



Mass spectrometric study of the negative and positive secondary ions emitted from ethanol microdroplets by MeV-energy heavy ion impact

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ABSTRACT

We have investigated the negative and positive secondary ions emitted from ethanol droplets by 4.0-MeV C^{3+} impact to reveal the characteristic features of the reaction processes induced by fast heavy ions at the liquid ethanol surface. Analysis of the secondary ions was performed by time-of-flight mass spectrometry for microdroplet targets in a high vacuum environment. Fragment ions, deprotonated cluster ions, and trace amounts of the reaction product ions are observed in the negative secondary ions. The main fragment anions are $C_2H_mO^-$ ($m = 1, 3, \text{ and } 5$) and C_2H^- generated by loss of hydrogen and oxygen atoms. The reaction product anions include deprotonated glycols, larger alcohols, and their dehydrated and dehydrogenated forms generated by secondary reactions between fragments and radicals. Furthermore, $C_3H_m^-$ ($m = 0-2$) and $C_4H_m^-$ ($m = 0 \text{ and } 1$) are observed, which could be produced through a plasma state generated in the heavy ion track. Deprotonated ethanol cluster ions, $[(EtOH)_n - H]^-$, are observed up to about $n = 25$. $[(EtOH)_n - H]^-$ have smaller kinetic energies than the protonated cluster ions $(EtOH)_nH^+$. This probably represents the effect of the positive Coulomb potential transiently formed in the ion track. We also discuss the size distributions and structures of the water- and CH_2OH -radical-attached ethanol cluster ions.

1. Introduction

Understanding the physicochemical reactions induced by fast heavy ions in liquids is important to better understand the underlying mechanism of biological radiation damage [1–3]. When a fast heavy ion passes through a liquid material, a large amount of energy is locally deposited along its trajectory at the nanoscale in a very short time. The reactions induced by fast heavy ions are drastically different from those induced by lower linear energy transfer radiation, such as electrons and X-rays. Various reaction pathways of the constituent molecules might be opened because of their highly excited and ionized states induced by heavy ion collisions, including multifragmentation and Coulomb explosion. Under these conditions, a large variety of fragments and radicals are generated as intermediate species. Because they are produced at high density, secondary reactions between these products will be enhanced. Furthermore, some of the fragmentation and secondary reactions might occur in the nanoplasma state transiently produced in the heavy ion track owing to localization of a large amount of deposited energy [4–7]. These reactions could generate unique product species

that are specific to fast heavy ion collisions. To understand the physicochemical reactions in detail, identification of the intermediate species is essential.

Methodologies using spectroscopic and chemical analysis [8,9] have been established by longtime research of radiation chemistry. However, it is difficult to identify the wide variety of complicated intermediate species produced by heavy ion irradiation using these methods. Mass spectrometry is another powerful method that allows systematic analysis of ionic products, including the unusual and unexpected complicated species that are difficult to identify by spectroscopic or chemical analysis. Information about ionic species is important because they play an important role in the damage and relaxation processes of biomolecules in liquids [10,11]. Furthermore, because secondary ions are ejected in the sub-nanosecond timescale after fast ion irradiation [12], information about the transient intermediate species generated in the corresponding timescale can be obtained. However, mass spectrometry is usually only applicable for gas-phase targets or solid surfaces because a high vacuum is required in the measurements. It is challenging to perform mass spectrometry of volatile liquid targets because of the high

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vapor pressures. By fast atom bombardment under low temperature conditions, secondary ion mass spectrometry (SIMS) of liquid-phase targets has been performed by measuring frozen targets when they were melting in vacuum [13–15]. To directly apply mass spectrometry to liquid targets, we used a liquid-jet technique to produce targets for MeV-energy ion beams [16–20]. The secondary ions emitted from liquid jets of water [16], ethanol [17], and aqueous solutions of some molecules [18,19] were analyzed by time-of-flight (TOF) mass spectrometry.

Recently, we developed an experimental setup using liquid microdroplets as new targets for fast heavy ions to perform mass spectrometry at lower gas pressure [21]. We adapted a technique using spontaneous Rayleigh breakup of a liquid jet [22,23] to obtain a continuous dense droplet beam that was suitable for irradiation of a continuous or high-frequency pulsed ion beam extracted from an electrostatic accelerator. We performed the first SIMS measurements of the positive secondary ions emitted from ethanol droplets.

In this work, we extended the abovementioned method to observe the negative secondary ions emitted from ethanol droplets by 4.0-MeV C^{3+} impact. Measurements of negative ions have the advantage of detecting trace amounts of secondary ions because of less disturbance from product ions originating from the background gases and vapors, which conceal this information in the measurements of positive ions. The product ion species and their TOF peak profiles were analyzed to reveal the characteristic features of the reaction processes after penetration of a fast heavy ion at the liquid ethanol surface. Positive secondary ions were also measured under the same conditions. By comparing the emission rates and kinetic energies of the protonated and deprotonated cluster ions, their production and emission mechanisms are discussed. Note that in the present experiment, the droplet formation system used in our previous study [20] was replaced by a new system using ultrasonic atomization, which reduces the fluctuations of the target density and improves the sensitivity.

