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## Wavelength-dependent study of strong-field Coulomb explosion of hydrogen

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**Abstract.** We present the first systematic wavelength-dependent study of laser Coulomb explosion of deuterium molecules at various peak intensities and polarizations. We measured the kinetic energy spectra of  $D^+$  for laser wavelengths in the range 480–2000 nm. In addition to the well-known enhanced ionization channel present for all wavelengths, we observe a new high-energy band at short wavelengths. This new band exhibits wavelength dependence, with fragment energy decreasing with increasing wavelengths until it merges with the enhanced ionization band for 800 nm and longer. We attribute the emergence of this band to a new pathway that involves resonant three-photon coupling to the first excited electronic state of the molecular ion during the Coulomb explosion process. This pathway should be accounted for in controlling molecular dynamics of hydrogen by intense laser pulses.

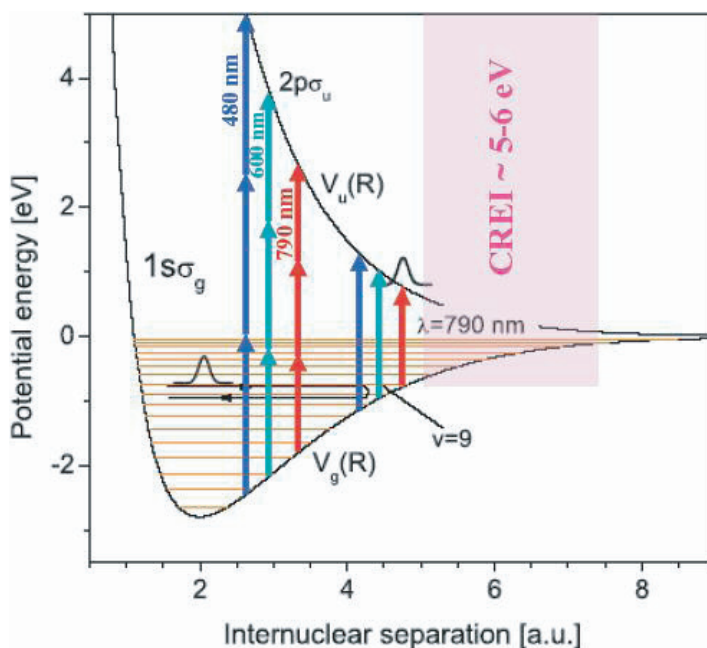
The interaction of isolated neutral hydrogen molecules with intense laser pulses is of fundamental interest for strong-field molecular physics. It has been studied very extensively both experimentally and theoretically over the last 20 years. A wealth of phenomena was discovered and some measure of qualitative understanding of its rather complex behavior

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has been achieved during this time (see [1] and included references for review). However, quantitative agreement between the experimental data and results of various theoretical models remains elusive. The complexity stems from the strongly non-perturbative nature of multiphoton intense field interactions, further complicated by strong coupling of electronic and nuclear motions of the molecule by the oscillating laser field. The energy absorbed from the field by electrons through excitation/ionization is very efficiently transferred to nuclear degrees of freedom (vibrations and rotations) on a timescale comparable to or faster than the pulse duration. A realistic theoretical model must include motions of both electrons together with molecular vibrations and rotations, an extraordinary difficult problem, which has not yet been solved.

