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Journal

Physical Review A, 95(1)

ISSN

2469-9926

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Publication Date

2017

DOI

10.1103/physreva.95.012501

Peer reviewed

Mapping and Controlling Ultrafast Dynamics of Highly Excited H₂ Molecules by VUV-IR Pump-Probe Schemes

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(Dated: November 2, 2016)

We used ultrashort femtosecond vacuum ultraviolet (VUV) and infrared (IR) pulses in a pump-probe scheme to map the dynamics and non-equilibrium dissociation channels of excited neutral H₂ molecules. A nuclear wave packet (NWP) is created in the $B^1\Sigma_u^+$ state of the neutral H₂ molecule by absorption of the 9th harmonic of the driving infrared laser field. Due to the large stretching amplitude of the molecule excited in the $B^1\Sigma_u^+$ electronic state, the effective H₂⁺ ionization potential changes significantly as the nuclear wave packet vibrates in the bound, highly electronically and vibrationally excited B potential energy curve. We probed such dynamics by ionizing the excited neutral molecule using time-delayed IR/VUV radiation. We identified the non-equilibrium dissociation channels by utilizing 3D momentum imaging of the ion fragments. We found that different dissociation channels can be controlled, to some extent, by changing the IR laser intensity, and by choosing the wavelength of the probe laser light. Furthermore, we concluded that even in a benchmark molecular system such as H₂^{*}, the interpretation of the non-equilibrium multiphoton/multicolor ionization processes is still a challenging task, requiring intricate theoretical analysis.

I. INTRODUCTION

The rapid development of laser technology, ultrashort vacuum ultraviolet (VUV) and extreme ultraviolet (XUV) sources in combination with advanced detection techniques, such as momentum imaging spectroscopy, has opened new opportunities for unraveling and controlling ultrafast molecular dynamics of non-equilibrium systems [1–7]. Recent studies showed how femtosecond VUV and XUV radiation can be used to reveal transient nuclear and electron dynamics in diatomic molecules [8–12] as well as in more complex molecular systems [13, 14]. To probe such dynamics, the majority of the pump-probe style experiments accomplished to date utilize pairs of XUV-IR pulses [8, 15–18] but also a combination of VUV-XUV pulses [19–22]. These experiments have led to the observation of novel ultrafast phenomena in molecules and allowed for the temporal characterization of known dissociation processes [21]. Moreover, new dissociation channels that had not been predicted previously have been observed [8, 16, 17]. However, even in rather simple diatomic and triatomic systems, the multitude of degrees of freedom as well as the complexity of the coupled electron and nuclear wave packet motion usually prevent a full theoretical treatment and, hence, limit our ability to fully understand and predict such complex dynamics.

Thus far, the majority of ultrashort XUV experiments, which were supported by comprehensive theoretical calculations, were focused on the ionization of H₂ leading to the ground and the first excited state of H₂⁺ (or D₂⁺) due to the simple geometry and a small number of degrees of freedom. However, very little attention has been paid to the Rydberg dynamics of a hydrogen molecule around the single and double ionization thresholds. Near those thresholds, the complexity significantly increases due to the dense electronic states, coupled nuclear and electronic motion, and electron-electron correlations that drive rapid dissociation processes. Due to the high excitation energy of these electronic states in the neutral H₂ molecule, this simple molecular system could not be studied by standard spectroscopy tools used in femtosecond chemistry, such as UV pulses generated through frequency doubling and tripling by non-linear effects in crystals. Meanwhile, ultrashort physics has been mostly focused on the development of so-called above-threshold harmonics or XUV radiation sources. Hence, in order to investigate the dynamics of a fundamental system such as the excited neutral hydrogen molecule, potent attosecond VUV sources have to be constructed and combined with modern spectroscopy techniques, and new theoretical methods have to be developed to bridge the gap in our understanding between ultrashort physics and femtosecond chemistry.

Only recently, the first experiments on excited neutral hydrogen molecules were performed. In a work by Ranitovic et al. [23], VUV attosecond coherent control methods were used to excite and steer the dynamics of highly

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excited electronic states in a D_2^* molecule on an attosecond time scale. In another pump-probe experiment, short VUV/XUV pulses were used to excite a broad range of neutral states in the D_2 molecule that were ionized subsequently by a second XUV pulse [24].

