PHYSICAL REVIEW A **81**, 051402(R) (2010)

Investigating two-photon double ionization of D_2 by XUV-pump–XUV-probe experiments

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(Received 25 February 2010; published 24 May 2010)

We used a split-mirror setup attached to a reaction microscope at the free-electron laser in Hamburg (FLASH) to perform an XUV-pump–XUV-probe experiment by tracing the ultrafast nuclear wave-packet motion in the $D_2^+(1s\sigma_g)$ with <10 fs time resolution. Comparison with time-dependent calculations shows excellent agreement with the measured vibrational period of 22 ± 4 fs in D_2^+, points to the importance of accurately knowing the internuclear distance-dependent ionization probability, and paves the way to control sequential and nonsequential two-photon double-ionization contributions.

DOI: 10.1103/PhysRevA.81.051402 PACS number(s): 33.80.Eh

Remarkable developments in femtosecond laser technology have significantly advanced our understanding of ultrafast processes in physics and chemistry [1]. Among the recent, most fascinating achievements are few-cycle laser pulses in the near infrared (IR), now implemented in pump-probe schemes imaging the subfemtosecond nuclear wave-packet (WP) motions in molecules [2,3]. In addition, the feasibility of localizing electrons in simple molecular reactions has been demonstrated by controlling the carrier envelope phase of such fields [4]. Other advances include the generation of attosecond [extreme ultraviolet (XUV)] pulses that deliver unique insight in nuclear and electronic dynamics in molecules [5–7] in IR-XUV (or vice versa) pump-probe experiments.

In this Rapid Communication we report the realization of a femtosecond XUV-pump–XUV-probe scheme that opens a new chapter in ultrafast science by exploiting the huge flux of about 10^{12} photons/pulse of the free-electron laser at Hamburg (FLASH). We trace in real time the femtosecond nuclear WP dynamics in a prototype system, the $1s\sigma_g$ ground state of D_2^+, populated with about 95% by absorption of one photon (38 eV) from the pump pulse as depicted in Fig. 1(a). The dynamics is captured by the time-delayed XUV probe pulse which "sequentially" ionizes D_2^+ and results in its Coulomb explosion with the kinetic energy release (KER) of the fragments, both measured in the reaction microscope (REMI), and is proportional to the inverse of the internuclear distance (R) at the instant of the second ionization.

The D_2 molecule has been chosen because of its prototype character for exploring the interplay between electronic and nuclear motion in two-photon double ionization (TPDI) and the availability of sophisticated calculations. TPDI of H_2/D_2 has sparked considerable interest in theory just recently [8,9] and pioneering experiments using single XUV pulses have been reported [10,11]. In Ref. [11] at 38-eV photon energy, we demonstrated in a combined experimental and theoretical investigation that "sequential" (involving real intermediate states) and "direct" (via virtual levels) TPDI pathways can be separated by measuring the KER of the $D^+ + D^+$ fragments. By making use of the inherent nuclear motion of the vibrationally excited molecular ion, initiated by the first ionization step, contributions at lower KERs were related to sequential double ionization since the WP has moved to larger distances by the time the second photon is absorbed. A quantitative determination of the time interval between both photoabsorption events, however, was not possible.

Here, together with model calculations, we trace the WP motion and, thus, the absorption of the second photon in TPDI in real time. By choosing specific time delays we are able to select instances in time for the second ionization step where the D_2^+ nuclear WP is either close to the outer or the inner classical turning point in the bound $1s\sigma_g$ potential curve. This way we extract information about the R dependence of the ionization probability and, in comparison with theory, it points to future ways to extract absolute direct TPDI cross sections.

Our experimental setup at FLASH [12] is comprised of a REMI [13] equipped with an on-axis backreflection split-mirror setup for focusing and pulse-pair creation. In contrast to already existing pulse-splitting schemes based on broad-band grazing incidence mirrors [14,15], our setup consists of a spherical multilayer mirror (1-in. Mo/Si mirror, 50-cm focal length, <10-μm focus diameter) that is cut into two identical "half-mirrors" (so-called "half-moon" geometry). The mirror has a reflectivity of 40%, sharply peaked around 38 eV so that higher-order harmonic radiation from the FEL is efficiently suppressed. While one half-mirror is mounted at a fixed position, the other one is movable along the FEL beam axis by

