Identification of a Previously Unobserved Dissociative Ionization Pathway in Time-Resolved Photospectroscopy of the Deuterium Molecule

Wei Cao, Guillaume Laurent,* Itzik Ben-Itzhak, and C. Lewis Cocke
J. R. Macdonald Laboratory, Department of Physics, Kansas State University, Manhattan, Kansas 66506, USA
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A femtosecond vacuum ultraviolet (VUV) pulse with high spectral resolution (< 200 meV) is selected from the laser-driven high order harmonics. This ultrafast VUV pulse is synchronized with an infrared (IR) laser pulse to study dissociative ionization in deuterium molecules. At a VUV photon energy of 16.95 eV, a previously unobserved bond-breaking pathway is found in which the dissociation direction does not follow the IR polarization. We interpret it as corresponding to molecules predissociating into two separated atoms, one of which is photoionized by the following IR pulse. A time resolved study allows us to determine the lifetime of the intermediate predissociation process to be about 1 ps. Additionally, the dissociative ionization pathways show high sensitivity to the VUV photon energy. As the VUV photon energy is blueshifted to 17.45 eV, the more familiar bond-softening channel is opened to compete with the newly discovered pathway. The interpretation of different pathways is supported by the energy sharing between the electron and nuclei.

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The development of ultrafast laser techniques enables us to observe and steer dynamical processes in quantum systems with unprecedented time resolution. The optical pump-probe approach with femtosecond laser pulses allows monitoring of the bond-breaking processes in a chemical reaction [1,2], leading to the era of femtochemistry. The discovery of high order harmonics and their application for ultrafast EUV pulse generation has extended our time-resolved tools to the subfemtosecond scale, resulting in the birth of attosecond science [3–5]. The development of shorter light bursts is essential to capturing ultrafast motion in the microscopic world.

On the other hand, in spectroscopic studies high energy resolution synchrotron radiation has been regularly used to probe atoms and molecules, and the energy structure of the corresponding quantum system can be deduced from the absorption spectra. Although the two aspects of a quantum system, namely time evolution and energy structure, are both of great importance, their relationship is governed by the uncertainty principle. The precise determination of time is accompanied by downgrading the precision of the energy information, and vice versa. Thus, an outstanding question is: Is it necessary to treat the time and energy resolution on equal footing in order to gain more comprehensive or new information of a physical process?

In this Letter we take the prototypical fragmentation process, the light-induced dissociative ionization (DI) of a deuterium molecule, as an example. During the bond-breaking process, photons absorbed by the molecule break it apart into a deuteron, a photoelectron and a deuterium atom, leaving the system in the double continuum, where both the electron and nuclei are in the continuum. The more massive hydrogen isotope D_2 is used because the ionic fragment D^+ can be separated from the background H^+, providing experimental data with better quality.

Most previous work on the DI process has used either ultrashort laser pulses [6–9] or monochromatic synchrotron radiation [10]. Two rather significant issues of the DI study are which pathway does the system follow to reach the final products (identification), and how can one control these pathways. The first issue is usually addressed by using synchrotron radiation. By combining with coincidence techniques, different DI pathways can be deduced from the registered final fragments coming from the same molecule [10]. However, monochromatic synchrotron radiation lacks temporal structure and thus loses dynamic control ability. As for the second issue, ultrafast laser pulses have been considered as promising tools for dynamic control over DI. A very pivotal experiment of this kind is asymmetric bond-breaking control. By changing the carrier-envelope phase of a few-cycle near infrared laser pulse [11], or by varying the timing of ultrafast attosecond pulses relative to the phase of an additional infrared (IR) field [7,8], deuterons produced in the DI process can be predominantly ejected in one direction or the other. Since this dynamic control relies on the interference of different pathways [12], the disentanglement of the mixed pathways is not feasible, and thus the direct identification of DI pathways becomes difficult.

