanol under an intense laser field, but fail to reproduce it theoretically by considering only the fragmentation of a  $C_2H_6O$  radical cation. It is difficult for the  $C_2H_6O^{2+}$  isomers in singlet state to undergo fragmentation, except for the  $H_2$  elimination from ethanol dication, to generate  $CH_3COH^{2+}$ . However, the fragmentation can take place easily from the  $C_2H_6O^{2+}$  isomers in triplet state. There exist low energy channels of the  $C_2H_6O$  dication in singlet state, to generate  $CH_3COH^{2+}$ ,  $CH_4^+$ ,  $CHOH^+$ ,  $CH_3^+$ ,  $CHOH_2^+$ ,  $CH_2^+$ ,  $CH_2OH_2^+$ ,  $COH^+$ ,  $H^+$ ,  $CH_2CHOH_2^+$ ,  $CH_2CH^+$  and  $H_3O^+$ . However, with similar consideration, the low energy channels of  $OH^+$ ,  $CH_3CH_2^+(T)$ ,  $CH_2CH_2^+$ ,  $H_2O^+$ ,  $CH_2O^+$  and  $CH_2OH_2^+$ , are available only in triplet state. The inter-conversions between any two  $C_2H_6O^{2+}$  isomers in both singlet and triplet states are easier than their fragmentation reactions, except for  $CH_2^+$  and  $\beta$ -H eliminations from those dications in triplet state. © 2006 Elsevier B.V. All rights reserved.

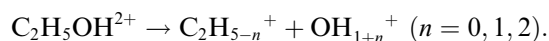
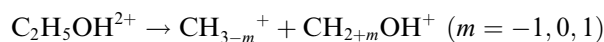
**Keywords:** Ethanol dication; Doubly charged cation; Theoretical study; Conformation; Fragmentation

## 1. Introduction

Early in 1957, a radiolysis and mass spectrometry study [1] of ethanol had already been performed. However, up to now, many researches [2–14] still focus on the fragmentations of ethanol, but employ different ionization tools, especially the dissociative ionization reactions induced by an intense laser [11–14]. The fragmentation under an intense laser field involves complicated dynamics because there exist many different ionization mechanisms, such as multiphoton ionization, tunnel ionization and over-the-barrier ionization (field ionization). Therefore the fragmentation precursors can be cations, dications or higher multiple charged ions which may even give rise to a coulomb explosion. Considering only the fragmentation

of  $C_2H_6O^+$  isomers, our previous theoretical results [15] fail to generate reasonable intensities for the fragments, such as  $H^+$ ,  $CH_3^+$ ,  $CHO^+$ ,  $CH_2O^+$ ,  $CH_2OH^+$ ,  $C_2H_3^+$ ,  $C_2H_4^+$ , etc., which are observed in the mass spectra of ethanol. Furthermore, the dissociative precursors other than the  $C_2H_6O^+$  isomers can be generated under a strong laser field. With such consideration, the fragmentation calculation of an ethanol cation beyond single charge should be taken into consideration, to provide a better description of the mass spectra.

The dissociative ionization studies of ethanol under an intense laser field [11–14], suggest that some fragments are generated due to a coulomb explosion of the ethanol dications. The observations [14] of the coincidence momentum imaging (CMI) maps suggest six explosion paths for the doubly charged parent ion, and they are:



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In order to understand the mechanism of these fragmentation reactions, we carried out the calculations of an ethanol dication and its related conformers. In this study, we focus on the fragmentation reactions involving only C–C bond and C–O bond cleavages. With this study, we hope to shed some light on elucidating the possible dissociation channels of an ethanol dication under an intense laser.

## 2. Computational method

The geometry optimization and vibration frequencies of an ethanol dication, and the related intermediates, transition states and fragments were performed at the B3LYP/6-31+G(d,p) level. A series of single point energy calculations were carried out at both the CCSD(T)/6-31+G(d) and MP2(FC)/G3MP2Large methods. In MP2 calculations of open shell systems, we replaced the MP2 energies with the corresponding spin-projected PMP2 values. The energies ( $E$ ) were obtained by using

$$E = \text{ZPE} + E(\text{CCSD(T)}/6-31+G(d)) \\ + E(\text{PMP2}/\text{G3MP2Large}) \\ - E(\text{PMP2}/6-31+G(d)),$$

where the ZPE are obtained by using B3LYP/6-31+G(d,p) level without scaling. It is similar to the well-known procedure, G3(MP2)(+)-RAD(p) method [16], for the treatment of charged, open shell systems. All calculations were performed by using the G03 package [17].

## 3. Results and discussion

The sources of the  $\text{C}_2\text{H}_6\text{O}^{2+}$  can be generated by further ionizing the  $\text{C}_2\text{H}_6\text{O}^+$  isomers. From our previous study

[15], there are five possible candidates which, in order of their stability, are  $\text{CH}_2\text{CH}_2\text{OH}_2^+$  (32),  $\text{CH}_3\text{CHOH}_2^+$  (18),  $\text{CH}_3\text{CH}_2\text{OH}^+$  (1),  $c\text{-CH}_3\text{CH}_2\text{OH}^+$  (2) and  $\text{CH}_4\text{CH}_2\text{O}^{2+}$  (44) with their relative energies in kcal/mol as  $-8.3$ ,  $-4.37$ ,  $0.0$ ,  $2.15$  and  $48.7$ , respectively, where the bold numbers in parenthesis are their sequence numbers in the previous study [15] to manifest the source of the  $\text{C}_2\text{H}_6\text{O}^{2+}$ . They are shown in Fig. 1. For example, **d-1-S** and **d-1-T**, where **d** represents a dication; **1** indicates the sequence number of the  $\text{C}_2\text{H}_6\text{O}^+$  isomer from which this dication is generated; and **S** and **T** are denoted as the singlet and triplet state, respectively. Fig. 2 presents the optimized structures of the  $\text{C}_2\text{H}_6\text{O}^{2+}$  isomers in singlet and triplet states, and their corresponding internal energies related to  $\text{CH}_3\text{CH}_2\text{OH}^{2+}$  (**d-1-S**); as well, their Mulliken atomic charges at B3LYP/6-31+G(d,p) level are also shown.

## 4. Structures and stability of the $\text{C}_2\text{H}_6\text{O}^{2+}$ isomers in singlet and triplet states

By comparing the structural difference and the relative stability between the  $\text{C}_2\text{H}_6\text{O}$  dications and their cation counterparts, one can understand the influence of further ionization of the  $\text{C}_2\text{H}_6\text{O}^+$  on the structures of the dications. The results indicate that the isomers of dications in singlet state are more difficult, than those in triplet state, when it comes to retaining the skeleton structure of their corresponding  $\text{C}_2\text{H}_6\text{O}^+$  counterparts. For example, two  $\text{CH}_3\text{CH}_2\text{OH}^{2+}$  isomers in singlet state, as shown in Fig. 2(a) and (c), should be complexes of  $\text{CH}_3\text{COH}^{2+}$  with  $\text{H}_2$  because both of them have two obviously elongated  $\text{C}_\alpha\text{-H}$ s, these two  $\alpha\text{-H}$ s are close to each other, and are structurally quite different from their  $\text{C}_2\text{H}_6\text{O}^+$  counterparts.

