Investigating two-photon double ionization of D_2 by XUV-Pump – XUV-Probe experiments at FLASH

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Abstract:

Using a novel split-mirror set-up attached to a Reaction Microscope at the Free electron LASer in Hamburg (FLASH) we demonstrate an XUV-pump – XUV-probe ($\hbar\omega = 38\ eV$) experiment by tracing the ultra-fast nuclear wave-packet motion in the D_2^+ ($1s\sigma_g$-state) with <10 fs time resolution. Comparison with time-dependent calculations yields excellent agreement with the measured vibrational period of 22±4 fs in D_2^+, points to the importance of the inter-nuclear distance dependent ionization probability and paves the way to control sequential and non-sequential two-photon double ionization contributions.

Breathtaking developments in femtosecond laser technology have revolutionized our understanding of ultra-fast 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 fastest nuclear wave-packet (WP) motions in molecules [2, 3]. In addition, the localization of 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 (XUV) pulses that deliver unique insight in nuclear and electronic dynamics in molecules [5, 6, 7] in IR-XUV (or vice versa) pump-probe experiments.

In this letter we report the realization of a femtosecond XUV-pump – XUV-probe scheme opening a new chapter in ultra-fast science. Capitalizing the huge flux of about 10^{12} photons/pulse of the Free-electron LASer at Hamburg (FLASH), exceeding the one of present high harmonic sources by orders of magnitude, we split the FEL pulse via a back-reflecting, cut-in-halves, multilayer mirror set-up. Its individual parts can be moved with respect to each other with sub-micron precision, thus producing two replica of the same FEL pulse. Those are directed onto the supersonic jet inside a reaction microscope (REMI) that allows the 3D momentum determination of low-energy electrons and of ions with large solid angle [8]. We then trace in real-time the femtosecond nuclear wave-packet dynamics in a model 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 "sequentially" ionizing D_2^+, thus causing Coulomb explosion with the kinetic energy release (KER) of the fragments, both measured in the REMI, proportional to the inverse of the inter-nuclear distance (R) at the instant of ionization.

In the present, pioneering work the simplest molecule, D_2, has been chosen because of its prototype character to explore 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 [9, 10] and first experiments using single XUV-pulses have been reported [11, 12]. In [12] 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 kinetic energy release (KER) of D^++D^+ fragments. 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 wave packet has moved to larger distances until the second photon is absorbed. A quantitative determination of the time interval between both photo-absorption 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, point to future ways to extract absolute direct TPDI cross sections.

Our experimental setup at FLASH [14] comprises a REMI [13] equipped with an on-axis back-reflection split-mirror setup for focusing and pulse-pair creation. In contrast to already existing pulse splitting schemes based on broad-band gracing incidence mirrors [15, 16], our setup consists of a spherical multi-layer mirror (1 inch 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 such 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

means of a high precision piezo-stage. 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, where a sharp ca. ±5 fs wide maximum in the ionization yield at zero delay-time was observed superimposed on a broad ca. ±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 centre 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 MCP detector (diameter 120 mm, position resolution 0.1 mm) and recorded as function of the pump-probe time delay. From the measured TOF 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 dissociation 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 the probe) to the total double ionization yield at the present intensities [12]. In the case of sequential ionization a nuclear wave-packet 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 wave packet is converted into kinetic energy (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 photo-absorption 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 wave packet in the $D_2^+(1s\sigma_g)$ potential the corresponding KER values are between 6 eV 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 18.5 eV, corresponding to the equilibrium inter-nuclear distance R_e of neutral D_2. This interpretation is in agreement with our recent single pulse measurement, where we demonstrated that direct and sequential TPDI pathways can be separated due to their specific KER distributions [12].

The KER spectrum measured with the pump-probe setup is shown in Fig. 1(b) as function of the time delay between both FEL pulses. Two pronounced horizontal bands around $E_{KER} \cong 18$ and 10 eV are observed which can be attributed to ionization of D_2^+ at the inner or outer classical turning-points, respectively. Assuming that a nuclear WP in D_2^+ is launched by the absorption of one photon from the pump-pulse projecting the D_2 vibrational ground state onto the D_2^+ potential surface close to the inner turning point in a Franck-Condon transition which is then probed during the time-delayed probe-pulse by further ionization, we expect a time dependent oscillatory behaviour for the KER distribution. The result of a projection of the 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 wave-packet as well as sequential double ionization is probed at different instants of time. A similar behaviour, though with slightly lower contrast is observed in the high KER band for a projection of all events with 15 eV < E_{KER} < 21 eV (Fig. 2(b)). This is expected, since the

ionization probability of the $1s\sigma_g$ state for 38 eV photons is decreasing at small R reducing the visibility of the oscillations for the high-energy KER peak.

