Carrier-envelope-phase dependence of asymmetric C—D bond breaking in C_2D_2 in an intense few-cycle laser field

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ABSTRACT

The carrier envelope phase (CEP) dependence in the C—D bond breaking of C_2D_2 induced by an intense few-cycle laser pulse is investigated. The ejection direction of D^+ ions generated from the Coulomb explo-sion, $C_2D_2^{2+} \rightarrow C_2D^+$ and D^+, exhibits the CEP dependent asymmetry, while its CEP dependence is out of phase by π with respect to the CEP dependence of the recoil momentum of $C_2D_2^+$. From a recollisional double ionization model, the asymmetry in the ejection direction of D^+ was ascribed to the laser-assisted C—D bond weakening in the few-cycle laser field.

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1. Introduction

When molecules are exposed to an ultrashort intense laser field, their responses are sensitively dependent on characteristics of the laser field such as its intensity, wavelength, and duration [1–3]. When the duration of 800 nm light pulses becomes as short as a few femtoseconds, the electric field of light oscillates only a few times, and another parameter called carrier-envelope-phase (CEP) becomes important for the characterization of the pulse. Indeed, a variety of CEP dependent photo-induced phenomena have been reported in recent years [4–11]. For example, it has been shown that, when photoionization proceeds in a few cycle laser pulses, emission of photoelectrons from rare gas atoms towards right or left along the laser polarization direction becomes asym-metric depending on the CEP [4], and the origin of the asymmetry and its dependence on the intensity and duration of laser pulses were discussed theoretically [5]. This right–left asymmetry be-comes evident in high-order above-threshold ionization (ATI) and this high-order ATI process itself has been used to determine the relative CEP of few-cycle laser pulses [6].

The CEP effect has also been found in the direction of fragment ions generated from diatomic molecules such as D_2 [7,8] and CO [9]. When D_2 was exposed to an intense few-cycle laser field, D^+ was found to be ejected asymmetrically in space depending on the CEP, and this CEP dependence was ascribed to an asymmetric charge distribution induced within a molecule in the few-cycle la-ser field [10]. Such variation of the charge distribution within a molecule was also investigated using H_2^+ [11].

In the case of polyatomic molecules, such changes in the charge distribution induced within a molecule may lead to changes in the nature of chemical bonds, affecting the subsequent chemical bond breaking processes. Therefore, by the irradiation with a few-cycle laser pulse, their decomposition processes are expected to become dependent on the CEP. In the present study, in order to examine how sensitively such photo-induced chemical bond breaking processes are influenced by the CEP of a few-cycle laser pulse, we investigate two-body decomposition of doubly charged deuterated acetylene, $C_2D_2^{2+} \rightarrow C_2D^+ + D^+$, induced by an intense few-cycle laser pulse. By comparing the CEP dependence of the asymmetry in the C—D bond breaking with the CEP dependence of the momentum recoil of $C_2D_2^+$ upon the ionization, the origin of the CEP dependence in the breaking processes of the two originally equivalent C—D bonds in $C_2D_2^{2+}$ is discussed.

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2. Experiment

The bandwidth of the output pulses of a femtosecond Ti:sapphire laser system (5 kHz, 0.7 mJ, 800 nm, 30 fs) was broadened by focusing the pulses into a hollow-core fiber (inner diameter: 330 um, length: 1.5 m) filled with an Ar gas (0.47 atm) through self-phase-modulation. By this fiber compression process [12], the spectral bandwidth was broadened so that it becomes 350 nm at full-width at tenth-maximum at the center wavelength of $\sim$740 nm.

By compensating the phase dispersion by a set of chirped mirrors (BBCOMP, FEMTOOPTICS), few-cycle pulses were generated. The generated few-cycle pulses were split into two by a beam splitter. One of the split laser beams was focused by a concave mirror (f = 250 mm) onto a Xe gas in a gas-cell in a single-shot phase meter [6].

