

Intense-Laser-Field Ionization of the Hydrogen Molecular Ions H_2^+ and D_2^+ at Critical Internuclear Distances

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Fragmentation of H_2^+ and D_2^+ in ion beams has been studied with short intense laser pulses (100 fs, $I = 5 \times 10^{13} - 1 \times 10^{15}$ W/cm²) and by a high-resolution two-dimensional velocity imaging technique. In the Coulomb explosion channel, at intensities just above the threshold for this process, we observe a clear structure in the kinetic energy spectra not previously found or predicted. The peaks can be attributed to single vibrational levels. We interpret this observation as a dissociative allocation of the electron to a proton followed by enhanced ionization at a well-defined “critical” overstretched internuclear distance. When using longer pulses we observe three separate Coulomb explosion velocity groups corresponding to critical distances of about 8, 11, and 15 a.u.

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As the simplest molecule, the hydrogen molecular ion H_2^+ is of fundamental importance in molecular physics. The interaction of H_2^+ with intense ultrafast laser light has revealed novel effects such as bond softening, above-threshold dissociation, and bond hardening in light-induced molecular potentials [1]. One of the most intriguing phenomena is the strong enhancement of molecular ionization at large internuclear separations and particularly at specific, so-called critical internuclear distances R_c [2–4]. Although the origin of critical distances is quantum mechanical, the mechanism involved can be understood by a simple semiclassical model of an electron in the combined potential of two protons and a static electric field, as it is described later in this Letter. The maxima in the ionization rate at critical distances have been predicted by accurate numerical simulations in the charge-resonance enhanced ionization model [2] for one- and two-electron molecular systems such as H_2^+ , H_3^{2+} , H_4^{2+} , etc. [5]. This seems to be a more universal phenomenon, since enhanced ionization has also been predicted for certain critical internal angles θ_c in nonlinear molecules [5] and has also been found in multielectron systems [6]. Moreover, critical distances play a crucial role in the processes of high harmonic generation (HHG) and above-threshold ionization (ATI) in molecules. However, despite numerous experiments, the maxima in the ionization rate at critical distances in H_2^+ have hitherto not been experimentally confirmed.

To answer the question of the existence of the critical distances, in this Letter we report a study of the Coulomb explosion of H_2^+ and D_2^+ in ultrashort intense laser fields using fast beams of molecular ions and a high-resolution photofragment velocity imaging technique. To date most of the related experiments have been carried out on neutral H_2 molecules. It was assumed that the first ionization step leading to H_2^+ occurs on the rising edge of the laser pulse and that H_2^+ is then fragmented by the same laser pulse. Because of the interplay between the two steps, the starting conditions were unknown, thus preventing a clear inter-

pretation of the results. Only a very recent study has shown that the H_2^+ vibrational population is actually intensity dependent with basically only the vibrational levels $v = 0-4$ populated [7]. Furthermore, the relatively high peak intensity required for the ionization of H_2 hindered the studies at lower intensities. This explains why the vibrational structure in the photodissociation ($\text{H}_2 + nh\nu \rightarrow \text{H} + \text{H}^+$) [8,9] and the Coulomb explosion (CE) channel ($\text{H}_2^+ + n'h\nu \rightarrow \text{H}^+ + \text{H}^+ + e^-$), as reported here, could not be observed.

In order to avoid the interplay between the ionization and fragmentation steps mentioned above, to have a definite and known population distribution of the molecular ions over the vibrational levels, and to reduce the intensity variations in the interaction region, we expose mass-selected ionic beams of H_2^+ and D_2^+ to femtosecond laser pulses. In an earlier experiment of this kind we have been able, for the first time, to resolve the contributions from different vibrational levels in the energy spectra of the neutral fragments in the dissociation channel [8]. Theoretically predicted novel effects of bond softening, level shifting, and trapping (bond hardening) have been studied state specifically [8] and compared with *ab initio* simulations starting from the time-dependent Schrödinger equation (TDSE) [10,11].

