Dissociative double ionization of formic acid in intense laser fields

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ABSTRACT

We have investigated dissociative double ionization of formic acid by intense 100 fs laser pulses at 800 nm, using ion–ion coincidence momentum spectroscopy. Neither changing the laser power nor switching the laser polarization from linear to circular affected energy distributions of the ion pair. This observation is interpreted as implying the occurrence of sequential enhanced ionization.

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1. Introduction

The advancement of ultrafast laser technology in last three decades enables us to obtain intense ultrafast laser pulses that can be used to multiply ionize molecules. After the ionization, the multiply ionized molecule suddenly dissociates due to Coulombic repulsive forces between the positively charged constituents in the molecule, producing multiply fragmented ions [1]. The multiple ionization and subsequent Coulomb explosion (CE) of molecules attracted much interest partly because the multiply charged molecular ion dissociates so quickly that the geometry of the ion just before the explosion may be determined from the observation of momentum correlations among the fragment ions in coincidence measurements [2–4]. Double ionization of a small molecule is the simplest form of multiple ionization and most double ionization can be understood by assuming that the electrons are removed sequentially, where there is first a quick ejection of one electron and then the resulting singly charged molecular ion can still interact with the optical field during the pulse duration [5]. The CE of certain molecules has been found to occur when the fragment are separated by a critical distance R_c, which is much larger than a equilibrium separation R_e in the neutral molecule. This phenomenon is explained by the well known enhanced ionization (EI) or Charge-Resonance Enhanced Ionization (CREI) [6–8]. However, below the laser saturation intensity for the single ionization, rare gas atoms and several small molecules showed evidence for non-sequential double ionization [9,10]. Double ionization yields were measured as a function of laser intensities and showed significant enhancement above the yields calculated using the Ammosov–Delone–Krainov (ADK) tunneling model [11], when linearly polarized laser pulses were used. The ADK model is based on the single active electron approximation and it does not include electron–electron

correlations which is the significant feature in non-sequential double ionization [12]. At present, the electron rescattering model is often used to explain these non-sequential double ionizations, where a fraction of the ejected electrons in strong laser fields are driven back by the oscillating electric fields of the laser pulse to collide with their parent ions [13]. Since the rescattering is impossible when the circularly polarized laser pulses are used as the ionization radiation, the measurement of polarization effect on the double ionization is a useful tool in the identification of the non-sequential double ionization [14]. The simplest carboxylic acid, with well known photodissociation channels, formic acid is a good target for researching the dissociative double ionization dynamics of organic molecules, since it is easy to be doubly ionized and then decomposed into ion pairs at relatively lower laser intensity near the onset of the double ionization, as indicated later. Furthermore it has larger ionization energy (11.3 eV) as an organic molecule, and then higher electron collision energy is expected at the time of re-collisions.

In this Letter, we report the energy distribution of ion pairs produced by two-body Coulomb explosions of doubly charged formic acid ions. In the measurements, formic acid is doubly ionized in an intense laser field with linearly and circularly polarized infrared laser pulses at low laser intensity, below the saturation for single ionization. The observed energy distribution leads to the conclusion that process leading to the ion pairs is sequential enhanced double ionization.

2. Experiment

Our experiments were carried out using 800 nm 100 fs laser pulses from a Ti:sapphire laser system with intensities ranging from 60 to 240 TW/cm². The polarization of the laser pulse is originally linearly polarized but can then be transferred to the circular polarized light using a $\lambda/4$ waveplate. The laser beam was focused by an $f = 60$ mm lens to ionize the sample gas. Formic acid vapor was effusively introduced into the chamber where the working