Electrons generated via the high-order ATI processes were ejected either towards the right direction or toward the left direction along the laser polarization direction, and were guided to the right-side micro-channel plate (MCP) detector or to the left-side MCP detector, respectively. By plotting the right–left asymmetry in the electron yield in the high-energy region of the photoelec-tron spectrum with respect to that of the low-energy region for every laser shots, a round-shaped map called 'an asymmetry parameter plot' [6] was obtained. From the phase angle ϕ and the radius r of the circular plot, the relative CEP [13] and the duration of the laser pulses [14] were estimated, respectively. The phase dispersion of the laser pulses were adjusted finely by a pair of wedge plates placed before the phase meter, and the shortest pulse duration at full-width at half-maximum of the few-cycle laser pulses was estimated to be 4.5 fs from $r \sim 0.8$ of the circular plot [14].

The other split laser beam was guided into a vacuum chamber for ion momentum imaging, and was focused by a concave mirror (f = 150 mm) onto a molecular beam of deuterated acetylene C_2D_2. Because the width of the molecular beam is sufficiently small compared to the confocal length, the effect of the Gouy phase shift is expected to be negligibly small in the measure-ments of the CEP dependence. The phase dispersion of the pulses was adjusted by a pair of wedge plates placed before the chamber so that the highest count rate of the ion signal was obtained. The peak intensity at the focus in the ion momentum imaging cham-ber was estimated to be 0.34 PW cm^{-2} from the pulse duration, the pulse energy ($\sim$50 μJ/pulse) and the radius of the focal area

44 μm) recorded by a beam profiler. Parent ions and fragment ions generated from deuterated acetylene at the focus were guided by a static electric field toward a two-dimensional posi-tion sensitive detector (HEX120, RoentDek) in the velocity map imaging conditions [15]. From the flight time and the position of ions on the detector, the momenta $\boldsymbol{p} = (p_x, p_y, p_z)$ of the ions were determined, where the x–z plane is taken to be parallel to the surface of the detector, the z-axis is parallel to the laser polar-ization direction, and the y-axis is in the direction from the cross-ing point of the molecular beam and the laser beam toward the detector.

For every laser shot, both the asymmetry data from the phase meter and the momentum data of ions from the ion momentum imaging chamber were collected simultaneously by a data acquisition board (TDC8HP, RoentDek) so that those data were tagged to each other. Because the optical path lengths from the beam splitter to the two apparatuses are not the same, the CEP value recorded by the phase meter has a certain offset with respect to the absolute CEP, ϕ_{CEP}, at the laser focus in the momentum imaging chamber. The absolute CEP values were predicted from the recoil momentum of $C_2D_2^+$ as described in the next section.

3. Results and discussion

3.1. Estimation of absolute CEP

The momentum distribution of parent ions $C_2D_2^+$ detected in addition to the fragment ions shows that its width along the polarization direction is $\sim 18 \times 10^3$ u ms^{-1}, which primarily represents the temperature of the sample gas, and that the mean value of the momenta, ($\bar{p}_{C_2D_2^+}$), along the laser polarization direction was found to vary by $\sim$60 u ms^{-1} with the estimated absolute CEP, ϕ_{CEP}, as plotted in Figure 1, in which the abscissa has already been converted from the recorded relative carrier envelope phase to the estimated absolute CEP ϕ_{CEP} based on the discussion in this section. The uncertainties associated with the mean momentum values were estimated to be $\sim$5 u ms^{-1} based on the number of signal counts $\sim 3 \times 10^6$ within the respective bins of the CEP values.

The recoil momentum of $C_2D_2^+$ ($\bar{p}_{C_2D_2^+}$) can be described as a function of ϕ_{CEP} if it is assumed by neglecting the Coulomb attraction between the ejecting electron and $C_2D_2^+$ that (i) the momenta of both the ejected electron and the generated parent ion $C_2D_2^+$ at the moment of the tunneling ionization are zero and (ii) the recoil momentum gained by $C_2D_2^+$ after the interaction with the laser pulse is proportional to the vector potential $A(t)$ of the laser pulse at the moment of the ionization. By adopting this model, the value of the CEP, ϕ_{CEP}, with which the electric field of a few cycle laser pulse is written using the temporal envelope $E_0(t)$ and the angular frequency ω of the laser pulse as:

$$E(t, \phi_{CEP}) = E_0(t)\cos(\omega t + \phi_{CEP}) \quad (1)$$

can be estimated from the observed CEP dependence of the recoil momentum of $C_2D_2^+$ as discussed below.

