Near-infrared femtosecond laser ionization of the acetic acid dimer

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Fragment ions produced after the ionization of the acetic acid dimer $(CH_3COOH)_2$ in a near-infrared intense femtosecond laser field were measured using time-of-flight mass spectrometry. The two-body Coulomb explosion (CE) process $(CH_3COOH)_2^{2+} \rightarrow 2CH_3COOH^+$ with a kinetic energy release of 3.4 eV, similar to the case of $(HCOOH)_2^{2+}$ (Hoshina et al., 2012), was identified. The two-body CE of $(CH_3COOH)_2^{2+}$ was induced when the laser polarization direction was perpendicular to the C···C intermolecular axis in contrast to the case of $(HCOOH)_2^{2+}$. The preferential configurations may be those that deform dimer structures close to dimer dications during the double-ionization process.

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1. Introduction

Photoionization using non-resonant femtosecond laser pulses enables the production of multiply charged molecular ions without intensive fragmentation [1–3]. This is in contrast to photoionization by irradiation with long-pulsed lasers, where intensive fragmentation occurs in singly charged molecular ions through the ladder-switching process [4], rather than further ionization to form multiply charged molecular ions. In this decade, rearrangement and fragmentation dynamics within intact dications is an interesting target of femtosecond laser ionization, and it has been demonstrated that fast intramolecular hydrogen rearrangement precedes dissociation in small-sized organic molecular dications. This fast rearrangement results in the opening of a variety of fragmentation pathways of organic molecules. Two-body Coulomb explosion (CE) processes of skeletal structures after such fast hydrogen migration processes have been securely identified for doubly ionized acetonitrile [5], methanol [6,7], ethane [8,9], and allene [10] by femtosecond laser pulses through ion correlation detection. The branching of dissociation pathways in methanol dication $CH_3OH^{2+} \rightarrow CH_{(4-n)}^+ + OH_n^+$ ($n = 1,2,3$) [6,7] is a simple example of the CE pathways that are preceded by the fast hydrogen transfer. The timescale of the hydrogen transfer was estimated to be shorter than 60 fs [11], which is within the femtosecond laser pulse duration. The formation of triatomic hydrogen molecular ion H_3^+ was similarly found to be caused by the metastable decomposition

of a long-lived dication whose dissociation time is sufficiently long for hydrogen scrambling [8,9,12]. Theoretical works have also supported the characteristic intramolecular hydrogen dynamics before the decomposition of organic molecules [13,14], in which isomerization barriers are lower than those connected with the dissociation path.

Recently, we applied femtosecond laser ionization to hydrogen-bonded complexes of hydrocarbon molecules and investigated if the complexes can be multiply ionized while maintaining their forms as dimers, trimers, and so on, and then be dissociated by any new pathways [15,16]. In the case of ethanol complexes, the enhancement of multiple ionization followed by the explosive production of multiply charged atomic fragment ions was observed when trimers or larger complexes were formed [15]. Conversely, molecular fragment ions ejected by the CE process were minimally observed, suggesting high internal energy deposition through the heating of complexes.

In contrast, in the case of the formic acid dimer, which is a cyclic dimer with two hydrogen bonds, the two-body CE pathway $(HCOOH)_2^{2+} \rightarrow 2HCOOH^+$ was identified; i.e., the dimer was doubly ionized and dissociated into two monomer ions by a CE [16]. In a quantum chemical calculation of $(HCOOH)_2^{2+}$, a metastable dissociation pathway was found with a kinetic energy release (E_{KER}) of 3.4 eV, which showed a good agreement with the observed value of 3.6 eV. Interestingly, the structure of the metastable state of $(HCOOH)_2^{2+}$ requires a large change from the neutral state; the two monomers rotate 47° in the same direction so that the carbonyl oxygen atoms move close to each other. This suggests that a structural change along the vibrational mode assigned as in-plane bending in conrotatory rotation [17] may be induced during

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double ionization by intense laser fields so as to approach the dication structure and follow the potential energy surface of the two-body CE pathway.