In this Letter we have investigated the CE channel with high resolution in an analogous way, which resulted in novel observations deviating from previous experiments on H_2 and also H_2^+ : by the Coulomb explosion of the dissociating molecules, we again observe the vibrational structure in the kinetic energy spectra of the CE fragments. Additionally, three CE groups have been discovered in the fragment velocity distributions, providing evidence of several critical distances. Preliminary data of this study have been presented at an international conference [12].

The experimental method was described in our previous publication [8] and in more detail by Wunderlich *et al.* in our Ar_2^+ studies [13]. Here we give details relevant to the

present experiment. The molecular ions are generated in a dc electric discharge of H_2 or D_2 gas. The vibrational distribution of H_2^+ has been determined to be approximately in accordance with the Franck-Condon excitation from the ground vibrational state of H_2 [8]. The molecular ions are accelerated to 11 keV, mass selected, and collimated to a beam with a rectangular shape of $25 \times 300 \mu\text{m}$ along the vertical axis and the horizontal axis, respectively. A Ti:sapphire laser system generated pulses at a central wavelength of 791 nm with a duration of about 100 fs (full width at half maximum) and a pulse energy of 1.6 mJ in the interaction region. The laser beam with its vertical polarization is focused on the horizontally running ion beam at 90° by a $f = 30$ cm achromatic lens. The peak laser intensity in the interaction region was calculated by direct measurements of the laser power, pulse duration, and beam profile. The peak intensity was varied in the range from 5×10^{13} to 1×10^{15} W/cm² by shifting the focusing lens along the laser propagation axis. With the laser beam diameter much larger than the ion-beam width of $25 \mu\text{m}$, the spatial intensity variations in the interaction region were limited basically to only one dimension. The neutral and charged fragments are detected on a two-dimensional multichannel plate (MCP) detector mounted perpendicularly to the ion beam at a distance of 95 cm from the interaction zone. The intensified charge pulses from the MCP generate flashes on a phosphor screen that are recorded by a charge-coupled device camera. A kinetic energy resolution of about 60 meV was achieved in the CE channel. The image on the MCP detector represents the projection of the fragments' three-dimensional velocity distribution.

Figure 1 shows such an image resulting from the fragmentation of H_2^+ at an intensity of 1×10^{15} W/cm². The dissociation and CE fragmentation channels are clearly distinguished. The semicircular distribution around

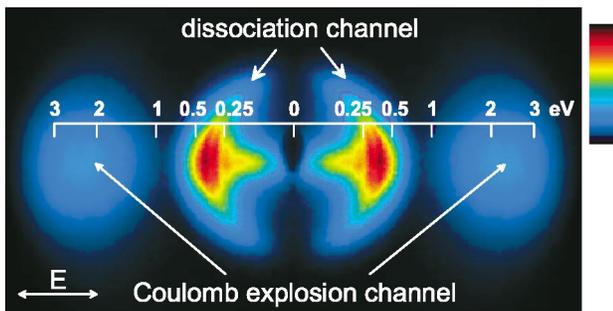


FIG. 1 (color). Velocity distribution of H_2^+ fragments as projected onto the two-dimensional detector at a peak laser intensity of 1×10^{15} W/cm². The two fragmentation channels are discerned by their kinetic energies and angular distributions. The laser polarization is in the detector plane along the horizontal axis of the image. The kinetic energies of the fragments ejected along this axis are marked by the inserted scale. The measured right-hand side is mirrored to simulate the real complete distribution.

0.5 eV is characteristic of low-intensity dissociation occurring at the rising edge of the laser pulse. The aligned fragments below 0.2 eV stem from the dissociation of the levels $v = 5-7$ due to molecular bond softening [8]. The narrow feature around 0.4 eV results from a net two-photon process, in which we have meanwhile identified fragments from the single vibrational level $v = 3$ [9].