As discussed previously [16,17], the Coulomb attraction between the ejecting electron and the parent ion could have a non-negligible effect [18] on the calibration of CEP. Therefore, we regard ϕ_{CEP} obtained by the assumptions above as an estimated absolute CEP that could have a certain offset from the absolute CEP. In the present study, a Gaussian shape was assumed for the envelope function $E_0(t)$. All the physical quantities appearing in Eq. (1) and those in the equations hereafter are expressed in atomic units.

When the pulse duration is 4.5 fs and $\phi_{CEP} = \pi/2$, the electric field becomes $-E_0(t)\sin(\omega t)$ as shown in Figure 2(a). If it is as-sumed that the tunneling ionization proceeds at the local maxima of the electric field amplitude, the recoil momentum of $C_2D_2^+$ proportional to the vector potential becomes slightly negative by the ionization at the extrema A and A′ of the electric field, while it becomes positive by the ionization at the extrema B and B′ of the electric field. The magnitude of the positive value of the vector potential at the extrema B and B′ is about 2.4 times as large as the magnitude of the negative value of the vector potential at the extrema A and A′.

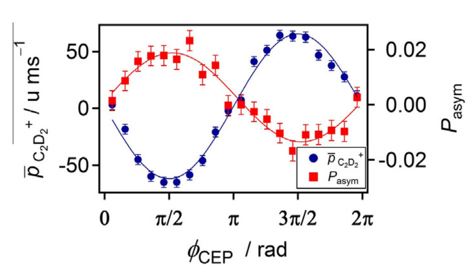

Figure 1. The asymmetry parameter P_{asym} (squares) and the mean momentum of $C_2D_2^+$, $\bar{p}_{C_2D_2^+}$, along the laser polarization direction (triangle) plotted as a function of the estimated absolute CEP, ϕ_{CEP}.

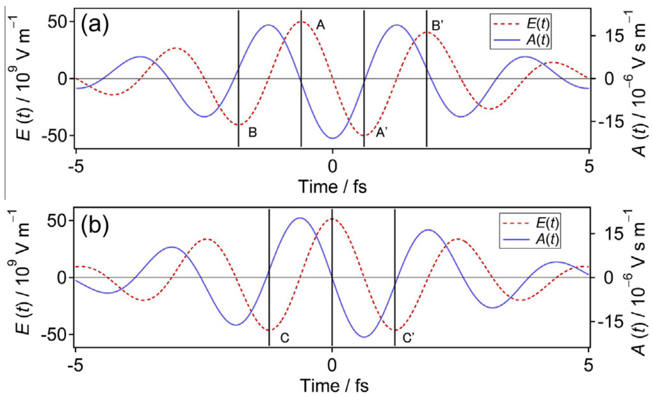

Figure 2. The waveforms of the electric fields and the vector potential of laser pulses with the pulse duration of 4.5 fs (FWHM) when the CEP is $\pi/2$ (a) and 0 (b).

In order to judge whether the averaged recoil momentum of $C_2D_2^+$ is shifted towards the positive or negative direction, it becomes necessary to estimate the ionization probabilities at each moment during the laser pulse. For the estimation of the ionization rate, we adopt the ADK rate formula [19]:

$$w_{\mathrm{ADK}}(t_0, \phi_{\mathrm{CEP}}) = a\left(\frac{2(2I_{\mathrm{p}})^{\frac{3}{2}}}{|E(t_0, \phi_{\mathrm{CEP}})|}\right)^{2\frac{Z_{\mathrm{C}}}{\sqrt{2I_{\mathrm{p}}}}-|m|-1} \times \exp\left(-\frac{2(2I_{\mathrm{p}})^{\frac{3}{2}}}{3|E(t_0, \phi_{\mathrm{CEP}})|}\right), \quad (2)$$

where I_{p} is the ionization potential, $|E(t_0, \phi_{\mathrm{CEP}})|$ is the absolute value of the amplitude of the electric field of light at time t_0, m is a magnetic quantum number, and a is a constant. In the present case, $Z_{\mathrm{C}} = 1$, $I_{\mathrm{p}} = 11.4$ eV, and $|m| = 1$ are chosen because the ionization is expected to proceed by the ejection of an electron dominantly from the highest occupied π_{u} orbital of a neutral molecule whose orbital energy is -11.4 eV.