To address both issues, i.e., identification and control, in a single experiment, a light source preserving both temporal and spectral resolution would be a straightforward requirement. In this work, we compromise the time and energy resolution of the electromagnetic field used for initiating the DI process of D_2 molecules. A 100 fs quasimonochromatic vacuum ultraviolet pulse near

17 eV is combined with a 50 fs IR pulse (802 nm) to interact with deuterium molecules. This pump-probe approach enables a study which is energy resolved by tuning the vacuum ultraviolet (VUV) photon energy, and time resolved by adjusting the delay between the VUV and IR pulses. Two unique features in the DI process of D_2 molecules have been discovered. First, a previously unobserved fragmentation mechanism is found in which the dissociation direction does not follow the IR polarization. VUV-induced predissociation precedes ionization by the IR pulse in this DI mechanism. A time-resolved study allows the determination of the lifetime of the predissociation process. Second, as the VUV photon energy is tuned from 16.95 eV to 17.45 eV, a shift made possible by the high spectral resolution we achieve for the VUV, the molecular fragmentation shows a transition from a single dominant fragmentation pathway to two competing pathways. In the second pathway, the VUV pulse removes an electron and populates the ground electronic state of the cation molecule D_2^+. With an additional IR photon, the cation molecule is promoted to a repulsive excited electronic state leading to molecular fragmentation. This process is known as the bond-softening (BS) mechanism [13,14].

The VUV light source is based on laser driven high order harmonics. A 3 mJ, 50 fs, 802 nm infrared (IR) laser pulse from a Ti:sapphire laser system is split by a beam splitter. Part of the pulse energy is focused into a semi-infinite gas cell (the cell length is much longer than the confocal length of the driving pulse) filled with xenon gas for high order harmonic generation. A grating-based monochromator consisting of a pair of identical holographic blazed gratings (3600 lines/mm) followed by a slit is installed after the harmonic generation cell, allowing the selection of the 11th harmonic (~17 eV). The other part of the laser pulse energy is combined with the 11th harmonic pulse to form a Mach-Zehnder interferometer [15]. Both the 11th harmonic pulse and the IR probe pulse are focused independently onto the gas target in a reaction microscope [16,17]. Both ions and electrons produced in the interaction are registered as shown in Fig. 1(a).

The 11th harmonic pulse duration is determined to be ~100 fs based on the IR-assisted photoionization of argon gas. The photon energy of the 11th harmonic is calibrated with the photoelectron spectrum of a gas-phase argon target as shown in Fig. 1(b). The typical harmonic photon has an energy of 16.95 eV and a bandwidth of 100 meV that is able to resolve the spin-orbit splitting of the $^2P_{1/2}$ and $^2P_{3/2}$ ionic states of Ar^+. By varying the focal position of the driving laser pulse with respect to the exit of the semi-infinite gas cell, the mean VUV photon energy is tunable [19] from 16.95 eV to 17.45 eV. Note that the blueshifted harmonic generally shows a slightly broader effective spectral width of ~150 meV.

Figure 1(c) shows the potential energy curves (PECs) of D_2. Considering that the weak VUV pump interacts with

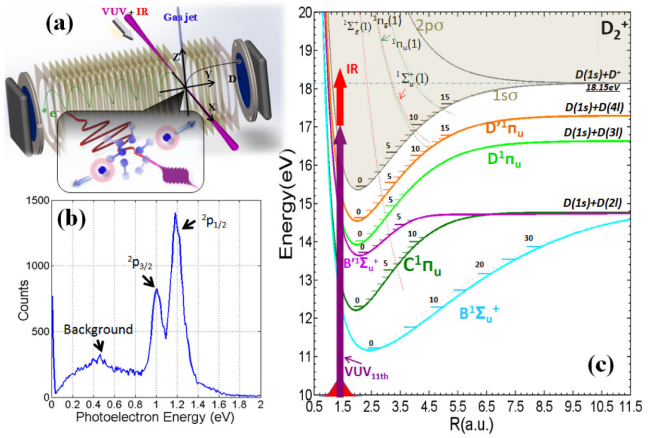

FIG. 1 (color online). (a) The schematic illustration of the reaction. (b) Photoelectron spectrum of argon from the 11th harmonic. (c) Part of the D_2^+ and D_2 PECs adapted from Ref. [18] and references therein. The dotted lines represent the doubly excited states.

the target via a single photon process, it is energetically forbidden to produce D^+ fragments with the 11th harmonic alone. A delayed IR probe pulse can feed additional photon(s) and thus open the DI channel. The key ingredients of our optical initiator, i.e., the VUV pump near 17 eV and IR probe, thus have to cooperate with each other to fragment the molecules. How the pump and probe cooperate and how to steer that cooperation are the main questions to be addressed in this work.