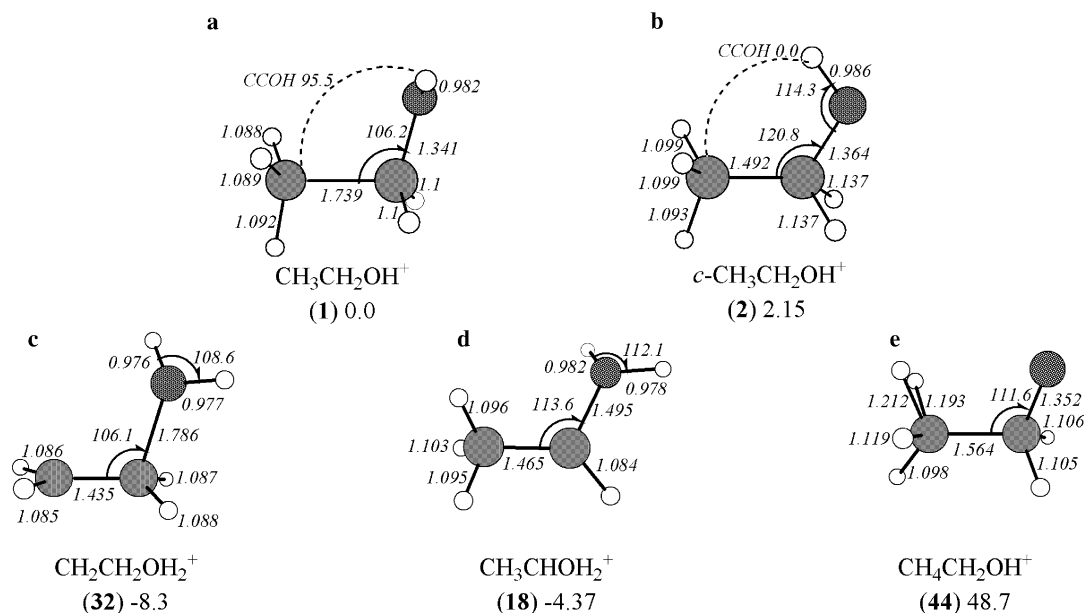


Fig. 1. The structures of  $\text{C}_2\text{H}_6\text{O}^+$  isomers containing the C–C–O skeleton with distance in Å and angle in degree. The numbers in italic type are the geometrical parameters.

