Reaction processes of negative secondary ions emitted from methanol microdroplets by fast heavy-ion irradiation

Y. Mizunami[1], T. Majima[1], T. Teramoto[2], H. Tsuchida[3], and M. Saito[3]
[1]Department of Nuclear Engineering, Kyoto University
[2]Institute for Radiation Sciences, Osaka University
[3]Quantum Science and Engineering Center, Kyoto University

We have performed a mass spectrometric study of negative secondary ions emitted from methanol microdroplets by MeV-energy heavy ion irradiation. We previously found that C_2HO^- and $C_2H_3O_2^-$ are produced by association reactions between negative fragment ions and neutral fragments. In this work, using *ab initio* calculations, we evaluated the barrier heights of these reactions. In addition, we studied the isomerization reaction pathway from CH_3OCO^- to CH_3COO^- after the association reaction between CH_3O^- and CO occurs.

1. Introduction

When MeV-energy heavy ions pass through aggregates such as liquids and biological materials, a large amount of energy (~ keV/nm) is locally deposited along the ion track. As a result, various violent molecular reactions are induced near the ion track. To investigate the complex reactions, we have performed a mass spectrometric study of secondary ions emitted from microdroplets prepared under a high vacuum chamber [1]. Recently, we have used methanol droplets as a model molecule for understanding the fundamental reaction processes. We identified various positive and negative secondary ions [2] and revealed some formation processes of negative product ions by comparing the results of CH_3OH and CH_3OD droplets [3]. We suggested that C_2HO^- is produced by the association reaction of CH^- and CO or that of C^- and HCO radical. In addition, we suggested that $C_2H_3O_2^-$ is generated by the reaction between CH_3O^- and CO. In this work, using *ab initio* calculations, we evaluate the barrier heights of these association reactions to confirm the validities of the reactions. Furthermore, the molecular structures of $C_2H_3O_2^-$ are investigated.

2. Quantum chemical calculations

To evaluate the reaction processes and the structures of the secondary ions predicted from our experiments, we performed *ab initio* calculations. All calculations are performed by Gaussian16 [4]. The molecular geometries were optimized, and the reaction pathways were analyzed by a configuration interaction (CISD) method with an augmented correlation-consistent polarized Valence-only Double-Zeta (aug-cc-pVDZ) basis set.

3. Results and Discussion

Figure 1 shows the calculation results that a distance between the O atom in CH_3O^- and the C atom in CO was changed step by step. The geometry was optimized at each step. It is suggested that this association reaction has no energy barrier. In the same way, Fig.2 shows the results of CH^-+CO and C^-+HCO. The energy of the system was calculated at each point depending on the C-C distance. It is suggested that these reactions also proceed without energy barriers.

$C_2H_3O_2^-$ have several isomers. The binding energy of CH_3OCO^- from CH_3O^- + CO was estimated to be about 0.53 eV, as shown in Fig.1. It is suspected that CH_3OCO^- is dissociated because of the small binding energy. Therefore, $C_2H_3O_2^-$ is possibly isomerized to a more stable structure. Using the *ab initio* calculations, we found the isomerization pathway from CH_3OCO^- to CH_3COO^- (see Fig.3). This has an energy barrier of about 2.47 eV. We considered that the isomerization might proceed because the fragments near the ion track can have excess energy enough to overcome this barrier.

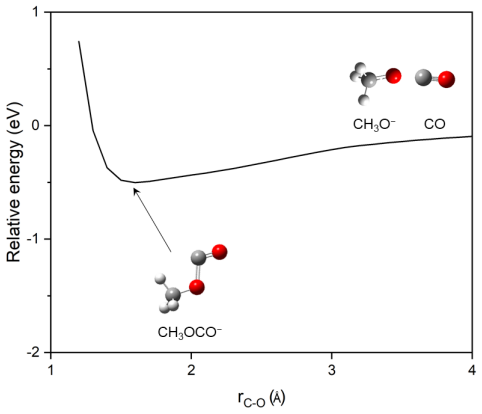

Fig.1 Calculated potential energy curves of $C_2H_3O_2^-$ by the association reactions of CH_3O^- and CO.

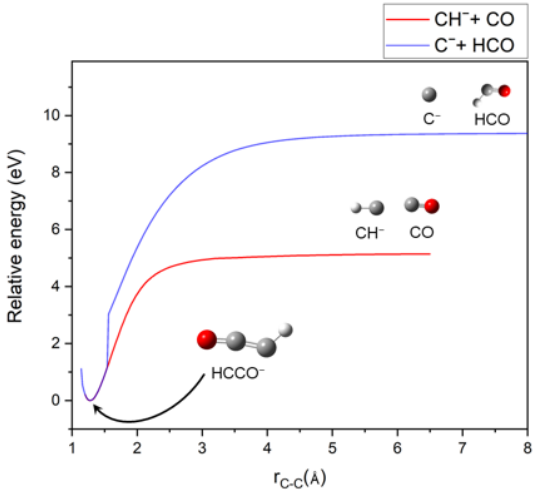

Fig.2 Calculated potential energy curves of C_2HO^- by the reactions of CH^- + CO (blue) and C^- + HCO (red).

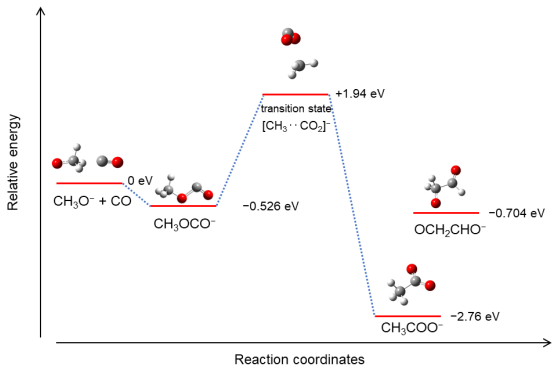

Fig.3 Calculated potential energy levels of $C_2H_3O_2^-$.

References

[1] T. Majima *et al.*, J. Chem. Phys. **153**, 224201 (2020).

[2] K. Kitajima *et al.,* NIM.B **424**, 10-16 (2018).

[3] Y. Mizunami *et al.,* QSEC sympo (2020).

[4] Gaussian 16, Revision C. 01, M. J. Frisch *et al.,* Gaussian Inc., Wallingford CT, (2016).