Time-resolved measurements with intense ultrashort laser pulses: a ’molecular movie’ in real time

A. Rudenko, Th. Ergler, B. Feuerstein, K. Zrost, C.D. Schröter, R. Moshammer and J. Ullrich
Max-Planck-Institut für Kernphysik, Saupfercheckweg 1 69117 Heidelberg, Germany
Artem.Rudenko@mpi-hd.mpg.de

Abstract. We report on the high-resolution multidimensional real-time mapping of H$_2^+$ and D$_2^+$ nuclear wave packets performed employing time-resolved three-dimensional Coulomb explosion imaging with intense laser pulses. Exploiting a combination of a “reaction microscope” spectrometer and a pump-probe setup with two intense 6-7 fs laser pulses, we simultaneously visualize both vibrational and rotational motion of the molecule, and obtain a sequence of snapshots of the squared ro-vibrational wave function with time-step resolution of ~ 0.3 fs, allowing us to reconstruct a real-time movie of the ultrafast molecular motion. We observe fast dephasing, or ‘collapse’ of the vibrational wave packet and its subsequent revival, as well as signatures of rotational excitation. For D$_2^+$ we resolve also the fractional revivals resulting from the interference between the counter-propagating parts of the wave packet.

1. Introduction
Molecular structure and its evolution in time are the key ingredients for our understanding of chemistry and biology on the microscopic level. Based on remarkable progress in short-pulse laser technology [1] the dynamics of numerous photo-induced processes ranging from bond-breaking in diatomic molecules to intramolecular rearrangement in large organic and biological complexes have become accessible in the recent past, opening the entirely new field of femtochemistry [2,3]. For different molecular systems the formation and time evolution of dissociating [4], rotational [5] and vibrational [6] wave packets have been investigated, and, under certain conditions, images of the squared nuclear wave function have become accessible [4,6].

Time-resolved studies of ultrafast molecular dynamics normally exploit the so-called ‘pump-probe’ scheme [2,3]. Here, a first (pump) laser pulse initiates a reaction, i.e. launches a continuum or bound-state molecular wave packet whose evolution in time is then recorded with a second (probe) pulse arriving after a well-defined and variable time-delay. Accordingly, the effective duration of the pulses has to be shorter than the time scale of the process of interest which, for most of the chemical or biological processes, is set by the internal vibrations of the reacting molecules.

Currently a lot of efforts is being undertaken in order to extend this kind of studies to the simplest of all molecules, the hydrogen (deuterium) molecular ion [7]. Apart from its apparent simplicity, some specific properties make H$_2^+$ (D$_2^+$) an ideal model laboratory system for exploring laser-molecule interactions. First, there exists only one bound potential curve, i.e. the electronic ground state, whereas all other electronically excited states are purely repulsive and converge towards the Coulomb 1/R curve, where R is the internuclear distance (see Fig. 1). Second, the degeneracy of the two lowest
electronic states 1s$\sigma_g$ and 2p$\sigma_u$ at large internuclear distances leads to a strong dipole interaction of these levels in the presence of external electrical fields, which is essential for the coupling of the system to laser radiation.

However, for these most fundamental molecular systems vibrational dynamics proceed on the 10 fs scale, which is still well below the 25 fs laser pulses of “ultrashort” commercial systems. As a consequence, time-resolved studies of hydrogen (deuterium) nuclear wave packets represent a severe experimental challenge. Therefore, early pump-probe experiments on these systems were essentially restricted to their dissociating (continuum) part [8,9]. In order to trace the wave packet’s motion in the bound state a novel approach known as the ‘molecular clock’ scheme, where the electrons ionized via tunneling and driven back to the parent ion by the oscillating laser field are used as an ultrafast probe, either observing “recollision”-induced electron-impact fragmentation [10,11], or high-harmonic radiation [12], was suggested. Though providing superior sub-fs time-resolution, this method is (i) intrinsically restricted to fixed return times given by the laser frequency, (ii) by definition explores the molecular motion in the presence of a strong disturbing field and (iii) cannot be used to study the long-time propagation of the wave packet. Therefore, within the last three years a series of “classical” pump-probe experiments with sub-10 fs time resolution have been carried out by different research groups [13-21], and clear signatures of the bound-state vibrational [13-20] and rotational [20,21] motion have been traced.