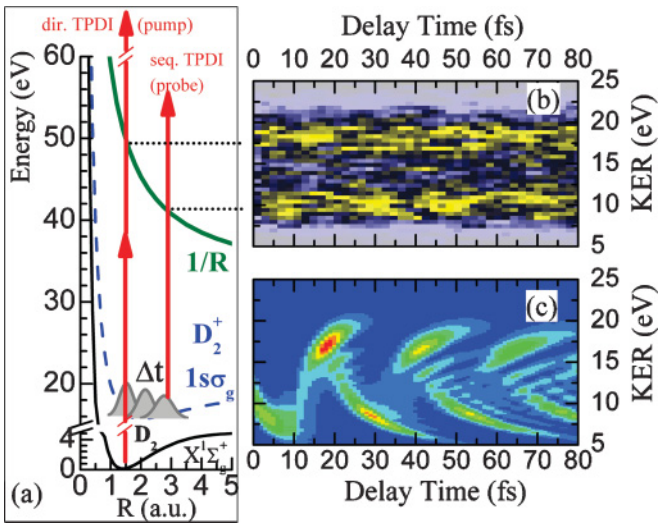

FIG. 1. (Color online) (a) Illustration of the dominant dissociative pathways for direct and sequential TPDI of D_2. (b) Density plot for the experimental KER spectrum of coincident $D^+ + D^+$ fragments as a function of delay time up to 80 fs. (c) The same as (b), but for theoretical results.

means of a high precision piezostage. In this way a time delay between both reflected light pulses is adjustable within a range of ±1500 fs at a resolution of better than 1 fs. The time overlap of both pulses was determined in a separate measurement on delay-dependent multiple ionization of N_2 [16], where a sharp about ±5-fs-wide maximum in the ionization yield at zero delay time was observed superimposed on a broad, about ±30 fs, background structure. During the experiment the intensity of the incoming FEL beam (10-mm diameter) was equally distributed over both half-mirrors and the foci were merged inside a dilute and well-localized beam (less than 1-mm diameter) of cold D_2 molecules in the center of our REMI. With a focus diameter of ∼10 μm and pulse energies of a few μJ at an estimated average pulse duration of ∼30 fs, we reached peak intensities of $I \cong 10^{13}$–10^{14} W/cm^2 at a photon energy of 38 ± 0.5 eV. Ionic fragments were projected by means of an electric field (40 V/cm) onto a time- and position-sensitive detector (diameter, 120 mm; position resolution, 0.1 mm) and recorded as a function of the pump-probe time delay. From the measured time of flight and position of each individual fragment the initial momentum vectors were reconstructed. The energy resolution in the KER spectra is better than 50 meV for all fragment energies detected.

The dominant fragmentation pathways for direct and sequential TPDI of D_2 are illustrated in Fig. 1(a) and both are expected to contribute with comparable amplitude in each individual pulse (pump as well as probe) to the total double-ionization yield at the present intensities [11]. In the case of sequential ionization a nuclear WP in $D_2^+(1s\sigma_g)$ is launched due to ionization by the first photon and then, either within the same pulse or induced by the time-delayed replica, projected onto the repulsive $D^+ + D^+$ Coulomb potential after absorption of the second photon. According to the reflection principle, and neglecting the bound-state nuclear kinetic energies, the R-dependent shape of the WP is converted into KER that is released in the Coulomb explosion of the deuterons. Thus, the KER spectrum carries information about the time delay between the two subsequent photoabsorption events or, turning it around, information about the actual shape of the molecular WP at the instant of the second ionization step. Considering the fact that D_2^+ may get ionized at any R, ranging from the inner up to the outer classical turning point of the WP in the $D_2^+(1s\sigma_g)$ potential, the corresponding KER values are between 6 and 20 eV. In the case of direct TPDI, where the molecule is promoted directly from the neutral ground state into the double-ionization continuum by instantaneous absorption of two photons via intermediate virtual states, the observed KER spectrum exhibits a peak at 18 eV, corresponding to the equilibrium internuclear distance R_e of neutral D_2. This interpretation is in agreement with our recent single excitation pulse measurement, where we demonstrated that direct and sequential TPDI pathways can be separated due to their specific KER distributions [11].

