Electron Localization in Molecular Fragmentation of H_2 by Carrier-Envelope Phase Stabilized Laser Pulses

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Fully differential data for H_2 dissociation in ultrashort (6 fs, 760 nm), linearly polarized, intense (0.44 PW/cm^2) laser pulses with a stabilized carrier-envelope phase (CEP) were recorded with a reaction microscope. Depending on the CEP, the molecular orientation, and the kinetic energy release (KER), we find asymmetric proton emission at low KERs (0–3 eV), basically predicted by Roudnev and Esry, and much stronger than reported by Kling *et al.* Wave packet propagation calculations reproduce the salient features and discard, together with the observed KER-independent electron asymmetry, the first ionization step to be the reason for the asymmetric proton emission.

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The dissociation of molecular hydrogen upon interaction with intense, ultrashort laser pulses has become a prototype reaction for molecular research in strong fields with numerous experimental and theoretical efforts (see, e.g., [1–5]) with increasing focus towards controlling chemistry. Interest has been fueled by theory since H_2 (D_2) or H_2^+ (D_2^+) represent the simplest molecules, with *ab initio* calculations looming on the horizon. At the same time, these molecules—being among the fastest—pose utmost challenges to experimentalists, successfully met in experiments with 6 fs pulses tracing the wave packet propagation in D_2 [6] and in H_2^+ [7] as well as pointing towards the possibility to fully characterize [8,9] and control [10–12] ultrafast motion on the laser electric field-dressed molecular potential curves.

More recently, an experiment on D_2 [2] demonstrated the possibility to control the emission direction of the D^+ fragments by varying the carrier-envelope phase (CEP), constituting a first experimental realization for subfemtosecond control of electronic motion in a molecular reaction. Here, after ionization of D_2 in a first step [Fig. 1(a)], the emerging electron oscillates in the field and can recollide with the parent D_2^+ thereby exciting it to the dissociating $2p\sigma_u$ state by inelastic scattering. Assuming that this happens during the first recollision with a probability of 100%, the wave packet travels down the repulsive curve to the point where the difference in energy between the bound $1s\sigma_g$ and the repulsive $2p\sigma_u$ potentials fits the photon energy. Photons in the tail of the laser pulse then effectively couple these two states and resonantly transfer the remaining electron between them. In the course of the ongoing further dissociation, the internuclear distance R and the potential barrier between the two protons then increase, eventually reaching the point where the electron density remains localized at one of the two nuclei [10,13]. Starting early on the steep $2p\sigma_u$ potential leads to the high deuteron kinetic energies between 3–8 eV observed in the experiment [2].

While this certainly marks an important step forward, many questions have remained open: To what extend might the effect be due to the CEP-dependence of the first ionization step rather than due to the coupling as discussed in [14]? Why has it not been observed for low dissociation energies as predicted theoretically [1]? Though a weak asymmetry for HD has been found between a kinetic energy release (KER) of 1 and 2 eV [3], it remains unclear whether this is due to bond softening or a very low KER recollision contribution to the asymmetry. Would charge localization depend on the orientation of the molecules, and does the electron, emitted during the ionization and "triggering the reaction," show an asymmetry as well? If so, will its CEP-dependence be related to "charge localization" [14]? Last but not least, since two electrons are

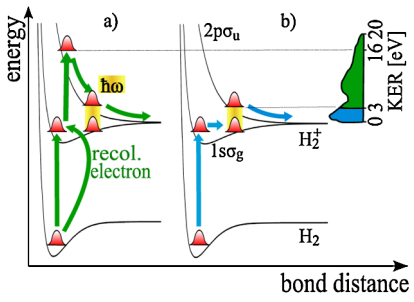

FIG. 1 (color online). Simple models for the dissociation of H_2^+ (a) with and (b) without a recolliding electron. The yellow shaded area is the region, where the laser can resonantly couple the two ionic states.

involved, what is the role of electron-correlation as exposed in [15]?

In order to shed light onto some of these questions, in this Letter we report on a kinematically complete experiment on H_2 using 6 fs CEP-controlled pulses. We find CEP-dependent asymmetries in the dissociation of H_2^+ at low KERs between 0–3 eV not to be explained by the recollision model developed in [2]. So far, unobserved effects depending on the initial orientation of the H_2 molecule as well as asymmetric electron ejection both become accessible with our technique.

Moreover, since we produce a wave packet on the H_2^+ potential curve in the first ionization step, not considered in previous theoretical models [1,16], we have performed wave packet propagation simulations [8,9,11], which widely reproduce our experimental data, providing not only insight into the origin of CEP-dependent effects for dissociating molecules in general but, in addition, point towards subfemtosecond chemical control schemes through electron localization in pump-probe scenarios.