In this study, we investigate the multiple ionization of an acetic acid dimer, which is of the same series of carboxylic acid dimers as the formic acid dimer—with a double-hydrogen bond (the binding energy is 0.58 ± 0.07 eV [18], see Figure 1(a))—by near-infrared (NIR) femtosecond laser ionization and time-of-flight (TOF) mass spectroscopic detection. It has been reported that a stable state of the acetic acid dimer cation is similar in structure to the formic acid cation and dication, where each monomer rotates in the same direction; however, in vertical ionization by vacuum ultraviolet (VUV) radiation, it has been suggested that a structural change in this stable state is unlikely due to the fast intermolecular proton transfer [19]. In the acetic acid system, we focus on whether the two-body CE process $(CH_3COOH)_2^{2+} \rightarrow 2CH_3COOH^+$ occurs when ionized by NIR femtosecond laser pulses. Quantum chemical calculations are also performed to support the identification of the signal, and the requirements to induce the two-body CE process are discussed.

2. Experimental

Output pulses (800 nm, ~100 fs, 10 Hz, <1 mJ/pulse) of a Ti:Sapphire regenerative amplifying laser system (B.M. Industries, α-10) were focused on a molecular beam in a linear-type TOF mass spectrometer. The magnitude of the laser field at the focal point (60 μm diameter measured by a CCD camera with an objective lens) was estimated to be $\sim 1 \times 10^{14}$ W/cm² when the laser energy was 0.3 mJ/pulse. The ions produced by laser irradiation were extracted and accelerated for detection by a microchannel plate (MCP) detector attached to the end of a 100-cm-long flight tube. Static electric fields for the extraction and acceleration regions were typically adjusted to 125 and 1125 V/cm, respectively, to realize the Wiley–McLaren principle for ion convergence [20]. The ion signal was A/D converted and accumulated, typically for 2500 shots, by a digital oscilloscope with a sampling rate of 5 GS/s. The accuracy of our TOF spectra was estimated to be ± 0.03 m/z.

Vapors of CH_3COOH (Kanto Kagaku Co. >99.7%) were used as gaseous samples. The vapor at room temperature and the vapors seeded with He were introduced into the TOF tube by a pulsed valve (Parker Hannifin Ser. 9), which was synchronized with the laser pulses. The base pressure in the TOF tube was lower than 2×10^{-6} Pa, and the pressure when sample gas was introduced into the 50-kPa He seed gas was as high as 1×10^{-4} Pa. The laser beam power was adjusted using a combination of a polarizer and a half-wave plate. The polarization direction at the focal spot was adjusted using another half-wave plate.

3. Quantum chemical calculation

Quantum chemical calculations for the optimized structures and the electronic energy for the acetic acid dimer dication $(CH_3COOH)_2^{2+}$ were performed using the Gaussian 09 program [21]. Structural optimization and vibrational analysis were performed at the MP2/6-311+G(2d,p) level of theory, and single-point energies were calculated using the QCISD(T)/6-311+G(2df,2p) method. Zero-point energy corrections were performed using the harmonic frequencies calculated at the MP2/6-311+G(2d,p) level without a scaling factor. After surveying the stationary and transition points, the obtained structure of the transition state was confirmed to connect the metastable dication and the two separated monomer cations through the intrinsic reaction coordinate method [22]. The counterpoise method was used to account for the basis set superposition error (BSSE)[23] for dimer structures.

Table 1
Calculated energies (eV) of metastable and transition states for $(HCOOH)_2^{2+}$ and $(CH_3COOH)_2^{2+}$ and experimentally determined total kinetic energy release (eV) for CE pathways $(HCOOH)_2^{2+} \rightarrow 2HCOOH^+$ and $(CH_3COOH)_2^{2+} \rightarrow 2CH_3COOH^+$.