The ADK ionization rate estimated using Eq. (2) at the extrema A and A′ of the field is 3.1 times as large as the rate at the extrema B and B′ under the present experimental conditions ($\Delta t \sim 4.5$ fs, $I = 0.34$ PW cm^{-2}, 740 nm). Because the absolute value of the vector potential at the peaks B, B′ is 2.4 times larger than that at the extrema A and A′, the mean recoil momentum of $C_2D_2^+$ is expected to become negative by the simple addition of the contributions from the extrema A, A′, B, and B′, that is, $(2.4 \times 1.0) - (1.0 \times 3.1) = -0.7$. In the same manner, when $\phi_{\mathrm{CEP}} = 3\pi/2$, the recoil momentum of $C_2D_2^+$ is expected to become positive, that is, $-(2.4 \times 1.0) + (1.0 \times 3.1) = 0.7$.

On the other hand, when $\phi_{\mathrm{CEP}} = 0$, the electric field becomes $E_0(t)\cos(\omega t)$ as shown in Figure 2(b) and the vector potential becomes an odd function. Consequently, the contributions of the momentum recoil from the peaks C and C′ may cancel each other out, resulting in zero recoil momentum of $C_2D_2^+$.

For more quantitative discussion, we need to take into account the fact that the ionization proceeds not only at the extrema of the electric field but also at each moment within the laser pulse. By adopting the ADK ionization rate of Eq. (2), the CEP dependence of the averaged recoil momentum, $\bar{p}_{\mathrm{calc}}$, is evaluated by the formula:

$$\bar{p}_{\mathrm{calc}}(\phi_{\mathrm{CEP}}) = \frac{\int_{-\infty}^{\infty}\int_{t_0}^{\infty} w_{\mathrm{ADK}}(t_0, \phi_{\mathrm{CEP}})E_0(\tau)\cos(\omega\tau + \phi_{\mathrm{CEP}})\mathrm{d}t_0\mathrm{d}\tau}{\int_{-\infty}^{\infty} w_{\mathrm{ADK}}(t_0, \phi_{\mathrm{CEP}})\mathrm{d}t_0}, \quad (3)$$

as a function of ϕ_{CEP} as shown in Figure 3. This figure shows that $\bar{p}_{\mathrm{calc}}$ takes a sine-type function, that is, $\bar{p}_{\mathrm{calc}}$ becomes zero when $\phi_{\mathrm{CEP}} = 0$ and π, and takes local minimum (negative) at $\phi_{\mathrm{CEP}} = \pi/2$

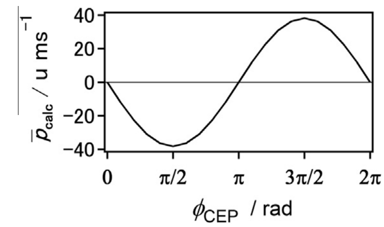

Figure 3. The calculated recoil momentum of $C_2D_2^+$, $\bar{p}_{\mathrm{calc}}$, obtained for a laser pulse with the pulse intensity of $I = 0.34$ PW cm^{-2}, the pulse duration of 4.5 fs, and the center wavelength of 740 nm.

and local maximum (positive) at $\phi_{\mathrm{CEP}} = 3\pi/2$. Even though the amplitude of $\bar{p}_{\mathrm{calc}}$ is approximately ~60% of the experimental value of $\bar{p}_{C_2D_2^+}$, the overall behavior is reproduced well by this simple calculation in which the Coulomb attractive interaction and the angular dependence of the ADK ionization rate are neglected.