In the experiment, linearly polarized ultrashort (6 fs, 760 nm), intense (0.44 PW/cm^2) laser pulses with stabilized CEP were focused by a spherical silver mirror (f = 60 mm) onto a dilute (10^8 particles/cm^3) supersonic H_2 jet in an ultrahigh vacuum (2×10^{-11} mbar) chamber. The reaction volume along the pulse propagation was well localized via two slits; thus, avoiding integration over different CEPs due to the Gouy effect [17].

In the reaction microscope (for details, see [18]), created electrons and ions were guided by weak electric ($\approx$2 V/cm) and magnetic ($\approx$0.8 mT) fields along the laser-polarization axis onto two position-sensitive channel plate detectors. Three-dimensional momentum vectors of all charged particles are reconstructed from the measured times of flight and positions on the detector, allowing us to extract kinematically complete electron-ion coincidences, and, thus, obtain information on channel separation, emission angular dependences, etc., not accessible by any other technique. For the ions, we reached a momentum resolution of $\Delta P_{\|} = 0.1$ a.u. in the longitudinal direction (i.e., parallel to the laser-polarization axis), $\Delta P_{T1} = 0.5$ a.u. in direction of the H_2 gas jet, and $\Delta P_{T2} < 0.1$ a.u. in direction perpendicular to both. Only the longitudinal momentum component was analyzed for the electrons in this first experiment, since here ionization phase information might be imprinted and a resolution of $\Delta Pe_{\|} = 0.05$ a.u. was achieved.

Experimentally, the CEP-dependent difference in the proton emission direction manifests itself via an asymmetry in the number of detected protons along the laser-polarization axis (up or down in our experiment). Thus, it can be characterized by an asymmetry parameter $A = (N_{\mathrm{up}} - N_{\mathrm{down}})/(N_{\mathrm{up}} + N_{\mathrm{down}})$, where N_{up} (N_{down}) is the number of protons emitted to the upper (lower) hemisphere. In Fig. 2, the asymmetry parameter A is plotted as a function of the KER and the CEP of the pulse. As the absolute value of the CEP is not known, the abscissa in the experimental spectra represent relative phases.

We find clear changes in the asymmetry for different CEPs at KERs in the range between 0–3 eV as shown in Fig. 2. Furthermore, we see a tilt in the asymmetry stripes, i.e., a dependence of charge localization on the KER and, thus, on the dissociation channels involved, both not observed in [1]. Moreover, by inspecting different orientation angles α between the dissociating molecule and the laser-polarization direction, we see that the tilted stripes shift with respect to the CEP. Finally, a pronounced asymmetry in the emission of the electron is observed as shown in Fig. 3(c).

Definitively, the model developed in [2] and depicted in Fig. 1(a) can not explain our results as the recolliding electron would lead to higher KERs. As already discussed in [1], the low energy of the fragments in our experiment points to bond softening as dissociation mechanism. Here, in accordance with the results of [1], the intensity-dependence of the opening of the energy gap between the light-induced states could give an explanation for the energy-dependence of the asymmetry parameter.

This led us to the following model illustrated in Fig. 1(b). The laser ionizes the H_2 molecule creating a vibrational wave packet on the $1s\sigma_g$ potential curve of H_2^+ that starts to move towards the outer turning point. By the time it reaches the internuclear distance where the photon energy matches the energy gap between the bound and repulsive ionic states, the remaining electric field in the tail of the laser pulse couples the two states [19]. Population gets transferred between the two states, and the dissociation finally leads to a localization of the bound electron [10]. Therefore, two localized states $|\sigma_{\pm}\rangle$ can be defined

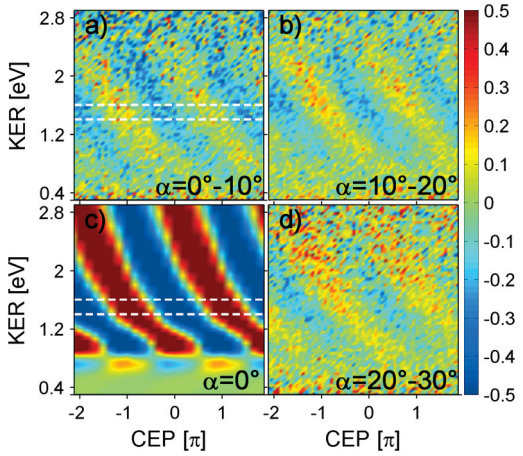

FIG. 2 (color). The asymmetry parameter A in dependence of the KER and the CEP for emission angles α between (a) 0°–10°, (b) 10°–20°, and (d) 20°–30° with respect to the laser-polarization axis. (c) shows the result of our time-dependent Schrödinger equation calculations (see text). As only relative CEP were measured, the axes of the experimental data were shifted to fit the calculation. The dashed lines in (a) and (c) mark the KER range for the projections shown in Figs. 3(a) and 3(b).