In this work, we investigate the temporal evolution of the ionization probability of an excited neutral hydrogen molecule and its non-equilibrium dissociation channels by using a coherent train of intense VUV attosecond pulses and 3D momentum imaging. This Attosecond Pulse Train (APT) enables us to coherently excite a nuclear wave packet in the neutral H_2 molecule and the ground state of H_2^+ . The dynamics are probed by measuring the total H_2^+ and H^+ yield modulations as a function of the relative delay between the pump and IR and VUV probe pulses. We identify the non-equilibrium dissociation channels by measuring and interpreting the 3D momentum images of the H^+ ions. Excited neutral H_2 molecules are easy to understand in a static picture but become very complex as the system moves out of its equilibrium position. Understanding the non-equilibrium dynamics in such molecules is an important step for developing concepts and tools necessary for extending such investigations to larger molecular systems.

In this article, we first show that intense VUV attosecond pulse trains (APTs) can be used to initiate and map the dynamics of an excited neutral H_2 molecule. By measuring the H^+ and H_2^+ yield dependence as a function of the delay between the VUV APT and a femtosecond IR or VUV (IR/VUV) probe pulse, we unravel the ionization probability dynamics and hence map the vibrational motion of the excited neutral molecule. Furthermore, we apply advanced 3D momentum imaging to visualize and identify the dissociative pathways formed in non-equilibrium H_2 molecules upon ultrafast VUV excitation and consecutive dissociation initiated by IR/VUV radiation. Finally, we demonstrate that the yield of the various pathways can be alternated by controlling the relative intensities of the IR and the VUV pulses in these two color experiments.

II. EXPERIMENT

Our experimental apparatus combines an intense source of ultrashort IR/VUV/XUV pulses with a high resolution 3D momentum imaging spectrometer. We focus a high-power infrared pulsed laser (808 nm, 25 mJ, 45 fs, 50 Hz) with a curved mirror ($f = 6$ m) into an argon filled 10 cm long gas cell to create a high-flux, coherent VUV photon beam ($\sim 10^9$ phot/shot) via High Harmonic Generation (HHG) [25–27]. For the experiments reported here, the generated broad spectrum of harmonics was spectrally controlled by varying the HHG gas cell pressure (10 Torr), by applying an additional gas filter cell (81 cm long, 3 Torr Ar pressure), and by using a B_4C coated focusing mirror. This results in a pump pulse spectrum predominantly consisting of the

3rd to the 9th order harmonics (4.7 - 14 eV), with a small leakage of higher orders. We estimate an intensity of $\sim 2 \times 10^{10}$ W/cm² for the 9th harmonic. In the probe arm, a MgF_2 filter eliminates all orders above the 7th harmonic. We estimate a pulse duration of the APT of around 15 fs. The infrared (IR) intensity in the target can be adjusted by rotating the polarization axis of the IR beam with a half-wave plate as only s-polarized infrared light is reflected of the silicon mirror surfaces at Brewsters angle for 800 nm (75° normal incidence). This results in an almost cross-polarized configuration with horizontal VUV polarization (i.e. along the z-axis) in the pump and the probe arm and vertical IR polarization (along the y-axis), as shown in Fig. 3. A custom, in-vacuum split-mirror interferometer creates VUV - VUV/IR pulse pairs for pump-probe studies with a relative delay range up to several picoseconds, and 170 attosecond (as) resolution. In the experiments presented here, the fundamental IR beam was present in the pump and probe arms but did not play a role in the pump step due to the high excitation energy of the H_2 molecule and the moderate IR intensity ($\sim 3 \times 10^{11}$ W/cm²). The IR pulse duration was around 45 fs. In the experimental end-station, the 3D momenta of the H_2^+ and H^+ ions were measured using a COLTRIMS type spectrometer [28]. The incoming VUV/IR beam was missing a supersonic jet of H_2 molecules, located in the center of the spectrometer, and was tightly back-focused into the target jet by a spherical mirror ($f=15$ cm, B_4C coating). A time-and-position-sensitive detector at the end of the spectrometer was used to record the yield and the 3D momenta of the H_2^+ and H^+ ions. The VUV beam was spectrally analyzed using an XUV spectrometer located upstream from the end-station. The experimental geometry and the apparatus are described in more detail in a separate publication [29].