In general, the oscillation (amplitude ~ 20 counts) occurs on top of a significant background of about 100 counts consisting essentially out 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 details in [12]). (ii) the same is true for the probe pulse alone, even though this contribution should be negligibly small for ideal overlap between both pulses since the pump-pulse will ionize all molecules in its focus with a probability close to one. (iii) since the FWHM of the envelope of "many" individual SASE pulses (***S***elf-***A***mplification by ***S***timulated ***E***mission) has been estimated (and measured [16]) to be ~ 30 fs, longer than the round-trip time of the D_2^+ wave-packet, a pump-probe experiment should deliver a mostly flat, time-independent behaviour!

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 explained in the light of several recent measurements [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). Non-linear autocorrelation measurements with our split-mirror setup [18], 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 as short as 4 fs on a broader background that can be simulated with SASE pulses at averaged FWHM of 25 fs with spikes as sharp as 3.7 fs.

In the light of these results we have calculated the kinetic energy release 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

(full width) cosine-square-like 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. [21] 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 [21] (in particular, the R-dependent photo-ionization probability is taken into account). This model is expected to yield an appropriate description of sequential (pump-probe) double ionization. Direct TPDI is not included in our calculation. 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 in good qualitative agreement with the experimental observation. Results obtained with slightly longer pulses, containing spikes as those of the SASE pulses, are very similar.

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 (~16 fs, ~ 40 fs) or outer (~9 fs, ~30 fs) turning point, respectively, we can generate the background contributions for the high and low-energy KER part separately and subtract them from the respective time dependent traces shown in Fig. 2. Comparison with the equivalent theoretical projections (dashed lines) yields good agreement 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, being 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 just integrating time traces (after background subtraction) for selected KER values. The results for ΔKER = ±1 eV are shown in Fig. 3. In good agreement with theory, we find a decrease of the cross section for the high KER (large R) bins compared to those for low KERs (small R).

We would like to emphasize that the WP motion might provide the key to unambiguously determine the cross section for direct TPDI in the future. Using slightly reduced photon energies (~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- 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 to extract the direct TPDI cross section, which is much more difficult to calculate but a subject of considerable interest for theory [9, 10]. 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 LCLS.

In summary, a femtosecond XUV-pump – XUV-probe experiment has been demonstrated and time-dependent sequential two-photon double ionization of D_2 at 38 eV has been explored. Measuring the KER via coincident D^++D^+ fragmentation detection we image the $1s\sigma_g$ D_2^+ bound-state vibrational wave-packet, launched by ionization in the pump-pulse via its reflection on the Coulomb potential and trace 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 novel 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 (20 eV < $\hbar\omega$ < 200 eV at FLASH) pump-step. Levels of interest are e.g. metastable dication states like in N_2^{2+} [20] or doubly excited D_2^{**} decaying within femtoseconds, thus, being coupled to the nuclear motion beyond the Born-Oppenheimer approximation [21]. Moreover, light-induced conformational changes in molecules (isomerization) [22] or investigations of the dynamics at conical intersections [23, 24] will become accessible. (ii) At high-enough photon energies, the nuclear wave-packet as a whole is projected from position (R) to momentum space allowing for its complete imaging, 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, that can be straight forward calculated by perturbation theory very different from IR-XUV setups aiming at attosecond resolution where the dynamics might be strongly influenced by strong non-perturbative IR fields [6]. (iv) Measuring the emitted electron in coincidence will allow time-dependent "imaging of molecules from within" either by site-selectively launching the electron from specific atoms in the molecule and inspecting its diffraction pattern or by emitting it from non-localized well-defined molecular states [25].

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Figure captions:

Fig. 1: (a) Illustration of the dominant dissociative pathways for direct and sequential TPDI of D_2 at 38 eV. (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.

Fig. 2: 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.