Of particular interest is the strong-field double ionization of  $\text{H}_2$  ( $\text{D}_2$ ). Removing both electrons produces a pair of bare protons (deuterons), which gain additional kinetic energy through pure Coulomb repulsion (Coulomb explosion). The resulting kinetic energy uniquely reflects the internuclear separation at which the final ionization took place. As in atoms, the second ionization in  $\text{H}_2$  can proceed either through non-sequential or sequential mechanisms depending on the pulse parameters [2]. Non-sequential ionization (when the second electron is knocked out by the re-colliding first electron) is important for less intense linearly polarized pulses. It was used to characterize the re-colliding electron wavepackets [2] and to observe ultrafast nuclear motion on sub-laser-cycle timescale ('molecular clock' [2]–[4]). Sequential double ionization is the dominant mechanism at higher intensities and also for circularly polarized field, when re-collision is not possible and shake-up/shake-off was shown to play only a minor part [5]. While electron re-collision happens on the sub-cycle timescale yielding high-energy (15–18 eV total) ions, a significant delay may occur between the first and second ionizations, with internuclear distance increasing substantially during that time. For sufficiently long pulses (>20 fs for  $\text{H}_2$  and >30 fs for  $\text{D}_2$ ) the molecular ion can reach the 'critical distance' of 5–8 au (at which the tunneling ionization rate is dramatically enhanced especially for molecules aligned parallel to the field [6, 7]) when the laser electric field is still strong enough to ionize. In this case, the kinetic energy release (KER) spectra are centered around 5–6 eV reflecting the mostly  $R$ -dependent ionization rate (enhanced ionization). For few-cycle (<10 fs) pulses this enhanced ionization is suppressed, as the molecular ion simply does not have enough time to expand, and higher energy fragments are generated [2, 8], more reflective of the real distribution of internuclear distances. Coulomb explosion with few-cycle pulses was successfully used to image vibrational [9, 10] and rotational [11] nuclear wavepackets in hydrogen in real time, and it holds some promise for studying the time-dependent structure of larger molecules [12, 13].

Both re-collision-based 'molecular clock' and time-resolved Coulomb explosion imaging of nuclear wavepackets rely critically on correct understanding of the real reaction pathways taken by the molecules being probed. For instance, to convert the time-dependent KER spectra into the corresponding nuclear wavefunction density, it is common to neglect the kinetic energy gained by the fragments on the potential energy surface of the molecular ion. The common understanding of the Coulomb explosion process (see figure 1) involves (i) tunneling ionization of the neutral molecule, that places the nuclear wavepacket into the ground electronic state ( $\sigma_g$ ) of the molecular ion; (ii) the evolution of the resulting wavepackets in the presence of the oscillating laser field, including bond softening [14] of the molecular ion due to one-photon coupling of its ground and excited ( $\sigma_u$ ) electronic states; and (iii) sequential tunneling ionization of the remaining electron, described by the angle- and  $R$ -dependent ionization rate. The intermediate bond softening step does contribute to the final kinetic energy



**Figure 1.** Energy level diagram for  $D_2^+$ . The lower  $\sigma_g$  surface is populated by tunnel ionization from the neutral molecule. The vibrational wavepacket moves outward where it can encounter strong resonant laser coupling to the  $\sigma_u$  surface. For shorter laser wavelengths, the three-photon coupling gives additional kinetic energy due to the steepness of the  $\sigma_u$  surface. In the charge resonant enhanced ionization (CREI) region, removal of the remaining electron is highly probable, leading to two  $D^+$  fragment ions that are detected.

of the fragments, but this contribution ( $\leq 1$  eV at 800 nm) is much smaller than the energy of Coulomb repulsion and does not change the overall interpretation of the KER spectra. Also this one-photon coupling (or curve crossing in the complementary Floquet picture [15]) occurs at larger  $R$ , where the slopes of potential energy curves are less steep, so that the additional bond softening energy and the total KER spectra only weakly depend on laser wavelength.