III. RESULTS

Figure 1 shows the simplified Potential Energy Curves (PECs), excitation/ionization pathways, and the experimental and theoretical results of the Nuclear Wave Packet (NWP) dynamics of an excited neutral H_2 molecule. The VUV part of the beam, in particular the 9th harmonic, was tuned to excite the $B^1\Sigma_u^+$ electronic state of the target. The 3rd, 5th, and 7th harmonics of the fundamental laser light (808 nm) are not resonant with the lowest bound electronic states of H_2 . The low infrared field intensity ($\sim 3 \times 10^{11}$ W/cm²) does not allow a non-linear absorption of more than three IR photons. Hence, the IR field and harmonic orders below the 9th play no significant role in the excitation process. Moreover, photon frequencies that can directly ionize H_2 , such as the 11th and the 13th harmonic or a non-resonant combination of VUV and IR frequencies (e.g. 9th + 2 IR), were minimized but contribute a time-independent background (at the present pulse duration of 45 fs) to the

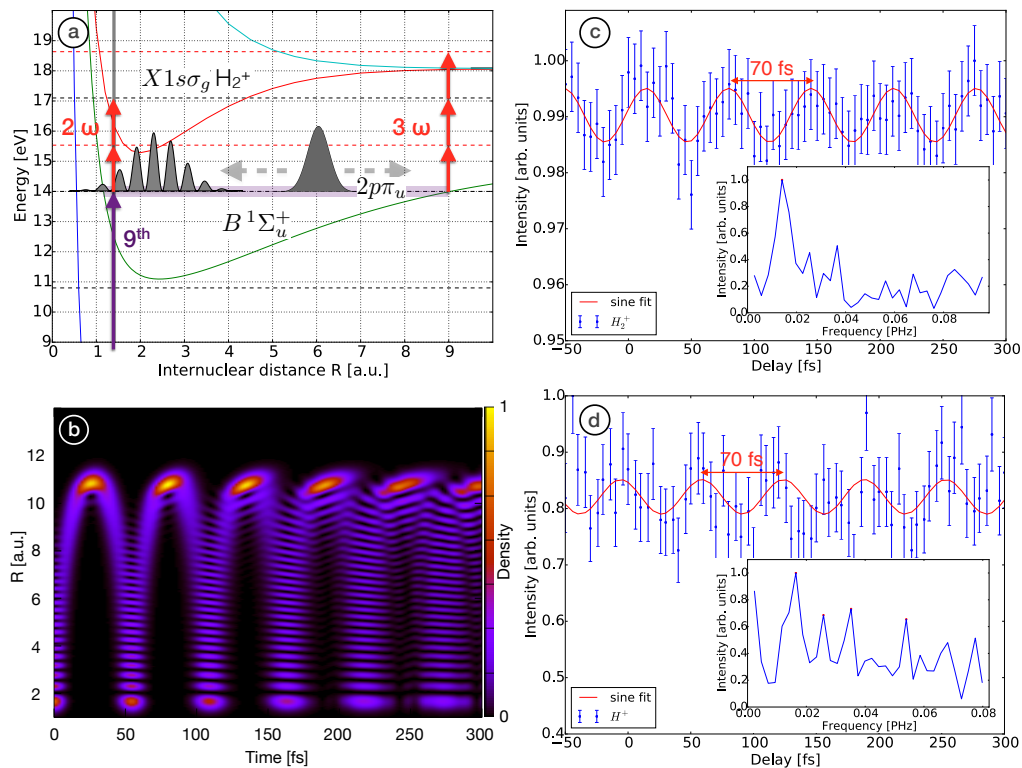


FIG. 1. (color online) (a) Schematic of the NWP dynamics in the $B^1\Sigma_u^+$ state potential energy curve of H_2 . (b) Simulation of the wave packet propagation (see text). (c) H_2^+ yield and (d) H^+ yield with corresponding Fourier transform power spectra (insets).

modulation of the total H_2^+ and H^+ yields. Upon the ultrafast excitation/ionization, we create a coherent superposition of several NWPs in the excited neutral molecule and the ground state of H_2^+ . For the interpretation of the data presented here, it is sufficient to consider the vibration of the nuclear wave packet in the $B^1\Sigma_u^+$ state of the neutral H_2 molecule with a vibrational period of ~ 60 fs, excited by the 9th harmonic VUV pump pulse. The vibrational period was estimated from the simulation shown in Fig. 1(b). As the excited neutral molecule is stretching, we use a time-delayed VUV/IR probe pulse to couple the $B^1\Sigma_u^+$ electronic state directly to the dissociative continuum, resulting in the creation of an H^+ ion and a neutral H atom. The H^+ ion energy, the ionization probability, and the angular momentum depend on the internuclear distance at which the ionization event occurs. The effective ionization potential of the excited neutral molecule is defined by the energy difference between the potential energy curves of the H_2^+ ground state and the $B^1\Sigma_u^+$ state. As can be seen in Fig. 1(a), this potential changes as a function of the internuclear distance. As indicated by red (gray) arrows, two IR photons are sufficient for ionizing the H_2^* molecule from the $B^1\Sigma_u^+$ state at small internuclear distances (small Rs), while at least three IR photons are required for ionization at large Rs. Meanwhile, the 3rd harmonic as a probe pulse, has sufficient energy to ionize the $B^1\Sigma_u^+$ at all in-

ternuclear distances.