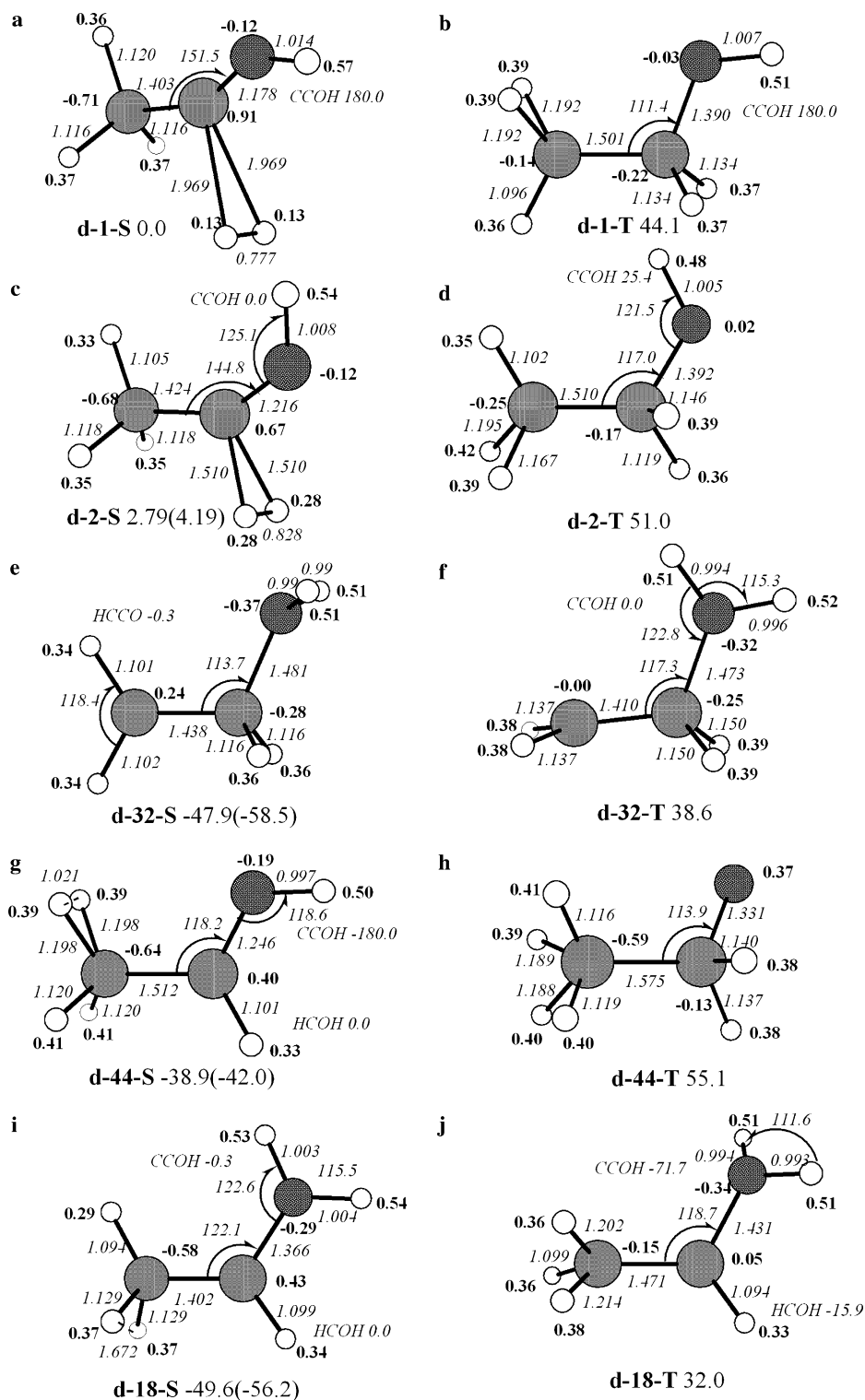


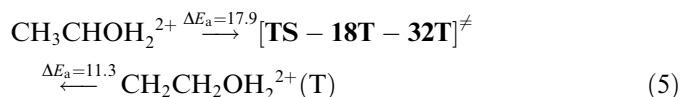
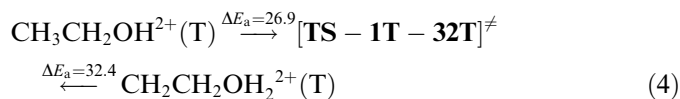
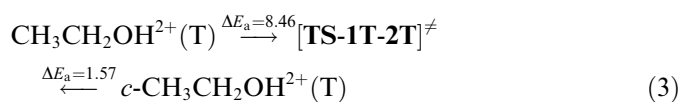
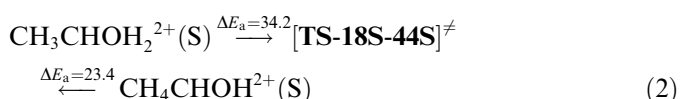
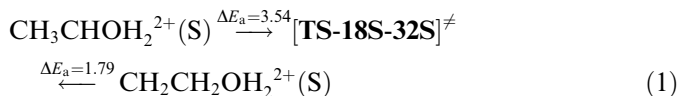
Fig. 2. The structures and relative energies of  $\text{C}_2\text{H}_6\text{O}^{2+}$  isomers containing the C–C–O skeleton in singlet state (left-hand side) and in triplet state (right-hand side), with energy in kcal/mol, distance in Å and angle in degree. The numbers in italic type are the geometrical parameters and the Mulliken charges using B3LYP/6-31+G(d,p) method are in bold type. And the energy in parenthesis is the energies calculated with CCSD method instead of CCSD(T) method in our calculated procedure.

The main skeletons of  $\text{CH}_2\text{CH}_2\text{OH}_2^{2+}$  and  $\text{CH}_3\text{CHOH}_2^{2+}$  in triplet state resemble more their  $\text{C}_2\text{H}_6\text{O}^+$  counterparts, than those found in singlet state. For example, the two dihedral angles (CCOH/CCOH') of **44**, **d-44-T** and **d-44-**

**S** are  $-46.7/175.8$ ,  $-71.7/150.1$  and  $0.0/180.0$ , respectively. These indicate that further ionization from a  $\text{C}_2\text{H}_6\text{O}^+$  precursor must undergo some structural change to generate its dication counterpart in singlet state. Furthermore, the

order of stability of isomers of  $C_2H_6O^{2+}$  in triplet state is similar to that of their  $C_2H_6O^+$  counterparts, except for the order of  $CH_2CH_2OH_2^{2+}$  (T) and  $CH_3CHOH_2^{2+}$  (T). However, the energy differences between these two are small. The two  $CH_3CH_2OH^{2+}$  isomers in singlet state are the most unstable among all of the  $C_2H_6O^{2+}$  isomers in singlet state since their positive charges are concentrated on 7 atoms, while the charges of the other isomers are distributed over 9 atoms. The conformers of dication in singlet state are more stable than their counterparts in triplet state, and both of them can generate the same products if they undergo the similar fragmentation reaction. Therefore, the energy required to undergo the fragmentation reactions for dications in triplet state are lower than for those in singlet states. Therefore, in an intense laser field, the contribution made by the fragmentation from the  $C_2H_6O^{2+}$  isomers in triplet state cannot be ignored.

It is important to know the kinetics of isomerization among dication isomers since this gives information about the possible parent ions for the fragmentation reactions. We omitted any conversion between the two  $CH_3CH_2OH^{2+}$  isomers in singlet state because their  $H_2$  eliminations with energetic barriers should take place before the conversions do. There are two types of isomerization in singlet state and three in triplet states. The related mechanisms are listed in the following equations, and the optimized structures of the corresponding transition states are shown in Fig. 3.



The conversion barriers between two  $CH_3CH_2OH^+$  conformers by rotating the C–O bond are 3 and 0.85 kcal/mol, while the similar barriers in triplet state are 8.46 and 1.57 kcal/mol (see Eq. (3)). This is due to the fact that the energy difference between these two isomers of  $CH_3CH_2OH^{2+}(T)$  is bigger than that between their cation counterparts but, even with a longer C–O bond-length,  $CH_3CH_2OH^{2+}(T)$  does not rotate more easily than does  $CH_3CH_2OH^+$ . As for the conversion between  $CH_2CH_2OH_2$  and  $CH_3CHOH_2$  cations through the H-migration between  $\alpha$ -C and  $\beta$ -C, the dication species have lower barriers than do the cation counterparts, with the energy barrier being 31.9 kcal/mol and 35.8 kcal/mol for the cations. Furthermore, these two dications in singlet state (Eq. (1)) can inter-convert more easily than those in triplet state (Eq. (5)). Therefore, no obvious correlation was uncovered between the charge of cations and the difficulty of isomerization among the isomers.

## 5. The fragmentations from $C_2H_6O^{2+}$ isomers in the singlet state

The dissociation energies of the  $H_2$  elimination from two  $CH_3CH_2OH^{2+}$  conformers in singlet state, **d-1-S** and **d-2-S**,