2. Experimental method

The experiment was performed using a 2 MV tandem-type Pelletron accelerator at the Quantum Science and Engineering Center of Kyoto University. A schematic of the experimental setup is shown in our previous report [21], except for the part to produce ethanol droplets that was changed in the present study. A schematic of the new apparatus for producing and transporting ethanol droplets is shown in Fig. 1. The ethanol droplets were generated by ultrasonic atomization of pure ethanol liquid (> 99.5 vol%, Wako Pure Chemical Industries, Ltd., Osaka, Japan) using an ultrasonic oscillator (NB59S-DP, Seiko Giken

Inc., Nagano, Japan) at the frequency of 1.6 MHz in a glass container (KF Cross NW 40, EVAC Glass). The container was filled with argon gas to a pressure of 1 atm and maintained at this pressure by continuous gas flow. The droplets were injected into the vacuum chamber together with the argon gas through a 200- μ m inlet hole. The argon gas acts as a carrier gas to guide transport of the droplets in the aerodynamic lens [24]. The aerodynamic lens consists of four apertures with diameters of 3.0, 3.0, 2.5, and 2.5 mm. The droplets then travelled through the differential pumping stage divided by a 2-mm skimmer and a 2-mm aperture before entering the collision chamber. Downstream of the collision chamber, the droplets were captured by a liquid nitrogen cold trap. The droplet temperature in the collision chamber was estimated to be about 190–220 K using the model proposed by Smith et al. [25], which considers the temperature decrease caused by evaporative cooling. In this estimation, the flight time of the droplets in vacuum was assumed to be 10–20 ms based on simulation of the transmission of the droplets through the aerodynamic lens [24]. The estimated temperature is sufficiently higher than the freezing point of ethanol (\sim 160 K). The vacuum pressure in the collision chamber was maintained at around 1×10^{-4} Pa during the measurements. The base pressure when the valve between the inlet hole and the aerodynamic lens was closed was about 2×10^{-6} Pa. The present system provides more stable droplet beam flow and the fluctuations of the target density are smaller for a longer time than the previous method using breakup of a liquid jet ejected from a glass capillary, which is sensitive to the displacement of the capillary from the center axis of the 200- μ m inlet hole [21]. In the present experiment, argon gas was used as the carrier gas rather than atmospheric air used in the previous experiment [21] to reduce the analytical complexity of the mass spectrum, in which product ions originating from the carrier gas are strongly involved.

A 4.0-MeV C^{3+} ion beam was collimated to about $2 \text{ mm} \times 2 \text{ mm}$ by two sets of four-jaw slits and chopped by an electrostatic deflector to about 30 ns width at repetition rates ranging from 1 to 40 kHz. The secondary ions ejected from the droplet surfaces were analyzed by TOF mass spectrometry. The negative and positive secondary ions were measured by reversing the polarity of the electric field in the spectrometer. A pulse signal synchronized by beam chopping was used for the start trigger of the TOF measurements. During the measurements, the incident ion-beam current was monitored by a Faraday cup downstream of the beam line. The current was integrated by a digital current integrator (ORTEC model 439) in each measurement. The intensities of the TOF spectrum were normalized by the integrated beam current.

The droplet size in the collision region was evaluated by measuring the energy spectrum of forward-scattered ions with a semiconductor detector at a scattering angle of about 34 mrad, as demonstrated in our

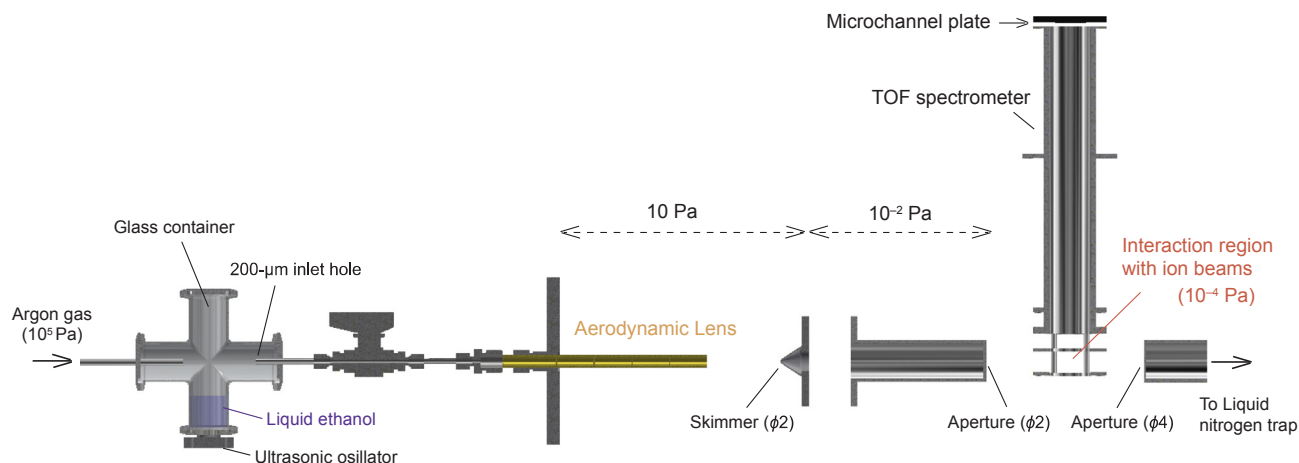


Fig. 1. Schematic diagram of the experimental setup to produce ethanol microdroplets by the ultrasonic atomization technique combined with argon gas flow. The droplets are transported into a collision chamber through an aerodynamic lens and a differential pumping system.

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