The observed sinusoidal behavior of the recoil momentum of $C_2D_2^+$ is fitted to a sinusoidal function $-\sin(\phi_{\mathrm{obs}} + \phi_0)$ using the adjustable offset parameter, ϕ_0, from which the estimated absolute phase was obtained as $\phi_{\mathrm{CEP}} = \phi_{\mathrm{obs}} + \phi_0$. The variation of the recoil momentum as a function of the absolute CEP shown in Figure 1 was obtained after this correction of the abscissa.

3.2. Asymmetric breaking of C—D bonds

The momentum image of the ions detected at $m/z = 2$ is shown in Figure 4. The signals appearing in the inner region $|\boldsymbol{p}| < 30 \times 10^3$ u ms^{-1} can be assigned to D^+ ions generated from singly charged parent ions by the dissociation process, $C_2D_2^+ \to C_2D + D^+$. The intense central region of this image con-tains a significant contribution from hydrogen molecular ions, H_2^+, generated from a residual H_2 gas in the ion momentum imaging chamber. The outer circular distribution appearing in the range 30×10^3 u ms^{-1} < $|\boldsymbol{p}|$ < 50×10^3 u ms^{-1} is assigned to D^+ ions generated from the Coulomb explosion process of doubly charged ions, $C_2D_2^{2+} \to C_2D^+ + D^+$, as reported in a previous study in which a coincidence detection of these fragment ions was performed [20]. Hereafter, we focus our attention on the outer circular distribution, and define an asymmetry parameter P_{asym} of the emission of D^+ as:

$$P_{\mathrm{asym}}(\phi_{\mathrm{CEP}}) = \frac{I_{\mathrm{upper}}(\phi_{\mathrm{CEP}}) - I_{\mathrm{lower}}(\phi_{\mathrm{CEP}})}{I_{\mathrm{upper}}(\phi_{\mathrm{CEP}}) + I_{\mathrm{lower}}(\phi_{\mathrm{CEP}})}, \quad (4)$$

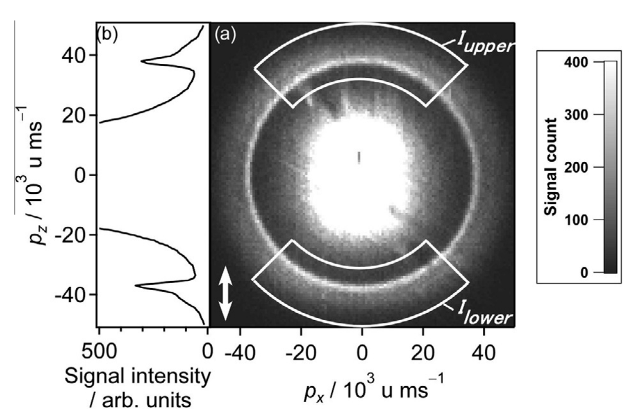

Figure 4. (a) The momentum image of D^+ generated from C_2D_2 by few-cycle laser pulses by accumulating all the data in the respective bins of the CEP values. The vertical double-headed arrow represents the laser polarization direction. Only the signals in the range of $|p_y| < 5 \times 10^3$ u ms^{-1} are depicted to show clearly the outer circular distribution. (b) The projection of the momentum image onto the p_z axis in the range $|p_x| < 5 \times 10^3$ u ms^{-1}.

where:

$$I_{\rm upper}(\phi_{\rm CEP}) = \int_{p_1}^{p_2}\int_{0}^{\theta_0}\int_{0}^{2\pi} I(p,\theta,\phi,\phi_{\rm CEP})p^2 \sin\theta\,{\rm d}p\,{\rm d}\theta\,{\rm d}\phi \quad (5)$$

and:

$$I_{\rm lower}(\phi_{\rm CEP}) = \int_{p_1}^{p_2}\int_{\pi-\theta_0}^{\pi}\int_{0}^{2\pi} I(p,\theta,\phi,\phi_{\rm CEP})p^2 \sin\theta\,{\rm d}p\,{\rm d}\theta\,{\rm d}\phi \quad (6)$$

represent the signal intensities in the two corresponding areas each of which is surrounded by the solid line in Figure 4. The integrand $I(p, \theta, \phi, \phi_{CEP})$ in Eqs. (5) and (6) denotes the three dimensional momentum distribution in the polar coordinate system, where $p(=|\boldsymbol{p}|)$ is the radius, θ is the polar angle with respect to the z axis parallel to the laser polarization direction, and ϕ is the azimuthal angle. The range of the integral with respect to p is from $p_1 = 30 \times 10^3$ u ms^{-1} to $p_2 = 50 \times 10^3$ u ms^{-1}. The angle θ_0 defines the range of the signals included in the integral, that is, the signals of D^+ ions ejected from $C_2D_2^{2+}$ within the polar angle range of $[0, \theta_0]$ are sampled in the analysis.