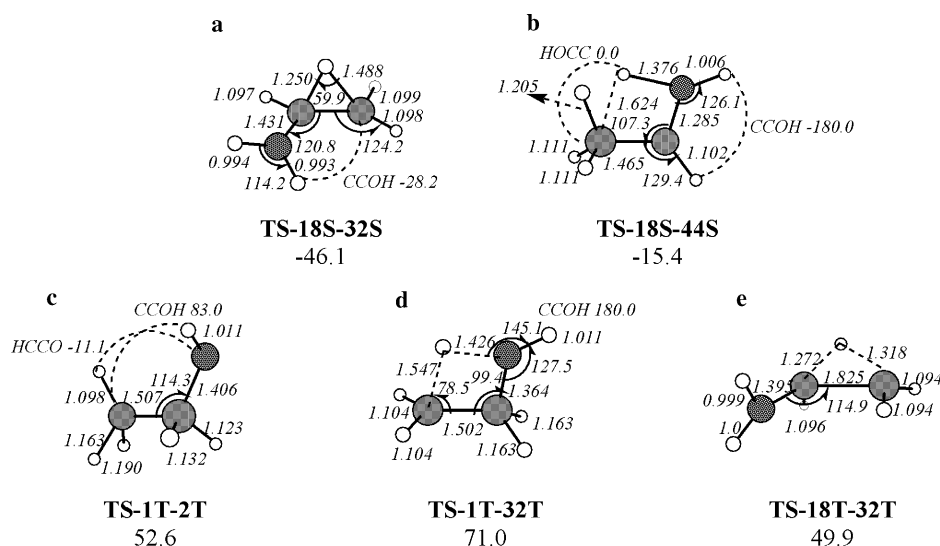
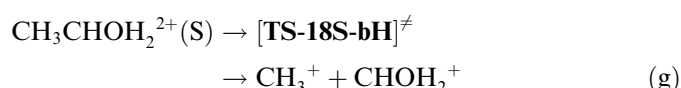
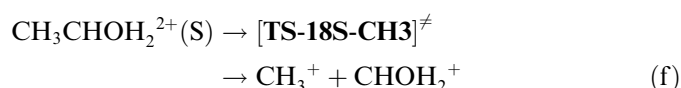
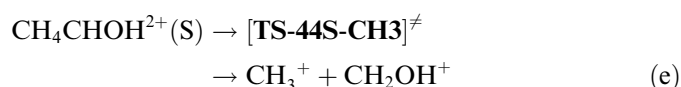
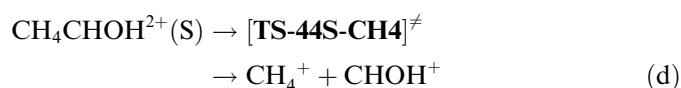
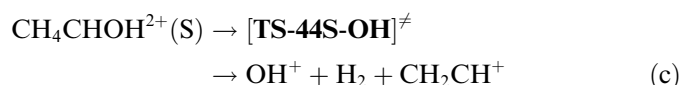
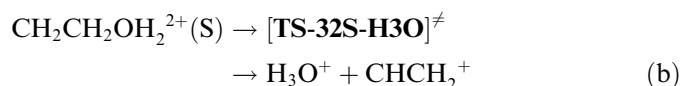
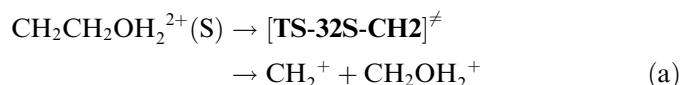


Fig. 3. The optimized structures of the transition states for the isomerization of  $C_2H_6O^{2+}$  in singlet and triplet states, with energy relative to **d-1-S** in kcal/mol, distance in Å and angle in degree.

are  $-1.23$  and  $-4.02$  kcal/mol, respectively, and both produce  $\text{CH}_3\text{COH}^{2+}$ . There exist chances to generate  $\text{H}_2^+$  instead of  $\text{H}_2$ , but according to the charge analysis,  $\text{H}_2$  should be the dominate product. Since no barrier was found to eliminate  $\text{H}_2$  from **d-1-S** via **TS-2S-H2**, and the energy of **TS-2S-H2** after ZPE correction, is lower than its precursor, **d-2-S**; the parent dications of  $\text{CH}_3\text{COH}^{2+}$  can be either **d-1-S** or **d-2-S**.  $\text{CH}_3\text{COH}^{2+}$  can undergo further fragmentation to generate  $[\text{CH}_3^+ + \text{COH}^+]$  via **TS-CH3COH-CH3** with the energy barriers and dissociation energies being  $22.3$  and  $-62.5$  kcal/mol, respectively. Other possible products are  $[\text{CH}_3\text{C}^+ + \text{OH}^+]$ , via **TS-CH3COH-OH** with the energy barriers and dissociation energies being  $183.7$  and  $61.3$  kcal/mol, respectively. Therefore, it is reasonable to propose that **d-1-S** or **d-2-S** can produce  $[\text{H}_2 + \text{CH}_3^+ + \text{COH}^+]$  and  $[\text{H}_2 + \text{CH}_3\text{C}^+ + \text{OH}^+]$  directly via **TS-CH3COH-CH3** and **TS-CH3COH-OH**, respectively.

By breaking the C–C or C–O bond,  $\text{CH}_2\text{CH}_2\text{OH}_2^{2+}$ , (**d-32-S**)  $\text{CH}_3\text{CHOH}_2^{2+}$  (**d-18-S**) and  $\text{CH}_4\text{CHOH}^{2+}$  (**d-44-S**) can be the precursors for generating the fragment combinations,  $[\text{CH}_2^+ + \text{CH}_2\text{OH}_2^+]$ ,  $[\text{H}_3\text{O}^+ + \text{CHCH}_2^+]$ ,  $[\text{OH}^+ + \text{H}_2 + \text{CH}_2\text{CH}^+]$ ,  $[\text{CH}_4^+ + \text{CHOH}^+]$ ,  $[\text{CH}_3^+ + \text{CH}_2\text{OH}^+]$  and  $[\text{CH}_3^+ + \text{CHOH}_2^+]$ . Also, the bond-length of  $\text{C}_\beta\text{-H}$  in  $\text{CH}_3\text{CHOH}_2^{2+}$  (**S**) (**d-18-S**) is pretty long, implying that  $\beta\text{-H}$  loss should take place rather easily. These fragmentation reactions are summarized in the following.

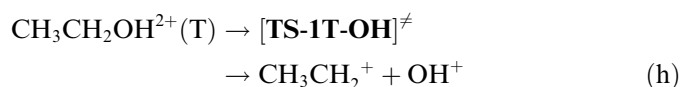


The corresponding dissociation energies in the above six reactions from (a) to (g) are  $17.7$ ,  $-94.1$ ,  $54.4$ ,  $-8.99$ ,  $-87.1$ ,  $1.41$  and  $23.7$  kcal/mol, respectively. The structures of the corresponding TSs and relative fragments for reaction (a)–(g) are presented in Figs. 4 and 6. Their calculated energy barriers are  $-212.5$ ,  $51.0$ ,  $-4070.4$ ,  $4.44$ ,  $30.8$ ,  $63.7$  and  $81.3$  kcal/mol, respectively. However, those that are

underlined are quite unreasonable. It is because a very elongated bond exists between the two to-be fragments in the transition state of the fragmentation, and the unreasonable energy contribution comes from the CCSD(T) level in our calculated procedure, as shown in Table 1. Therefore, the energies are calculated with the CCSD method instead of the CCSD(T) method. Finally, the corresponding energy barriers and reaction energies are summarized in Table 2. Our calculated result indicates that  $\text{CH}_4\text{CHOH}^{2+}$  (**d-44-S**) can undergo an OH-elimination by breaking the C–O bond, followed by a  $\text{H}_2$  elimination. Interestingly, one of  $\alpha\text{-Hs}$  is rather close to  $\text{H}_2\text{O}$  when the C–O bond is broken from  $\text{CH}_2\text{CH}_2\text{OH}_2^{2+}(\text{S})$ . Besides,  $\text{CH}_3^+$  elimination happens not only in  $\text{CH}_3\text{CHOH}^{2+}(\text{S})$  by breaking the C–C bond directly but also in  $\text{CH}_4\text{CHOH}^{2+}$  (**d-44-S**) by the migration of one of its  $\beta\text{-Hs}$  from  $\beta\text{-C}$  to  $\alpha\text{-C}$ , followed by the C–C bond breakage. The latter reaction has a lower energy barrier,  $30.8$  kcal/mol, compared to the former,  $60.7$  kcal/mol. However, the dominate path to generate  $\text{CH}_3^+$  in  $\text{C}_2\text{H}_6\text{O}^{2+}$  isomers in singlet state cannot go through the fragmentation reaction (e) and (f), but should involve the following two processes, starting instead from  $\text{CH}_3\text{CH}_2\text{OH}^{2+}(\text{S})$ . First,  $\text{CH}_3\text{CH}_2\text{OH}^{2+}(\text{S})$  undergoes the  $\text{H}_2$ -elimination and then goes through **TS-CH3COH-CH3**, with the energy barrier being  $22.3$  kcal/mol. The results also indicate that the fragmentations cannot take place easily in the dications in singlet state even with a lot of reaction energy released, such as in reactions (b) and (e).

