Ion-Energy Dependence of Asymmetric Dissociation of D_2 by a Two-Color Laser Field

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Two-color (800 and 400 nm) short (45 fs) linearly polarized pulses are used to ionize and dissociate D_2 into a neutral deuterium atom and a deuteron. The yields and energies of the ions are measured left and right along the polarization vector. As the relative phase of the two colors is varied, strong yield asymmetries are found in the ion-energy regions traditionally identified as bond softening, above-threshold dissociation and rescattering. The asymmetries in these regions are quite different. A model based on the dynamic coupling by the laser field of the gerade and ungerade states in the molecular ion accounts for many of the observed features.

Short, intense laser pulses can fragment molecules via a variety of mechanisms. Controlling the fragmentation pathways by manipulating the pulse shape is a major theme of ultrafast science today. If the laser pulse possesses a left-right asymmetry (we imagine the polarization vector to be horizontal and the observer to view the process along the propagation direction of the laser beam), the emission of the fragments may reflect this asymmetry. Kling *et al.* [1] found that sufficiently short carrier-envelope-phase (CEP)-locked pulses, which have an intrinsic left-right asymmetry, produce a strong left-right asymmetry in the direction of emission of D^+ ions in the dissociative ionization of D_2. The mechanism at play was the rescattering excitation of the $2p\sigma_u$ excited state (hereafter referred to as "*u*") of the D_2^+ ion, followed by the coherent coupling of the $2p\sigma_u$ and $1s\sigma_g$ (hereafter referred to as "*g*") states of the ion by the laser field during the dissociation. This coupling results in a final-state wave function which is a coherent superposition of the *g* and *u* states, forming a wave function which is preferentially on the right or left charge center. Physically, as the dissociation proceeds, the electron wave function becomes "localized" on one side or the other when the interatomic barrier rises sufficiently to block further oscillation back and forth [2]. In principle, the IR field can be used to control in which direction the charged particle is emitted.

In this Letter we report that a two-color field applied to D_2 produces a very strong left-right asymmetry in the emission of D^+ ions from D_2 which is very dependent on the ion energy. We identify the asymmetry associated with "one-photon" (bond softening, BS [3]), "two-photon" (above-threshold dissociation, ATD [3], and rescattering (RES) processes [4] (see Fig. 1). The asymmetries in these channels are quite different. We analyze these results in terms of a model which evaluates the time dependent *g*-*u*

coupling caused by the laser field, and find quantitative agreement with the data.

The observation that a two-color laser field generates asymmetric ion yield from molecular hydrogen was previously reported more than a decade ago. Sheehy *et al.* [5] observed such an asymmetry in HD with very long (ps) pulses. A similar result was found by Thompson *et al.* [6] with much shorter (100 fs) pulses and higher intensities. Both groups concluded that the ions seemed to be preferentially emitted when the relative phase of the two colors was such that the electric field at the time of emission was maximum and directed opposite the favored ion emission direction ("nonintuitive" direction). This conclusion was
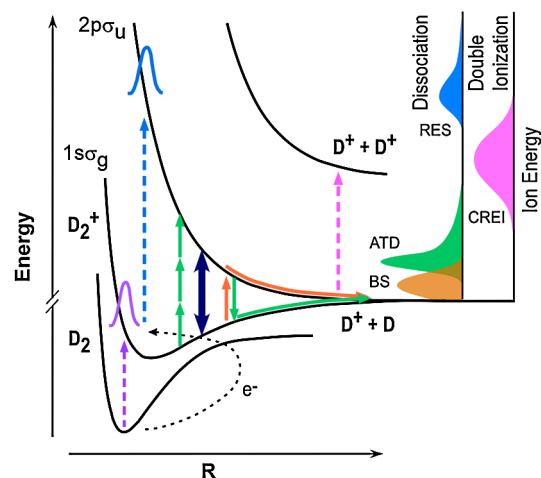

FIG. 1 (color online).   Schematic of dissociation processes for D_2 (not to scale). Traditional BS and ATD processes are indicated by thin arrows. The additional process enabled by the second harmonic is indicated by the thicker double-ended arrow. Rescattering is indicated by a dashed arrow.

based on the assumption that the (low-energy) electron emission was in the "intuitive" direction. A physical explanation was proposed by Posthumus *et al.* [7]. More complete theoretical analyses [8,9] explained the observation that the electrons and ions were observed to be emitted in the same direction, but concluded that it was the electrons, not the ions, which were emitted in the "nonintuitive" direction. These calculations also showed that the ion emission was expected to be very ion-energy dependent, but there was no data on this issue with which to compare this aspect of their theoretical results.

