Electron-nuclear correlation in above-threshold double ionization of molecules

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We report on the experimental observation of photon energy sharing among two electrons and two ions ejected from a doubly ionized molecule exposed to an intense ultraviolet femtosecond laser pulse. Although two electrons are successively released one after the other, bridged by the nuclear motion via their interactions, photon energy sharing among four particles is observed as multiple energy conservation lines in their joint energy spectrum. For sequential double ionization of H_2, the electron-nuclear joint energy spectrum allows us to identify three pathways towards the charge-resonance enhanced ionization of the stretching H_2^+ in strong laser fields. By counting the photon number absorbed by the molecule, we trace the accessibility, enhancement, and suppression of various pathways. The correlated electron-nuclear motion provides profound insights of the complicated strong-field dynamics of molecules.

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I. INTRODUCTION

Despite the great success of the Born-Oppenheimer approximation, the correlated electron-nuclear motion plays a crucial role in the strong-field dynamics of molecules. As the primary stage of the light-molecule interaction, correlated deposition of the absorbed photon energy into the electronic and nuclear degrees of freedom is an important example governing the molecular fate. It was observed not only for the single-photon ionization of molecules exposed to synchrotron radiation [1–3], but also recently for strong-field multiphoton single ionization of molecules [4–10] via the correlated interaction of the outgoing electron with the nuclei. As compared to the single ionization, exchanging and sharing of energies from multiple absorbed photons between two freed electrons are expected in nonsequential above-threshold double ionization (ATDI) [11–14], which was recently observed experimentally in both atoms and molecules [15,16]. Beyond the photon energy sharing between one freed electron and its parent ion, in which case two parts are closely correlated, does the photon energy sharing between two electrons and two nuclei still hold, especially when the two electrons do not directly correlate each other but release out sequentially during the ATDI process? An experimental examination is in urgent need to give a clear statement.

In addition to the electron-nuclear energy sharing, molecules exposed to strong laser fields exhibit many fascinating phenomena, e.g., bond softening and hardening [17–19], above-threshold dissociation [20,21], light-induced electron self-diffraction [22,23], and charge-resonance enhanced ionization (CREI) [24,25]. As compared to atoms, the ionization rate of a molecule orientated parallel to the laser field is significantly enhanced when the molecule stretches to a critical range of internuclear distance. From the multiphoton point of view, the enhanced ionization of a molecule can be alternatively understood as a manifestation of enhanced multiphoton ionization on the basis of the Floquet potentials, including the $1/R$ Coulomb explosion curves dressed by the laser field, i.e., above-threshold Coulomb explosion, as proposed in Ref. [26]. Additionally, the role of the time-dependent coupling of the electronic and nuclear motion in refining the ionization rate of a stretching H_2^+ in strong laser fields was recently revealed [27]. While most of the theoretical works focused on the simplest one-electron H_2^+ [25,28–31], the experiments were mainly performed using the neutral target of H_2 molecules [32–36], where the enhanced ionization occurs in the second ionization step during the stretching of the H_2^+ created in the first ionization step. The thorough understanding of photon energy sharing between two electrons and two nuclei will give comprehensive understanding of molecular dissociative ionization in strong laser fields.

In this paper, we experimentally demonstrate the photon energy sharing among four particles, i.e., two electrons and two ions, in multiphoton ATDI of H_2 exposed to an intense UV femtosecond laser pulse. As compared to the conventional time-resolved pump-probe technique, we reveal the dissociative ionization dynamics of molecules by taking the advantage of the electron-nuclear joint energy spectrum (JES). Multiple energy conservation lines spaced by the photon energy are observed in the electron-nuclear JES. We identify three pathways, i.e., the direct, one-photon, and net-two-photon pathways as denoted in Fig. 1, towards the enhanced ionization of the stretching H_2^+ created in the first ionization step. The photon energy deposition between the electron and nuclei in the first ionization step governs the stretching of H_2^+ and thus the releasing dynamics of the second electron. With the increasing of the number of photons absorbed by the molecule, the double ionization channel with higher nuclear kinetic energy release (KER) becomes accessible and the yield is relatively increased. Our results strengthen our understanding of the correlated electron-nuclear dynamics in absorbing multiple photons and provide an illuminating insight into the general phenomenon of charge-resonance enhanced ionization of molecules exposed to strong laser fields.