## 6. The fragmentations from isomeric $\text{C}_2\text{H}_6\text{O}^{2+}$ in triplet state

In comparison with the fragmentations of  $\text{C}_2\text{H}_6\text{O}^{2+}$  isomers in singlet state, we study these reactions in triplet state, by breaking the C–C bond to generate  $\text{CH}_4^+$ ,  $\text{CH}_3^+$  and  $\text{CH}_2^+$ , or by breaking C–O bond to generate  $\text{OH}^+$ . The most possible precursors of these fragmentations are selected according to the structures of  $\text{C}_2\text{H}_6\text{O}^{2+}$  isomers in triplet state. First, the generation of  $\text{CH}_3^+$ , by breaking the C–C bond, can start from two  $\text{CH}_3\text{CH}_2\text{OH}^{2+}(\text{T})$  isomers (**d-1-T** and **d-2-T**) and one  $\text{CH}_3\text{CHOH}_2^{2+}(\text{T})$  isomer (**d-18-T**). However, only **d-2-T** is studied because its C–C bond is the longest and should be the weakest one among these isomers. The  $\text{H}_2\text{O}^+$ ,  $\text{CH}_2^+$  and  $\text{CH}_4^+$  eliminations can take place in  $\text{CH}_2\text{CH}_2\text{OH}_2^{2+}(\text{d-32-T})$ ,  $\text{CH}_2\text{CH}_2\text{OH}_2^{2+}(\text{d-32-T})$  and  $\text{CH}_4\text{CH}_2\text{O}^{2+}(\text{d-44-T})$ , respectively. However, only the transition state for the  $\text{OH}^+$  elimination from  $\text{CH}_3\text{CH}_2\text{OH}^{2+}(\text{d-1-T})$  was found. And, the bond-length of  $\text{C}_\beta\text{-H}$  in  $\text{CH}_3\text{CHOH}_2^{2+}(\text{T})(\text{d-18-T})$  is pretty long, implying that  $\beta\text{-H}$  loss should be rather easy. Thus, we calculated the fragmentation reactions in triplet state and summarize these reactions in the following.



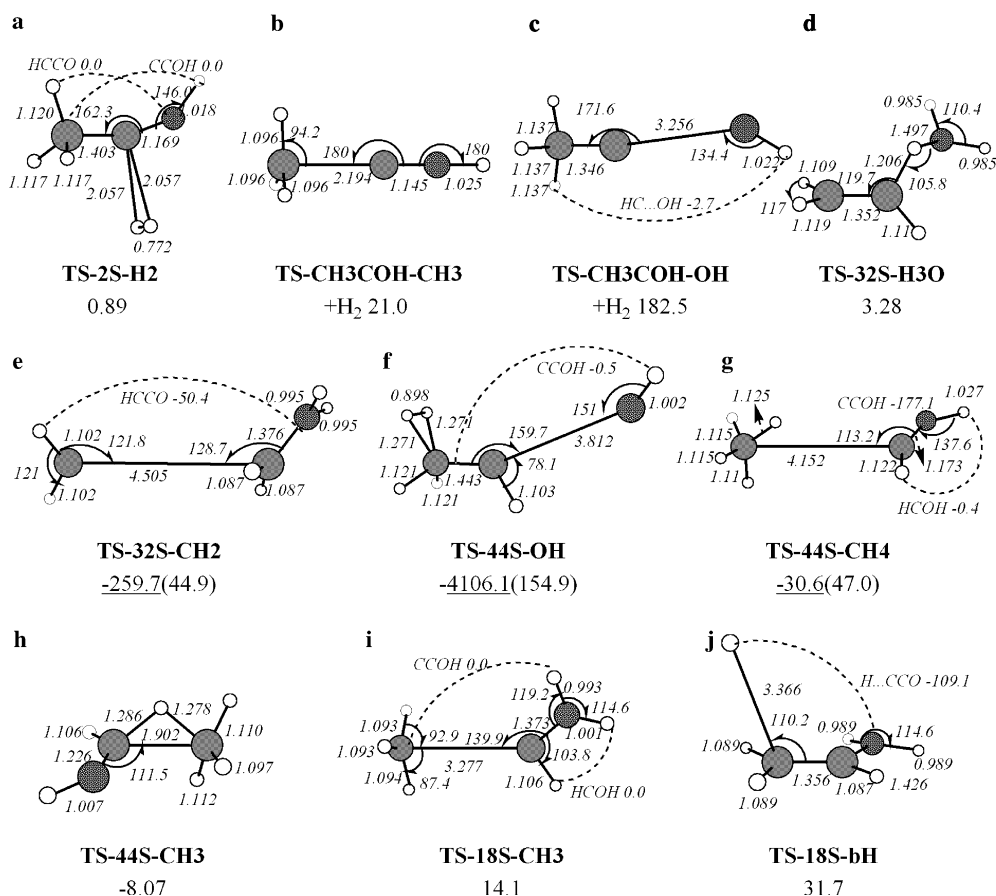


Fig. 4. The optimized structures of the transition states for the fragmentation of  $C_2H_6O_2^+$  isomers in singlet state, with energy relative to **d-1-S** in kcal/mol, distance in Å and angle in degree. The numbers in parenthesis are the relative energies using CCSD level. And the energy in parenthesis is the energies calculated with CCSD method instead of CCSD(T) method in our calculated procedure.