Here we present the results of a high-resolution multidimensional real-time mapping of H$_2^+$ and D$_2^+$ nuclear wave packets performed employing time-resolved three-dimensional Coulomb explosion (CE) imaging [22-24]. Exploiting a combination of a “reaction microscope” spectrometer [25,26] and a pump-probe setup with two intense 6-7 fs laser pulses, we simultaneously visualize both vibrational and rotational motion of the molecule, and obtain a sequence of snapshots of the squared ro-vibrational wave function with the time-step resolution of $\sim$ 0.3 fs, allowing us to reconstruct a real-time movie of the ultrafast molecular motion. For both H$_2^+$ and D$_2^+$ we observe fast dephasing, or ‘collapse’ of the vibrational wave packet and its subsequent revival, and the signatures of rotational excitation. For D$_2^+$ we also resolve the structures due to the fractional revivals resulting from the interference between the counter-propagating parts of the wave packet.

2. Experiment

A sketch of the experimental setup and the scheme of our CE imaging procedure is shown in Fig. 1. A coherent superposition of the H$_2^+$ (D$_2^+$) ro-vibrational states is prepared via tunnelling ionization of the neutral D$_2$ molecule in its ground state by an intense (3-5x10$^{14}$ W/cm$^2$) linearly polarized 6-7 fs laser pulse. Created molecular ions either dissociate along the field modified 2p$\sigma_u$ potential curve or remain bound in the 1s$\sigma_g$ potential. Both, continuum and bound parts of the wave packet are then projected onto the repulsive Coulomb curve by ionizing the H$_2^+$ (D$_2^+$) ions with an even more intense (up to 10$^{15}$ W/cm$^2$) probe pulse arriving after a certain time delay and, thus, ‘exploding’ the molecule. The measured energy release consists of the Coulomb energy and the kinetic energy at the moment of explosion. Since for the bound wave packet the latter component is rather small, the internuclear distance $R$ can be directly reconstructed from the measured deuteron energy using the Coulomb law. Simultaneous determination of the emission angle with respect to the direction of the laser polarization (see Fig. 1c) yields information on the orientation of the internuclear axis at the moment of explosion. Due to the cylindrical symmetry of the problem with respect to the laser polarization axis, these two observables contain the complete three-dimensional information on the probability density distribution of the nuclear wave packet.

Measurements were performed using linearly polarized radiation from a Kerr-lens mode locked Ti:sapphire laser at 795 nm central wavelength with 25 fs pulse width (FWHM) and 3 kHz repetition rate, which was spectrally broadened in a neon-filled hollow fiber (80 cm length, 200 $\mu$m inner diameter) and then compressed to 6-7 fs full width at half maximum (FWHM) by chirped mirrors and a prism-compressor sequence. The central wavelength of the output pulses was 760 nm. The main pulse sits upon a background of $\sim$ 5% of the peak intensity lasting for $\sim$ 100 fs. Pulse to pulse intensity
fluctuations were monitored during the experiment and did not exceed 5%. The laser beam was fed through a Mach-Zehnder type interferometer with one arm variable in length, providing two pulses separated by a time delay which can be scanned from 0 to 3300 fs with a resolution of better than 0.3 fs. By measuring the interferometric autocorrelation directly at the reaction volume using the ion rate as non-linear signal we verify in situ the length of the pulse and the absolute time zero of the delay determined by the symmetry axis of the autocorrelation pattern [27]. The latter was not noticeably changed during ~ 50 hours data acquisition time, confirming the excellent long-term interferometric stability of our system. Both laser beams were focused to a spot size of ~ 5 µm into the collimated supersonic molecular gas jet at the center of an ultra-high vacuum chamber (2x10^{-11} mbar). Charged reaction fragments were guided onto two position-sensitive channel plate detectors by weak electric (9 V/cm) and magnetic (7 G) fields applied along the laser polarization axis. From the respective time-of-flights and positions on the detectors the full momentum vectors of the coincident recoil ions and electrons were calculated. By inspecting momentum conservation for multi-photon single ionization along the jet propagation, its internal temperature was determined to be about 3 K such that molecules are well prepared in their vibrational ground state before the interaction. A more detailed description of the spectrometer and the coincidence measurement scheme can be found in [26-28].

Figure 1. (color online) (a) A sketch of the experimental setup. (b) Scheme of the pump-probe experiment and the relevant potential curves of H₂ and H²⁺. The curves are shown for a field-free situation. (c) Schematic of the experimental geometry. θ denotes the measured ion emission angle (and, thus, the orientation of the internuclear axis) relative to the laser polarization direction.
3. Results and discussion

Fig. 2 displays the measured kinetic energy spectrum of the protons as a function of the time delay between the 6 fs pump and the probe pulses. For delays below 100 fs the data manifest slight modulations with the laser period due to the interference between the ~5% intensity pedestal with the main pulse. Apart from that, three major contributions can be distinguished in the spectrum. First, there is an intense band at 0 - 1 eV kinetic energy, which originates from the dissociation of H₂⁺.

