Supplementary Information

Dissociation Path Competition of Radiolysis-Ionization induced Molecule Damage under Electron Beam Illumination

Zenghua Cai, Shiyou Chen and Lin-Wang Wang

1. Method of calculating τ_{ij}

The decoherence time τ_{ij} can be represented as:

$$\tau_{ij}(t_0) = \sqrt{\frac{2(kT)^2}{S_{ij}(t_0)}},$$
(S1)

in which, k is the Boltzmann constant. T is the temperature. $S_{ij}(t_0)$ can be calculated using the following formula:

$$S_{ij}(t_0) = \left\langle \left\| \frac{d}{dt}(E_i(t_0,t) - E_j(t_0,t)) \right\|^2 \right\rangle_t,$$
(S2)

$$E_i(t_0,t) = \langle \phi_i(t_0) | H(t) | \phi_i(t_0) \rangle.$$
(S3)

$\phi_i(t_0)$ is the wave function of the adiabatic state i at time t_0. H(t) is the Hamiltonian of the system at time t. $\langle X \rangle_t$ represents the average of variable X.

2. Definition of the Dissociation Time

For the dissociation channel $C_2H_6O_2^+ \rightarrow CH_3O^+ + CH_3O$, it needs to break down the C-C bond, *i.e.*, bond 1 in Fig. S1(a). In our rt-TDDFT simulation, we recorded the change of C-C bond length with the time, as shown in Fig. S1(c). If the bond length of the C-C bond exceeds the 1.3 times of its original bond length and will not fluctuate any more, then the time is defined as the dissociation time, *i.e.*, 154.5 fs for the dissociation of ionized $C_2H_6O_2^+$ as shown in Fig. S1(c). From Fig. S1(c), we can also see the process of the fluctuation before 154.5 fs. All the bond lengths of the ground state $C_2H_6O_2$ molecule are listed in Fig. S1(b) for reference.

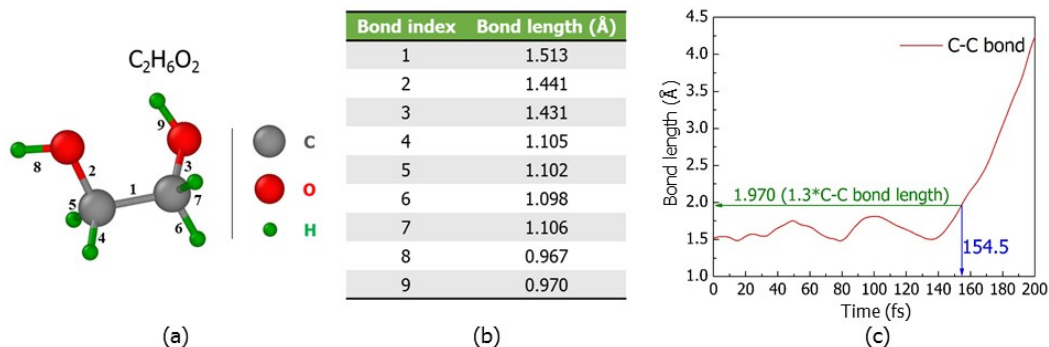| Bond index	Bond length (Å)
1	1.513
2	1.441
3	1.431
4	1.105
5	1.102
6	1.098
7	1.106
8	0.967
9	0.970

(a)　　　　　　(b)　　　　　　(c)

Fig. S1. (a) The ground state structure of $C_2H_6O_2$ molecule. All the bonds have been labeled using the Arabic numerals. (b) The bond length (Å) of each bond as labeled in

(a). (c) The change of the C-C bond length with the time in one specific rt-TDDFT simulation which ends up with the $C_2H_6O_2^+ \rightarrow CH_3O^+ + CH_3O$ dissociation.
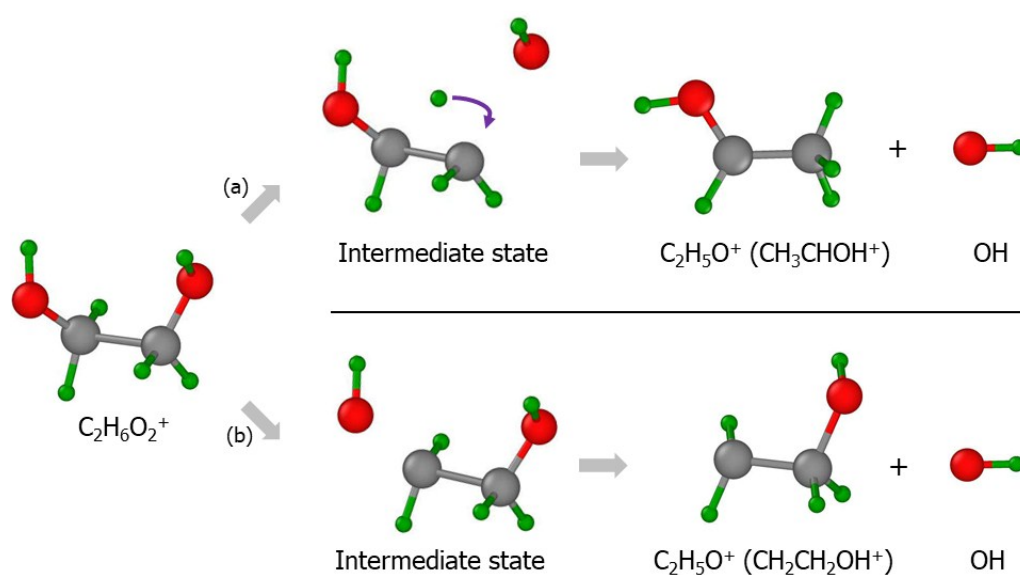

