Visualizing recurrently migrating hydrogen by few-cycle intense laser pulses

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Abstract. Ultrafast hydrogen migration in deuterated acetylene dication (C\textsubscript{2}D\textsubscript{2}\textsuperscript{2+}) is studied by the pump-probe Coulomb explosion imaging with few-cycle intense laser pulses (9 fs, 0.13 PW/cm\textsuperscript{2}, 800 nm). The temporal evolution of the momenta of the fragment ions produced by the three-body explosion, C\textsubscript{2}D\textsubscript{2}\textsuperscript{2+} → D\textsuperscript{+} + C\textsuperscript{+} + CD\textsuperscript{+}, shows that the migration proceeds in a recurrent manner: The deuterium atom first shifts from one carbon site to the other in a short time scale (∼ 90 fs), and then migrates back to the original carbon site by 280 fs, in competition with the molecular dissociation.

1. Introduction

Ultrafast laser spectroscopy based on the pump-and-probe scheme is a powerful tool to unveil complex ultrafast dynamics of polyatomic molecules [1]. The evolution of the nuclear wavepacket created by the pump laser pulse is projected onto a reference electronic state by the time-delayed probe pulse, which realizes the real-time tracking of the chemical reaction. Recent advances in laser technology have enabled us to utilize ultrashort intense laser pulses (<10 fs, ∼10\textsuperscript{15} W/cm\textsuperscript{2}) as a new probe to image the ultrafast structural deformation in reaction processes. Molecules exposed to such intense laser pulses promptly eject several electrons by non-resonant interactions and undergo rapid bond breaking (called Coulomb explosion) on the repulsive Coulombic potential energy surface of the highly charged states [2]. Since the momenta of the resultant fragment ions reflect sensitively the geometrical structure of the target molecule [3, 4, 5], the Coulomb explosion provides direct access to the instantaneous structure in the course of reaction processes, as demonstrated for dissociating diatomic [6, 7] and triatomic molecules [8, 9].

The isomerization of neutral acetylene [10, 11, 12, 13] and its ionic species [14, 15, 16, 17, 18] between the acetylene (HCCH) and vinylidene (H\textsubscript{2}CC) configurations has been extensively studied as a prototype of the hydrogen migration proceeding via the shift of a hydrogen atom from one carbon site to the other, while reports of direct time-scale measurements are sparse [15, 12]. Here we report the real-time visualization of ultrafast hydrogen migration in acetylene dication by employing the pump-probe Coulomb explosion imaging [8, 9]. In order to track the
ultrafast migration of deuteron atoms between the acetylene and vinylidene configurations,

\[ \text{DCCD}^{2+} \leftrightarrow \text{D}_2\text{CC}^{2+}, \]

we employed a pair of few-cycle intense laser pulses (9 fs, 0.13 PW/cm², 800 nm).

Our experimental scheme is shown in Fig.1. The pump laser pulse is used to doubly ionize the target molecule as well as to trigger the hydrogen migration. The structural change of \( \text{C}_2\text{D}_2^{2+} \) is then probed by another intense laser pulse, introduced with a time delay \( \Delta t \) to ionize \( \text{C}_2\text{D}_2^{2+} \) to \( \text{C}_2\text{D}_2^{3+} \). The three-body Coulomb explosion process from \( \text{C}_2\text{D}_2^{3+} \),

\[ \text{C}_2\text{D}_2^{3+} \rightarrow \text{D}^+ + \text{C}^+ + \text{CD}^+ \]

is monitored for each explosion event by the coincidence momentum imaging method [19] to identify the location of the deuterium atom migrating between the two carbon sites.

Here we focus our attention to the angle \( \theta_{12} \) between the momenta of the resultant \( \text{D}^+ \) and \( \text{C}^+ \) fragment ions, \( \mathbf{p}_1(\text{D}^+) \) and \( \mathbf{p}_2(\text{C}^+) \). For the acetylene configuration, the angle \( \theta_{12} \) is expected to be small due to its linear geometry, whereas large \( \theta_{12} \) values should be observed when the hydrogen migration proceeds towards the vinylidene configuration (see Eq. (1)). A classical simulation of the three-body Coulomb explosion shows that the acetylene (\( \alpha = 0^\circ \)) and vinylidene (\( \alpha \sim 140^\circ \)) configurations [18] lead to the Coulomb explosion with different momentum angles, \( \theta_{12} = 0^\circ \) and \( 130^\circ \), respectively.