	Metastable[a]	Transition state[a]	E_{KER} (ΔE_{KER})[b]
$(HCOOH)_2^{2+c}$	2.69	3.40	3.6 (1.0)
$(CH_3COOH)_2^{2+}$	2.28	3.04	3.2 (0.8)

[a] Calculated at the QCISD(T)/6-311+G(2df,2p)//MP2/6-311+G(2d,p) level of theory including the BSSE correction. Zero-point energies are corrected using vibrational frequencies calculated at the MP2/6-311+G(2d,p) level of theory.
[b] Values of E_{KER} were determined from the analysis of TOF spectra, and those of ΔE_{KER} were derived as the full width at half maximum.
[c] Values for $(HCOOH)_2^{2+}$ are taken from Ref. [16].

Figure 1(b) shows the metastable structure of $(CH_3COOH)_2^{2+}$ optimized at the MP2/6-311+G(2d,p) level. In contrast to the neutral dimer shown in Figure 1(a), which has a cyclic structure through double hydrogen bonds, in the dication dimer, the two acetic acid molecules rotate in the same direction so that the carbonyl oxygen atoms approach each other, and the dication no longer forms hydrogen bonds. Alternatively, an attraction force between the two acetic acid ions in the dimer dication is caused by a weak O—O bond with a length of 1.478 Å, as shown in Figure 1(b), similar to that of the O—O covalent bond in hydrogen peroxide, 1.475 Å [24], and that of $(HCOOH)_2^{2+}$, 1.464 Å [16]. This stabilization through an O—O bond is caused by ejecting one electron from each acetic acid to form two acetic acid cations, each with an unpaired electron localized on the carbonyl oxygen. The metastable structure is found to dissociate into two monomer cations via a transition state, whose structure is shown in Figure 1(c).

The calculated energies of $(CH_3COOH)_2^{2+}$ are summarized in Table 1 and compared with those of $(HCOOH)_2^{2+}$. The energies relative to the dissociation limit calculated using the QCISD(T)/6-311+G(2df,2p)//MP2/6-311+G(2d,p) level are 2.28 and 3.04 eV for the metastable and transition states, respectively. These values are smaller than those of $(HCOOH)_2^{2+}$, which are 2.69 and 3.40 eV, respectively. The stability of these dimer dications are determined as a result of the compromise between the Coulombic repulsion force and the intermolecular O···O attraction force that forms a covalent bond. Indeed, the mean charge distance 4.69 Å for $(CH_3COOH)_2^{2+}$ obtained from the calculation is larger than that of $(HCOOH)_2^{2+}$ 4.14 Å, resulting in smaller internal energy for $(CH_3COOH)_2^{2+}$ caused by Coulombic repulsion.

4. Results and discussion

4.1. Overview of observed TOF spectra

Figure 2 shows the TOF spectra measured by changing the stagnation pressure from 5 kPa, corresponding to the vapor pressure of acetic acid, to 50 kPa seeded by He, while the femtosecond laser energy was fixed at 0.3 mJ/pulse, resulting in 1×10^{14} W/cm² at the focal point. The spectra shown by the red and blue lines are those measured when the laser polarization direction (ε_L) is parallel and perpendicular to the TOF axis (z_{TOF}), respectively.

We first analyzed fragmentation of monomers in Figure 2(a) to discriminate that of dimer in Figure 2(b)–(d). In the TOF spectra measured without He seed gas, shown in Figure 2(a), the parent molecular ion signal, CH_3COOH^+, at $m/z = 60$ is observed as a dominant peak. Fragment signals that can be clearly identified in the spectrum are CH_3^+ at $m/z = 15$, CH_3CO^+ at $m/z = 43$, and $COOH^+$ at $m/z = 45$, all of which are produced through simple dissociative ionization processes through CH_3COOH^+, i.e., CH_3—COOH or $CH_3C(O)$—OH bond breakings as reported in the VUV experiment [25]. The signals of $COOH^+$, CH_3^+, and CH_2^+ have miniscule side peaks at both sides of their central peaks when $\varepsilon_L || z_{TOF}$,