The KER spectrum measured with the pump-probe setup is shown in Fig. 1(b) as a function of the time delay between both FEL pulses. Two pronounced horizontal bands around $E_{\mathrm{KER}} \cong 18$ and 10 eV are observed which can be attributed to ionization of D_2^+ at the inner or outer classical turning points, respectively. Since the absorption of one photon from the pump pulse launches a D_2^+ nuclear WP, which is then probed during the time-delayed probe pulse by further ionization, we expect a time-dependent oscillatory behavior for the KER distribution. The result of a projection of the two-dimensional (2D) data in Fig 1(b) over the low KER band (from 6 to 12 eV) onto the time axis is shown in Fig. 2(a). The periodic maxima occur whenever the probe pulse meets the vibrating molecule at large R. Hence, by varying the delay time the D_2^+ vibrational WP as well as sequential double ionization is probed at different instants of time. A less pronounced, barely visible oscillation is observed in the high KER band for a projection of all events

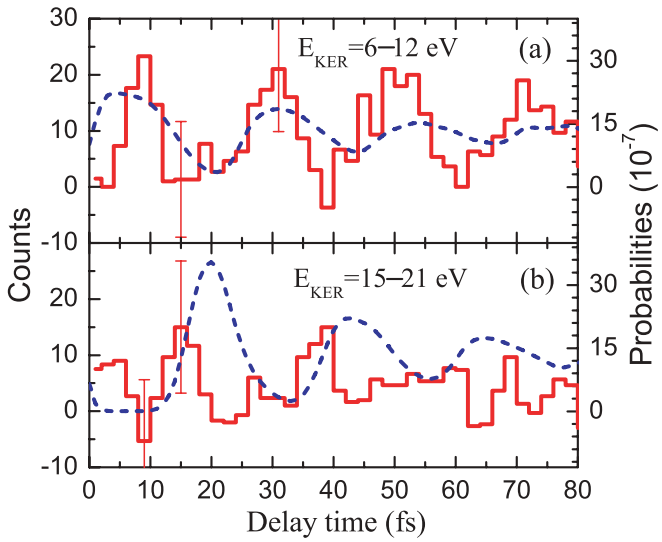

FIG. 2. (Color online) Pump-probe delay-time dependence of ion yields in different KER regimes as indicated in the figure, after proper background subtraction, as described in the text. Dashed lines: theoretical ionization probabilities (right ordinate) for the corresponding KER ranges.

with 15 eV $< E_{\mathrm{KER}} <$ 21 eV [Fig. 2(b)]. To some extent this is expected because at small R (i.e., high KER) the contribution from the direct double-ionization process is largest [11] and the corresponding probability does not oscillate with delay time because no vibrational WP is launched in the $1s\sigma_g$ state. Thus, among other reasons, it might be the larger (time-independent) background that dilutes the expected oscillations in the high KER range [Fig. 2(b)].

In general, the oscillation (amplitude ~20 counts) occurs on top of a significant background of about 100 counts (already subtracted in Fig. 2), consisting essentially of three contributions. (i) The FEL pump pulse is strong enough to generate direct as well as sequential TPDI at high KER. At the same time the pulse duration is long enough, ~30 fs, to produce one-pulse sequential TPDI contributions at low KER as well (see the details in [11]). (ii) The same is true for the probe pulse alone, even though this contribution should be negligibly small for an ideal overlap between both pulses since the pump pulse will ionize all molecules in its focus with a probability close to unity. (iii) Because the full width at half maximum (FWHM) of the envelope of "many" individual self-amplified spontaneous emission (SASE) pulses has been estimated (and measured [15]) to be ~30 fs, which means longer than the round-trip time of the D_2^+ WP, a pump-probe experiment should deliver a mostly flat, time-independent behavior.

The question why the ~20 fs motion of nuclear WPs can be mapped at all, even observing structures as sharp as ~7 fs, can be answered in light of several recent measurements [14,15,17] on the single-shot characteristics and the coherence length of the SASE pulses, showing that they contain single spikes as short as <7 fs (limited by the experimental resolution). Nonlinear autocorrelation measurements for multiple ionization of N_2 with our split-mirror setup [16], where the same pulse is used for pump and probe and, thus, the width of the most prominent peak of the spiky internal pulse structure sets the limit for the achievable time resolution, deliver signals shorter than 7 fs. A more detailed discussion of these results combined with basic model calculations for nonlinear autocorrelation with atoms and molecules, taking into account the spiky structure of the statistically fluctuating FEL pulses, will be the subject of a forthcoming publication [16].