Figure 1(b) shows the calculated NWP dynamics in the $B^1\Sigma_u^+$ state of the H_2 molecule, excited by the 9th harmonic. In this simulation, the probability density of the internuclear distance of the H-H bond of the excited neutral molecule is shown as a function of time. The temporal evolution of the NWP was calculated by projecting the H_2 molecule ground state onto the $B^1\Sigma_u^+$ electronic state through a dipole transition with 14 eV energy, corresponding to an excitation by the 9th harmonic in the Franck-Condon (FC) region. The hereby created NWP is then propagated in time on the potential energy curve of the $B^1\Sigma_u^+$ state. In this experiment, we probe the time-dependent ionization probability of the excited neutral H_2 molecule by mapping the NWP dynamics of the $B^1\Sigma_u^+$ state as a function of the relative time delay between the VUV pump and the VUV/IR probe pulses. Figure 1(c) and (d) show the measured H_2^+ and H^+ yields as a function of the pump-probe time delay. The oscillation period of the total H_2^+ experimental yield is extremely sensitive to the exact energy of the 9th harmonic. We measured a period of ~ 70 fs, close to the simulated vibrational period of the $B^1\Sigma_u^+$ state excited by the 9th harmonic of the driving IR field. The period of the oscillation was determined from the Fourier transform of the time-dependent ion yield, as shown in the insets of Figure 1(c) and (d).

The oscillation of the ion yield can be explained by the change of the effective ionization potential which results in a varying number of IR photons required for ionization as described earlier and illustrated in Fig. 1(b). Additionally, different ionization processes occurring at small and large stretching amplitudes of the excited neutral molecule contribute to the observed effect. At a constant IR pulse intensity, the molecular dynamics of the moving wavepacket thus prompts different ionization probabilities at different R s. The ionization process initiated by a 3rd harmonic probe pulse does not depend on the internuclear distance as the photon energy of 4.5 eV is sufficient to ionize the $B^1\Sigma_u^+$ state of H_2^* at all internuclear distances. However, at large R s, the $B^1\Sigma_u^+$ electronic state is coupled directly to the dissociative continuum (by IR or 3rd harmonic absorption), which results in a decrease of the total H_2^+ yield. We conclude that the observed maxima in the H_2^+ ion yield correspond to ionization events taking place at small R s, while the minima in the total yield occur when the NWP is located at the outer turning point of the $B^1\Sigma_u^+$ potential energy curve.

The modulation of the H^+ yield in Fig. 1(d) shows a similar oscillation period as the modulation of the total H_2^+ yield, with the exception of a change in the absolute phase. This phase difference stems from the different dissociation processes at small and large internuclear distances. At small internuclear distances, the photon energy is not sufficient to reach the dissociative $2p\sigma_u$ curve, thus the above described ionization processes result in a stable H_2^+ ion. H_2^+ can, however, dissociate through a delayed sequential process occurring at R s close to the equilibrium internuclear distance. Here, the VUV pump pulse first excites the $B^1\Sigma_u^+$ state. Then, the probe pulse couples the $B^1\Sigma_u^+$ state to the bound $X^1s\sigma_g$ ground state of H_2^+ . This ionization creates an additional NWP in the $X^1s\sigma_g$ state that dissociates with the highest probability at the outer turning point by absorption of an additional IR photon. This NWP takes about 7.5 fs to reach the outer turning point in the $X^1s\sigma_g$ potential before the molecule is efficiently dissociated by the same IR probe pulse.

In order to better understand the dissociation processes, we show all optically allowed electronic states accessible with the pump VUV pulse in Figure 2. The vertical arrows indicate the energy of the VUV pump pulse (purple and blue), and the couplings of the neutral and the ion states via the 3rd harmonic (yellow (light gray) arrows) as well as the IR field (red (dark gray) arrows) leading to the dissociation into H^+ and H . We see that the VUV pulse (i.e. the 9th harmonic) can coherently excite several other electronic states (i.e. C, B, etc.), each with completely different NWP dynamics. While the Fourier transforms of the total H_2^+ and H^+ yields indicate the presence of several other, faster NWPs, the vibration of the $B^1\Sigma_u^+$ state is the only one with a long vibration period. Several dissociation channels contribute to the total H^+ yield when the H_2 molecule is exposed to a combination of VUV pump - VUV/IR probe pulses.