In the experiment, the IR probe intensity is 2×10^{12} W/cm^2 and the DI caused by the IR probe alone can be neglected. We first fix the delay so that the IR arrives after the VUV pulse (~9000 fs), where the DI yield saturates. Figure 2 shows results of the measurement using a 16.95 eV VUV pump pulse. Two polarization configurations are utilized; i.e., the IR polarization direction is parallel or perpendicular to that of the VUV beam, respectively. The measured D^+ fragment has a kinetic energy peaking around 0.2 eV. The energy sharing between the nuclei and the electrons follows energy conservation [dashed line in Fig. 2(d)]: $E_{e^-} + E_D + E_{D^+} = E_{e^-} + 2E_{D^+} = \hbar\omega_{11} + \hbar\omega_0 - E_{diss}$, where $E_{diss} = 18.15$ eV is the dissociation limit into $D(1s) + D^+$. Figure 2(d) indicates that the major reaction involves a two photon process, i.e., the net absorption of one VUV photon and one IR photon, with the electron carrying almost zero kinetic energy. A unique feature of this process, compared with the familiar BS mechanism, is that the D^+ fragmentation direction does not follow the IR polarization direction [Fig. 2(a) and Fig. 2(b)], but rather the VUV polarization direction.

We invoke a predissociation mechanism to interpret the new DI pathway in Fig. 2. When the D_2 molecule is exposed to photons with energies greater than the first ionization threshold (15.4 eV), it can be singly ionized into

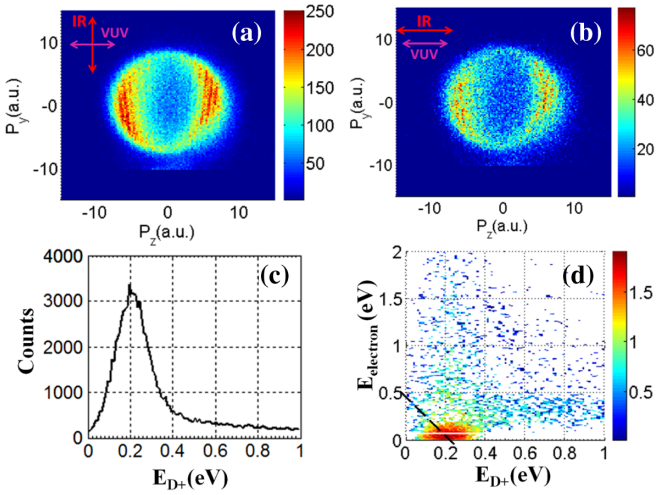

FIG. 2 (color online). Dissociative ionization experiment with a 16.95 eV photon as the pump. D^+ momentum distribution with the IR polarization (a) perpendicular and (b) parallel to the VUV polarization; (c) Kinetic energy of D^+ fragment; (d) D^+ and e^- energy correlation map (logarithmic scale). Note that measurements (c) and (d) are almost identical for the two polarization configurations. We choose the perpendicular polarization configuration for presentation. The calibration uncertainty for 0.7 eV photoelectrons is 0.05 eV.

the $1s\sigma_g$ cation state as expected. However, other processes can compete with direct ionization. For instance, singly excited Rydberg states of neutral D_2, which are termed as superexcited states [20], can be populated through electronic excitation. Doubly excited states can also contribute but are precluded for the VUV photon energies used. It has been reported that the superexcited states of the hydrogen molecule are very weakly coupled by nonadiabatic couplings to energetically allowed dissociation channels consisting of one ground state and one highly excited hydrogen atom [21,22]. Therefore after photon excitation these states remain stable for some time but eventually dissociate into two separated atoms. If an IR photon is introduced at a later time, the excited atom can be photoionized producing a D^+ fragment, appearing to be a new DI mechanism but with dissociation leading the ionization in time. Now, we use the electron-ion energy sharing to check the validity of this interpretation. According to this mechanism, a 16.95 eV VUV photon will populate vibrational states on an electronic curve with a $D(n=1)+D(n=4)$ dissociation limit. Then the superexcited molecule can predissociate into two atoms [$D(n=1)$ and $D(n=3)$] with each of them carrying a kinetic energy of $E_{D^+}=(16.95-16.6)/2\approx 0.2$ eV. The kinetic energy of the associated photoelectron is $E_{e^-}=\hbar\omega_0-I_p(n=3)=1.54-1.51=0.03$ eV. Furthermore, since the predissociation process is induced solely by the VUV pulse, the dissociation direction is expected to be independent of the IR polarization. These predictions agree well with the measurement shown in Fig. 2 within the system resolution.