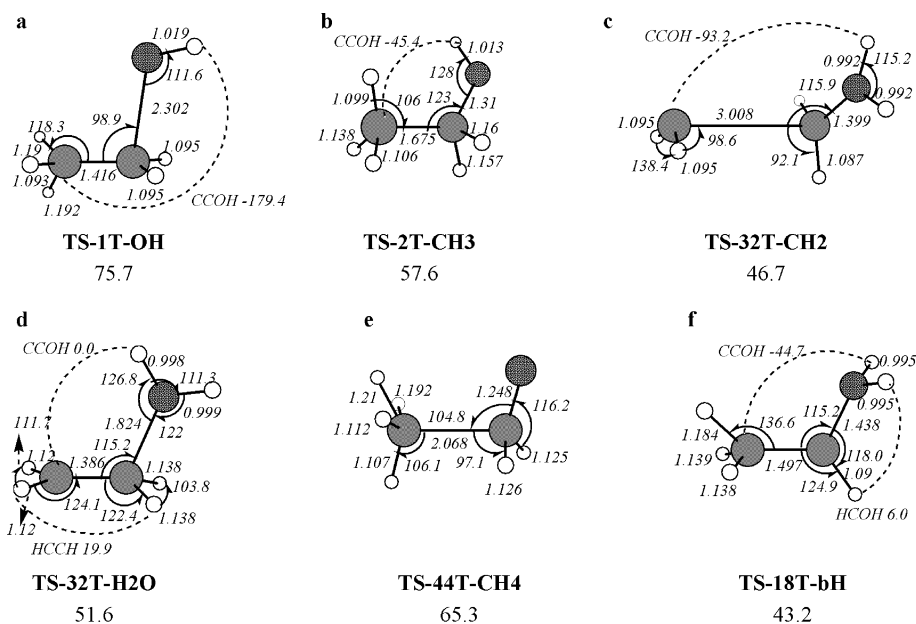


Fig. 5. The optimized structures of transition states for the fragmentation of  $C_2H_6O_2^+$  isomers in triplet state, with energy relative to **d-1-S** in kcal/mol, distance in Å and angle in degree.



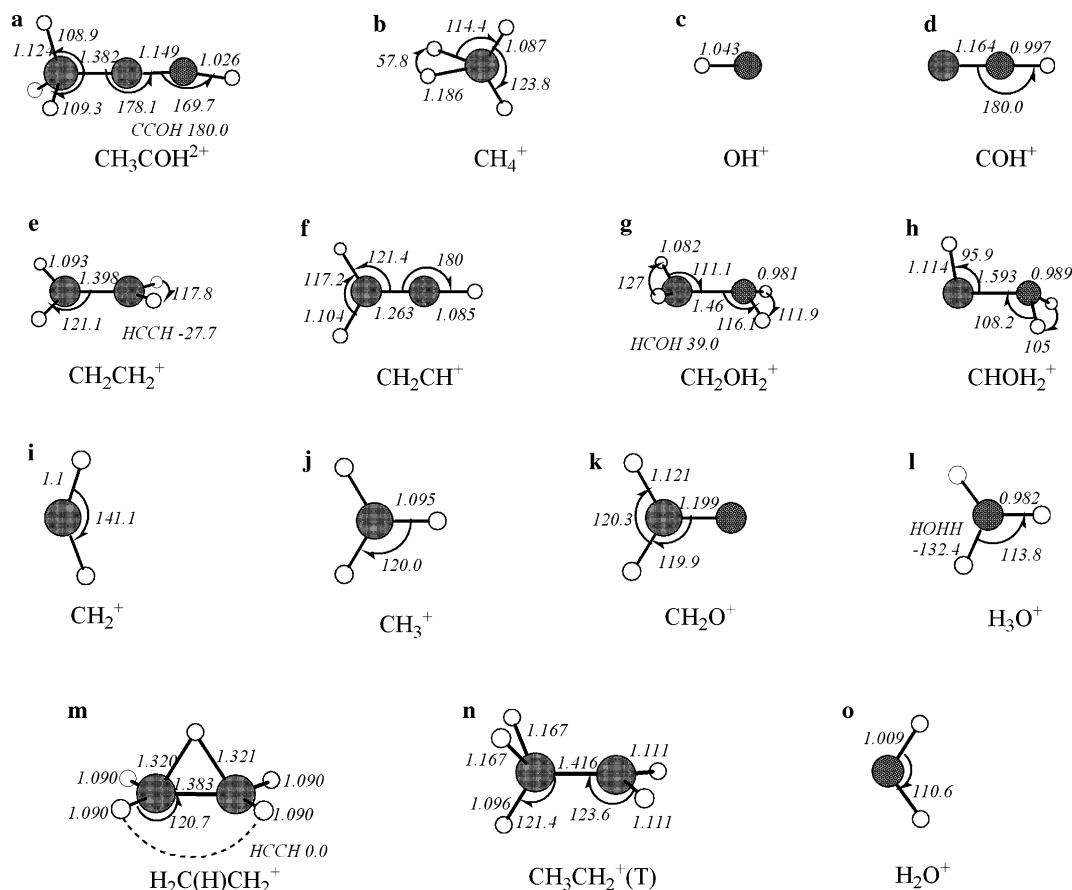


Fig. 6. The optimized structures of the fragmentation products, with distance in Å and angle in degree.

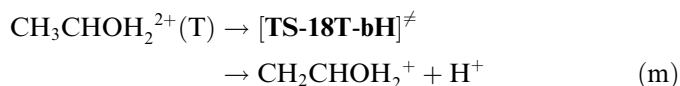
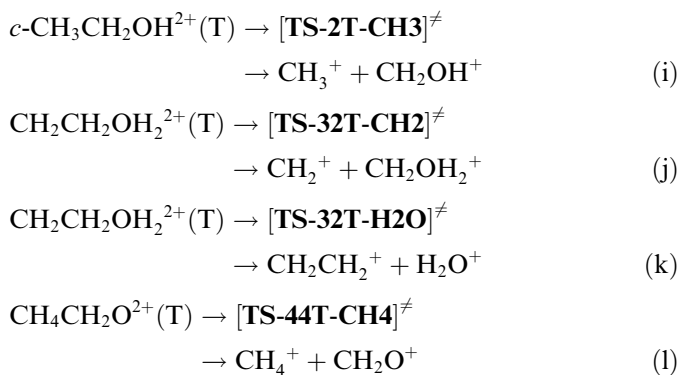
Table 1

The energy barriers of fragmentations of  $C_2H_6O^{2+}$  isomers in several energy calculated levels using 6-31+G(d) basis sets with ZPE correction, unit in kcal/mol

Eqs.	B3LYP <sup>a</sup>	MP2	MP3	MP4SDQ	CCSD	CCSD(T)	MP2 <sup>b</sup>
(a)	102.8	131.9	141.0	102.9	103.4	<u>-212.5</u>	132.6
(b)	42.9	54.4	56.4	53.4	53.1	51.0	54.6
(c)	192.1	250.5	236.7	227.6	196.9	<u>-4070.4</u>	253.7
(d)	76.1	96.5	109.4	84.4	89.1	<u>4.44</u>	100.3
(f)	65.4	66.0	60.0	58.8	57.7	60.0	69.7

<sup>a</sup> 6-31+G(d,p) basis sets.

<sup>b</sup> G3MP2Large basis sets.