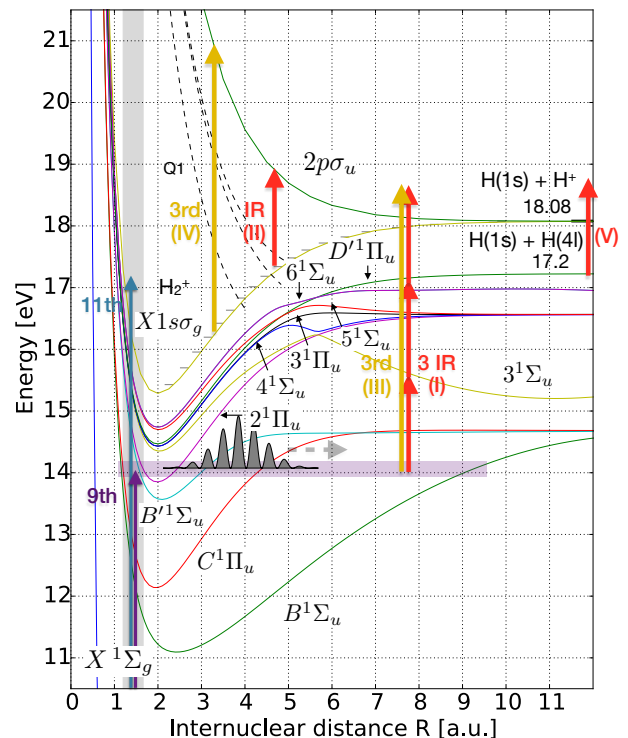


FIG. 2. (color online) Potential energy curves of H_2/H_2^+ accessible by a single photon (VUV) excitation/ionization. Vertical arrows in purple (9th harmonic) and blue (11th harmonic) indicate the energy of the pump VUV pulses. Red (dark gray) (IR) and yellow (light gray) (3rd harmonic) arrows indicate the observed non-equilibrium transitions resulting in dissociative ionization into $H^+ + H$.

Upon the VUV excitation, both the IR field as well as the 3rd harmonic have sufficient intensity and energy to initiate the dissociation process of the molecule. Since the IR and the VUV pulses are orthogonally polarized, the competing dissociation channels, corresponding to the absorption of the VUV-IR and VUV-VUV pulse combinations at the same R s, can be identified by resolving the ionization step by means of the 3D momentum distributions of the H^+ ions measured with the time- and position sensitive COLTRIMS detectors. The dipole character of the electronic transitions, caused by the absorption of photons in the broadband (IR-to-XUV) spectrum, imposes selection rules on the transitions allowed between the electronic states, which result in different emission patterns of the created ions with respect to the polarization axis of the ionizing radiation. For example, at $R = 7.8$ a.u., the $B^1\Sigma_u^+$ state can be coupled directly to the dissociative continuum by the 3rd harmonic. An ion with the same energy, but completely different 3D momentum components, is created by the absorption of three IR photons due to their different polarization direction. Additionally, those two channels can have different probabilities when a sequential coupling of H_2 to the transient Rydberg states occurs.