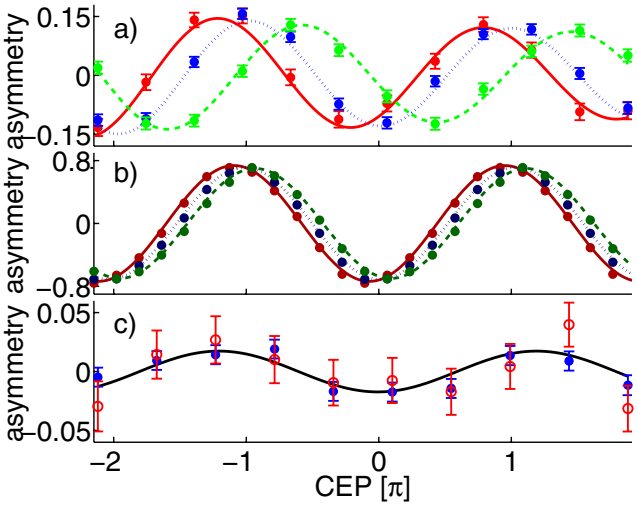

FIG. 3 (color online). Projections of the asymmetry for KERs between 1.4 and 1.6 eV. (a) Experimental data for different emission angles. Red solid line: 0°–10°, blue dashed line: 10°–20°, green dash-dotted line: 20°–30° with respect to the laser-polarization axis. (b) Results from TDSE calculations. Red solid line: $I_1 = 0.44$ PW/cm^2, blue dashed line: $I_2 = 0.41$ PW/cm^2, green dash-dotted line: $I_3 = 0.36$ PW/cm^2. (c) Electrons detected in coincidence with protons of 1.4 to 2.0 eV (red open symbols) and 2.6 to 3.2 eV (blue filled symbols), respectively. The asymmetry was integrated over an electron kinetic energy of 0–20 eV.

for the electron being at the upper (+) or lower (−) nucleus as $|\sigma_\pm\rangle = (|1s\sigma_g\rangle \pm |2p\sigma_u\rangle)/\sqrt{2}$. Such a scenario would lead to proton energies between 0 and 2 eV [20] as we observe them in our experiment. Moreover, we create a (non-Franck-Condon) coherent wave packet, different from the incoherent average over stationary vibrational states considered in [1]. According to Fig. 5 of [1], averaging over vibrational states will wash out the asymmetry. Thus, one might expect that the localization of this wave packet in space and time when reaching the coupling region leads to a higher contrast in the asymmetry parameter.

In order to substantiate these ideas towards providing a quantitative comparison with the experiment, we have numerically solved the time-dependent Schrödinger equation (TDSE) by using a Cranck-Nicholson split-operator method (for details see [8,9,11]). We calculated the tunnel ionization probability by using the Ammosov-Delone-Krainov (ADK) theory [11,21], for the transition of H_2 into the $1s\sigma_g$ state at the five most intense maxima of a Gaussian laser field $E(t) = \epsilon(t)\cos(\omega t + \phi_{\mathrm{CEP}})$ and propagated the corresponding bound state wave packets. The CEP and KER-dependent dissociation probabilities were then evaluated separately for each one of the wave packets launched at the different field maxima and added up incoherently. This simplification is necessary because in our model, the emitted electron was not taken into account explicitly, such that the relative phases of the sequentially launched nuclear wave packets are not available. Such an approximation was further supported by the experimental finding that the asymmetries in Fig. 2 did not depend on the longitudinal momentum of the emitted electron. This might be understood in terms of a recent experiment [22], where we demonstrated that for ultrashort, CEP stabilized pulses, the probability of realizing any specific electron longitudinal momentum value can be interpreted as an interference between essentially two wave packets released at two times symmetrically centered around a zero crossing of the laser electric field. This makes it in principle impossible to retrieve the electron release phase in the field from its final momentum.

Figure 2(c) illustrates the outcome of our simulations displaying distinct and clearly visible asymmetries in good qualitative agreement with the experiment even though intensity averaging over time is taken into account. An averaging over the focal volume, however, was not done, which explains that the asymmetry is more pronounced in the calculation than in the experiment. The wave packet propagating on the $1s\sigma_g$ potential curve needs approximately 10 fs to reach the point where the laser can effectively couple the two ionic states. At this time, the field strength of the laser decreased to about 1.4×10^{13} W/cm^2. Nevertheless, this field strength is sufficient to induce a coupling between the $1s\sigma_g$ and $2p\sigma_u$ state [14] and, therefore, leads to the observed CEP-dependence.