Fig. 3: KER dependent $D_2^+(1s\sigma_g)$ ionization probability for 38 eV photons obtained by integrating, after background subtraction, the KER spectrum of Fig. 1(b) in the time-delay interval 0-80 fs. Lines: Results of theoretical calculations (right ordinate) using the Franck-Condon approximation (FCA) or taking explicitly the R-dependent ionization (non-FCA) into account (see also [12]).

Fig. 1

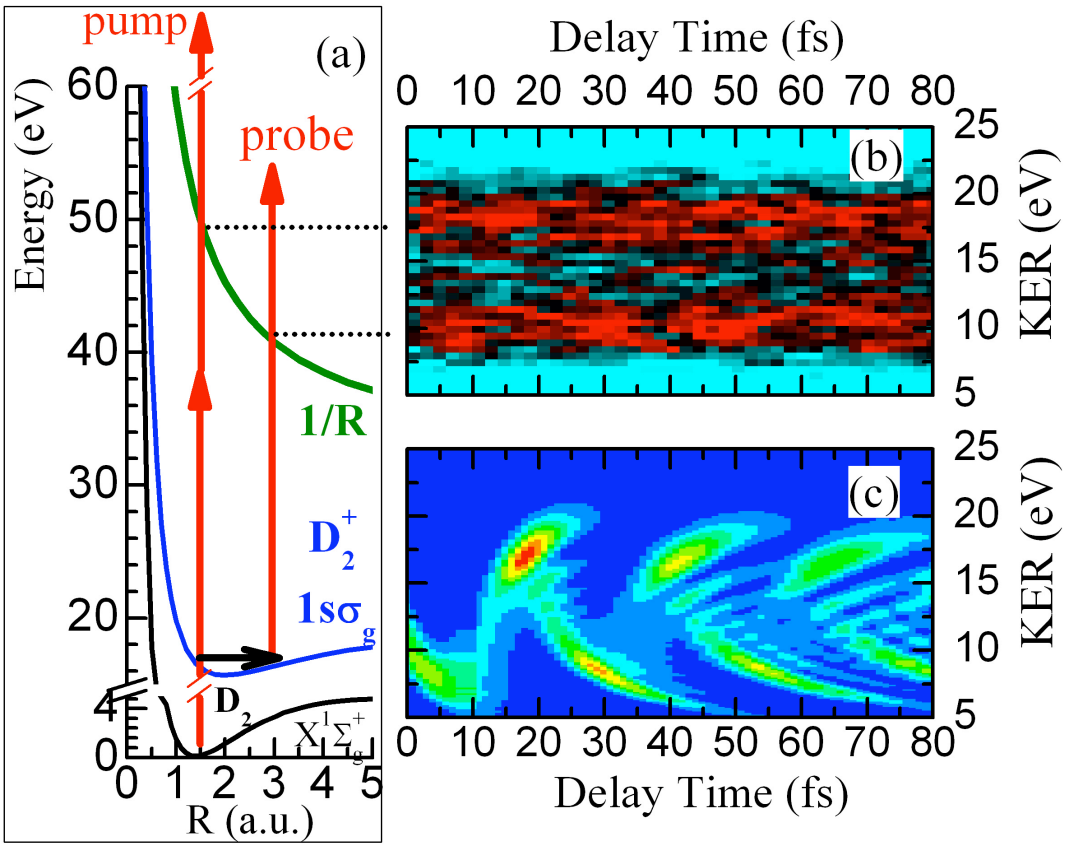

pump
probe
(a)
Energy (eV)
60
50
40
30
20
4
0
1/R
D2+
1sσg
D2
X1Σ+g
0 1 2 3 4 5
R (a.u.)
Delay Time (fs)
0 10 20 30 40 50 60 70 80
(b)
25
20
15
10
5
KER (eV)
(c)
25
20
15
10
5
KER (eV)
0 10 20 30 40 50 60 70 80
Delay Time (fs)