Here, the CE channel of H_2^+ and D_2^+ has been extensively studied at different laser intensities. Figure 2 shows the CE kinetic energy distributions for H_2^+ . Sharp peaks have been observed in both H_2^+ and D_2^+ at near-threshold intensities for CE. The main peaks also appear in spectra at slightly higher intensities, with variations being within the error bars (indicated for the uppermost plot). Above 1×10^{14} W/cm² the structure begins to vanish, and only modulations in the spectra are observed. At the lowest intensities the signal is very weak, a factor of ~ 50 smaller than in the dissociation channel. The spectra here contain only 10^3-10^4 fragments generated by $\sim 10^6$ laser pulses. No fragments have been observed in this velocity range when we selectively recorded only the neutral fragments from the photodissociation channel, thus ruling out the possibility that the structure is due to photodissociation by the absorption of three or more photons.

The resemblance of the spectra in Fig. 2 to the vibrational structure that we observe in the dissociation channel [8] hints at the same physical origin. In Fig. 3(a) the energy differences between the CE peaks are compared with the spacings of vibrational levels participating in the one-photon dissociation process. (The possible contribution of the net two-photon process can be neglected since it is essentially unobservable in the dissociation channel at these intensities [8,9].) In this way the main peaks in

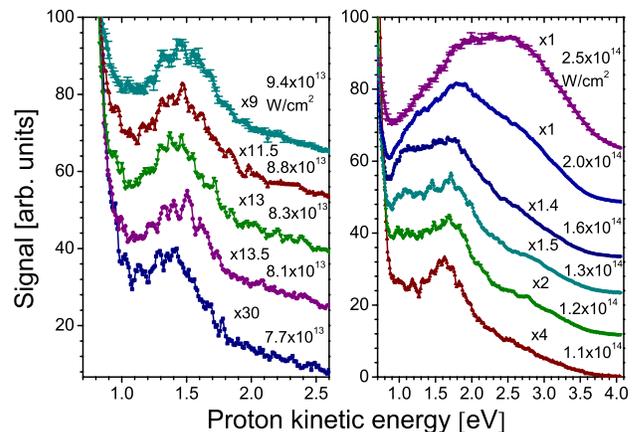


FIG. 2 (color online). Kinetic energy spectra of protons from the Coulomb explosion of H_2^+ . The spectra are obtained by radial integration of the velocity distributions over $\pm 2^\circ$ around the laser polarization axis. The error bars shown for the uppermost spectra are calculated from the difference in spectra for integration over positive and negative angles. Peak laser intensities are given in the figure together with the scaling factors of the proton yield.

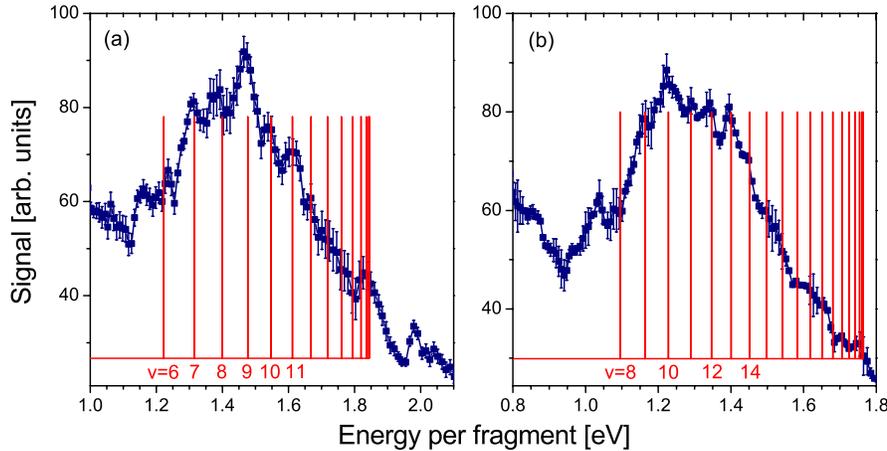


FIG. 3 (color online). Coulomb explosion spectra of (a) H_2^+ at an intensity of $8.8 \times 10^{13} \text{ W/cm}^2$; (b) D_2^+ at an intensity of $6.4 \times 10^{13} \text{ W/cm}^2$. The vertical lines mark the fragment energies as expected after one-photon absorption from different vibrational levels, followed by a Coulomb explosion at a critical distance.