The P_{asym} values obtained by Eqs. (4)–(6) with $\theta_0 = \pi/4$ are plotted in Figure 1 as a function of the estimated absolute phase ϕ_{CEP} derived in the preceding section. Even though the extent of the asymmetry is small, the variation of about 1.6% is identified with the uncertainties of less than about 0.5%. When the angle range θ_0 is decreased and increased by $\pi/18$ from $\theta_0 = \pi/4$, the phase of the resultant sinusoidal functions are shifted respectively to the negative and positive directions by only 0.06π, showing that the CEP dependence of P_{asym} is not sensitively varied by the range of θ_0. It should be noted that the CEP dependence of P_{asym} and that of the recoil momentum of $C_2D_2^+$ are out of phase with each other by around π as shown in Figure 1.

3.3. Recollisional double ionization

In order to discuss the origin of the CEP dependence in the asymmetric C—D bond breaking, resulting in the asymmetry in the ejection direction of D^+, we need to consider the double ioniza-tion process occurring in the intense laser field by the recollision of a part of the electrons ejected through the tunneling ionization. When a doubly charged parent ion, $C_2D_2^{2+}$, is generated through the electron recollision process, the motion of the recolliding electron after the tunneling ionization is calculated by solving the equation of motion of the electron whose position on the z axis is z_e:

$$\frac{{\rm d}^2 z_e}{{\rm d}t^2} = -E(t), \quad (7)$$

when the Coulomb attraction between the electron and the rest of the molecule is neglected.

Typical classical trajectories of the re-colliding electrons generated just after the peak positions of the electric field obtained by solving Eq. (7) are plotted in Figure 5(a-1) and (b-1) for the few-cycle pulses with $\phi_{CEP} = \pi/2$ and $\phi_{CEP} = 0$, respectively. Thus, the timing of the recollision t_r as well as the kinetic energy $E_{recol}(t_r, t_0)$ of the recolliding electron generated at $t = t_0$ and recolliding at $t = t_r$ can be evaluated by the trajectory calculations.

In order to induce double ionization followed by the bond breaking to produce D^+, the kinetic energy of the recolliding electron needs to be larger than the threshold energy to produce the lowest dissociative electronic state of $C_2D_2^{2+}$ from C_2D_2. Because the lowest dissociative state of $C_2D_2^{2+}$ is considered to be the $^3\Pi_u$ state [21] and the vertical ionization energy from $C_2D_2^+$ to produce this dissociative state is 25 eV, we consider only those recolliding electrons whose energy is larger than $I_p(C_2D_2^+) = 25$ eV at the moment of the recollision.

From the simulation, we derived the kinetic energies of electrons at the moment of the recolliding events as shown in Figure 5(a-2) and (b-2), and found that the electrons generated through the tunneling ionization can gain kinetic energies larger than 25 eV only when they are produced in the hatched temporal ranges shown in Figure 5(a-1) and (b-1). As long as electrons with such high kinetic energies are considered, the timing of the tunneling ionization and the timing of the recollision have one-to-one correspondence.

In order to estimate quantitatively the yield of the double ionization by the recollision, we need to derive (i) the probabilities of the tunneling ionization at $t = t_0$ and (ii) the probabilities of the double ionization at the moment of the recollision at $t = t_r$. The probabilities of the tunneling ionization can be estimated by the ADK formula of Eq. (2), and are plotted in Figure 5(a-3) and (b-3). The yield of the double ionization by the recollision can be estimated using the electron impact ionization cross-section [17,22], as described below.