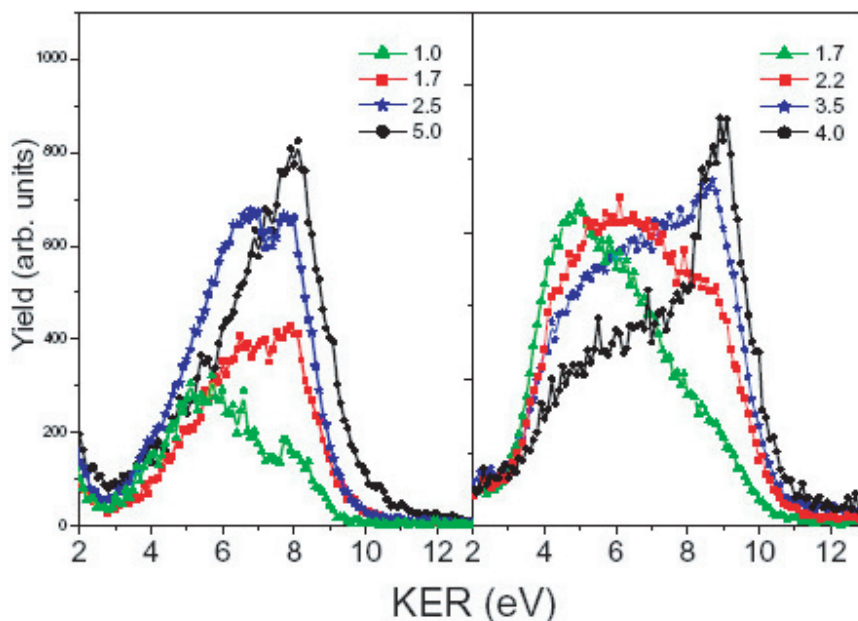
Another possible  $H_2^+$  dissociation pathway is the above-threshold dissociation (ATD, [14, 16]), which is a net two-photon process involving consecutive three- and one-photon couplings (Floquet curve crossings) and resulting in somewhat more energetic fragments. While ATD is clearly seen in  $(D^+ + D)$  dissociation KER spectra, it is thought to be less probable than bond softening, and in any case it would add too little to kinetic energy to make it identifiable in the broad Coulomb explosion KER spectra. Therefore, until very recently the general expectation (confirmed by all available experimental data) was that KER spectra of hydrogen Coulomb explosion fragments with sufficiently long pulses reflect mostly  $R$ -dependent tunneling ionization rates for molecular ions and only weakly depend on laser intensity and wavelength.

This general picture was put into question by the very recent unexpected results reported by Staudte *et al* [17]. They presented high-resolution KER spectra measured with 35 fs 800 nm pulses for Coulomb explosion of  $H_2$  and  $D_2$ , which exhibited a very clear multi-peak structure not seen in any prior studies. The explanation suggested by Staudte *et al* and supported by the consequent theoretical paper by Chelkowski *et al* [18] involves interference between one-photon

and net-two-photon (three-photon absorption and one-photon reemission) excitation pathways, resulting in spatially modulated nuclear wavepackets, which are reflected by the final ionization onto the fragment KER spectra. This interpretation is supported by KER spectra measured for 1200 and 1400 nm wavelengths, also presented in [17]. For such interference to be seen in the energy domain, the energy separation between the wavepackets taking the two interfering routes must be less than their inherent spectral width. This is obviously the case for 800 nm and longer wavelengths. Looking at the  $\text{H}_2^+$  potential energy curves in figure 1, one can easily see that increasing the photon energy will affect kinetic energies generated by the two pathways differently. The three-photon resonance occurs at smaller  $R$ , where the curves are steeper and the corresponding kinetic energy will be more dependent on  $\lambda$ . One should expect that at some sufficiently short wavelength the two pathways would no longer interfere, but instead should produce two well separated KER bands. The hint of the two bands is already seen in 800 nm spectra reported in [17].