In light of these results, we have calculated the KER for sequential double ionization of D_2 as a function of the pump-probe delay time by solving the time-dependent Schrödinger equation (TDSE) separately for the two ionization steps using 10-fs-cosine square-shaped XUV pulses. Single ionization by the pump pulse ($D_2^0 \Rightarrow D_2^+$) is treated essentially without approximations by including all electronic and vibrational (dissociative) degrees of freedom (see, e.g., [18] and references therein). In particular, the electron-electron interaction is included. The time integration is stopped just at the end of the pump pulse and the resulting nuclear WP, freely propagated in time until the onset of the probe pulse, serves as a starting point for the calculation of the second ionization step ($D_2^+ \Rightarrow D^+ + D^+$), in which the presence of the first ejected electron is ignored. The corresponding one-electron TDSE is solved again essentially without approximations by using a method similar to that described in [18] (in particular, the R-dependent photoionization probability is taken into account). This model is expected to yield an appropriate description of sequential (pump-probe) double ionization. The delay-time-dependent KER spectrum calculated for 10^{12} W/cm^2 at 38 eV clearly shows the WP motion [Fig. 1(c)] over the whole KER range, closely resembling the temporal and spatial evolution of the $D_2^+(1s\sigma_g)$ vibrational WP that is created after the pump pulse. Results obtained with slightly longer pulses, containing spikes such as those of the SASE pulses, are very similar. The fact that the oscillatory structure in the theoretical KER spectrum is considerably more pronounced than in experiment [Fig. 1(b)] is a result of the discussed single pulse-induced double-ionization processes that are not included in theory. At high KER in particular the direct TPDI gives rise to a time-independent background contribution.

In order to enable a quantitative comparison with theory, we have subtracted the background contributions from the experimental data for low (6–12 eV) and high (15–21 eV) KER contributions by exploiting the time-dependent WP motion. For times where the WP is at the inner (about 16 fs and 38 fs) or outer (about 9 fs and 30 fs) turning point, respectively, we can generate the background contributions for the high- and low-energy KER parts separately and subtract them from the respective time-dependent traces shown in Fig. 2. Comparison with the equivalent theoretical projections yields good agreement, thus demonstrating that the model has captured the essential physics. A Fourier analysis of the low-energy KER oscillations, where we have slightly better statistical significance, yields periods of 22 ± 4 fs and 23.8 fs for experiment and theory, respectively, which is in very good agreement with the expected 22-fs oscillation period of a freely propagating nuclear WP in $D_2^+(1s\sigma_g)$ [19].

We can further extract experimental information on the R dependence of the ionization probability for the $D_2^+(1s\sigma_g)$ ground state by 38 eV photons by integrating (up to 80 fs) the time traces of Fig. 1(b) for selected KER values. This was done after a background correction to effectively subtract direct (time-independent) two-photon double ionization leaving behind those events that emerge from two-pulse sequential ionization only. The results for $\Delta\mathrm{KER} = \pm 1$ eV are shown in Fig. 3 together with theoretical ionization probabilities using the Franck-Condon approximation (FCA) and the R-dependent non-FCA from [11]. The theoretical curves are normalized to the experimental results (same

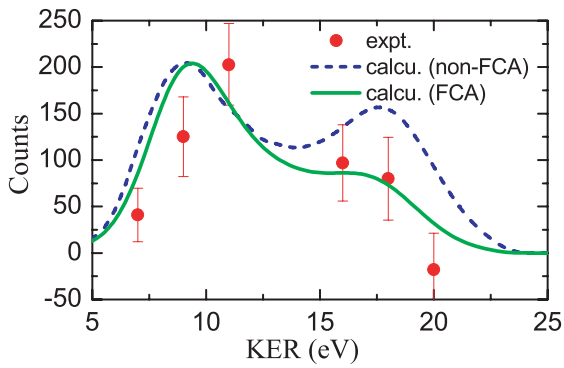

FIG. 3. (Color online) KER-dependent $D_2^+(1s\sigma_g)$ ionization probability obtained by integrating the KER spectrum of Fig. 1(b), after background subtraction, in the time-delay interval 0–80 fs. Lines: theoretical results (see text).

maximum values). In qualitatively good agreement with theory we find a decrease of the probability at high KERs (small R) compared to low KERs (large R) with a slight preference for the non-FCA result.

We would like to emphasize that the WP motion might provide the key to unambiguously determining the cross section for direct TPDI in the future. Using slightly reduced photon energies ($\sim$30 eV) sequential TPDI is not allowed at small R [see Fig. 1(a)]. Then, any experimental observation of high KER events at times (e.g., at 30 fs) where the WP is at large R (small KER) must be entirely due to direct TPDI induced by the pump pulse and/or the probe pulse. The ratio of the integrated direct TPDI signal (high KER events) to the sequential one, together with the theoretically available sequential TPDI probability, will allow us to extract the direct TPDI cross section which is much more difficult to calculate and the subject of considerable interest for theory [8,9]. This is true for not too intense pulses ($<10^{13}$ W/cm^2) such that sequential three-photon processes do not significantly contribute. The method would profit from shorter pulses ($<$10 fs) recently demonstrated at the Linac Coherent Light Source.