the spectra at intensities between 8×10^{13} and $1 \times 10^{14} \text{ W/cm}^2$ could be well matched with the vibrational “comb” after its origin was shifted by the same energy of 1.06 eV for all spectra. Similarly, the more closely spaced peak structure that we have found in the CE spectra of D_2^+ could be well described by the D_2^+ vibrational comb shifted by 0.98 eV [Fig. 3(b)].

We interpret these findings as follows. After the laser excitation, the molecular ion dissociates and the nuclei gain a kinetic energy that at large internuclear distances is equal to $E_{\text{diss}}(v) = (h\nu - |E_v|)/2$, where E_v is the binding energy of the vibrational state v . In the next step, the stretched, dissociating molecule is ionized at a large critical internuclear distance R_c , where ionization is strongly enhanced [2–4,6]. The remaining positively charged nuclear fragments repel each other due to the Coulomb interaction. The measured fragment kinetic energy is thus equal to $E = E_{\text{diss}}(v) + e^2/(2R_c)$. The first term describes the vibrational comb in Fig. 3, while the second term, the CE energy, corresponds to the shift of the comb from its origin.

From the determined shift of the “comb,” we conclude that ionization and the subsequent Coulomb explosion in H_2^+ occur at a critical distance of ~ 13 a.u. In order that the vibrational structure from the dissociation process remains preserved after ionization, the critical distance found must be sharp and the same for all vibrational levels. Roughly, a spread in the critical distance ΔR_c of more than 1 a.u. would cause smearing of the contributions from single vibrational levels. However, the peaks in the CE spectra appear to be broader than in the dissociation channel, suggesting that the nuclear probability distribution prior to ionization is affected by the width of the critical distance. We note that, owing to the small differences in the spacing of vibrational levels, the values of vibrational quantum numbers attributed to the peaks may differ by ± 1 in H_2^+ and ± 2 in D_2^+ , which also implies a corresponding uncertainty in the critical distances determined. The method also showed no shifting of the lower vibrational levels towards smaller energies as observed in the dissociation channel.

Enhanced ionization at large critical distances has been theoretically predicted by the charge-resonance enhanced ionization model. Numerical simulations for H_2^+ based on the TDSE show that for the internuclear distances $R > 4$ a.u. the ionization rate rapidly increases, exhibiting maxima at certain critical internuclear distances [2]. Depending on the calculation technique and laser parameters, a different number as well as values of critical distances have been reported (e.g., [2,14]). In the semiclassical picture, the electron experiences a double-well potential created by two protons and tilted by the laser electric field (e.g., Fig. 2 in Ref. [2]). For a certain internuclear distance, the electron localized at one nucleus will have a high probability of tunneling from the upper electronic state through the inner barrier. A sufficient population in the upper state is provided by strong coupling (charge resonance) between the bonding $1s\sigma_g$ and the dissociative $2p\sigma_u$ states at large internuclear distances. Since the electron in H_2^+ and D_2^+ experiences the same potential, the same critical distances are expected in H_2^+ and D_2^+ . This is in agreement with similar comb shifts found in Figs. 3(a) and 3(b), with small differences that can be attributed to the different laser peak intensities.

We also considered a possible role of the ionized electron returning to the ionic core and giving rise to effects such as ATI and HHG. The successive electron returns could shield the nuclear potential and weaken Coulomb repulsion, thus causing modulations in the CE spectra. However, a similar structure was also observed with elliptically polarized light that should prevent the electron from returning to the nuclei.

It is not surprising that the clearest structure in the spectra is observed at the lowest peak intensities. At intensities close to the threshold for CE, only a very narrow range of intensities above the threshold intensity can contribute to the measured signal. In contrast, at higher peak intensities the intensity distribution in the interaction region causes fragmentation at different intensities, hence broadening and washing out the structure.