Here, we present a wavelength-dependent study of  $\text{D}_2$  Coulomb explosion. We measured KER spectra of  $\text{D}^+$  fragments at 480, 600, 800, 1300 and 2000 nm, while also varying laser polarization from linear to circular. The experiments were conducted at the Advanced Laser Light Source (ALLS) facility located in Varennes, Quebec. Laser pulses were generated by a high-power TOPAS optical parametric amplifier (OPA). The OPA was pumped by 800 nm, 70 fs, 7 mJ pulses generated by a Ti : sapphire system from Thales Lasers at 100 Hz repetition rate. An additional nonlinear mixing stage was used to generate wavelengths shorter than 800 nm. For all wavelengths the pulse duration was estimated to be 100–110 fs. After some attenuation by neutral density filters, the laser pulses were focused by a spherical mirror (10 cm focal length) into a well collimated supersonic jet of target molecules inside the uniform-electric-field ion imaging spectrometer. Resulting ions were collected and their momenta were measured by a time- and position-sensitive delay-line anode detector (Roentdek) at the end of the spectrometer. The supersonic jet propagation direction and laser beam propagation direction were orthogonal to each other and both orthogonal to the spectrometer axis. The laser polarization could be changed from linear to circular by rotating an appropriate quarter-waveplate. The laser peak intensities at the focus were determined from  $\text{Ar}^+$  ion momentum measurements with circular polarization as described in [19].

Figure 2 shows KER spectra measured for 480 and 600 nm linearly polarized laser pulses of different peak intensities. At our experimental conditions the energy resolution for all presented  $\text{D}^+$  spectra is  $\leq 0.2$  eV. In addition to the enhanced ionization band at 5–6 eV present in all spectra for both wavelengths, another band of ion energies appears at around 9 eV for 480 nm and near 8 eV for 600 nm. This band becomes more prominent as peak intensity increases and becomes dominant at the highest intensities. The position of the band for each wavelength seems to be independent of intensity. To eliminate any contribution from re-scattering double ionization, also known to produce high-energy fragments, we varied the ellipticity of the laser pulse from linear to circular while keeping its total energy constant. Figure 3 shows KER spectra measured for 480 nm pulses of different ellipticities, with peak intensity kept at  $4 \times 10^{14} \text{ W cm}^{-2}$ . The increase in ellipticity also results in a decrease in peak electric field by as much as  $2^{1/2}$  for circular polarized pulses ( $\varepsilon = 1$ ), when the peak electric field is the same as in linearly polarized pulses of half the intensity. The high kinetic energy (KE) band is observed for all ellipticities up to circular polarization, thus excluding the possibility that it originates from a rescattering pathway. The ratio of the two bands depends on ellipticity by following almost exactly the intensity dependence observed for linearly polarized pulses with

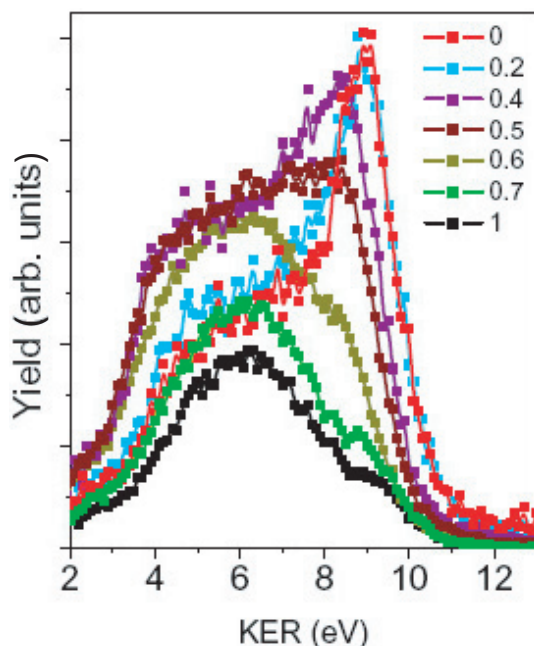


**Figure 2.** KER of  $D^+$  fragments measured for 600 nm (left panel) and 480 nm (right panel) linearly polarized laser pulses of different laser intensities. Intensities are indicated in units of  $10^{14} \text{ W cm}^{-2}$ . Pulse duration is 100 fs. The new channel is apparent around 8–9 eV.

similar peak electric fields. It is therefore the peak electric field, and not polarization, which mostly determines the branching ratio between the two Coulomb explosion pathways. Both pathways yield highly anisotropic fragment angular distributions, with fragments ejected mostly along the laser polarization direction. The design of our ion spectrometer did not allow precise measurement of the fragments' angular distributions. However by rotating the laser polarization in respect to the time-of-flight axis of the spectrometer we determined that the high-KE channel is more directional than even the enhanced ionization process, another argument against the rescattering mechanism [2].