Second, one can see a broad structure at 2 – 4 eV energy, with pronounced vertical or slightly tilted stripes. This band is due to CE of the bound molecular ion. For very small delays it is shifted towards larger proton energies due to the higher laser intensities achieved in case of constructive interference between both pulses [16,28]. Dissociation and CE within the probe or the pump pulse alone produce delay-independent background below 1 eV and at 2 – 4 eV, respectively. Finally, a clear delay-dependent structure starting from the same energy region as the Coulomb explosion band discussed above close to zero time, and propagating towards lower and lower energies with increasing delay can be observed. At about 150 fs it merges with the dissociation band. This path reflects the process, where the H₂ molecule undergoes dissociative ionization in the first pulse, and the dissociating H₂⁺ ion is ionized by the second one (the so-called ‘delayed ionization’ [9,16,27]). After the first pulse the nuclei of the dissociating molecule fly apart resulting in lower kinetic energies for larger delays. After ~150 fs this line merges with the dissociation band.

In the CE band at 2-4 eV a series of clear stripes can be observed for delays of 0-75 and 200 – 300 fs, which degenerate into an unstructured band for delays between about 80 – 150 fs as well as beyond ~350 fs. These stripes (separated by ~17 fs) reflect the oscillatory motion of the H₂⁺ vibrational wave packet created by the first pulse. A coherent superposition of several H₂⁺ vibrational states, prepared by the first pulse, dephases, or ‘collapses’ after a few oscillations due to the unequal spacing of the vibrational levels in the anharmonic molecular potential. However, after about 200 fs the wave packet partly regains its original form, exhibiting again an apparent periodicity of ~18 fs. This phenomenon is known as a quantum wave packet revival (see [29,30] for reviews) and arises in weakly anharmonic systems with a long-time preserved coherence. This revival structure can be also distinguished for the dissociation band, reflecting the situation where the molecular ion remains bound after the pump pulse, and is dissociated by the probe. Thus, under current experimental conditions vibrational wave

Figure 2. (color online) Proton energy spectrum as a function of the delay between the pump (3x10¹⁴ W/cm²) and the probe (6x10¹⁴ W/cm²) pulses. The data are integrated over all emission angles.
packets can be probed via both CE and dissociation channels. It should be noted that the real contrast of the revival structure in the dissociation channel is considerably higher than the one that is visible in Fig. 2, since at the revival time it is already merged with the ‘delayed ionization’ band, where no revival structure is expected [18].

Fig. 3a shows the results of the same experiment performed with D₂ target. All the structures discussed above for H₂ can be also observed in this Figure. The CE explosion band is shifted towards higher energies due to somewhat higher laser intensity for both the probe and the pump pulses [28]. The stripes reflecting vibrational motion are much more pronounced even though slightly longer pulses (7 instead of 6 fs) have been used in the D₂ experiment. This is a clear consequence of slower nuclear motion in D₂⁺, where the stripes separation of ~24 fs is observed. Noteworthy, as it can be seen from Fig. 2 and 3, the revival time for D₂⁺ is about factor of two longer than for H₂⁺, i.e. it scales with the mass ratio and not with the square root of it, as the vibrational period [30].

Figure 3. (color online) (a) D⁺ energy spectrum as a function of the delay between the pump (5×10¹⁴ W/cm²) and the probe (10¹⁵ W/cm²) pulses. The data are integrated over all deuteron emission angles with respect to the polarization axis. (b) same as (a) but only for the emission angles 0-10° relative to the polarization axis. Black line shows the total delay-dependent CE yield for these angles. Arrows indicate minima in the CE band due to rotational motion. Inset: Zoom into the region of the fractional revivals (shown with linear colour scale).
For the delays between 200 and 400 fs some substructure seems to appear in the CE band. Zooming into this region (see the inset of Fig. 3), one can clearly resolve a periodic pattern, with the maxima spaced by ~12 fs. This feature originates from the fractional revival of the vibrational wave packet. Here, the wave packet consists essentially of two copies of the initial one, each shifted against the other by half of the vibrational period. Dynamical interference between these two "counterpropagating" waves produces a periodic pattern at a frequency doubled compared to the fundamental vibrational one [5,29,30].