In order to identify the contributions of different chan-

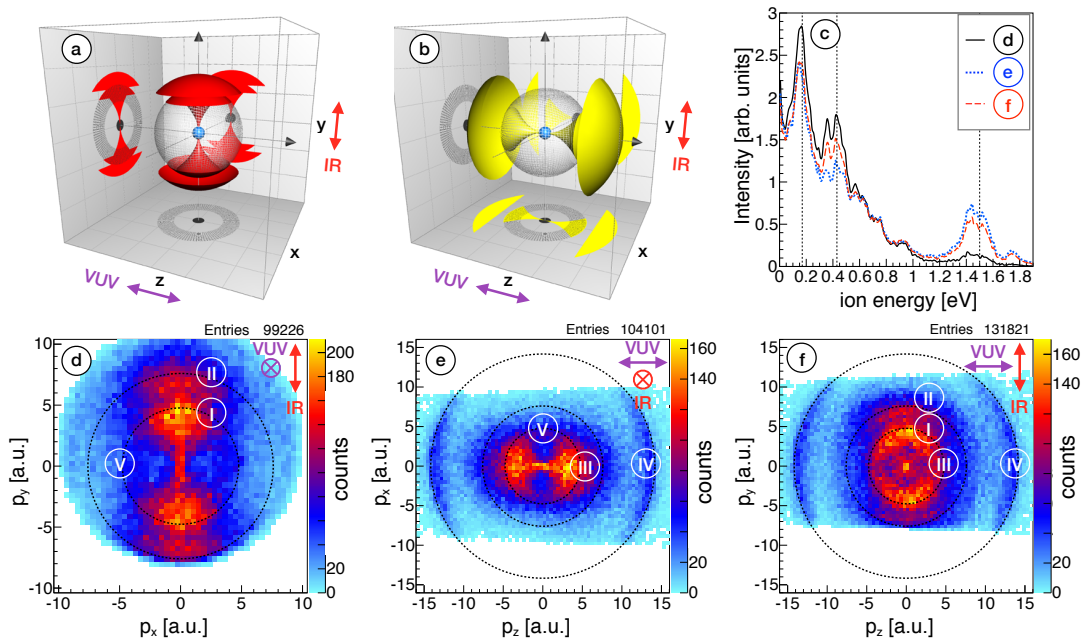


FIG. 3. (color online) (a) Sketch of the 3D ion momenta caused by VUV pump - IR probe and (b) VUV pump - VUV probe transitions. (c) Measured H^+ ion energies corresponding to projected slices through the momentum sphere in all three spatial directions shown below ((d) black solid, (e) blue dotted, and (f) red dashed line). Intensities corrected for the momentum dependent detection phase space. The identified non-equilibrium channels are labeled with roman numerals.

nels, we take advantage of the crossed polarization geometry of our apparatus. The polarization axis of the IR beam is oriented along the y -axis while the polarization of the VUV radiation is oriented along the z -axis. This geometry allows us to distinguish the VUV pump - IR probe channels from those initiated by a VUV-VUV pump-probe sequence. Ionization of the H_2^+ ground state, as well as parallel transitions in general, occur preferentially for ions oriented along the polarization axis, as a consequence of the higher electron density.

In Figures 3(a), we schematically illustrate how the dipole selection rules for two orthogonally polarized VUV pump - IR probe pulses and (b) parallel polarized VUV pump - VUV probe pulses would influence the H^+ 3D momentum distributions. In Figs. 3(d) to (f) we show slices of the experimental 3D H^+ momenta averaged over all time delays, as shown in Fig. 1(d). The corresponding H^+ kinetic energies are shown in Figure 3(c). Labelled red and purple arrows indicate the polarization directions of the IR and the VUV radiation in and out of the paper plane.

By looking at the H^+ ions emitted in the P_x - P_y plane with low momentum in the P_z -direction (see Figure 3(d)), we can identify the ions that were excited by a VUV pulse and dissociated by the IR probe pulse, since the IR polarization was oriented along the P_y -axis. On the other hand, the ions dissociated by the VUV pulse are predominantly emitted in the P_z -direction (i.e. out of the P_x - P_y plane) and thus do not contribute to the momentum distributions in this plane. The same principle can

be applied to obtain the channels corresponding to the VUV pump - VUV probe sequence. For example, Figure 3(e) shows the momentum slices in the P_y - P_z plane, where the contribution from the IR pulse is minimized. All significant reaction channels are labeled with roman numerals and listed in Table I.

TABLE I. Dissociation reactions of H_2 .

I.a	$X^1\Sigma_g^+ \xrightarrow{9th} B^1\Sigma_u^+$	$\xrightarrow{3IR} 2p\sigma_u + e^-$
I.b	$X^1\Sigma_g^+ \xrightarrow{9th} B^1\Sigma_u^+$	$\xrightarrow{2IR} 3^1\Pi_u \xrightarrow{IR} 2p\sigma_u + e^-$
II	$X^1\Sigma_g^+ \xrightarrow{11th} X^1s\sigma_g + e^-$	$\xrightarrow{IR} 2p\sigma_u + e^-$
III	$X^1\Sigma_g^+ \xrightarrow{9th} B^1\Sigma_u^+$	$\xrightarrow{3rd} 2p\sigma_u + e^-$
IV	$X^1\Sigma_g^+ \xrightarrow{11th} X^1s\sigma_g + e^-$	$\xrightarrow{3rd} 2p\sigma_u + e^-$
V	$X^1\Sigma_g^+ \xrightarrow{11th} D'^1\Pi_u$	$\xrightarrow{non-ad. coupl.} H(1s) + H(3l)$ $\xrightarrow{IR} H(1s) + H^+ + e^-$