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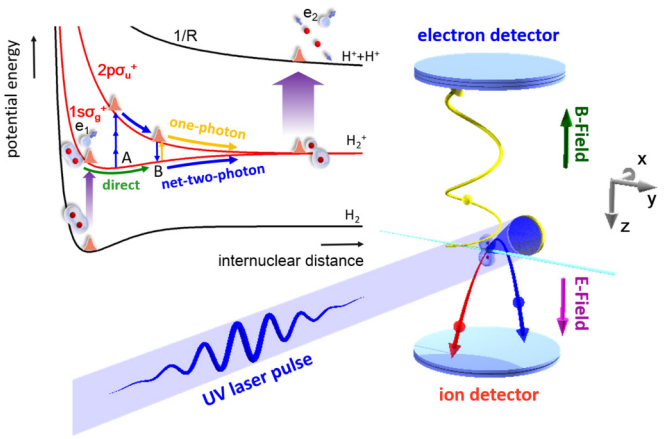

FIG. 1. Schematic illustration of the experimental setup and the various pathways of the multiphoton double ionization of H_2 in a strong laser field.

II. EXPERIMENTAL SETUP

As schematically illustrated in Fig. 1, the experiments were performed in an ultrahigh vacuum reaction microscope setup of cold-target recoil ion momentum spectroscopy (COLTRIMS) [37], where the photoionization-created ions and electrons were measured in coincidence by two time- and position-sensitive detectors at the opposite ends of the spectrometer. The three-dimensional momenta of the ejected electrons and ions are reconstructed from the times-of-flight and positions of the measured impacts during the offline analysis. In order to obtain a well-spaced above-threshold-ionization (ATI) spectrum of the photoelectron, a linearly polarized UV pulse ($\lambda = 395$ nm) was produced by frequency doubling of a near-infrared pulse (25 fs, 790 nm, 10 kHz) in a 150-μm-thick β-barium borate (BBO) crystal. The z-polarized UV pulse propagating along the x axis was afterwards sent into the vacuum chamber and focused onto a supersonic gas jet of H_2 by a concave silver mirror with a focusing length of $f = 75$ mm inside the apparatus. The intensity of the 60-fs UV pulse was estimated to be 1.1×10^{14} W/cm^2 in the interaction region. The corresponding Keldysh parameter was calculated to be $\gamma = \sqrt{(I_p/2U_p)} \approx 2.2$, where I_p is the ionization potential of H_2 and U_p is the ponderomotive energy of a free electron in the oscillating laser field.

III. RESULTS AND DISCUSSION

To reveal the correlated electron-nuclear sharing of the absorbed photon energy, we investigate the Coulomb-exploded double ionization channel of $H_2 + n\omega \rightarrow H^+ + H^+ + e_1 + e_2$, hereafter denoted as $H_2(1,1)$. Atomic units (a.u.) are used throughout unless otherwise stated. To suppress the false coincidence, a momentum conservation gate of $|p_{z,e1} + p_{z,e2} + p_{z,ion1} + p_{z,ion2}| < 0.5$ is applied for the measured electrons and ions along the time-of-flight direction of the spectrometer. Figure 2(a) shows the JES of the sum energy of two electrons, i.e., $E_{e1} + E_{e2}$, versus the sum energy of two ions, i.e., E_N, of the $H_2(1,1)$ channel. Multiple diagonal lines spaced by the photon energy are clearly observed, indicating the sharing of multiphoton energies

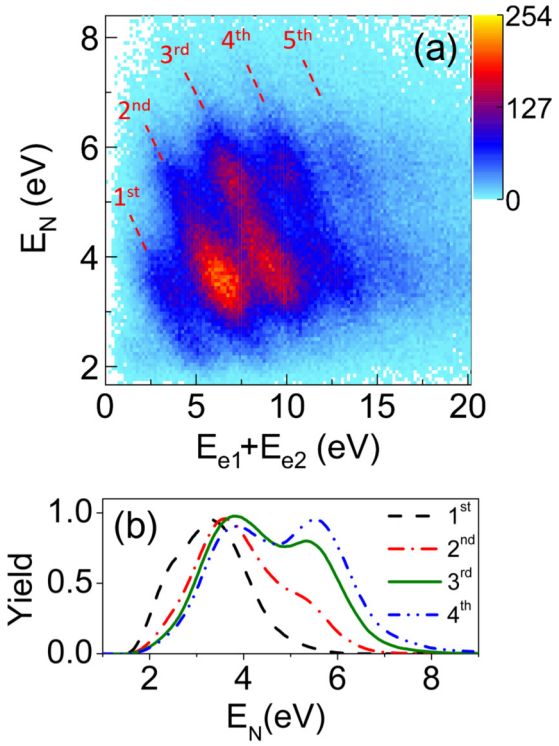

FIG. 2. (a) Electron-nuclear JES of the sum energy of two protons and the sum energy of two electrons of the $H_2(1,1)$ channel. (b) Nuclear KER spectra by projecting one of the first four diagonal energy conservation lines as labeled in (a), normalized by their own maxima.

among the ejected electrons and nuclei in the ATDI of H_2. Hence, multiphoton ionization dominates in our experiments, although the tunneling process should also exist, which might blur the discrete ATI structure to a certain extent [5,6]. Each energy conservation (diagonal) line in the JES indicates that the H_2 system as a whole absorbs a constant number of photons. The excess photon energy over the double ionization threshold is deposited into the nuclei and electrons in a correlated manner. As compared to the photon energy sharing between two electrons in nonsequential ATDI of atoms and molecules [15,16], the JES in Fig. 2(a) shows an experimental observation of photon energy sharing among two electrons and two ions in a multiphoton ATDI of a molecule exposed to strong laser fields.

