Control of Electron Excitation and Localization in the Dissociation of $H_2{}^+$ and Its Isotopes Using Two Sequential Ultrashort Laser Pulses

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We study the control of dissociation of the hydrogen molecular ion and its isotopes exposed to two ultrashort laser pulses by solving the time-dependent Schrödinger equation. While the first ultraviolet pulse is used to excite the electron wave packet on the dissociative $2p\sigma_u$ state, a second time-delayed near-infrared pulse steers the electron between the nuclei. Our results show that by adjusting the time delay between the pulses and the carrier-envelope phase of the near-infrared pulse, a high degree of control over the electron localization on one of the dissociating nuclei can be achieved (in about 85% of all fragmentation events). The results demonstrate that current (sub-)femtosecond technology can provide a control over both electron excitation and localization in the fragmentation of molecules.

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Controlling the electrons and fragments in a reaction is one of the exciting goals of photochemistry and attosecond physics. It is nowadays possible to steer the fragmentation pathways of molecules using ultrashort laser pulses [1]. The advent of carrier-envelope phase-locked few-cycle pulses and single subfemtosecond pulses [2–4] has further prepared the ground to control electron wave packets and coherently coupled electronic states in atoms and molecules [5–8]. It is therefore appealing to ask whether the combined control of pathway selection and electron localization in the fragments is feasible with current laser technology. In this Letter, we address this question via the solution of the time-dependent Schrödinger equation for the simplest molecules, namely, the hydrogen molecular ion and its isotopes, interacting with a sequence of two ultrashort laser pulses.

These molecules represent fundamental diatomic molecules with a well-known electronic structure. In the past few years, progress in experimental techniques has made it possible to clarify the photodissociation dynamics of $H_2{}^+$, HD^+, and $D_2{}^+$ by a single intense laser pulse [9–12]. The laser induced dynamics of the molecule include two major pathways, namely, dissociation and dissociative ionization, via several mechanisms, e.g., above threshold dissociation [13], bond softening [14,15], bond hardening [16], charge-resonant enhanced ionization [17,18] or above threshold Coulomb explosion [19]. The challenge to control both the electronic excitation and localization during the fragmentation of the molecule can be therefore expressed in the following question: Is it possible to dissociate the molecule without ionizing it *and* localize the electron at one of the two dissociating nuclei?

Recently, the aspects of controlling the dissociation pathway by shaped pulses [20] or the electron localization by ultrashort few-cycle phase-locked pulses [6,7] have been addressed but separately. Below, we consider the combined control of both aspects by applying a different control strategy based on the use of two time-delayed coherent pulses [21]. This will allow us to select the dissociation route and avoid ionization of the molecule with a first pulse and to steer the electron between the two dissociating nuclei with a second time-delayed pulse. We find that in nearly 85% of all fragmentation events, the electron can be purposefully located at a specific nucleus.

For our numerical simulations we have used the three-dimensional model for the hydrogen molecular ion and its isotopes interacting with an intense linearly polarized pulse [6,22,23]. It accounts for the interaction of the electron with the external field as well as non-Born-Oppenheimer effects. Rotation of the molecule is not considered since the molecule does not rotate significantly during the time of interaction with an ultrashort laser pulse up to a few tens of femtoseconds duration. Within this model, the time-dependent Schrödinger equation can be given as (Hartree atomic units, $e = m = \hbar = 1$ are used)

$$i\frac{\partial}{\partial t}\Phi(R, z, \rho; t) = [H_0 + V(t)]\Phi(R, z, \rho; t), \qquad (1)$$

where H_0 is the field-free Hamiltonian

$$\begin{aligned} H_0 = &-\frac{1}{2\mu}\frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_e}\left(\frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho}\frac{\partial}{\partial \rho}\right) \\ &+ \frac{1}{\sqrt{R^2 + \beta}} - \frac{1}{\sqrt{(z - z_p)^2 + \rho^2 + \alpha}} \\ &- \frac{1}{\sqrt{(z + z_n)^2 + \rho^2 + \alpha}}, \end{aligned} \qquad (2)$$