We start the description of the observed channels by identifying the dissociation processes responsible for the observed yield oscillation in the H^+ ion signal. As discussed earlier, the 9th harmonic creates a NWP in the neutral $B^1\Sigma_u^+$ state of H_2^* . At large internuclear distances (i.e. larger than 7 a.u.) the molecule can be ionized and dissociated through the $2p\sigma_u$ state by absorbing three IR photons (I.a). From the potential energy curves, we calculate the onset of this process at proton

momenta of ~ 4.5 a.u. as observed in Fig. 3(d) and (f). This momentum corresponds to ~ 0.2 eV of measured proton energy (see Fig. 3(c)). When this ionization process (I) occurs at larger internuclear distances, i.e. further stretching of the H-H* bond, it leads to smaller ion energies down to zero kinetic energy at asymptotic Rs where the excited electron is coupled to the flat PEC. This explains the continuous structure from 4.5 down to 0 a.u. in the H⁺ ion momentum distribution (i.e. notice the bowtie shape in Fig. 3(d)). Additionally, the infrared multi-photon dissociation of the $B^1\Sigma_u^+$ state can be enhanced by involving resonant intermediate states, splitting up the 3-IR photon ionization into two steps: a 2-IR-photon transition to the $3^1\Pi_u^+$ state followed by the ionization to the $2p\sigma_u$ state with an additional IR photon (I.b). This process yields the same proton energies as process I.a and, thus, is energetically indistinguishable.

As shown in Fig. 2, the transition from the excited neutral $B^1\Sigma_u^+$ state to the $2p\sigma_u$ repulsive state can also be initiated by the absorption of a single 3rd harmonic photon (III). Looking at Figure 3(e) we see a similar bowtie structure oriented along the z-direction (III), corresponding to the polarization direction of the VUV pulses, at momentum values below 5 a.u.. We note here that the P_x-P_z momentum plane is perpendicular to the polarization of the IR pulses (linearly polarized along the P_y-direction). Consequently, all channels appear in Figure 3(f) as the P_z-P_y plane contains both the VUV as well as the IR polarization directions.

The ion fragments observed at higher energy (~ 0.4 eV) in Fig. 3(d) can be assigned to the dissociation of the $X1s\sigma_g$ H₂⁺ ground state and do not contribute to the modulation of the total ionization yield caused by the excitation of the neutral molecule. The harmonic orders ≥ 11 , as well as a combination of the $9th + 2IR$, directly ionize the molecule to the $X1s\sigma_g$ state. This state can be dissociated subsequently through the $2p\sigma_u$ state by absorbing a single IR photon, leading to H⁺ ions with ~ 7 a.u. momentum (II). This dissociation pathway is well known and described as the bond-softening channel in the literature [30].

The dissociation of the $X1s\sigma_g$ ion state to the $2p\sigma_u$ state initiated by the 3rd harmonic (IV) leads to much higher energies than in the IR case because the resonant absorption and dissociation occurs at shorter internuclear distances, as indicated by the yellow (light gray) arrow in Figure 2. This channel forms a discrete ring in the ion momentum distribution at ~ 13 a.u. (IV) in Fig. 3(e). Such distributions are useful for analyzing the relative strengths of the VUV/IR pulses, as their individual contributions can be clearly separated in momentum space.

An additional discrete ring at ~ 4 a.u. is observed in all three momentum slices suggesting a dissociation process that leads to an isotropic momentum sphere (V). This channel is likely produced by the ionization of atomic hydrogen after pre-dissociation of highly excited neutral H₂. At the energy of the 11th harmonic, Rydberg states of the $n\pi^1\Pi_u$ series can be populated that are known to

dissociate through non-adiabatic coupling into the H(1s) + H(3l) limit (V) [31]. At large internuclear distances, the absorption of one infrared photon is sufficient to ionize the excited atomic hydrogen, resulting in an isotropic proton distribution with a discrete energy that depends on the photon energy of the initial excitation.