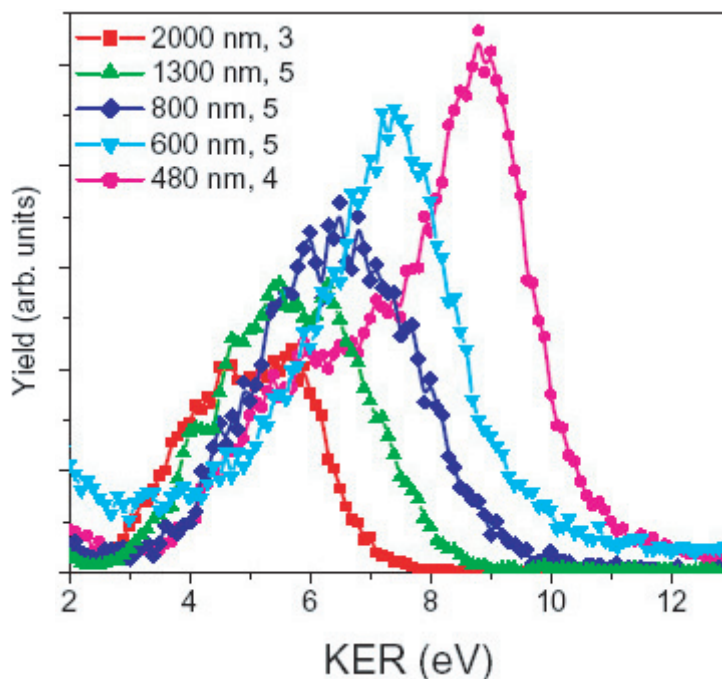
We also measured KER spectra at 800, 1300 and 2000 nm wavelengths (figure 4). At 800 nm and longer wavelengths, the two bands are too close in energy to be resolved in the spectra. However, the wavelength dependence is still evident from the decrease in the high-KER edge for longer wavelengths, suggesting that the pathway remains operational for all of them, and the resulting fragment energy strongly depends on the laser frequency. This wavelength dependence is consistent with the  $R$ -dependence of a three-photon resonance for various wavelengths: at a shorter wavelength the resonance occurs for smaller internuclear distance, resulting in the higher kinetic energy fragments. We hesitate to suggest a single specific mechanism responsible for this band, as at least two distinct pathways may account for our observations. Both of them involve three-photon resonance between  $\sigma_g$  and  $\sigma_u$  states of the hydrogen molecular ion.

For instance, the following scenario for Coulomb explosion of hydrogen is consistent with our data. After the neutral molecule is singly ionized, the vibrational wavepacket propagates on the field-dressed electronic potential energy surfaces of  $D_2^+$ ; staying mostly in the lowest two electronic states (field-free  $\sigma_g$  and  $\sigma_u$  states). When the resonant one- or three-photon coupling (only odd photon number transitions are allowed by symmetry) is efficient, a transition



**Figure 3.** KER spectra measured for 480 nm pulses of different ellipticities. The ellipticity is indicated and shows the squared ratio of two perpendicular components of the electric field:  $\varepsilon = 0$  corresponds to linear polarization,  $\varepsilon = 1$  for circular polarization. Peak intensity is  $4 \times 10^{14} \text{ W cm}^{-2}$ , pulse duration is 100 fs. The pulse energy was kept constant as the ellipticity was varied, so that the electric field decreased as the ellipticity increased. The changes in the spectra are entirely due to the decrease in the electric field, ruling out recollision as a factor.