For the above six reactions, the energy barriers are 31.6, 6.63, 8.11, 13.0, 10.2 and 11.2 kcal/mol, and the fragmentation energies are -79.3, -176.9, -68.8, -108.5, -113.3 and -57.9 kcal/mol, respectively.  $\text{CH}_3\text{CH}_2^+$  should be generated in triplet state through Reaction (h) although the energy released in singlet state is higher. It is because the structure of  $\text{CH}_3\text{CH}_2^+(\text{T})$ , as shown in Fig. 6(n), is similar to **TS-1T-OH**, but the structure of  $\text{CH}_3\text{CH}_2^+(\text{S})$  is quite different from **TS-1T-OH**, with a bridged H between two carbons, as shown in Fig. 6(m). The structures of the corresponding TSs and relative energies are presented in Fig. 5. The result indicates that all the reactions, except for the generation of  $\text{OH}^+$ , can take place rather easily from all the  $C_2H_6O^{2+}$  isomers in triplet state. Besides, in triplet state, there are no subsequent fragmentations which take place after migration or elimination reactions, as are found in singlet state.

## 7. An Overall comparison between the fragmentations and conversions of the $C_2H_6O^{2+}$ isomers in singlet and triplet states

Compared to the  $C_2H_6O^{2+}$  isomers in triplet state, the energy required to undergo further fragmentation reactions

Table 2

The energy barrier and reaction energy of the fragmentation of the C<sub>2</sub>H<sub>6</sub>O dications, with unit in kcal/mol

Fragmentations	$\Delta E_a$	$\Delta E$
<i>In singlet state</i>		
CH <sub>3</sub> CH <sub>2</sub> OH <sup>2+</sup> (S)( <b>d-1-S</b> ) → CH <sub>3</sub> COH <sup>2+</sup> + H <sub>2</sub>	—	−1.23
CH <sub>3</sub> CH <sub>2</sub> OH <sup>2+</sup> (S)( <b>d-1-S</b> ) → CH <sub>3</sub> COH <sup>+</sup> + H <sub>2</sub> <sup>+</sup>	—	−1.54
<i>c</i> -CH <sub>3</sub> CH <sub>2</sub> OH <sup>2+</sup> (S)( <b>d-2-S</b> ) → CH <sub>3</sub> COH <sup>2+</sup> + H <sub>2</sub>	—	−4.02
<i>c</i> -CH <sub>3</sub> CH <sub>2</sub> OH <sup>2+</sup> (S)( <b>d-1-S</b> ) → <i>c</i> -CH <sub>3</sub> COH <sup>+</sup> + H <sub>2</sub> <sup>+</sup>	—	−2.69
CH <sub>3</sub> COH <sup>2+</sup> → CH <sub>3</sub> <sup>+</sup> + COH <sup>+</sup>	22.3	−62.5
CH <sub>3</sub> COH <sup>2+</sup> → CH <sub>3</sub> C <sup>+</sup> + OH <sup>+</sup>	183.7	61.3
(a) CH <sub>2</sub> CH <sub>2</sub> OH <sub>2</sub> <sup>2+</sup> (S)( <b>d-32-S</b> ) → CH <sub>2</sub> <sup>+</sup> + CH <sub>2</sub> OH <sub>2</sub> <sup>+</sup>	104.1 <sup>a</sup>	17.7
(b) CH <sub>2</sub> CH <sub>2</sub> OH <sub>2</sub> <sup>2+</sup> (S)( <b>d-32-S</b> ) → H <sub>3</sub> O <sup>+</sup> + CHCH <sub>2</sub> <sup>+</sup>	51.2	−94.1
(c) CH <sub>4</sub> CHOH <sub>2</sub> <sup>2+</sup> (S)( <b>d-44-S</b> ) → OH <sup>+</sup> + H <sup>+</sup> + CHCH <sub>2</sub> <sup>+</sup>	200.1 <sup>a</sup>	54.4
→ OH + H <sub>2</sub> <sup>+</sup> + CHCH <sub>2</sub> <sup>+</sup>		113.0
(d) CH <sub>4</sub> CHOH <sub>2</sub> <sup>2+</sup> (S)( <b>d-44-S</b> ) → CH <sub>4</sub> <sup>+</sup> + CHOH <sup>+</sup>	92.9 <sup>a</sup>	−8.99
(e) CH <sub>4</sub> CHOH <sub>2</sub> <sup>2+</sup> (S)( <b>d-44-S</b> ) → CH <sub>3</sub> <sup>+</sup> + CH <sub>2</sub> OH <sup>+</sup>	30.8	−87.1
(f) CH <sub>3</sub> CHOH <sub>2</sub> <sup>2+</sup> (S)( <b>d-18-S</b> ) → CH <sub>3</sub> <sup>+</sup> + CHOH <sub>2</sub> <sup>+</sup>	63.7	1.41
(g) CH <sub>3</sub> CHOH <sub>2</sub> <sup>2+</sup> (S)( <b>d-18-S</b> ) → H <sup>+</sup> + CH <sub>2</sub> CHOH <sub>2</sub> <sup>+</sup>	31.7	23.7
<i>In triplet state</i>		
(h) CH <sub>3</sub> CH <sub>2</sub> OH <sup>2+</sup> (T)( <b>d-1-T</b> ) → OH <sup>+</sup> + CH <sub>3</sub> CH <sub>2</sub> <sup>+</sup> (T)	31.6	9.33
→ OH <sup>+</sup> + CH <sub>2</sub> (H)CH <sub>2</sub> <sup>+</sup> (S)		−79.3
(i) <i>c</i> -CH <sub>3</sub> CH <sub>2</sub> OH <sup>2+</sup> (T)( <b>d-2-T</b> ) → CH <sub>3</sub> <sup>+</sup> + CH <sub>2</sub> OH <sup>+</sup>	6.63	−176.9
(j) CH <sub>2</sub> CH <sub>2</sub> OH <sub>2</sub> <sup>2+</sup> (T)( <b>d-32-T</b> ) → CH <sub>2</sub> <sup>+</sup> + CH <sub>2</sub> OH <sub>2</sub> <sup>+</sup>	8.11	−68.8
(k) CH <sub>2</sub> CH <sub>2</sub> OH <sub>2</sub> <sup>2+</sup> (T)( <b>d-32-T</b> ) → H <sub>2</sub> O <sup>+</sup> + CH <sub>2</sub> CH <sub>2</sub> <sup>+</sup>	13.0	−108.5
(l) CH <sub>4</sub> CH <sub>2</sub> O <sup>2+</sup> (T)( <b>d-44-T</b> ) → CH <sub>4</sub> <sup>+</sup> + CH <sub>2</sub> O <sup>+</sup>	10.2	−113.3
(m) CH <sub>3</sub> CHOH <sub>2</sub> <sup>2+</sup> (T)( <b>d-18-T</b> ) → CH <sub>2</sub> CHOH <sub>2</sub> <sup>+</sup> + H <sup>+</sup>	11.2	−57.9