Fig. S2. (a) Pattern of dissociation of $C_2H_6O^+ \rightarrow CH_3CHOH^+ + OH$. (b) Pattern of dissociation of $C_2H_6O_2^+ \rightarrow CH_2CH_2OH^+ + OH$. Atomic labels are the same as those in Fig. S1(a).
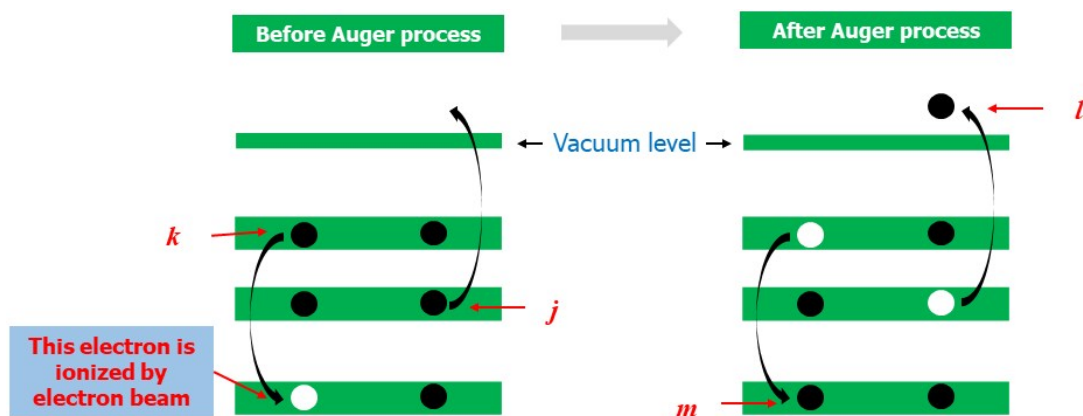

Fig. S3. The occupation of different electronic states before and after the Auger process.
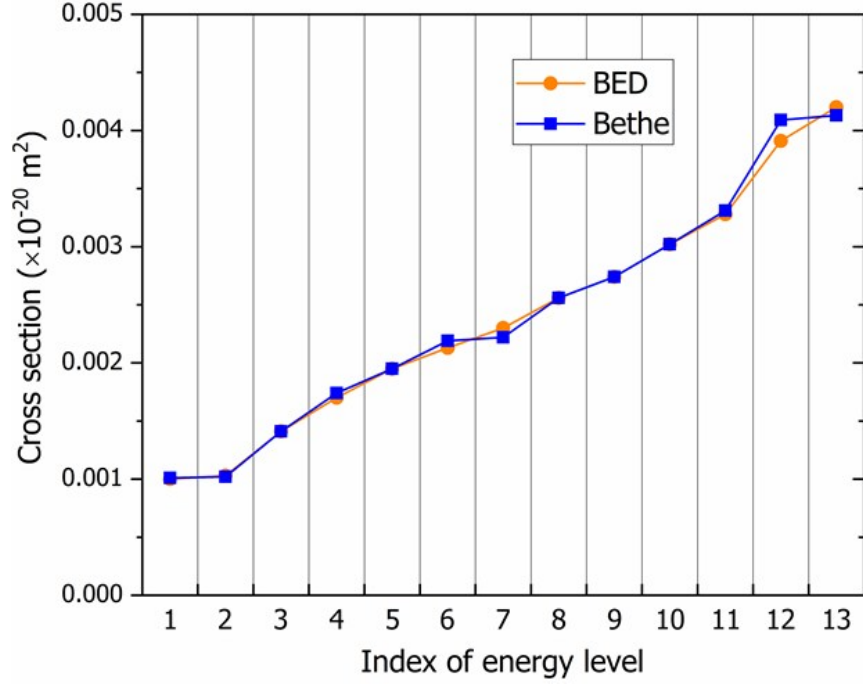
Fig. S4. The calculated ionization cross sections of all the 13 occupied levels of $C_2H_6O_2$ under the illumination of electron beams with 100 keV incident energies. The orange circle is calculated using BED model, while the blue square is calculated using Bethe model.

Table S1. All the possible Auger channels. For the Auger channel 13_3-9, 13, 3 and 9 represent the state k, m and j, respectively, as shown in Fig. S3.

Auger channel	Auger channel	Auger channel	Auger channel	Auger channel	Auger channel
13_3-9	13_2-3	11_2-7	9_2-10	7_2-8	5_2-11
12_3-9	13_2-6	11_2-8	9_2-12	7_2-9	4_2-9
11_3-9	13_2-7	11_2-11	9_2-13	7_2-11	4_2-11
11_3-13	13_2-9	11_2-12	8_2-8	7_2-13	4_2-13
9_3-11	13_2-11	11_2-13	8_2-10	6_2-8	3_2-13
9_3_12	13_2-10	9_2-5	8_2-11	6_2-9	5_1-12

9_3_13	12_2-9	9_2-6	8_2-12	6_2-11
8_3_13	12_2-12	9_2-7	7_2-5	6_2-13
7_3_12	11_2-4	9_2-8	7_2-7	5_2-7

Table S2．Total energies of all the fragments related to the single-ionization induced dissociation

Neutral fragment	Total energy (eV)	+1 charged fragment	Total energy (eV)
CH_5O	-667.384	$C_2H_6O_2^+$	-1263.908
CH_3O	-634.764	$C_2H_5O^+$	-815.607
CH_2O	-619.541	$C_2H_4O^+$	-797.931
CHO	-602.068	$C_2H_3O^+$	-782.829
CH_3	-201.465	CH_5O^+	-660.584
H_3O	-479.028	CH_3O^+	-627.147
H_2O	-465.822	CHO^+	-593.762
OH	-446.909	CH_3^+	-191.441
H	-13.586		