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pressure 6.0×10^{-10} mbar was maintained (base pressure 2.0×10^{-10} mbar) thus insuring that on average less than one molecule is ionized per laser shot. All ions were detected using an ion velocity imaging time-of-flight (TOF) spectrometer. The details of the spectrometer are described elsewhere [15]. Briefly this spectrometer is equipped with a position sensitive detector with multi-hit capability and allows us to extract the 3D momentum of individual ions based on the measured hit position and TOF of each ion. The TOF data are recorded by multichannel, multi-hit, time-to-digital converters. The start time for the TOF is obtained from a fast photodiode responding to the laser pulse and the stop signal is from the electronic pulse generated by a multichannel plate (MCP) detector. Photo-ion photo-ion coincidence (PIPICO) signals from the Coulomb explosion can be extracted by discriminating random coincidence contributions using momentum conservation conditions, because only energetic fragment ions are produced in the process.
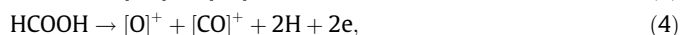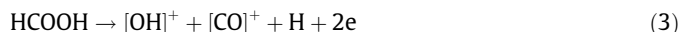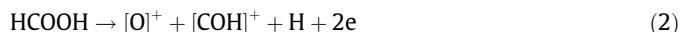
To estimate the peak laser field intensity, we measured the ratio of Xe^{++}/Xe^{+} using the ion TOF spectrometer, and compared the measured ratios to the values obtained by Talebpour et al. [16] for several different intensities below 100 TW/cm², where Xe^{++} is produced by the non-sequential double ionization. For higher values, the peak intensities are obtained by extrapolation and by assuming a linear relationship between the peak values and the power measured by the power meter.

3. Results and discussion

Fig. 1 shows the TOF mass spectrum of HCOOH irradiated by intense 800 nm laser pulses with linearly polarized laser light at 90 TW/cm², which is almost equal to the saturation intensity for the single ionization estimated from the atomic ADK theory [11]. However, organic molecules show much higher saturation intensities than those estimated by the atomic ADK model [17] and we believe that the present laser intensity (90 TW/cm²) is lower than the saturation intensity for single ionization. As described later, this laser intensity is just above the onset of the double ionization in our experimental condition, and it means that, if the rescattering plays a significant role in the double ionization, the contribution from the rescattering must be observed experimentally at this laser intensity. Parent ions and fragments obtained by the loss of one H atom are dominant. Additionally, some ion fragments including COH^{+}, CO^{+}, OH^{+}, and O^{+} are clearly observed. Here, we mainly focus on the ion pair fragmentations coming from the two-body dissociative ionization of $HCOOH^{2+}$ as indicated in the insert panels of Fig. 1. We have observed energetic ion fragments COH^{+}, OH^{+}, CO^{+} and O^{+} produced via the CE of the doubly charged parent species.

We also found that, with an increase in the laser intensity, the ion counts for O^{+} and CO^{+} in the mass spectra increased more strongly with intensity than did those for OH^{+} and COH^{+}.

The coincidence maps of the TOF of fragment ions are shown in Fig. 2 at the laser peak intensity of 90 TW/cm² and at a much higher laser intensity (240 TW/cm²). These maps indicate that doubly charged formic acid ions decompose into COH^{+}–OH^{+}, COH^{+}–O^{+}, CO^{+}–OH^{+}, and CO^{+}–O^{+} ion pairs. We also observed the $H_2O^{+} + CO^{+}$ ion pair coming from the hydrogen migration [18]. But we did not focus on it in this Letter because its yield is too low. We can infer that the four main channels are