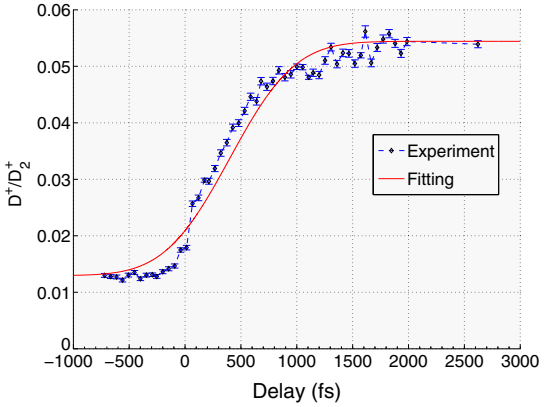

FIG. 3 (color online). D^+/D_2^+ ratio as a function of the VUV-IR delay. Positive delay indicates VUV preceding the IR pulse. The red curve is a fit with the function: $\int_{-\infty}^{\tau} dtA\exp((t-\tau_0)^2/T^2)+B$, where A and T are the amplitude and width of the Gaussian function, τ is the VUV-IR delay, and B and τ_0 are offsets along the vertical and horizontal axis, respectively. T is 650 fs in the fit.

We now proceed to a study of the dynamics of this process by exploiting our ability to vary the VUV-IR delay. Figure 3 shows the delay-dependent D^+/D_2^+ ratio with 16.95 eV photons as the pump. This ratio shows an enhancement when the IR pulse arrives after the VUV pulse, and saturates at about 2000 fs delay when most of the superexcited-state population has predissociated. Thus the lifetime of the predissociation is estimated to be about 1080 fs. The predissociation linewidths of selected superexcited states in H_2 have been reported using synchrotron radiation [22,23], from which the times for the predissociation processes can be deduced in the range from a few tens of femtoseconds to a few picoseconds depending on states involved. The present experiment is the first direct measurement of this time.

We will next demonstrate the onset of a second competing DI pathway by slightly tuning the VUV photon energy. The blueshifted 11th harmonic (17.45 eV) is applied to perform a similar measurement shown in Fig. 4. Two features are now observed in the kinetic energy spectrum of D^+ fragments, peaking around 0.08 eV and 0.4 eV, respectively. These two features exhibit very different momentum distributions. The D^+ fragment with lower kinetic energy dissociates preferentially along the VUV polarization direction, which is similar to the distribution in Fig. 2. The D^+ with higher kinetic energy, in contrast, preferentially dissociates along the IR polarization direction and thus displays the behavior of the BS mechanism. Therefore, we refer to the lower kinetic energy group as DI via predissociation, and the higher kinetic energy group as DI via BS.

The above identification can be confirmed with the electron-ion correlation measurement [Fig. 4(d)]. With a photon energy of 17.45 eV, the vibrationally excited states

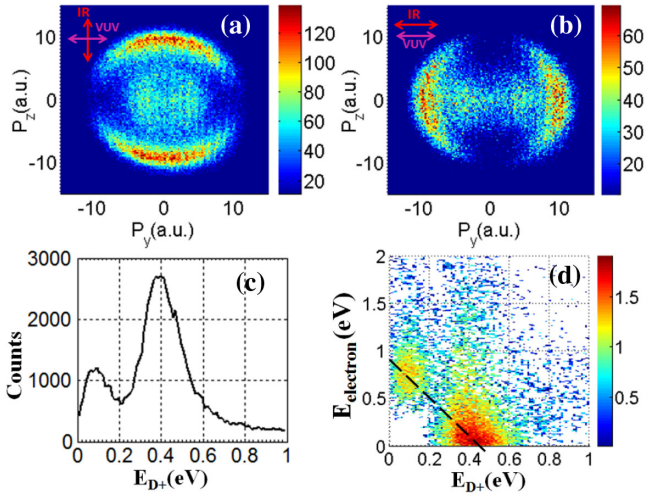

FIG. 4 (color online). Same as Fig. 2 but with the blueshifted 11th harmonic pulse (17.45 eV) as the pump.