The kinetic energies of these electrons at the moment of the recolliding events are plotted as a function of the recollision time as shown in Figure 5(a-4) and (b-4). We learn from the simulation that, after the propagation within the laser field, the widths of the time windows for the recolliding events become several times wider than the corresponding time windows of the generation of the electrons by the tunneling ionization, and that the recollision events occur around 1.4π after the event of the tunneling ionization, which is slightly smaller than 3π/2.

It has been known for electron impact ionization that the ionization cross-section near the threshold energy for the ionization increases almost linearly as a function of the excess kinetic energy [23–26]. Thus, the cross-section is approximated in the present study by a linear function of the excess energy of the recolliding electron as

$$\sigma(E_{\rm recol}(t_r)) \propto (E_{\rm recol}(t_r) - I_p(C_2D_2^+)), \quad (8)$$

where $I_p(C_2D_2^+) = 25$ eV is the ionization potential for generating the lowest dissociative state $^3\Pi_u$ [21] of $C_2D_2^{2+}$.

The yield $Y(t_r)$ of the doubly charged dissociative parent ions can thus be evaluated using the tunneling ionization probability of Eq. (2) and the recollisional ionization probability of Eq. (8) as:

$$Y(t_r) \propto w_{\rm ADK}(t_0)\cdot\sigma(E_{\rm recol}(t_r)), \quad (9)$$

where t_0 is determined uniquely by t_r. The resultant yields of $Y(t_r)$ are plotted in Figure 5(a-5) and (b-5) for $\phi_{CEP} = \pi/2$ and $\phi_{CEP} = 0$, respectively. When $\phi_{CEP} = \pi/2$, the largest contribution of the double ionization comes from the first recollision after $t = 0$, represented by the trajectory 1 in Figure 5(a-1). On the other hand, when $\phi_{CEP} = 0$, the first and the second recollisions after $t = 0$ represented by the trajectories 2 and 3 in Figure 5(b-1) contribute almost equally.

Considering the observation shown in Figure 1 that P_{asym} becomes maximum and minimum at $\phi_{CEP} = \pi/2$ and 3π/2, respectively, and that it becomes almost zero at $\phi_{CEP} = 0$ indicates that the recollisional events represented by the trajectory 1 in Fig-ure 5(a-1) play a decisive role in making the ejection direction of D^+ shifted towards the positive direction of the electric field, while the recollisional events represented by the trajectories 2 and 3 in Figure 5(b-1) cancel each other, resulting in zero asymmetry in the ejection direction of D^+.

3.4. Possible scenario of asymmetric ejection of D^+

In the collisional events represented by the trajectory 1 in Figure 5(a-1) for $\phi_{CEP} = \pi/2$, $C_2D_2^{2+}$ is produced slightly before the electric field of light changes from negative to positive. This means that the resultant $C_2D_2^{2+}$ experiences the positive half cycle of the electric field for about 1.2 fs, during which the C—D internuclear