2. Experimental

The output from a Ti:Sapphire femtosecond laser system (central wavelength 800 nm, pulse duration 35 fs, repetition rate 1 kHz) was introduced to a pulse compressor consisting of a hollow fiber filled with Ar (\( \sim 0.1 \) MPa) and a pair of chirped mirrors, to obtain sub-10 fs intense laser pulses (energy 0.4 mJ/pulse, band width \( > 3000 \) cm\(^{-1} \)) [20]. The pump and probe laser pulses were generated by a Michelson-type interferometer and focused onto an effusive molecular beam of \( \text{C}_2\text{D}_2 \) by a silver-coated concave mirror in an ultrahigh vacuum chamber (\( < 10^{-8} \) Pa).
Figure 2. (Colour online) Evolution of the momentum angle \( \theta_{12} \) (a) and the total kinetic energy release \( E_{\text{kin}} \) (b), obtained with \( \sim 10^7 \) laser shots for each pump and probe delay \( \Delta t \). Each distribution is normalized to the peak value. The scale shown as the inset in (b) represents the internuclear distance \( R_d \) between the two fragments produced by the two-body dissociation of \( \text{C}_2\text{D}_2^{2+} \), estimated [8] as \( R_d = 14.4 / \left[ E_{\text{kin}}(\Delta t) - E_{\text{kin}}(\Delta t = \infty) \right] \) by using Coulombic potentials, where \( E_{\text{kin}}(\Delta t) \) [eV] is the kinetic energy release observed at \( \Delta t \).

The dispersion by the optical materials (such as the chamber window) was pre-compensated to achieve the shortest pulse duration (\( \sim 9 \) fs) at the focal spot. The minimum time delay between the pump and probe pulses, \( \Delta t = 30 \) fs, was chosen to avoid the optical interferences between the pump and probe pulses [6].

The fragment ions produced from the target molecule were guided by four electrodes in velocity mapping configuration to a fast position sensitive detector (Roentdek Handels GmbH, HEX80), where all the fragment ions originating from a single parent ion were detected in coincidence. In order to detect securely the coincidence events originating from a single parent ion, the pressure in the vacuum chamber needs to be as low as \( \sim 10^{-8} \) Pa to keep the number of ion-detection events per laser shot sufficiently less than unity. The momenta of the respective fragment ions, \( P_1(\text{D}^+) \), \( P_2(\text{C}^+) \) and \( P_3(\text{CD}^+) \), were determined as three-dimensional vectors for each Coulomb explosion event from the \((x, y)\) position and the time of flight \( t \) at the arrival at the detector [19]. The momentum angle \( \theta_{12} \) and the total kinetic energy release \( E_{\text{kin}} \) can be calculated from the measured momenta as, \( \theta_{12} = \cos^{-1}\left[ P_1(\text{D}^+) \cdot P_2(\text{C}^+) / (p_1 p_2) \right] \) and \( E_{\text{kin}} = \sum p_i^2 / (2m_i) \), where \( m_i \) and \( p_i \) are the mass and the absolute value of the momentum for the \( i \)-th fragment ion, respectively.

3. Results and discussion
3.1. Visualization of hydrogen migration
The changes in the observed \( \theta_{12} \) distributions as a function of the pump-probe delay \( \Delta t \) are shown in Fig.2(a). Since the phase space available to the molecule sharply decreases as \( \sin \theta_{12} \) [5], the \( \theta_{12} \) distribution peaks at a finite value (\( \theta_{12} \sim 30^\circ \)) even when \( \text{C}_2\text{D}_2^{3+} \) is formed directly.
by the 9 fs pump laser pulse (bottom trace). As Δt increases, a shoulder-like feature emerges near θ12 = 120°, as expected for the isomerization from acetylene to vinylidene discussed above, and extends further to larger θ12 values. For further discussion, however, we need to take into account the dissociation of C2D22+, which is known to occur in a short time scale [16, 17] for the highly excited states. Indeed, in Fig. 2(b), the distribution of the kinetic energy release $E_{kin}$ shows the appearance of a new component at Δt = 60 fs on the lower energy side of the original peak ($E_{kin} \sim 18$ eV), which shifts to $E_{kin} \sim 8$ eV as Δt increases. The observed decrease in $E_{kin}$ is attributed to the dissociation induced by the pump laser pulse, since the Coulomb repulsion among the fragments is reduced by the increase in the internuclear distances. From the analysis of the momentum distribution in the $p_1(D^+)$- $p_2(C^+)$ correlation map performed along the lines described previously [8], we found that the low energy component originates dominantly (> 90%) from C2D22+, dissociating through the two-body pathways [17], C2D22+ → (i) D+ + C2D+, (ii) CD+ + CD+ and (iii) C+ + CD2+. This shows that the dynamics in C2D22+ is most sensitively detected in the present experimental scheme, with negligibly small contributions from those in lower charged species (C2D2+, C2D2).