where R is the internuclear distance, $z_p = m_n/(m_p + m_n)R$ and $z_n = m_p/(m_p + m_n)R$ are the positions of the proton and the second nucleus, respectively. $\mu = (1/m_p + 1/m_n)^{-1}$ and $\mu_e = (m_p + m_n)/(m_p + m_n + 1)$ are the reduced masses, with m_p and m_n the masses of the proton and the second nucleus. We have considered $H_2{}^+$, HD^+, and HT^+ oriented along the polarization axis. We have chosen the soft-core parameters $\alpha = 0.0109$ and $\beta = 0.1$ such that the model yields the experimental ground state energy and equilibrium distance of -0.6028 and 2.0 a.u., respectively. The interaction of the electrons with the two pulses is taken into account via $V(t)$ given in dipole approximation and length gauge as [24]

$$V(t) = [E_1(t) + E_2(t - \Delta t)] \times \left[\frac{m_p - m_n}{m_n + m_p} R + \left(1 + \frac{1}{1 + m_n + m_p}\right) z\right] \quad (3)$$

with $E_i(t) = E_{0,i} \exp[-(t/\tau_i)^2] \sin(\omega_i t + \phi_i)$, where τ_i is the pulse duration, ω_i is the central frequency, $E_{0,i}$ is the peak electric field amplitude, ϕ_i is the carrier-envelope phase of the i-th pulse, and Δt is the time delay between them. The applied fields are chosen to be linearly polarized along the molecular axis.

We have solved Eq. (1) on a grid using the Cranck-Nicholson method with a time step of $\delta t = 0.05$ a.u.. The grid ranges in R-direction from 0 to 20 a.u., for ρ from 0 to 24 a.u. and for z from -30 to 30 a.u. with 500, 80, and 200 points in the three directions, respectively. The ground state of the system (electronic $1s\sigma_g$ state and vibrational $\nu = 0$ state) has been obtained using imaginary time propagation. We have defined the two channels of dissociation as

$$P_+ : R > 10 \quad \text{and} \quad \sqrt{(z - z_p)^2 + \rho^2} < 5, \qquad : \mathrm{H} + n \quad (4)$$

$$P_- : R > 10 \quad \text{and} \quad \sqrt{(z + z_n)^2 + \rho^2} < 5, \qquad : p + A \quad (5)$$

where n and A stand for p, d, t and H, D, T, respectively. We define P_+ and P_- as the probabilities of directional localization of the electron along the positive (proton side) and negative (second nucleus side) z-axis, respectively. The grid is chosen large enough to account for any return of an ionized electron wave packet to the nuclei. We have employed absorbing boundaries using $\cos^{1/6}$-masking functions but stored the absorbed contributions as dissociation or dissociative ionization, respectively. The propagation of the wave function has been continued after the interaction with the pulses until the probabilities for all reaction channels are converged.

We aim to drive the molecular ion to dissociation without ionizing it with a first pulse and steer the electron between the two dissociating nuclei with a second time-delayed pulse. Let us first consider the excitation induced by the first pulse alone. The most promising strategy for a pathway selection appears to be a one-photon transition to the first dissociative $2p\sigma_u$ state. In our model, the energy gap between the ground and the first excited state at the equilibrium distance is 0.43 a.u., which corresponds to a wavelength of 106 nm and equals the seventh harmonic of a laser system operating at 742 nm.

In Fig. 1, we present the dissociation probabilities for electron localization at the proton (circles) and at the second nucleus (stars), respectively, for the interaction of ${H_2}^+$, HD^+, and HT^+ with an ultrashort ($\tau_1 = 0.425$ fs, FWHM) UV pulse at 106 nm and a peak intensity of 10^{13} W/cm^2. The desired pathway selection has been achieved since the probability for dissociative ionization is below the numerical noise level.