The whole CE band in Fig. 3a exhibits a slight long-term modulation. It becomes apparent in Fig. 3b, where only the deuterons emitted within 10° cone around the laser polarization axis (i.e., the events where the fragmenting molecules were aligned along the latter direction) are shown. White arrows indicate clear minima of the CE event rate, i.e., times when preferential molecular orientation departs from the polarization direction. Plotting the total CE yield for this angular interval as a function of the delay (black line in Fig. 3b), one can clearly see additional modulation on top of the vibrational revival structure. Considerable enhancement of this effect for a given molecular orientation points out that the most likely reason for this behavior is rotational motion of the molecule. For the case of H_2/D_2 despite numerous experimental and theoretical studies, the issue concerning its rotational excitation is still obscure, and so far no direct experimental evidence for dynamic alignment of H_2^+ in fs laser pulses exists (see [31] and references therein for a detailed discussion).

In order to trace this, in Fig. 4 we have plotted the time-dependent D^+ (Fig. 3a) and H^+ (Fig. 3b) rates (in the energy range between 3 and 4 eV) for various angular intervals δθ with respect to the laser polarization. For comparison, the corresponding angle-integrated rates are also shown. Evident differences for varying δθ are found, most strikingly around the vibrational revival times. Whereas here the data e.g. for D_2 for δθ = (0-10)° exhibit a clear dip, spectra for δθ = (20-30)° display a maximum which is shifted towards larger delays for δθ = (40-50)°. A pronounced angular dependence can be also observed in H_2. Thus, we undoubtedly observe signatures of rotational motion (i.e., dynamical alignment) in both H_2^+ and D_2^+, and prove that it can be induced even by an ultrashort 6-7 fs laser pulse. A more detailed analysis of the rotational wave packet taking into account θ-dependent ionization probability for linearly polarized pulses [32] will be presented elsewhere.

Figure 4. (color online) Angular-dependent CE yields of the D^+ (a) and H_2^+ (b) ions in the 3-4 eV energy interval as a function of the delay between the pump and the probe pulses. Upper curve in both panels shows yields integrated over all emission angles.

![Figure 4](image-url)
Finally, combining the vibrational and rotational motion in a polar representation and plotting the probability density as a function of both $R$ and $\theta$, the time-evolution of the ro-vibrational wave-packet can be visualized in a real-time “molecular movie”. Internuclear distance $R$ has been reconstructed from the measured CE energy using the Coulomb law. Kinetic energy of the wave packet at the moment of explosion has been neglected since for the bound molecule it is small compared to the CE energy [18,20,24]. Four subsequent “snapshots” of this motion for $D_2^+$ are presented in Fig. 5 (the full movie is available in the online version). The data are presented in polar coordinates $z$ and $\rho$ given by $z = |R \cos \theta|$ and $\rho = |R \sin \theta|$. In this representation for each point the distance from the coordinate origin gives the value of $R$, and the angle relative to the vertical axis reveals the orientation of the molecular axis with respect to the laser polarization.

![Figure 5. (color online) Snapshots of the three-dimensional $D_2^+$ probability distribution for different delays $\tau$ between the pump and the probe pulses. Because of the cylindrical symmetry with respect to the laser polarization direction the data are integrated over all azimuthal angles. Vertical axis ($z$) is parallel to the laser polarization. The shown polar coordinates $z$ and $\rho$ are given by $z = |R \cos \theta|$ and $\rho = |R \sin \theta|$, respectively. (a) $\tau = 0$ fs. (b) $\tau = 8.6$ fs. (c) $\tau = 17.2$ fs. (d) $\tau = 25.8$ fs. Each snapshot is integrated over a delay interval of 4.3 fs.](image)

In Fig. 5a the probability density is localized at low $R$, moving outwards for about half of the vibrational period (Fig. 5b). After reaching the outer turning point the wave packet splits into two parts, one moving further outwards (dissociating), while the other one remains bound (Fig. 5c). The latter part looses its localization while heading inwards (Fig. 5c) [20], and is restored again after a full vibrational period (Fig. 5d). One should of course keep in mind, that the probability distributions shown might still be unequally weighted at different $R$ and $\theta$ as a result of a possible $R$- as well as $\theta$-dependent ionization probability [32].

4. Conclusions and outlook

In this paper we have reported on the direct real-time mapping of $H_2^+$ and $D_2^+$ bound-state and dissociating wave packets using 6-7 fs pump-probe pulses with 0.3 fs time-step resolution in combination with an elaborated 3-D imaging spectrometer (“reaction-microscope”). We provide high-resolution data for the simplest and fastest molecular systems helping to advance strong-field theory and find unambiguous signatures of rotational excitation by few-cycle pulses. In good agreement with earlier theoretical predictions [24] we are able to visualize a fast dephasing (“collapse”) of the vibrational wave packet and its subsequent fractional or nearly complete reconstruction (revival).