We generate the two-color field by passing a vertically polarized 45 fs 800 nm pulse through a BBO crystal followed by a calcite crystal and a zero-order half-wave plate for the 800 nm radiation. The BBO crystal generates a horizontally polarized 400 nm component and the half-wave plate rotates the 800 nm polarization to horizontal as well, not changing the 400 nm polarization. A birefringent calcite crystal is placed between the BBO crystal and the half-wave plate to adjust the time delay between the two components. Scanning the relative phase ϕ of the 400 and 800 nm radiation is accomplished by rotation of the calcite around an optical axis. The two-color beam is focused onto a neutral deuterium gas and the resulting ions are imaged in a velocity-map-imaging (VMI) arrangement [10].

A density plot of the asymmetry for an intensity of $1.5(\pm 0.8) \times 10^{14}$ W/cm^2 of the 800 nm light is shown in Fig. 2. The ion asymmetry plotted is defined as

$$A(E, \phi) = \frac{Y_r(E, \phi) - Y_l(E, \phi)}{Y_l(E, \phi) + Y_r(E, \phi)}, \quad (1)$$

where $Y_l(E)$ and $Y_r(E)$ are the ion yields to the left and right, respectively. The ion energy (E) was deduced from the Abel-inverted images [11]. The absolute phase ϕ between the two colors was assigned from a measurement
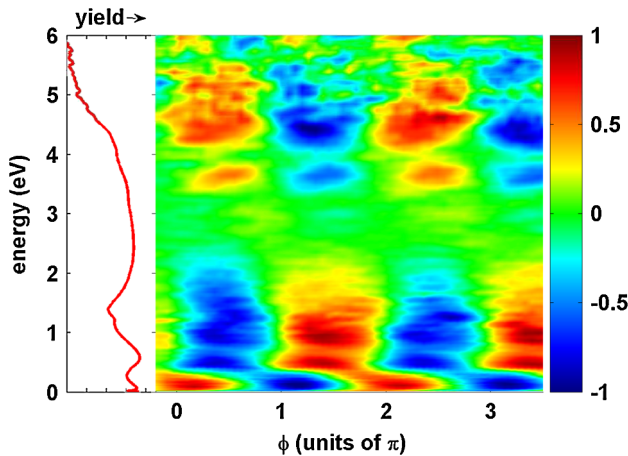

FIG. 2 (color online).   Density plot of the asymmetry of D$^+$ ion emission from D$_2$ as a function of ion energy and phase ϕ between 800 and 400 nm radiation. The panel on the left shows a log plot of the total ion yield as a function of ion energy with decades indicated by tic marks.

and analysis of the asymmetry of backscattering electrons from Xe [12]. Briefly, one would expect that electrons emitted when $\phi = 0$ (maximum field to the right: see phase and sign convention defined below) go first to the left, return, and rescatter to the left. At the time of rescattering the vector potential is such that it additionally gives a nearly maximal boost to the left. A quantitative analysis of this process shows that the maximum rescattering energy to the left in a two-color field does not quite occur at $\phi = 0$, but closer to $\phi = 50°$ for our conditions. This quantitative analysis was used to assign the absolute phase. We note that previous calibrations of ϕ based on the phase of the asymmetric emission of the direct electrons [5,6,13] is more difficult to interpret [9], since the vector potential at the time of maximum emission is passing through zero.

Figure 2 shows that the major regions of strong asymmetry lie in the one-photon (0–0.3 eV), two-photon (0.3–2 eV), and rescattering (4–6 eV) regions of the ion-energy spectrum. The strong group (see left panel) centered near an ion energy of 3 eV corresponds to charge-resonance-enhanced-ionization (CREI) [14], which is double ionization (two deuterons) and therefore cannot show asymmetry, as is seen in the data. Indeed, much of the yield on the upper side of the CREI peak is still due to CREI, but the asymmetry reveals an additional component for an ion energy near 4–5 eV which does show a large asymmetry and which we attribute to rescattering-induced dissociation. It is seen that maximal asymmetries in these three regions occur at different phases.