In summary, a femtosecond XUV-pump–XUV-probe experiment has been performed and time-dependent sequential two-photon double ionization of D_2 at 38 eV has been explored. By measuring the KER via coincident $D^+ + D^+$ fragmentation detection we imaged the $1s\sigma_g$ $D_2{}^+$ bound-state vibrational WP, launched by ionization in the pump pulse via its reflection on the Coulomb potential, and traced its motion with $<$10 fs time resolution. Comparison with sophisticated model calculations yields good overall agreement with the experimental delay-time-dependent KER spectrum, the observed vibrational period of 22 ± 4 fs, as well as with information on the R-dependent $D_2{}^+(1s\sigma_g)$ ionization probability.

Our XUV pump-probe scheme combined with many-particle imaging methods opens a variety of future possibilities. (i) Highly excited states can easily be reached within just one frequency-controlled XUV pump step, such as metastable dication states in $N_2{}^{2+}$ [20] or doubly excited $D_2{}^{**}$ [18]. Moreover, light-induced conformational changes in molecules (isomerization) [21] or investigations of the dynamics at conical intersections [22,23] will become accessible. (ii) At high-enough photon energies, the nuclear WP as a whole is projected from position (R) to momentum space allowing for its complete imaging, which is different from previous measurements with IR lasers [2] where the WP could not be traced at small R. (iii) Pump and probe steps are clean in the sense that they ideally involve one-photon absorption processes. (iv) Measuring the emitted electron by coincidence will allow time-dependent "imaging of molecules from within" [24].

The authors are greatly indebted to the scientific and technical teams at FLASH, in particular, the machine operators and run coordinators, who strive for optimal beam-time conditions. Support from the Max-Planck Advanced Study Group at CFEL is gratefully acknowledged. Y.H.J. is grateful for support from DFG Project No. JI 110/2-2, J.F.P.-T., E.P., F.Mo., and F.Ma. from the MICINN Project No. FIS2007-60064, M.S. from NSF Grant No. PHY-0652519, J.L.S.V. from UdeA and Colciencias, R.D. and T.J. from DFG Koselleck Project, and O.H., M.L., and M.F.K. from the DFG via the Emmy-Noether program and the Cluster of Excellence: Munich Center for Advanced Photonics. The European COST Action "CUSPFEL" (CM0702) is also acknowledged. Computations were carried out at Mare Nostrum BSC and CCC-UAM.

[1] A. Zewail, J. Phys. Chem. A **104**, 5660 (2000).
[2] T. Ergler *et al.*, Phys. Rev. Lett. **97**, 193001 (2006).
[3] C. R. Calvert *et al.*, J. Phys. B **43**, 011001 (2010).
[4] M. F. Kling *et al.*, Science **312**, 246 (2006).
[5] F. Krausz and M. Ivanov, Rev. Mod. Phys. **81**, 163 (2009).
[6] F. Kelkensberg *et al.*, Phys. Rev. Lett. **103**, 123005 (2009).
[7] E. Gagnon *et al.*, Science **317**, 1374 (2007).
[8] J. Colgan *et al.*, J. Phys. B **41**, 121002 (2008).
[9] F. Morales *et al.*, J. Phys. B **42**, 134013 (2009).
[10] K. Hoshina *et al.*, J. Phys. B **39**, 813 (2006).
[11] Y. H. Jiang *et al.*, Phys. Rev. A **81**, 021401(R) (2010).
[12] W. Ackermann *et al.*, Nat. Phot. **1**, 336 (2007).
[13] J. Ullrich *et al.*, Rep. Prog. Phys. **66**, 1463 (2003).
[14] W. F. Schlotter *et al.*, Opt. Lett. **35**, 372 (2010).
[15] R. Mitzner *et al.*, Phys. Rev. A **80**, 025402 (2009); Opt. Express **16**, 19909 (2008).
[16] Y. H. Jiang *et al.* (unpublished).
[17] U. Frühling *et al.*, Nat. Phot. **3**, 523 (2009).
[18] J. F. Pérez-Torres *et al.*, Phys. Rev. A **80**, 011402(R) (2009).
[19] C. D. Lin, X. M. Tong, and T. Morishita, J. Phys. B **39**, S419 (2006).
[20] Y. H. Jiang *et al.*, Phys. Rev. Lett. **102**, 123002 (2009).
[21] T. Osipov *et al.*, Phys. Rev. Lett. **90**, 233002 (2003).
[22] A. Stolow *et al.*, Chem. Rev. **104**, 1719 (2004).
[23] F. Martin, J. Phys: Conf. Ser. **88**, 012001 (2007).
[24] A. Landers *et al.*, Phys. Rev. Lett. **87**, 013002 (2001).