Rather than nonsequential double ionization, we note that the two electrons are mostly sequentially released, separated by molecular bond stretching in our experiments. As shown in Fig. 3(a), the successive releasing dynamics of the two electrons are confirmed by observing the dominated discrete islands appearing in the crossing of straight lines in the electron-electron JES of the $H_2(1,1)$ channel. Meanwhile, as shown in Fig. 3(c), the nuclear fragments mainly lie in the ranges from 2 to 8 eV (~97% of the events of double ionization) of the KER spectrum, which is quite typical for the enhanced ionization of H_2, as previously observed [26,32,34]. The events with nuclear KER higher than 8 eV are quite few (less than 2% of the events of double ionization) as compared to those with nuclear KER lower than 8 eV. Hence, the contribution from the fragmentation of H_2 happening along the

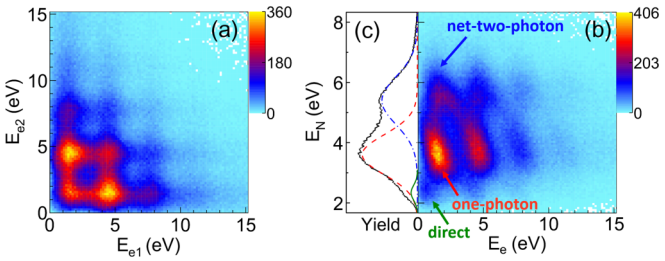

FIG. 3. (a) Electron-electron JES of two freed electrons of the $H_2(1,1)$ channel. (b) JES of the sum energy of two protons and the energy of one of the two electrons of the $H_2(1,1)$ channel. (c) Nuclear energy spectrum integrated over the electron energy where the fitted distributions of three identified pathways are plotted in different colors (solid green for direct, dashed red for one-photon, dash-dotted blue for net-two-photon). The titled arrows in (b) indicate the energy of the electron correlated to three different pathways towards the double ionization of H_2.

$1/R$ potential energy curve populated earlier than the opening of the CREI channel is minor in our experiments.

The exploding double ionization of H_2 can occur via a three-step process [38], as illustrated in Fig. 1. Initially, a neutral H_2 molecule in its ground state is multiphoton ionized, resulting in a vibrational wavepacket launched in the $1s\sigma_g{}^+$ state of $H_2{}^+$ by releasing an electron e_1. The ionization-created $H_2{}^+$ may stretch in the laser field via three different pathways: the direct pathway (bond stretching along the $1s\sigma_g{}^+$ curve), or the one-photon pathway (propagation on the $1s\sigma_g{}^+$ curve undergoes one-photon transition to the $2p\sigma_u{}^+$ curve at point B, followed by dissociation along the $2p\sigma_u{}^+$ curve), or the net-two-photon pathway (propagation on the $1s\sigma_g{}^+$ curve undergoes a three-photon transition to the $2p\sigma_u{}^+$ curve at point A, followed by propagation on the $2p\sigma_u{}^+$ curve and coupling back to the $1s\sigma_g{}^+$ curve at point B by emitting one photon, followed by dissociation along the $1s\sigma_g{}^+$ curve). As the stretching molecular ion passes through the critical range of internuclear separation, the charge-resonance-enhanced releasing of the second electron e_2 might occur, which takes place about 10 fs after the first ionization step [6], triggering the breakup of bare nuclei by Coulomb repulsion between two H^+ ions. The final state lies in the molecular double continuum as a Coulombic system comprised of two freed electrons and two ions. The diagonal lines in the electron-nuclear JES displayed in Fig. 2(a) stand for the conservation of the photon energy absorbed by the molecule which are shared by two electrons and two ions in the ATDI of the molecule.

Interestingly, as shown in Fig. 3(b), the JES of one electron and two nuclei allows us to identify the aforementioned three pathways of the stretching $H_2{}^+$ towards the enhanced releasing of the second electron around the critical internuclear separation. Three distinct sets of tilted strips with nuclear energy E_N in the ranges of 2–3 eV, 3–5 eV, and 5–8 eV, are observed, indicating three different dynamics involved in the ATDI of H_2 in our experiments. However, as shown in Fig. 3(c), the nuclear spectrum of the $H_2(1,1)$ channel integrated over the electron energy obscures much of the information revealed by the electron-nuclear JES, which provides deeper insights into the electron-nuclear dynamics than the sole nuclear spectrum does.