We have observed the following general features of this and other similar spectra: (i) The main features seen in the spectrum of Fig. 2 persist over the intensity range of 1–4 $\times$ 10^{14} W/cm^2, with only small differences; (ii) Spectra taken for an H$_2$ target show nearly identical asymmetry maps to those for D$_2$ at all intensities.

We have carried out a model calculation of the dissociation. The procedure is very similar to that used in Refs. [15,16]. We solve the two-state Schrödinger equation:

$$i\frac{\partial}{\partial t}\begin{pmatrix} \chi_g \\ \chi_u \end{pmatrix} = \begin{pmatrix} T_R + V_g(R) & D_{gu}(R)E(t) \\ D_{gu}(R)E(t) & T_R + V_u(R) \end{pmatrix}\begin{pmatrix} \chi_g \\ \chi_u \end{pmatrix},$$

where $T_R = -\frac{1}{2\mu}\frac{\partial^2}{\partial R^2}$, $V_g(R)$, and $V_u(R)$ are the Born-Oppenheimer potential curves for the g and u electronic states, and μ is the reduced mass of the nuclei. The dipole coupling between g and u states is designated by $D_{gu} = \langle \phi_g | er | \phi_u \rangle$. The two-color laser pulse is written as

$$E(t) = E_{0,800}\cos(\omega_{800}t)\exp\left[-2\ln2\left(\frac{t}{\tau}\right)^2\right]$$

$$+ E_{0,400}\cos[\omega_{400}(t + \Delta t)]$$

$$\times \exp\left[-2\ln2\left(\frac{t + \Delta t}{\tau}\right)^2\right],$$

where positive E is taken to be to the right. We use $\tau = 65$ fs, and $E_{0,800} = 0.0754$ a.u., $E_{0,400} = 0.0238$ a.u. and $\varphi = \omega_{400}\Delta t$. We identify the g and u components of the dissociative wave function and project onto the left and right atomic states. The energy spectrum is obtained by Fourier transforming the wave functions going to the left and right. The asymmetry parameter is defined as given in Eq. (1). The initial ionization step which launches the wave packet on the g curve occurs near the peak of each maximum of the pulse. In modeling this we launch only two wave packets, both near the center of the laser pulse envelope and on two successive maxima, one when the field is to the right and one to the left, with relative weights given by the ADK ionization rate [17]. We add the resulting probabilities incoherently, under the assumption that the ionized electron destroys the phase coherence of the nuclear wave packets.

In Fig. 3 we compare the results of the model with the data of Fig. 2 over the 0–2 eV region only, since the model as described to this point does not apply directly to the rescattering region. The agreement is qualitatively good, although there is a slight phase shift between experiment and theory in the "two-photon" region. We note that the calculated phase of the theoretical stripes slightly depends on the exact intensities used, while this dependence is less pronounced in the experiment. The most striking aspect of the results in Fig. 3 is the apparent discontinuity in the phase of the asymmetry near an ion energy of 0.3–0.4 eV. This energy is approximately the dividing line between one- and two- photon dissociation.