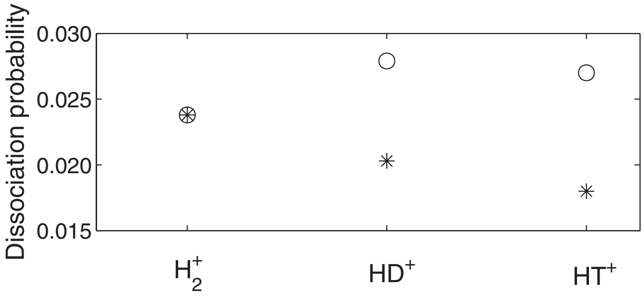

FIG. 1. Dissociation probabilities with an electron localization along the positive (proton side, circles) and the negative (second nucleus side, stars) z-axis as a function of the mass of the molecule due to the interaction with an ultrashort UV pulse at $\lambda_1 = 106$ nm, $\tau_1 = 0.425$ fs and $I_{0,1} = 10^{13}$ W/cm^2.

The results in Fig. 1 show that for ${H_2}^+$, the electron is localized with the same probability at either one of the nuclei, while for the hetero-nuclear molecules, we observe a slight asymmetry with preferred electron localization at the proton side. This asymmetry is not induced by the UV pulse since the results do not vary qualitatively with a change of the parameters of the pulse. Neither a variation of the peak intensity (10^{13}–10^{14} W/cm^2) nor small variations of the wavelength (100–120 nm) or of the pulse duration (up to $\tau_1 = 2$ fs) changes the relative probabilities significantly. The dissociation probabilities are found to be independent of the value of the carrier-envelope phase of the pulse. Generation of a UV pulse with these parameters appears to be feasible. In test simulations on high harmonic generation in atoms, we have found that the seventh harmonic driven by a 10 fs (FWHM) laser pulse at a Ti:sapphire wavelength (700—840 nm) would fulfill the requirements.

We next investigate the dissociation dynamics initiated by the first pulse. In order to follow the temporal evolution of the electron localization, we have to erase the bound state contributions from the total wave function. This is achieved by projecting out the initial ground state $\Phi(R, z, \rho)_{1s\sigma_g, \nu=0}$ at the end of the pulse and propagating the remaining wave function alone. Minor contributions from higher vibrational levels of the electronic ground state are found to be negligible. The electron localization probabilities are obtained from the remaining wave function by dividing the grid along the geometrical center of the nuclei and integrating the contributions in the respective zones of the coordinate space.

In Fig. 2, we present the temporal evolution of the electron localization probabilities at the proton (thick line) and the second nucleus (thin line) for (a) ${H_2}^+$, (b) HD^+, and (c) HT^+. The electron oscillates between

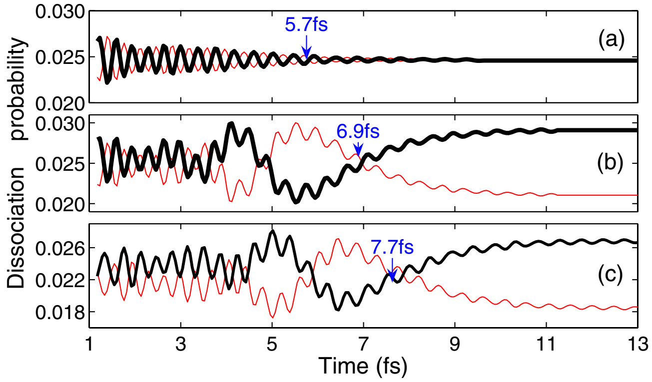

FIG. 2 (color online). Electron localization probabilities along the positive (proton side, thick line) and the negative z-axis (second nucleus, thin line) for (a) $H_2{}^+$, (b) HD^+, and (c) HT^+ as a function of time. Laser parameters are as in Fig. 1. The arrows mark the time when the interatomic barrier reaches the energy of the first excited state.

the two nuclei before the localization probabilities finally stabilize. This is due to the rise of the internuclear barrier as the distance between the two nuclei increases. As, within the present model, the electronic structure is identical for all molecules considered here; the height of the barrier crosses the energy of the first excited state $2p\sigma_u$ at $R_0 = 6.3$ a.u. However, the time to reach R_0 during the dissociation increases with the total mass of the fragments. The oscillation of the electron localization ceases beyond the respective times, indicated by the arrows.