Fig. 2

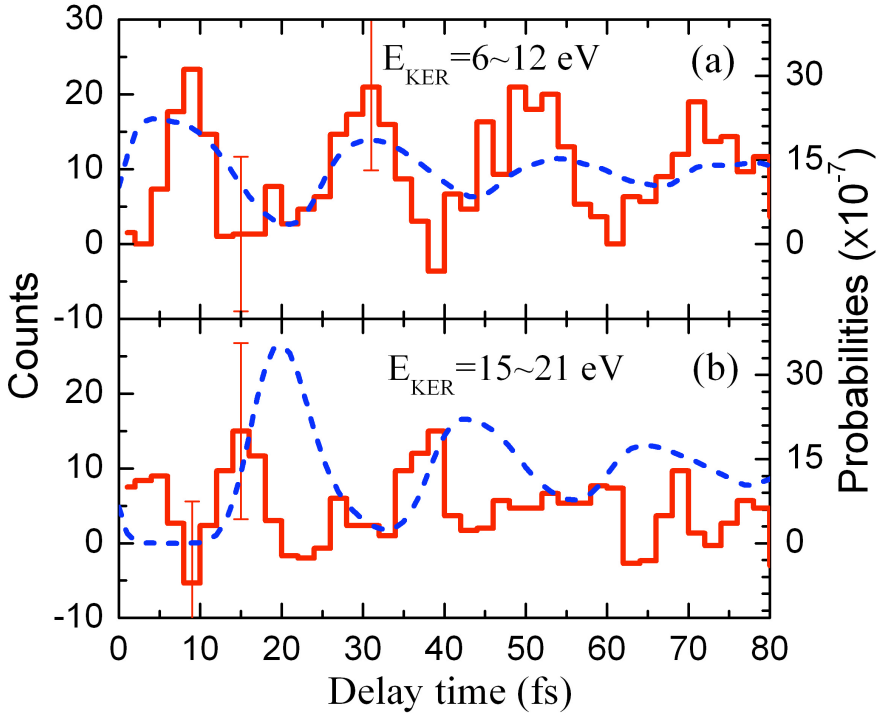
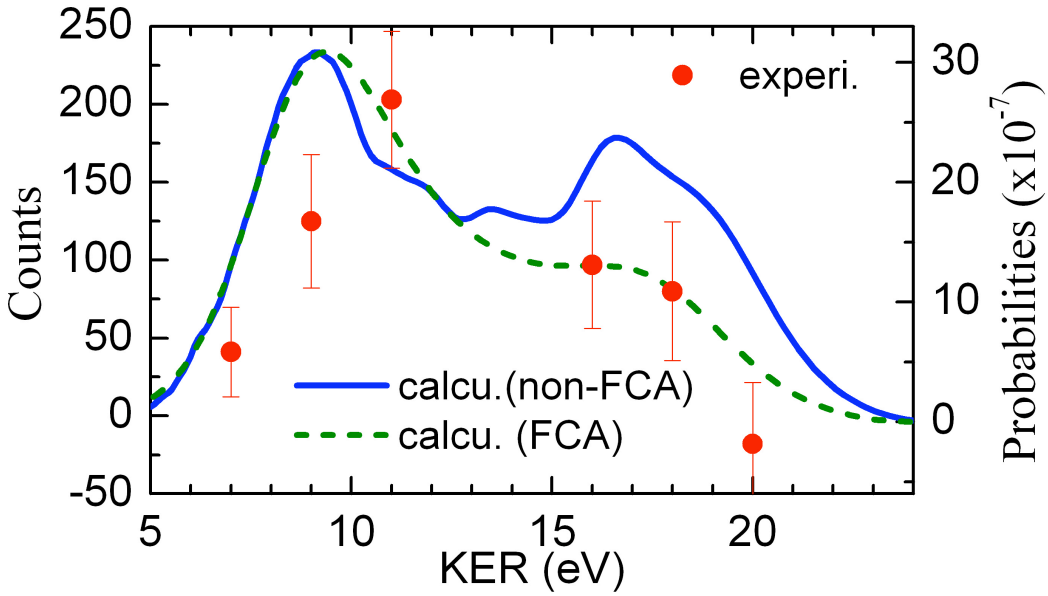

E_KER=6~12 eV
(a)
E_KER=15~21 eV
(b)
Counts
Probabilities (X10^-7)
Delay time (fs)
30
20
10
0
-10
15
0
10
20
30
40
50
60
70
80

Fig. 3


250
200
150
100
50
0
-50
Counts
5
10
15
20
KER (eV)
30
20
10
0
Probabilities (x10^{-7})
experi.
calcu.(non-FCA)
calcu. (FCA)