When using pulses of longer durations, we have clearly resolved additional groups in the velocity distributions of

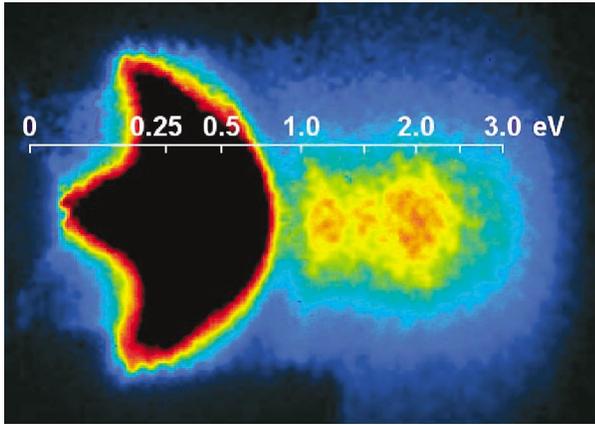


FIG. 4 (color). Projected velocity distribution of the fragments from the photodissociation and Coulomb explosion channel of D_2^+ at an intensity of 1×10^{14} W/cm² and pulse duration of 350 fs. Three Coulomb explosion groups are discerned corresponding to enhanced ionization at about 8, 11, and 15 a.u. The color scale is adjusted to the signal in the CE channel.

the CE fragments of H_2^+ and D_2^+ (Fig. 4). As the pulse duration is increased, the molecules are increasingly ionized at later times, i.e., at larger internuclear distances. This can be compared to a recent pump-probe experiment, in which dissociation was initiated by a pump pulse and the dissociating molecules were ionized by a probe pulse at variable delay times, i.e., at arbitrarily chosen nuclear distances [15]. However, no indication of critical distances was found in this work. The groups in Fig. 4 observed in our experiment strongly suggest ionization at critical distances of about 8, 11, and 15 a.u., where we assumed that prior to ionization the dissociating molecules had a kinetic energy of 0.3 eV. We note that the groups observed in Fig. 4 have significantly different widths of angular distributions, which supports the idea of ionization at different critical distances. The additional low-energy CE group was also recognized in the velocity distributions of measurements with shorter pulses, which in Fig. 2 can be seen as a hump at 1.1 eV at intensities around 1.5×10^{14} W/cm². With increasing intensity, the two humps merge together and shift to higher kinetic energies, corresponding to ionization at smaller internuclear distances.

So far only one ion-beam experiment on H_2^+ has been reported [16]. However, in this experiment the energy resolution for the CE fragments was low and no structure has been observed. Also no angular distribution of the CE channel that could be compared to our Fig. 1 has been reported. The numerous experiments starting on H_2 mentioned before show structure in neither the dissociation nor the CE channel, though the authors in recent works claim a resolution comparable to ours. The main reason seems to be the absence of population in the vibrational levels $v \geq 5$, which participate in one-photon absorption and hence in CE [7]. In addition, these studies were possible only at relatively high intensities, at which we do not find clear structure either. A weak structure in the CE spectrum

has been reported in one of the earliest experiments on H_2 by Zavriyev *et al.* [17], who ascribed it to vibrational trapping. However, many subsequent experiments on H_2 using a similar experimental technique have not confirmed their results. A recent experiment starting with H_2 [18] seems to give a weak indication of two maxima confirming two critical distances predicted in Ref. [2]. Numerous theoretical investigations on the dissociative ionization of H_2^+ have predicted nuclear kinetic energy spectra with a structure little related to our observations (e.g., [14]).

In conclusion, in the first high-resolution study of a Coulomb explosion directly on H_2^+ and D_2^+ we have observed sharp peaks in the kinetic energy spectra and additional isolated groups in the velocity images of the fragments. Our results strongly suggest the existence of critical internuclear distances of enhanced ionization. We hope that our findings will stimulate further theoretical simulations of the dissociation and ionization dynamics of H_2^+ .

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