$$HCOOH \rightarrow [OH]^{+} + [COH]^{+} + 2e \tag{1}$$

$$HCOOH \rightarrow [O]^{+} + [COH]^{+} + H + 2e \tag{2}$$

$$HCOOH \rightarrow [OH]^{+} + [CO]^{+} + H + 2e \tag{3}$$

$$HCOOH \rightarrow [O]^{+} + [CO]^{+} + 2H + 2e, \tag{4}$$

where neutral H atoms are produced in (2)–(4). However, coincidence patterns for the two-body dissociations are visible for the COH^{+}–O^{+}, CO^{+}–OH^{+}, and CO^{+}–O^{+} ion pairs in Fig. 2. This means that the momentum obtained by the H atoms are negligible compared with those for fragment ions. The ion pair counts from different channels were extracted from the PIPICO spectra by imposing the momentum conservation condition. The ratio of each ion pair count and the total parent count is shown in Fig. 3 at several different laser intensities. Since the single ionized parent ion ($HCOOH^{+}$) is the dominant species in the mass spectra, we use it to provide the reference counts to calculate the fragmentation yields for different Coulomb explosion channels. At low intensity (lower than 60 TW/cm²), all the ion pair yields were close to zero indicating that the probability of the double ionization is almost zero in this low intensity region. The calculated double ionization threshold using atomic ADK theory [11] also agrees with this experimental result. For the range of 60–240 TW/cm², the contribution of the double ionization increases as a function of peak laser intensity. From Fig. 3 we also see that the channel (1) is always the dominant process and its ion yield increases rapidly. Channel (4) is the weakest process compared to the others at low intensity. But with an increase in laser intensity, the contribution of the channel (4) relative to other channels increases significantly. This observation indicates that the two hydrogen are easily emitted at high laser intensity.

The kinetic energy release (KER) distributions for the COH^{+}–OH^{+} pair detected in the coincidence spectra are shown in Fig. 4 where formic acid is irradiated by linearly and circularly polarized laser pulses. In Fig. 4a we consider linearly polarized light with intensities ranging from 90 to 240 TW/cm². In Fig. 4b we compare linearly and circularly polarized light with the same electric field magnitude. The

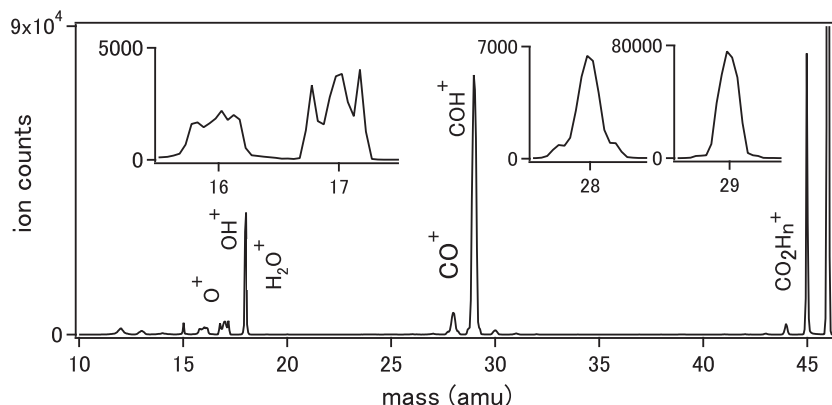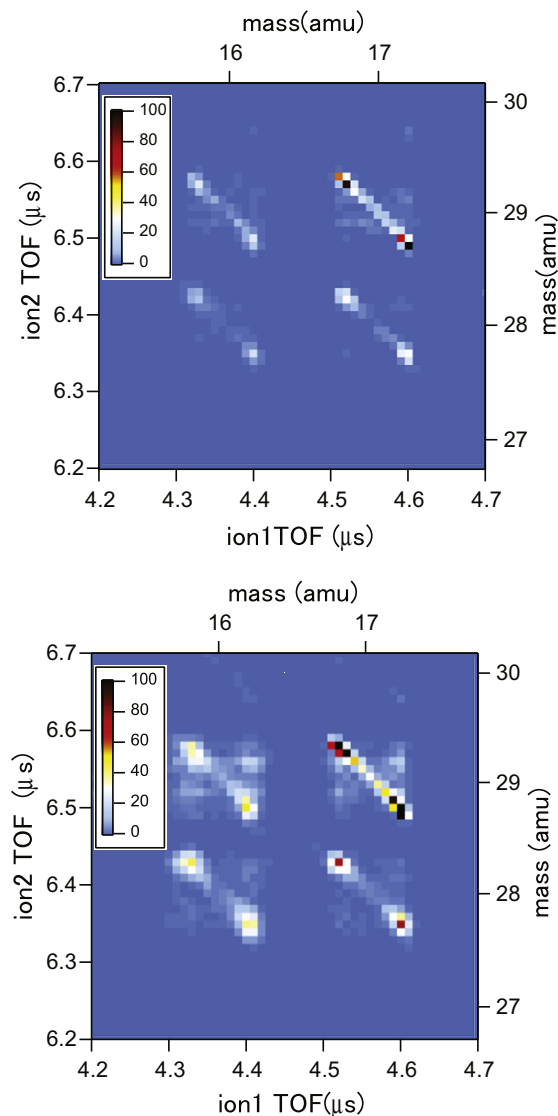**Fig. 1.** TOF mass spectrum measured with an estimate peak laser intensity at 90 TW/cm² and insert is expanded figure for main fragments: TOF mass spectra for O^{+} and OH^{+} (left) and that for CO^{+} and COH^{+} (right).