There is an apparent difference in the electron dynamics for the dissociating homo- and hetero-nuclear molecules. In the former case [Fig. 2(a)], one observes a fast oscillation around the final value of the localization probability, which is induced by the UV pulse. Because of the high frequency of the oscillation, any asymmetry in the electron localization at the beginning averages out as the interatomic barrier slowly rises. In contrast, in the heteronuclear cases, there is a second oscillation with larger amplitude. It is due to the separation of the center of the electron charge and the center of mass during the dissociation of the hetero-nuclear molecules, which creates a coupling between the $1s\sigma_g$ and $2p\sigma_u$ states. This can be seen, e.g., by changing to a reference frame moving with the center of charge, which introduces mixed terms in the kinetic operator and an asymmetric potential term in the Hamiltonian. These terms work as a permanent dipole inducing a coupling between the states (c.f. [25]).

We now turn to the control of the electron localization at the two dissociating nuclei. The results in Fig. 2 let us expect that there is a time window of a few femtoseconds to steer the electrons between the nuclei. In order to check our expectations, we have performed another set of simulations in which a second time-delayed two-cycle ($\tau_2 = 3.8$ fs) laser pulse at $\lambda = 800$ nm and $I_{0,2} = 3 \times 10^{12}$ W/cm^2 has been applied. We note that this weak pulse does not induce ionization or further dissociation.

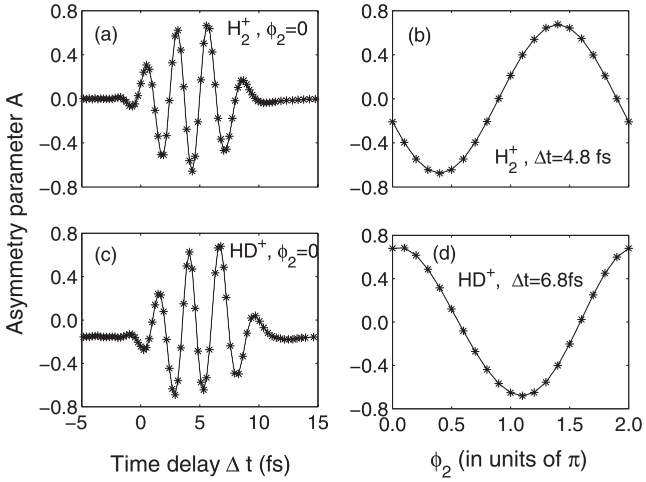

FIG. 3. Dependence of the asymmetry parameter A of electron localization on the two control parameters Δt and ϕ_2. Left hand panels: A as a function of the time delay Δt with $\phi_2 = 0$ for (a) $H_2{}^+$ and (c) HD^+. Right hand panels: A as a function of the carrier-envelope-phase ϕ_2 for (b) $H_2{}^+$ and $\Delta t = 4.8$ fs and (d) HD^+ and $\Delta t = 6.8$ fs.

In Fig. 3, we present the dissociation asymmetry $A = (P_- - P_+)/(P_- + P_+)$ for $H_2{}^+$ (upper row) and HD^+ (lower row) obtained after application of the two pulses. Note that A denotes the asymmetry in the directional localization of the electron along the positive (P_+, proton side) and the negative (P_-, second nucleus side) z-direction. The control over the electron localization is achieved by the delay Δt between the two pulses and the carrier-envelope-phase ϕ_2 of the second near-infrared pulse. This is seen from Fig. 3, where A is shown as a function of the time delay Δt at fixed $\phi_2 = 0$ for (a) $H_2{}^+$ and (c) HD^+ on the left hand side. The dependence of A on the carrier-envelope-phase ϕ_2 for a fixed time delay is shown on the right hand side [(b) $H_2{}^+$, $\Delta t = 4.8$ fs and (d) HD^+, $\Delta t = 6.8$ fs]. The parameters of the first UV pulse are as in Fig. 1. We may recall that the phase of the first pulse, and hence the relative phase of the two pulses, do not play a role for the electron localization. The desired control of the electron localization is indeed achieved. A maximum asymmetry of $A = 0.676$ for $H_2{}^+$ and $A = 0.681$ for HD^+ is found, which corresponds to an electron localization probability as high as about 84% of all fragmentation events.