For the single ionization of H_2 into $H_2{}^+$, as we already demonstrated [8], most of the electron energy is transferred to the nuclei via their interaction for the direct pathway. Hence, for the first ATI order indicated by the titled arrows in Fig. 3(b), the electron energy of the direct pathway is lower than that of the one-photon pathway. On the other hand, in the first ionization step, the nuclei share the photon energy with the emitted electron by creating a vibrational wave packet as an energy reservoir. Accordingly, the net-two-photon pathway, which initializes from lower vibrational levels of the $1s\sigma_g{}^+$ state than the one-photon pathway, correlates to the higher energy of the electron, as shown in Fig. 3(b). Therefore, the electron-nuclear JES displayed in Fig. 3(b) reveals three pathways towards the enhanced ionization of the stretching $H_2{}^+$ as their different photon energy sharing dynamics in the first ionization step.

In addition to the energy taken from e_1 in the first ionization step and accumulated as the molecular ion stretches to the critical internuclear distance along the potential curve, the nuclei further gain kinetic energy from the Coulomb explosion in the second ionization step including the energy taking from e_2. The energy sharing between the nuclei and e_2 can be understood as the internuclear-distance-dependent ionization potential of e_2 [30], i.e., the energy difference between the Coulombic repulsive curve of $1/R$ and the $1s\sigma_g{}^+$ (or $2p\sigma_u{}^+$) curve on which the nuclei propagate. By assuming that the e_2 is released in the same range of internuclear distance, the kinetic energy difference of the nuclei of the $H_2(1,1)$ channel produced via the one-photon and net-two-photon pathways is expected to be $\sim$1.7 eV. It agrees well with the energy separation between two dominated peaks (fitted by dashed red and dash-dotted blue curves) in the measured E_N spectrum shown in Fig. 3(c). The complicated structures of the band with E_N around 5 eV in Fig. 3(b) arise from the overlap of these two pathways.

The total energy of two electrons and two ions satisfies $E_{e1} + E_{e2} + E_N = n_s\omega + V_g\text{-}U_{p1}\text{-}U_{p2}$, where ω, V_g, and $U_{p1(2)}$ denote the laser frequency, the potential energy of the ground state of H_2, and the ponderomotive energies of e_1 and e_2, respectively. $n_s = n_1 + n_2 + n_d$ is the total photon number absorbed by the molecule, $n_{1(2)}$ is the photon number absorbed in the first (second) ionization step, and n_d is the photon number that $H_2{}^+$ absorbed during its stretching towards the critical internuclear separation ($n_{d.} = 0,1,2$ for the direct, one-photon and net-two-photon pathways). Each diagonal line in Fig. 2(a) stands for a constant number of n_s, which is composed of various combinations of n_1, n_2, and n_d. For a given energy conservation line in Fig. 2(a), the sum energy of two electrons associated with $n_1 + n_2$ decreases as the increasing of the nuclear energy E_N associated with n_d, since their sum n_s is a constant. For the first diagonal energy conservation line in Fig. 2(a) with electron-nuclear sum energy of $\sim$5 eV, the n_s is estimated to be 13 for the UV field with a photon energy of 3.1 eV by considering the double ionization threshold of $\sim$32 eV and the ponderomotive energy $U_{p1(2)}$ of more than 1.6 eV for each freed electron. Interestingly, as displayed in Fig. 2(b), the higher nuclear energy pathway becomes accessible with increased relative yield with the increase of n_s. For instance, the $H_2(1,1)$ channel is dominated by the direct and one-photon pathways for the first energy conservation line, with $n_s = 13$,

while the $H_2(1,1)$ channel via the net-two-photon pathway is opened for the second energy conservation line with $n_s = 14$. The yield of the net-two-photon pathway increases with the increase of n_s, which even exceeds the one-photon pathway for the fourth energy conservation line with $n_s = 16$. Meanwhile, the direct pathway is rapidly suppressed with the increase of n_s. Therefore, the opening and relative weights of various pathways towards the charge-resonance enhanced ionization of the stretching molecular ion depend on the total number of photons absorbed by the molecule and how the photon energy is deposited into the electrons and nuclei.

IV. CONCLUSION

In summary, we report the first experimental observation of photon energy sharing among two electrons and two ions in multiphoton ATDI of H_2 exposed to a strong laser field. The electron-nuclear JES allows us to identify three pathways of the stretching H_2^+ towards its enhanced ionization in the range of critical internuclear distance. Our results show that the accessibility, enhancement, and suppression of various pathways are dominated by the total number of photons absorbed by the molecule. The electrons share the excess photon energy over the double ionization threshold with the nuclei due to their interaction, allowing us to get deep insights into, for instance, the charge-resonance enhanced ionization of the stretching molecular ion, which generally occurs for molecules exposed to strong laser fields.

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