Mass spectrometric study of negative secondary ions emitted from ethanol microdroplet surfaces by fast heavy ions

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Synopsis We have performed a mass spectrometric study of negative secondary ions emitted from ethanol microdroplets in collisions of MeV-energy heavy ions to reveal complex ion species formed in the time scale of picoseconds. We observe various negative ions including deprotonated cluster ions, ethanol fragment ions and a trace amount of reaction-product ions. This is achieved with the aid of a new system using ultrasonic atomization with argon gas flowing for droplet formation. We discuss production processes of these negative secondary ions.

Study on reaction intermediates emitted from liquid surfaces by fast heavy ions provides us crucial insights on initial radiation reactions around the ion track in liquids. So far, a large number of studies using spectroscopic or chemical analysis have been performed to reveal physicochemical reactions of radical species as well as solvated electrons in water, alcohols and biological solutions [1]. However, it has been difficult to analyze most of the reaction intermediates with complex molecular structures. For mass-spectrometric analysis of complex product ions, we have previously developed an experimental setup to irradiate liquid-jet targets with a MeV-energy ion beam [2]. In addition, we developed another setup using microdroplets allowing us to perform ion-irradiation under a higher vacuum condition [3]. We reported time-of-flight mass spectra of positive secondary ions emitted from ethanol microdroplets by 2-MeV C^{2+}. In this work, we examine negative secondary ions with improved signal intensity by employing ultrasonic atomization with argon gas flowing for producing microdroplets. We discuss production processes of these negative ions.

The experiment was performed using a 2-MV tandem type Pelletron accelerator at the Quantum Science and Engineering Center, Kyoto University. Ethanol microdroplets produced by ultrasonic atomization in the atmosphere were transferred into a vacuum chamber through a differential pumping system and crossed with an ion beam of 4-MeV C^{3+} from the accelerator. The vacuum pressure in the collision chamber was kept around 10^{-4} Pa during the measurements. Negative ions emitted from droplet surfaces induced by collisions were analyzed by time-of-flight mass spectrometry.

We observed fragment ions generated via multiple desorption processes such as deprotonation ($C_2H_5O^-$), additional loss of hydrogen ($C_2H_3O^-$, C_2HO^-) and oxygen atoms (C_2H^-). A series of hydrocarbon ions such as $C_3H_m^-$ (m = 0–2) and $C_4H_m^-$ (m =0, 1) were also observed. They might be formed via reactions of C_2H^- with other neutral hydrocarbons [4]. In addition, deprotonated cluster ions $[(EtOH)_n–H]^-$ and ions formed by additional loss of CH_3 radicals $[(CH_2OH)(EtOH)_n–H]^-$ were observed up to n ~ 28 and 10, respectively. We also observed various trace amounts of ions possibly produced via additional reactions between radical species such as CH_2OH [5].

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References

[1] A. Mozumder 1999 *Academic Press, London, Fundamentals of Radiation Chemistry*
[2] M. Kaneda *et al.* 2010 *J. Chem. Phys.* **132** 144502
[3] T. Majima *et al.* 2015 *J. Phys. Conf. Ser.* **635** 012021
[4] S. Stoykov *et al.* 2001 *J. Phys. D: Appl. Phys.* **34** 2160
[5] G. R. Freeman, 1974 *NSRDS-NBS 48, Radiation Chemistry of Ethanol: A Review of Data on Yields, Reaction Rate Parameters, and Spectral Properties of Transients*

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