What is the origin of the control? To answer this question, we present in Fig. 4 the temporal evolution of the electron localization in (a) $H_2{}^+$ ($\Delta t = 6.9$ fs, $\phi_2 = 0$) and (b) HD^+ ($\Delta t = 7.2$ fs, $\phi_2 = 0$). The localization probabilities are obtained as in Fig. 2; the representation of the results agrees as well. It is seen that the electron follows the oscillating field (shown by the dashed-dotted line) as long as the interatomic barrier does not inhibit its free movement between the nuclei. As the barrier reaches the energy of the $2p\sigma_u$-state (c.f. arrows in Fig. 4), there is some probability for tunneling through the barrier before the

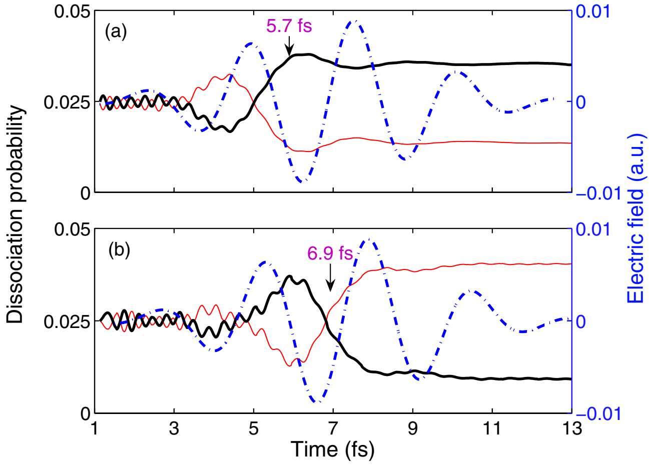

FIG. 4 (color online). Same as Figs. 2(a) and 2(b) but with a second time-delayed laser pulse. The electric field of the latter is shown by the dashed-dotted line. The time delay is (a) $\Delta t = 6.9$ fs and (b) $\Delta t = 7.2$ fs, respectively.

electron gets trapped in the Coulomb potential of one of the two nuclei.

The interpretation of a field-driven electron localization in the double-well potential provides an intuitive picture of the control scenario with the time delay and the carrier-envelope-phase of the second pulse as the principal control parameters. Our results also suggest that even longer near-infrared pulses can be used since the control of electron localization via the field is limited to a certain period due to the rise of the interatomic barrier. We have confirmed this expectation in test calculations using three-cycle pulses. Furthermore, the final asymmetry is expected to increase as the field intensity increases. We indeed observe a noticeable control of the electron localization starting at 10^{10} W/cm^2 with a maximum probability of 97% reached at 10^{14} W/cm^2, beyond which ionization of the dissociating molecule sets in.

Alternatively, the electron localization can be also interpreted via coherently coupled electronic states [8]. In the present control scheme, a coherent superposition of the ground and first excited states is prepared by the first pulse. Depending on the time delay, carrier-envelope-phase, and intensity of the second pulse, population is transferred between the two states, changing the electron localization between the two nuclei.

We may finally note that a substantially higher degree of control has been achieved with the present two-pulse scenario as compared to previous studies, in which one carrier-envelope- phase-locked pulse has been used [6,7]. In the latter, the electron is excited via rescattering (near a zero of the field) and steered between the nuclei during the rest of the pulse. In that case, the time delay between excitation and steering as well as the phase relation are fixed, constraining the control parameters. As shown in Fig. 3, it is the variation of these two parameters which facilitates the control in the present scheme.

In conclusion, we have shown that a control to a large degree of both electron excitation *and* localization in the dissociation of the hydrogen molecular ion and its isotopes is feasible with current laser technology. In numerical simulations, a final localization probability of 85% and more is found for an interaction of the molecules with two ultrashort laser pulses. The control is achieved via a dissociation pathway selection with a first UV pulse and a control of the electron localization with a second time-delayed infrared pulse. Since the dissociation time and, hence, the time window for a control increases with the mass of the fragments, we expect that the present control scheme is applicable in other molecules too.

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