In order to clarify how the isomerization from the acetylene to vinylidene configuration proceeds in undissociated C2D22+, the corresponding coincidence events need to be separated from those of the dissociating component. The distribution of all the coincidence events obtained at a fixed time delay (Δt = 280 fs) clearly shows the difference between the two components in the $E_{kin}$ - θ12 plane; a broad image extending from θ12 = 0° to 180° is observed for $E_{kin} \sim 8$ eV, whereas a dense distribution is identified at small θ12 values for $E_{kin} \sim 18$ eV. Accordingly, the dissociating component (defined with $E_{kin} < 13$ eV) exhibits a broad distribution $P_{uds}(θ_{12})$, which is attributed to the rotation of the fragment ions (e.g., C2D+) during the two-body dissociation process. On the other hand, a clear peak is observed at a small value θ12 = 40° in $P_{uds}(θ_{12})$ for the undissociated component (defined with $E_{kin} \geq 13$ eV). It is noted that $P_{uds}(θ_{12})$ contains the contribution from the background signals due either to the pump or to
the probe laser pulses, $P_{bg}(\theta_{12})$, which needs to be subtracted for further discussion: $P_{uds}^0 = P_{uds}(\theta_{12}) - P_{bg}(\theta_{12})$.

Figure 3(a) shows a two-dimensional map constructed from the distribution $P_{uds}^0(\theta_{12})$ obtained at different $\Delta t$. At the shortest time delay $\Delta t = 30$ fs, $P_{uds}^0(\theta_{12})$ exhibits a peak at small values around $\theta_{12} = 30^\circ$, as observed with the pump laser pulse only. Then, the distribution shifts to large $\theta_{12}$ values as $\Delta t$ increases until $\Delta t \sim 90$ fs when the distribution is peaked at $\theta_{12} \sim 120^\circ$ with a steep edge on the larger angle side. At a larger time delay, the $\theta_{12}$ distribution gradually shifts in the reverse direction towards the acetylene configuration to eventually form the distribution peak again at $\theta_{12} \sim 30^\circ$ with a broader distribution extending to $\theta_{12} \sim 120^\circ$. The observed time scale is consistent with the upper limit of the isomerization time of 60 fs for $\text{C}_2\text{H}_2^{2+}$ suggested by the experimental study on the inner-core ionization of carbon K-shell [16], since the migration is expected to become slower in $\text{C}_2\text{D}_2^{2+}$ because of the increase in the effective mass. After reaching the vinylidene configuration, the deuterium atom is found to undergo backward migration to the acetylene configuration with a longer time scale of 190 fs (= 280 - 90 fs) to form a broader distribution around the C-C skeleton.

3.2. Mechanism of recurrent hydrogen migration
Because of the high isomerization barrier from the acetylene to vinylidene ($\sim 2$ eV), the hydrogen migration is expected to proceed in the picosecond time scale in the lowest triplet ($X^3\Sigma_g^-$) or singlet ($a^1\Delta_g$) electronic states [18] (see Fig.4), which explains the component remaining in the acetylene configuration at $\Delta t = 90$ fs (see Fig. 3(b)). The ultrafast migration to vinylidene should, therefore, be attributed to the contribution from electronically excited states, which can be populated by the interaction with the non-resonant intense (0.13 PW/cm$^2$) pump laser pulse. In the first excited triplet state, $1^3\Pi$ (located 5.3 eV above the $X^3\Sigma_g^-$ state), for example, the acetylene configuration is unstable [18], so that the isomerization can proceed directly to reach the vinylidene configuration in a short time scale.

The subsequent backward isomerization to acetylene can be interpreted as the result of the internal conversion from the excited states to the ground $X^3\Sigma_g^-$ state. Once the vinylidene...
isomer is formed in the ground state in such a manner, the isomerization to the more stable acetylene isomer in the ground state [14, 17, 18] should rapidly proceed because the vibrational energy is sufficiently high to overcome the isomerization barrier (~0.4 eV [18]). The longer timescale of the backward migration as well as the broad distribution after the recurrence would be attributed to the spread of the nuclear wavepacket due to the intramolecular vibrational redistribution to other vibrational modes.

4. Summary

We demonstrated the real-time tracking of ultrafast hydrogen migration in the molecular frame with deuterated acetylene dication as the target. The time-resolved Coulomb explosion imaging employed here has wide applicability to unveil the intramolecular hydrogen dynamics, for instance in neutral molecules, by using a tunable ultrashort laser pulse to resonantly trigger photochemical reactions of interest. The direct visualisation of rapidly migrating hydrogen will provide a deeper understanding of chemical reactions of hydrocarbons as well as new prospects for efficient coherent reaction control with tailored laser pulses.

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