<sup>a</sup>  $E = ZPE + E(\text{CCSD}/6\text{-}31\text{+G(d)}) + E(\text{PMP2}/\text{G3MLarge}) - E(\text{PMP2}/6\text{-}31\text{+G(d)})$ .

is higher than those in singlet state, except for the H<sub>2</sub> elimination to generate CH<sub>3</sub>COH<sup>2+</sup> which can then serve as the precursor to generate [CH<sub>3</sub><sup>+</sup> + COH<sup>+</sup>] or other fragments. For example, the energy barriers for breaking the C–C bond to generate CH<sub>3</sub><sup>+</sup>, CH<sub>2</sub><sup>+</sup> and CH<sub>4</sub><sup>+</sup> from CH<sub>3</sub>CH<sub>2</sub>OH<sup>2+</sup>(T), CH<sub>2</sub>CH<sub>2</sub>OH<sub>2</sub><sup>2+</sup>(T) and CH<sub>4</sub>CH<sub>2</sub>O<sup>2+</sup>(T) are 6.63, 8.11 and 10.2 kcal/mol, respectively. However, those from the possible precursors of their counterparts in singlet state are 22.3, 104.1 and 92.9 kcal/mol, respectively. The energy required for the OH elimination in singlet and triplet states are 183.7 and 31.6 kcal/

mol, respectively. The energy barriers of H<sup>+</sup>-elimination from CH<sub>3</sub>CHOH<sub>2</sub><sup>2+</sup> in single and triplet states are 11.2 and 81.3 kcal/mol, respectively. To generate the same fragments, the C<sub>2</sub>H<sub>6</sub>O<sup>2+</sup> isomers in triplet state tend to undergo the fragmentation channels due to structural instability, while their counterparts in singlet state prefer to go through isomerization channels first. However, the internal energy of a dication is the determining factor in deciding the most probable channel. Therefore, we summarized the comparison between reactions in singlet and triplet states based on their energies related **d-1-S** as shown in

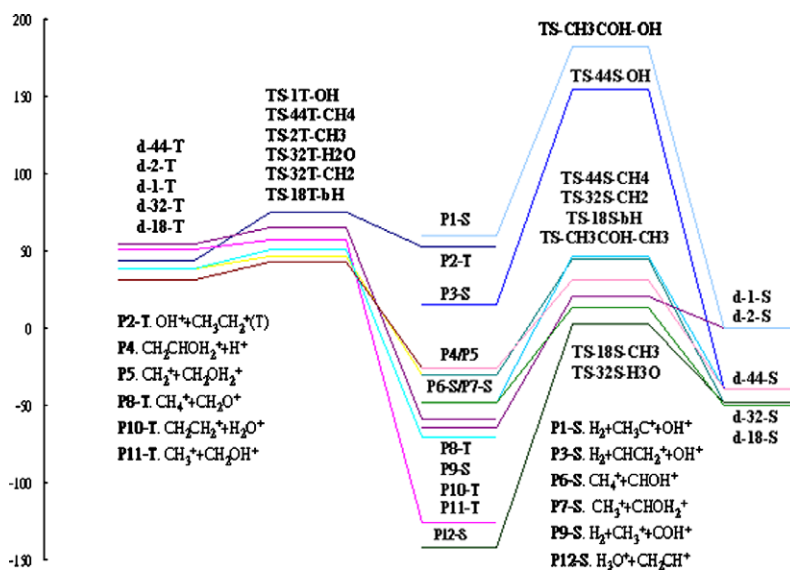


Fig. 7. The energy profile of fragmentations of the C<sub>2</sub>H<sub>6</sub>O dications, where the energy in kcal/mol is relative to **d-1-S**. The fragmentation reactions in triplet state are shown in the left-hand side and those in singlet state are listed in the right-hand side.



Fig. 7. Judged from the relative energies, the  $C_2H_6O$  dication in singlet state with low energy channels can generate  $CH_3COH^{2+}$ ,  $CH_4^+$ ,  $CHOH^+$ ,  $CH_3^+$ ,  $CHOH_2^+$ ,  $CH_2^+$ ,  $CH_2OH_2^+$ ,  $COH^+$ ,  $H^+$ ,  $CH_2CHOH_2^+$ ,  $CH_2CH^+$  and  $H_3O^+$ , while the  $OH^+$  and  $CH_3CH_2^+(T)$  fragments can be obtained easily from the fragmentation of those in triplet state. However,  $CH_2CH_2^+$ ,  $H_2O^+$ ,  $CH_2O^+$  and  $CH_2OH_2^+$  fragments can be obtained only through the fragmentation of the dication in triplet state. The conversions among the  $C_2H_6O^{2+}$  isomers in singlet state are easier than their fragmentations. Except for the  $CH_2^+$  and  $\beta$ -H eliminations, the conversions among the  $C_2H_6O^{2+}$  isomers in triplet state are easier than their fragmentations. Therefore, it is important to distinguish the fragmentations from the  $C_2H_6O^{2+}$  isomers in singlet or triplet states.

However, there are still some other possibilities which are not included in this study. First, fragmentations can take place other than the reactions considered above. Second, the sequential fragmentation reactions from the products of the above reactions can also contribute some other fragments not found in this study. Finally, the energetics of the dications found in this study can be quite different if the calculations were to be performed with an electric field because the electron distribution around the parent cation can be quite different with and without a laser field [18].

## 8. Conclusion

The fragmentation products generated from a  $C_2H_6O$  dication through the C–H, C–C and C–O bond cleavage are dependent on the electronic states of the reactant dications.  $CH_3COH^{2+}$ ,  $CH_4^+$ ,  $CHOH^+$ ,  $CH_3^+$ ,  $CHOH_2^+$ ,  $CH_2^+$ ,  $CH_2OH_2^+$ ,  $COH^+$ ,  $H^+$ ,  $CH_2CHOH_2^+$ ,  $CH_2CH^+$  and  $H_3O^+$  are generated probably from the  $C_2H_6O$  dications in singlet state, while  $OH^+$ ,  $CH_3CH_2^+(T)$ ,  $CH_2CH_2^+$ ,  $H_2O^+$ ,  $CH_2O^+$  and  $CH_2OH_2^+$  fragments can be obtained from the dications in triplet state. It is rather difficult for the  $C_2H_6O^{2+}$  isomers in singlet state to undergo fragmentation, except for the  $H_2$  elimination from  $CH_3CH_2OH^{2+}$  to generate  $CH_3COH^{2+}$ . However, fragmentation can take place rather easily from the  $C_2H_6O^{2+}$  isomers in triplet state.

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