between the two levels can occur. Once in a dissociative state, the ion's internuclear distance increases until it reaches the critical value ( $R_c$ ) when the second ionization takes place with high probability, followed by Coulomb explosion. The final KER will include the kinetic energy gained by fragments during dissociation and also kinetic energy of the Coulomb explosion itself ( $1/R_c$ ). The second component is independent of the laser wavelength, while the energy gained in dissociation depends on the internuclear separation ( $R$ ) at which the dissociative state is efficiently populated. For the one-photon pathway this  $R$  is relatively large for all wavelengths, and the energy gained is small in comparison to  $1/R_c$ . For the three-photon pathway the excitation occurs at shorter distances, where the potential is steep, resulting in higher kinetic energy and a strong wavelength dependence. The branching ratio between the two pathways will be determined by the relative one- and three-photon excitation rates and by the dynamic distribution of internuclear distances in the molecular ion. This mechanism is consistent with the model suggested by Chelkowski *et al* [18] to explain the results of Staudte *et al* [17] with one notable difference: they postulate interference of one-photon and net-two-photon pathways, when the latter pathway results from three-photon excitation followed by subsequent de-excitation at the one-photon resonance. The net-two-photon pathway would result in lower kinetic energy fragments inconsistent with our data. It is possible that for some reason, one-photon de-excitation is suppressed for higher laser frequencies and the net-three-photon pathway becomes dominant.



**Figure 4.** KER spectra obtained at the highest peak intensity for each experimental wavelength. The wavelengths are indicated together with intensities in units of  $10^{14} \text{ W cm}^{-2}$ . The peak seen below 2 eV is due to the bond softening ( $\text{D} + \text{D}^+$ ) channel.

Another possibility is that the second ionization may take place directly at shorter internuclear distances for shorter wavelengths. In this case the three-photon excitation to the  $\sigma_u$  state is only a virtual one, with ionization yield being strongly enhanced by the presence of the intermediate resonance. The fragments would gain their full kinetic energy on the Coulomb potential, and that energy will be very close to that of the previously discussed scenario, as the Coulomb and  $\sigma_u$  potentials are nearly parallel to each other.

Unfortunately, our data do not allow to distinguish between these two possibilities. In principle, the two pathways could be distinguished experimentally by measuring dependence of the KER spectra on pulse duration: for sufficiently short pulses the enhanced ionization pathway is suppressed [8], while the direct ionization mechanism should remain operational. Such a study would require very short ( $\leq 10$  fs) intense pulses of 500–600 nm wavelength, which are not yet available. In the absence of pulse-duration dependent data, a detailed theoretical analysis is needed to determine the exact ionization mechanism. Such analysis must also account for the effects of pulse duration and the depletion of the molecular ion by the final ionization, and it is far beyond the scope of this purely experimental study. While realistic numerical modeling of strong-field double ionization of a hydrogen molecule remains a formidable theoretical challenge, our new findings should stimulate theorists to extend their efforts beyond the 800 nm wavelength of Ti:sapphire lasers.

To summarize, we report the observation of a new wavelength-dependent band in the kinetic energy spectra of  $\text{D}^+$  that emerged as a result of a systematic wavelength-dependent experimental study of deuterium Coulomb explosion. We attribute this band to resonant three-photon coupling between two electronic surfaces in the molecular ion. The experimental

ability to vary the wavelength of intense femtosecond laser pulses provides a new tool to differentiate mechanisms that participate in dissociative ionization of molecules. Our results emphasize the importance of resonant pathways in ultrafast dynamics of molecules interacting with intense femtosecond laser pulses, and suggest new approaches to controlling these dynamics. The results also show that care must be taken in inferring bond lengths from Coulomb explosion experiments, which may have implications in molecular imaging techniques that employ ultrafast lasers.

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