in PECs with a $D(n=1)+D(n=5)$ dissociation limit can now be populated. These states eventually predissociate into a ground and an excited D atom with $n=4$. The kinetic energy of each atom is expected to be $E_{D^+} = (17.45-17.3)/2 \approx 0.08$ eV. The $D(n=4)$ atom has a binding energy of $I_P(n=4)=0.85$ eV; thus, an IR photon can photoionize the excited atom, releasing an electron with a kinetic energy of $E_e = 1.54-0.85 = 0.69$ eV. This energy sharing corresponds to D^+ fragments with lower kinetic energy. In a second pathway attributed to the BS mechanism, the VUV photon first strips a very slow electron and populates the $1s\sigma_g$ curve near $v=13$. An IR photon arriving thereafter can electronically excite the molecular cation to the repulsive $2p\sigma_u$ curve, eventually producing a D^+ fragment with kinetic energy around 0.4 eV. This energy sharing is consistent with the measured data with D^+ carrying most of the energy shown in Fig. 4(d). The two identified DI mechanisms are sketched in Fig. 5.

The high sensitivity of the onset of the BS channel to the VUV photon energy can be understood with the dressed

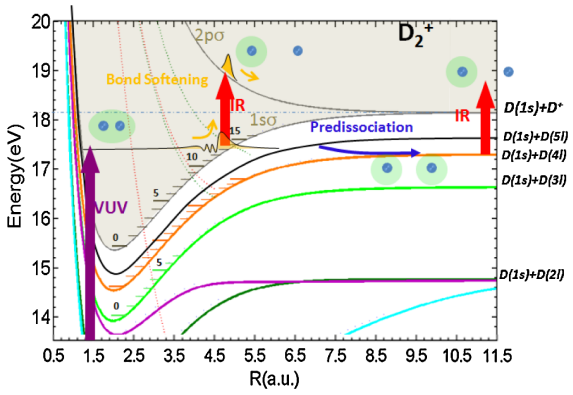

FIG. 5 (color online). The two DI mechanisms identified using the 17.45 eV photon as the pump.

state Floquet picture [24]. In order to enable the BS mechanism, the vibrational states populated by the VUV photon have to surpass the barrier formed by the avoided crossing of the dressed state PECs of D_2^+ for a net one photon process. This barrier is 17.2 eV for our IR intensity; thus, a VUV photon of 17.2 eV and above will be required to launch this process. This phenomenon reveals the significance of energy resolution in the VUV pump to single out particular DI pathways.

It is worth pointing out that the dissociation and ionization steps in both DI mechanisms are induced in a sequential manner. For DI via predissociation, the pump is responsible for the dissociation and the probe is responsible for the ionization, and this order is reversed in the case of DI via the BS mechanism. The disentanglement of the dissociation and ionization offers efficient ways to steer the DI process. By tuning the VUV-IR delay, the DI via predissociation can be eliminated, allowing the control of the branching ratio of the two DI pathways. By scanning the VUV photon energy progressively towards the $D(1s)+D^+$ dissociation limit, we anticipate the transition from one DI channel (DI via predissociation) being dominant to the other channel (DI via BS) dominating the total DI yield. This is because with sufficient VUV photon energy the BS mechanism is allowed to compete with DI via predissociation. As the VUV photon energy is approaching the $D(1s)+D^+$ dissociation limit, Rydberg atoms with progressively increasing primary quantum number n are produced via predissociation. The excited electron in the Rydberg atom tends to behave more like a free electron with increasing n, and is thus more immune to the external IR pulse. Therefore, the DI via BS mechanism is anticipated to become more dominant.

In conclusion, a tabletop VUV light source, which possesses both time resolution (100 fs) and energy resolution (< 200 meV), has been developed to investigate dissociative ionization processes. By combining the VUV with a delayed IR pulse, the onset of a previously unobserved DI pathway is demonstrated in D_2 molecules. In this mechanism, the molecule first gets excited by the VUV pulse and then predissociates into two separated atoms. A following IR pulse then photoionizes the excited atom. By adjusting the VUV-IR delay, the predissociation yield can be altered and thus the lifetime of the molecular predissociation process can be retrieved. This emphasizes the necessity of short temporal width VUV pulses. By varying the VUV photon energy from 16.95 eV to 17.45 eV, the DI process transits from a single dominant pathway to two distinguishable competing pathways. This highlights the significance of the spectral resolution of the VUV pulse for launching different DI pathways. This double dependence of the DI process, namely, the delay dependence and the photon energy dependence, reveals the significance of compromising between the temporal and energy resolution of the initiator pulse in a photochemical

reaction. We expect that this approach can be applied to more complex molecules, offering the possibility of time-resolved and channel-resolved studies of photochemical reactions.

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*Present address: Department of Electrical Engineering and Computer Science and Research Laboratory for Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA.

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