Following the identification of the various dissociation channels caused by the absorption of IR and VUV pulses, in Fig. 4, we demonstrate a rudimentary degree of control in the branching ratios of the described channels by adjusting the relative intensity of the IR/VUV probe pulses. In the top row of Fig. 4, we show the H⁺ ion momenta and energies for the case where only a moderate infrared field was applied, leading to relatively weak signals of channels (I) and (II) caused by the dissociative ionization driven by the infrared probe pulse. By increasing the infrared field strength by a factor of ~ 2 , as seen in the data shown in fig. 4(c) - (d), we were able to change the relative intensities of the various dissociation channels. This can be observed both in momentum space as well as in the 1D ion energy spectra shown in Figs. 4(b) and (d). In the bottom row, at large infrared intensity the IR mediated channels dominate and the peak corresponding to the VUV-VUV dissociation process (IV) has disappeared. These data suggest that a fine degree of control over non-equilibrium dissociative processes in excited neutral molecules could be achieved by further decreasing the duration of the femtosecond VUV pulses and by changing the wavelength and polarization of the probe laser pulses. Shorter pulses would allow to observe the wave packet motion and the resulting dissociation dynamics in higher excited states that have vibrational periods around 10 - 20 fs. By changing the wavelength, one can move the various transitions in and out of resonance. Such resonance behavior is expected from similar studies in D₂ [8, 23].

IV. CONCLUSION

In this work, we used ultrashort VUV-IR pump-probe schemes in combination with COLTRIMS 3D momentum imaging to time-resolve, map, and control the dynamics of neutrally excited H₂ molecules. We showed how the detection of the 3D ion momenta, in combination with polarization control over laser driven VUV radiation, can be used to unravel multiple ionization and dissociation channels produced by a combination of VUV and IR pulses. Additionally, we demonstrated that such processes can be controlled by varying the relative intensity and polarization of the IR and VUV pulses. Our results illustrate that non-equilibrium processes are complex in nature, even in rather simple molecules such as an excited neutral H₂ molecule, and require the development of non-trivial theoretical models for a quantitative interpretation of the data. These benchmark experiments can be used to test new theoretical models and are essential for developing the concepts necessary for the in-

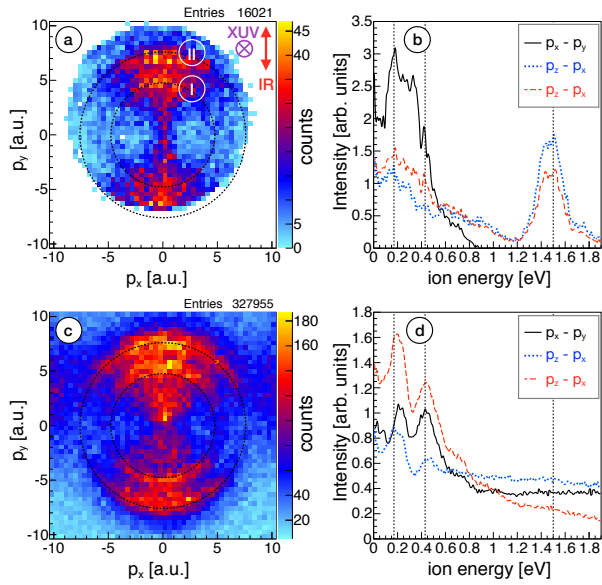


FIG. 4. (color online) H^+ momenta (a,c) and energies (b,d) for two measurements at low IR intensity (top row) and high intensity (bottom row) demonstrating the IR intensity dependent branching ratio of the dissociation channels. The energies for projections in all three spatial directions are shown as black solid, blue dotted, and red dashed lines.

terpretation of experiments involving the ionization and dissociation mechanisms of more complex molecules.

ACKNOWLEDGMENTS

We acknowledge many fruitful discussions and advice from R. Dörner, M. S. Schöffler, L. Ph. Schmidt as well as Wei Cao. We are indebted to O. Jagutzki and A. Czausch from Roentdek GmbH and T. Jahnke from Cronologic GmbH for outstanding support for their momentum imaging detectors readout and software. F. S. acknowledges financial support by Studienstiftung des deutschen Volkes. A.P. and F.M. acknowledge the European COST Action XLIC CM1204, the European Research Council Advanced Grant XCHEM no. 290853, and the MINECO Project no. FIS2013-42002-R. XMT was supported by Grand-in-Aid for Scientific Research from the Japan Society for the Promotion of Science and Interdisciplinary Computational Science Program in Center for Computational Sciences, University of Tsukuba. This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, and by the Division of Chemical Sciences, Geosciences, and Biosciences of the U.S. Department of Energy at LBNL under Contract No. DEAC02-05CH11231.

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