The experimental proof for that finding comes along three routes: First, the KER-dependence of the asymmetry—not seen in [2]—along with the fact that the emitted electron asymmetry does not depend on the KER (see below) rules out any direct relation to the first step which would ''not know'' along which way the molecule might finally dissociate. Second, we can directly inspect any asymmetry correlation between the ion fragments and the electron. Even though we definitively observe an effect (discussed in detail in [22]) of steering the electron more efficiently to one or the other momentum hemisphere, i.e., causing ''localization'' that might be imprinted in the subsequent dissociating step, we do not find, however, any KER-dependent relation to the dissociation asymmetry: Fig. 3(c) shows the asymmetry of the electron integrated over its energy and measured in coincidence with the proton for two different KER bands. Third, in experiments done with D_2, the observed asymmetry at low KER almost vanished and is much weaker for HD [3] compared to our present result. In our model, this isotope trend can be explained by the larger mass and, accordingly, the slower propagation of the wave packet in the heavier isotopes which reach the coupling region when there is much weaker or (almost) no laser field left. The less pronounced asymmetry in D_2 compared to H_2 was recently predicted in [16] and agrees well with our experimental findings. Also, this might explain why it has not been observed in [2]. On the other hand, for the mechanism proposed in [2], the wave packet starts early on the $2p\sigma_u$ state, traveling

quickly down the steep potential curve, thus reaching the coupling after only about 5 fs [see Fig. 1(a)] when the laser field is still strong enough.

Since the effective coupling strength is proportional to $\cos(\alpha)$, the dependence on the molecular orientation might be qualitatively explained as well in our model. Figure 3(b) confirms this assumption by showing the asymmetry for 6 fs Gaussian laser pulses with the intensities $I_1 = 0.44\ \mathrm{PW/cm^2}$, $I_2 = \cos^2(15°)I_1$, and $I_3 = \cos^2(25°)I_1$. The intensity I_2 (I_3) therefore roughly corresponds to an effective intensity which a molecule is exposed to at an angle of 15° (25°) between the molecular and the laser-polarization axis. This leads to a shift of the asymmetry which is qualitatively similar though less pronounced than the one observed in our experiment [Fig. 3(a)]. The explanation for that might lie in the fact that we impulsively create a rotational wave packet during ionization, not taken into account in the calculation, such that the effective angle in the coupling region might differ from the finally observed one (see also [23]).

In conclusion, we have observed a high-contrast charge localization as a function of the CEP in bond-softening dissociation of H_2^+ in a KER range between 0 and 3 eV. The dissociation asymmetries show a distinct dependence on the proton KER and of its emission angle. Our results reveal an isotope trend (including the former results by [3]), namely, that for H_2^+, the role of bond softening in the asymmetry is most pronounced. Whereas a clear asymmetry is observed for the first (ionization) step as well, through the asymmetrically emitted electrons, no indication of any correlation, neither trivial nor more subtle ones via possible phase retrievals from the electron momentum, could be established. This lack of correlation between the electronic and nuclear motion demonstrates that the asymmetry in the first step is not responsible for the observed dissociation asymmetry.

A set of numerical calculations qualitatively reproduces the experimental results and sheds light on the responsible bond-softening [19] mechanism: The efficient coupling between the $1s\sigma_g$ and the $2p\sigma_u$ states transfers population between them and, depending on the CEP, the population of the localized states $|\sigma_\pm\rangle$ changes, leading to the observed asymmetry. Although the laser field is rather weak in the coupling region, the appearance of a dissociation asymmetry proves that the laser-induced coupling is strong enough to effectively couple these two states as indicated in recent calculations [19].

Even though the asymmetry in our experiment shows a similar CEP and KER-dependence as in [1,16], the physical situation considered there, an incoherent sum of vibrational states, is different. Instead, we produce a wave packet in the first step [24] pointing towards further directions on the possible control of chemical reactions through attosecond steering of electrons in a new type of "pump-control" experiments (a similar scenario, using an attosecond pump pulse was discussed in [13]). Switching on the control laser at the time where the wave packet approaches the coupling region should strongly enhance the population transfer and the contrast of the asymmetry. Control then can be achieved by changing the delay between pump and control pulse. In general, one might envision that nuclear wave packets are efficiently guided through coupling regions via CEP stabilized pump-control-schemes steering the electronic motion on a subfemtosecond time scale.

Reaching even better statistical significance with more stable laser systems in the future, one would further like to revisit the issue of relating the phase of the emitted electron with the charge localization of the second one during dissociation. Even though we have not found any indication in this pioneering experiment, one keeps being intrigued by such a possibility.

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