As we have recently shown [20], tracing the $D_2^+$ ro-vibrational motion for time periods as long as 3 ps enables high-resolution Fourier analysis of the wave packet motion, and channel-selective decomposition of contributing individual vibrational and rotational states becomes possible yielding unprecedented detailed information on the wave packet generation. Moreover, internuclear-distance resolved Fourier analysis of the experimental data can retrace the shape of the lowest (field-modified) potential curve of the molecular ion, and, under certain conditions, can even reveal the nodal structure.
of the bound vibrational states [33]. Finally, the demonstrated possibility to diagnose in details the spatio-temporal structure as well as the spectral composition of an ultrafast molecular wave packet, along with the recent developments in adaptive pulse-shaping techniques represents an important advance in the arising field of wave packet engineering and strong-field coherent control.

Considering the rapid development of the attosecond technology and recent demonstration of stable isolated attosecond pulses [34], there is a realistic prospect for further improvement of the time resolution of pump-probe experiments. It was recently predicted [35] that using a 300 as VUV pulse as a probe will enable a “perfect” CE imaging procedure, ionizing the molecule with the same probability at any internuclear distance and, at the same time, with minimum momentum transfer (detectable by photoelectron momentum spectroscopy, which is implemented already in our current experimental arrangement). Thus, the dream of following in real time electronic motion and tracing the possible coupling between the nuclear and electronic degrees of freedom beyond the Born-Oppenheimer approximation, is deeming at the horizon.

References

[1] Brabec T and Krausz F 2000 Rev. Mod. Phys. 72 545
[2] Zewail A H 2000 J. Phys. Chem. 104 5660
[3] Hertel I V and Radloff W 2006 Rep. Prog. Phys. 69 1897
[4] Skovsen E, et. al. 2002 Phys. Rev. Lett. 89 133004
[5] Litvinyuk I V, et. al. 2003 Phys. Rev. Lett. 90 233003
[6] Katsuki G H, et. al. 2006 Science 311 589
[7] Posthuma J H 2004 Rep. Prog. Phys. 67 623
[8] Posthuma J H, et. al. 1999 J. Phys. B 32 L93
[9] Trump C, Rottke H, and Sandner W 1999 Phys. Rev. A 59 2858
[10] Niikura H, et al. 2002 Nature 417 917; 2003 Nature 421 826
[11] Alnaser A S, et al. 2003 Phys. Rev. Lett. 91 163002; 2004 Phys. Rev. Lett. 93 183202
[12] Baker S, et. al. 2006 Science 312 424
[13] Alnaser A S, et al. 2005 Phys. Rev. A 72 030702 (R)
[14] Légaré F et. al. 2005 Phys. Rev. A 72 052717
[15] Niikura H, Villeneuve D M and Corkum P B 2006 Phys. Rev. A 73 021402 (R)
[16] Ergler Th, et. al. 2006 J. Phys. B 39 S493
[17] Ergler Th, et. al. 2006 Phys. Rev. Lett. 97 103004
[18] Rudenko A, et. al. 2006 Chem. Phys. 329 193
[19] McKenna J, et. al. 2007 J. Phys.: Conf. Series 58 375
[20] Ergler Th, et. al. 2006 Phys. Rev. Lett. 97 193001
[21] Lee K F, Légaré F, Villeneuve D M, and Corkum P B 2006 J. Phys. B 39 4081
[22] Vager Z, Naaman R and Kanter E P 1989 Science 244 426.
[23] Chelkowski S, Corkum P B and Bandrauk A D 1999 Phys. Rev. Lett. 82 3416
[24] Feuerstein B and Thumm U 2003 Phys. Rev. A 67 063408
[25] Ullrich J, et. al. 2003 Rep. Prog. Phys. 66 1463
[26] de Jesus V L B, et. al. 2004 J. Electr. Spectrosc. Relat. Phenom. 141 127
[27] Ergler Th, et. al. 2006 Proc. of SPIE 6256 62560C
[28] Rudenko A, et. al. 2005 J. Phys. B 38 487
[29] Averbuch I Sh and Perelman N F 1991 Sov. Phys. Usp. 34 572
[30] Robinet R W 2004 Phys. Rep. 392 1
[31] Uhlmann M, Kunert T and Schmidt R 2005 Phys Rev. A 72 045402
[32] Tong M, Zhao Z X and Lin C D, 2002 Phys Rev. A 66 033402
[33] Feuerstein B, et. al. 2007 Phys. Rev. Lett. (in press)
[34] Sansone G, et al. 2006 Science 314 443
[35] Tong X N and Lin C D 2006 Phys. Rev. A 73 042716