Fig. 2. Photoion–photoion coincidence map at 90 TW/cm^2 (upper) and 240 TW/cm^2 (lower) with linearly polarized 800 nm laser pulses.

KER peaked at ∼4.9 eV (E_{exp}) for all spectra in Fig. 4. There is no clear difference in KER between linear and circular polarization at both laser intensities. The ion pair yield for the circular polarization is higher than that for the linear polarization, which means that the double ionization is not suppressed by the circular polarization pulse. Thus there is no indication of any effect due to rescattering in this experiment. The critical distance, R_c, between the ion pair before the Coulomb explosion can be estimated using the kinetic energy release value. The value of R_c is about 2.9 Å estimated by the Eq. (5) in the energy region of 90 and 240 TW/cm^2.

$$E_{Coul} = 14.4 Q_1 Q_2 / R \qquad (5)$$

R_c is about 2.1 times larger than the equilibrium distance of C–O, where R_e(CO) = 1.34 Å, in the neutral molecule. We calculate E_{Coul} by Eq. (5) with $R = R_e$ and then define the energy ratio as E_{exp}/E_{Coul}. The value of this energy ratio is 0.48 when R_e = 1.34 Å. This bond stretching phenomenon has been observed in the Coulomb explosion of diatomic and polyatomic molecules and can be understood using EI or CREI model [19–21]. Since the polyatomic effect should be considered in the CE phenomenon for this kind of organic molecules, we modify the crude point charge CE model to calculate the
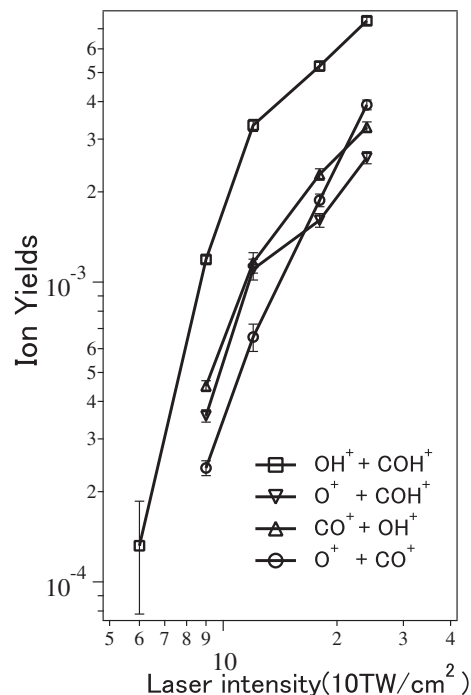
Fig. 3. Power dependence of the ion pair yields for different channels.
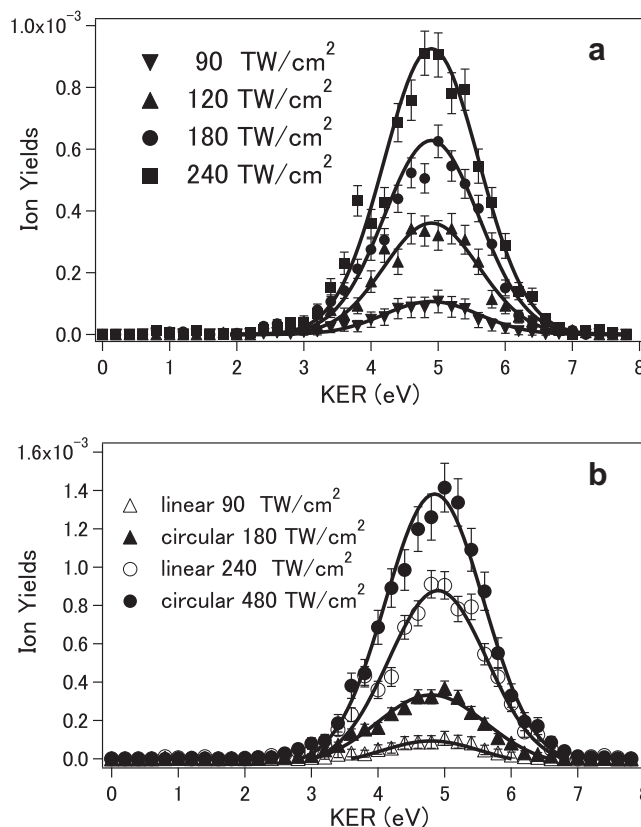
Fig. 4. Kinetic energy release (KER) of COH$^+$ and OH$^+$ at different peak laser intensity with linear polarization (a) and circular polarizations (b), solid line is fitted with GAUSSIAN.