We suggest a possible simplified interpretation of these results. It is well known that the asymmetry is caused by the interference between g and u states: both must be populated at the same ion energy to produce an asymmetry at that energy. In a one-color field, BS leads to the u state only and no asymmetry is produced (see Fig. 1). In a two-color laser field, however, the molecule has two ways to absorb the energy of one ω_{800} photon: The molecule can absorb one ω_{800} photon and dissociate through the u channel (BS); alternatively, it can first absorb one ω_{400} and then emit one ω_{800} photon, dissociating through the g channel. These two dissociation routes both produce ion-energy below 0.3 eV. Similarly, in a one-color field, ATD leads to the g state only and no asymmetry is produced. With two colors there are two pathways to absorb the energy of two ω_{800} photons: the molecule can directly absorb three ω_{800} photons and emit one ω_{800} photon, dissociating through the g state (ATD); alternatively, the molecule can absorb a single ω_{400} photon, dissociating through the u state. Both these channels create an ion with energy above 0.3 eV, ranging up to about 2 eV. The relative phase between 800 and 400 nm components of the electric field determines the relative phase of the two amplitudes contributing to each of the above energy regions. Thus it is not surprising that there could be a
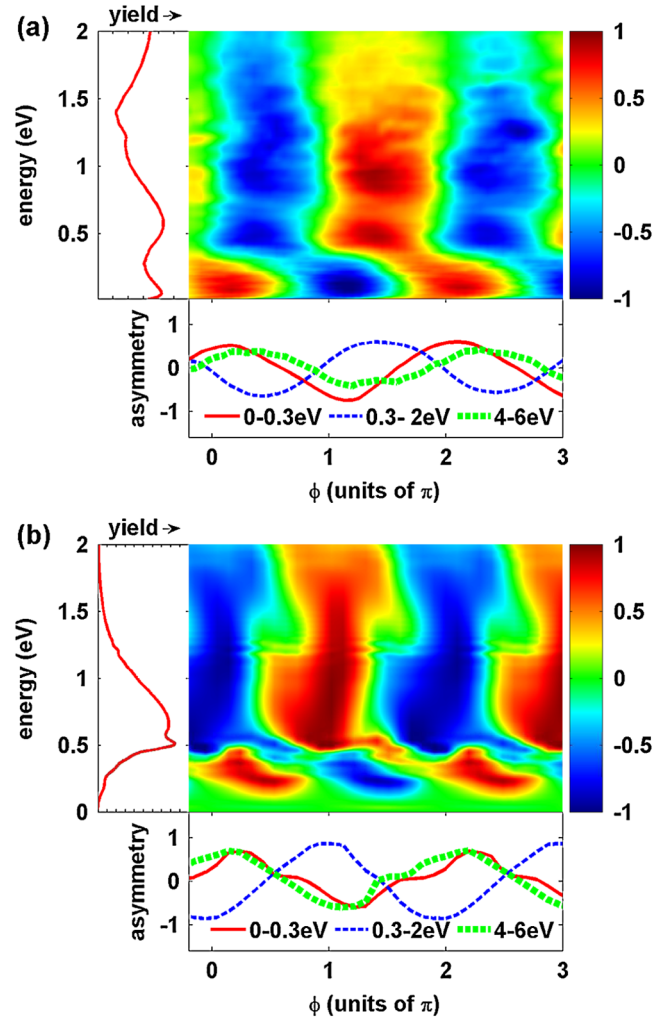

FIG. 3 (color online). Similar to Fig. 2: comparison of experiment (a) and theory (b) for the one and two-photon regions of ion energy (0–2 eV). The left hand panels show log plots of the measured (calculated) energy spectra integrated over all phases, while the bottom panels show the asymmetries integrated over one-photon (0–0.3 eV) and two-photon (0.3–2 eV) regions of the spectrum. Also shown in the bottom panels are plots measured and calculated for the rescattering region from Fig. 2 (4–6 eV).

discontinuity in the phase dependence at approximately the energy which separates these two energy regions, since different amplitudes are in play above and below this energy. The robust nature of the relative phase shift between these regions suggests that a simple classical argument might also be applicable. For example, the time the nuclear wave packet takes to reach the localization distance (near 6 a.u.) is different for these two regions and thus the location of the oscillating electron wave packet which is frozen when this distance is crossed would be expected to be different, giving rise to different asymmetries.

The rescattering region requires further modeling, since an additional electron-scattering step is required. We in-

corporate this into our model by launching the same wave packets discussed above, allowing them to evolve on the *g* potential for approximately 2/3 of an optical cycle (the return time for the rescattering electron) and then promoting them suddenly to the *u* potential curve. We then use the same two-state solution of the Schrödinger equation to follow the wave function to a mixture of *g* and *u* dissociation. The resulting predicted asymmetry is shown as a dashed (green) curve in Fig. 3(b), where it is seen to be in excellent agreement with corresponding asymmetry from the experiment shown in the lower panel of Fig. 3(a). This mechanism is similar to that proposed in Ref. [1] to explain the results for the CEP controlled pulse

In conclusion, we have measured the asymmetry of the ion emissions in the dissociation of D_2 by a two-color field, and have found that the dependence of the asymmetry on the relative phase of the two colors is very dependent on the energy of the emitted ion. Clearly different dissociation mechanisms give rise to very different asymmetries. No simple general correlation between the direction of the field at the time of the initial ionization and the direction of ion emission can be assigned without looking at the specific dissociation mechanism. Unfortunately this means that the concept of an intuitive direction for the ion emission [5–9] is of limited use. The experimental results are in good agreement with a simple two-state model analysis.

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