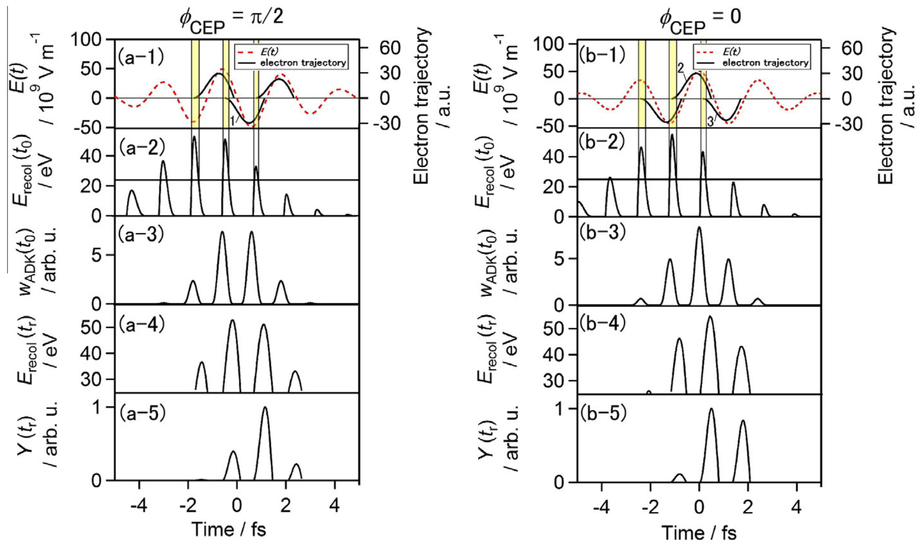

Figure 5. The timings of the tunneling ionization and the recollision within a few cycle laser electric field with $\phi_{CEP} = \pi/2$ (left) and $\phi_{CEP} = 0$ (right), and the yield of the recollisional double ionization. (a-1) and (b-1): The electric waveform of a few cycle laser pulse and typical trajectories of the recolliding electrons. (a-2) and (b-2): The recollision energy of the electrons at the tunneling ionization time. The horizontal line denotes the minimum energy required for the formation of dissociative $C_2D_2^{2+}$. (a-3) and (b-3): The ADK ionization rate at the tunneling ionization time. (a-4) and (b-4): The recollision energy of the electron at the recollision time. (a-5) and (b-5): The yield Y_0 of doubly charged parent ions at the recollision time.

distance may be stretched to a certain extent. When the principal molecular axis of $C_2D_2^{2+}$ is approximately parallel to the polarization direction of the electric field of light, the C—D chemical bond on the positive side of the electric field is considered to be weak-ened because the electron density at the C—D chemical bond is ex-pected to become lower due to the positive electric field. This laser field-assisted chemical bond weakening induces the larger separa-tion of the C—D internuclear distance on the positive electric field side. Even though the displacement occurring during this very short period of time may be at most ~0.1 Å, this small displace-ment may promote the charge separation between D^+ and C_2D^+, resulting in the eventual D^+ emission, by the time when the electric field becomes negative again to assure $P_{asym} > 0$ as shown in Fig-ure 1. For $\phi_{CEP} = 3\pi/2$, the propensity of the ejection of D^+ toward the negative direction of the electric field of light, that is $P_{asym} < 0$, can be explained in a similar manner.

In the case of $\phi_{CEP} = 0$, the recollision events represented by the trajectory 2 may induce preferentially the ejection of D^+ towards the negative direction of the electric field from the same mecha-nism above, while those represented by the trajectory 3 may in-duce preferentially the ejection of D^+ towards the positive direction of the electric field, resulting in the cancellation of the two contributions, that is, $P_{asym} = 0$, which is consistent with the observation in Figure 1.

When a doubly charged parent ion, $C_2D_2^{2+}$, is generated through the electron recollision process, an electron in the π_u HOMO orbital is considered to be ejected through a tunneling ionization as the first step. It was reported recently [27] that the tunneling ionization rate from π_u HOMO orbital of acetylene takes a local minimum when the molecular axis is parallel to the laser polarization direction and a local maximum when it is perpendicular to the laser polarization direction. The present observation suggests that the yield of the tunneling ionization from the π_u orbital is sufficiently large even when the axis is parallel to the laser polarization direction so that the subsequent recollisional ionization produces $C_2D_2^{2+}$.

4. Summary

In the present study, from the coincidence measurements of the ion signals and the CEP signals obtained using few-cycle pulses, we have investigated the CEP dependence of the ionization of C_2D_2. We have found that the two different CEP dependent phenomena; one is the asymmetry in the direction of the recoil momentum of $C_2D_2^+$ and the other is the asymmetry in the direction of the emission of D^+ after the Coulomb explosion, and that these two types of CEP dependences are out of phase with each other by π. The asymmetry in the recoil momentum of $C_2D_2^+$ is interpreted by the direction of the vector potential at the moment of the tunnel ionization, and is used to derive the estimated absolute CEP based on the assumption that the Coulombic attraction between the ejecting electron and $C_2D_2^+$ can be neglected. The fact that the observed asymmetry in the emission direction of D^+ is interpreted as phenomena originating from the laser-assisted C—D bond weakening in $C_2D_2^{2+}$ suggests that the estimated absolute CEP is close to the absolute CEP under the present experimental conditions.

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