Coulomb energy by replacing the R in the point charge CE model with the distance between the center of charge on the two fragments. Here we define the fragment center of charge as the Eq. (6),

$$(x, y) = \frac{\sum q_i(x_i, y_i)}{\sum q_i} \qquad (6)$$

where q_i is the charge population, and (x_i, y_i) is the coordinate of the atoms composing the fragment in molecular frame. The natural bond orbital (NBO) charge analysis method is used to calculate the electron population on every atom of the $HCOOH^{2+}$. Using the charge population and the geometry of the neutral ground molecule, we get a revised equilibrium distance R_e between the charge center of COH^+ (C (0.64), H (0.37), O (0.35)) and OH^+ (O (0.05), H (0.59)). The value of the revised R_e is about 2.2 Å. With this value for R_e we obtain an energy ratio of about 0.76. According to the [22], the CE occurs at the critical internuclear distance $R_c = a\sqrt{R_e}$, and the factor $a = \sqrt{R_e}/(E_{exp}/E_{Coul})$ is nearly independent of molecule. In our case, the value of a is about 2.0 calculating with the revised R_e, which is consistent with the reference ($a \approx 2.3$). We also calculated the CE energy for another organic molecules, $C_2H_4^{2+}$ using the same NBO method to check whether this method is reliable. The NBO based R_e is 2.0 Å, leading to the factor $a = 2.1$, as calculated with the published experimental KER value [23]. The value of a is also consistent with the reference. Thus we infer that the R_c calculated by experimental KER should be the distance between center of charge of the fragments and not the length of a certain bond.

Another three ion pairs were also investigated in our experiment. Strictly speaking, it is impossible to impose the momentum conservation condition because the ejected neutral H atoms carry some amount of the momentum. However, from the coincidence patterns shown in Fig. 2, we extracted the momentum data of CO^+–OH^+, HCO^+–O^+ and CO^+–O^+ pairs and found that the momentum sums also centered 0 but with a little wider distribution, so a relaxed momentum conservation condition is used to extract the true coincidence and to get the KER values for three channels. The KERs of all four channels are basically the same. This may indicate the following possible dissociative processes. The first possibility is that the hydrogen atoms are ejected from the singly charged parent ions. Assuming sequential double ionization within the temporal pulse duration (100 fs), this H ejection from the intermediate ionic state can easily happen before the CE after production of the dicationic ion, and it may do not affect the Coulomb potential of the C–O dimension so much. Hydrogen atoms can also be ejected from the doubly charged parent ions or from the fragments after CE.

4. Summary

The two-body dissociative ionization process of doubly charged formic acid ($HCOOH^{2+}$) induced by intense femtosecond laser fields has been investigated using ion–ion coincidence momentum spectroscopy. The circularly polarized laser pulse does not suppress the ion pair yield and the KER does not depend on the laser polarization and intensity. These indicate that the sequential double ionization plays a dominate role in this special case. The experimental KER value showed that the CE occurs at a critical distance R_c through sequential enhance ionization and the revised R_e considering the polyatomic effect is calculated using the NBO method.

Acknowledgements

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