

## Dissociation Dynamics of $\text{H}_2^+$ in Intense Laser Fields: Investigation of Photofragments from Single Vibrational Levels

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We present a photodissociation experiment on  $\text{H}_2^+$  with ultrashort laser pulses ( $\geq 130$  fs) at peak intensities of  $\leq 1.5 \times 10^{14}$  W/cm<sup>2</sup>. Since in an ion beam setup  $\text{H}_2^+$  is produced in a discharge source spatially separated from the light interaction zone interference with neutral  $\text{H}_2$  can be excluded in the interpretation. As the beam setup allows a high energy resolution of photofragments, effects predicted by the light induced potential theory can be tested in detail. The one-photon trapping effect was detected and the angular distributions of fragments from single vibrational levels were measured. Fragment energy spectra deviate strongly from those obtained by experiments on  $\text{H}_2$ .

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Exciting nonlinear effects as above threshold ionization and dissociation were discovered when molecules were exposed to high intensity femtosecond laser fields during the last decade. Investigating the fragment energies of small molecules like  $\text{H}_2^+$ ,  $\text{D}_2^+$ , and  $\text{Na}_2$  in such high laser fields as  $10^{13}$  to  $10^{15}$  W/cm<sup>2</sup>, different nonlinear dissociation effects are discernible [1–4]. These include dissociation by one photon and more photons ( $\text{H}_2^+ \rightarrow \text{H} + \text{H}^+$ ), and the ionization-dissociation effect known as Coulomb explosion ( $\text{H}_2^+ \rightarrow \text{H}^+ + \text{H}^+ + e^-$ ). For small light intensities the dissociation rate is linear with intensity and is well described by Fermi's golden rule (FGR), whereas at higher intensities up to  $10^{14}$  W/cm<sup>2</sup> the light induced potential (LIP) theory explains the nonlinear dissociation behavior [5]. In LIP the light field is treated equivalent to inner molecular potentials in the Hamiltonian.

However, so far all related experimental work has been done on neutral  $\text{H}_2$  [1,2] or on  $\text{H}_2^+$  generated by a laser prepulse [3]. In the first case it is assumed that  $\text{H}_2^+$  is formed in a very fast ionization process at the leading edge of the pulse. The interpretation of the dissociation process mostly neglects the influence of the ionization process. In fact, the independence of the two processes cannot be experimentally controlled and the exact temporal evolution of the two processes involved is still a subject of investigation. Recent calculations show that the photoionization process has strong influence on the subsequent dissociation [4]. Furthermore in the prepulse experiments only a part of  $\text{H}_2$  is ionized to  $\text{H}_2^+$  [6].

LIP gives distinct predictions for the dissociation rates of different vibrational levels, such as bond softening for lower vibrational levels (enhanced dissociation) and stabilization for higher vibrational levels (reduced dissociation) [5].

We performed an ion beam experiment on  $\text{H}_2^+$ , which determines its nonlinear dissociation rate directly, since there is no nonlinearity originating from the optical ionization process. The populations of the different vibrational levels of  $\text{H}_2^+$  were separately experimentally determined. Furthermore, a sufficiently high momentum and angular

resolution of the photofragments yield exact information about the dissociation of single vibrational levels. In particular, our observed fragment energy spectrum deviates strongly from measurements done on  $\text{H}_2$  before [1,2]. A part of this work was already reported as conference proceedings [7].

In our experiment,  $\text{H}_2^+$  ions have been produced in a dc electric discharge ion source. An ion beam was extracted, accelerated to 11.1 keV, and then mass selected in a sector magnetic field. After strong collimation the monochromatic  $\text{H}_2^+$  beam was crossed by the focused laser beam at a right angle. Laser pulses of a chirped pulse amplification laser system with a repetition rate of 1 kHz at various pulse energies up to 1.0 mJ were focused by a hollow mirror. We used a glass reflex of the laser beam for measuring the intensity distribution in the focus with a pinhole of 1  $\mu\text{m}$  diameter. Our focus diameters were greater than the height of the rectangular molecular ion beam (50  $\mu\text{m}$ ) and Rayleigh lengths were large compared to the width of the molecular beam (300  $\mu\text{m}$ ) which reduced the intensity volume effect.

The neutral dissociation fragments H originating from the dissociation channel  $\text{H}_2^+ \rightarrow \text{H}^+ + \text{H}$  were projected onto a two-dimensional microchannel plate-detector screen positioned at a distance of 80 cm behind the interaction region. The screen was read out by a charge-coupled device camera. Fragments from a single vibrational level lie spatially distributed on a sphere which expands on its way to the screen and generates a circularly shaped pattern when projected on the screen (Fig. 1). Thus we get the two-dimensional momentum projection of the fragments (Fig. 1). Choosing the laser polarization axis perpendicular to the axis of the molecular beam, the projection contains full information about the three-dimensional momentum distribution of the photofragments. The energy resolution  $\Delta E/E$  we achieved was about 1%. Undissociated  $\text{H}_2^+$  molecules were deflected by an electric field into a Faraday cup. In order to account for small fluctuations we recorded the  $\text{H}_2^+$ -ion current on that Faraday cup as a measure of the number of molecules in the laser focus

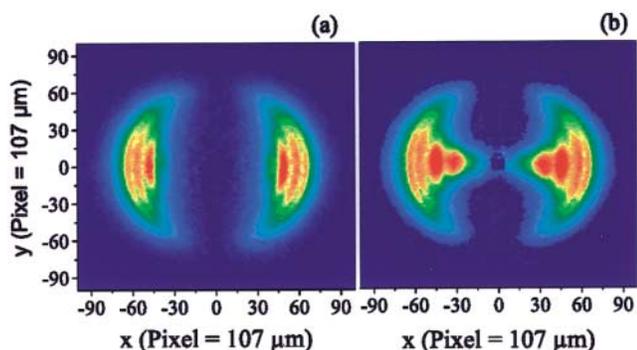


FIG. 1 (color). Two-dimensional momentum projection of neutral photofragments at a pulse energy of 1.0 mJ and a wavelength of 785 nm. (a)  $\tau = 575$  fs,  $I_0 = 3.5 \times 10^{13}$  W/cm<sup>2</sup>; (b)  $\tau = 135$  fs,  $I_0 = 1.5 \times 10^{14}$  W/cm<sup>2</sup>.

during a measurement. These time integrals of the beam current were used for normalization of the measured fragment distribution.

Experiments with low intensity pulses (harmonics of a Nd:YLF laser,  $\tau = 300$  ns,  $I_0 \leq 2 \times 10^6$  W/cm<sup>2</sup>) at wavelengths of 527 and 263.5 nm were carried out to determine the population of rovibrational levels  $\nu > 3$  of the  $H_2^+$  molecules in the beam. Computational simulations of the dissociation spectra were carried out starting with a rovibrational population corresponding to the formation process of  $H_2^+$  by electron impact ionization [8] of  $H_2$  in the ion source and using calculated photodissociation cross sections according to [9]. Only small variations of the population assumed had to be done to fit the experimental curves.

Our interpretation of the experimental results takes only the electronic ground state ( $1s\sigma_g$ ) and the first excited state ( $2p\sigma_u$ ) of  $H_2^+$  into account, since the transition moment coupling them is large and higher electronic states are energetically well separated [5]. In order to investigate nonlinear dissociation rates as expected from the LIP we compare measurements recorded with equal pulse energies but different pulse lengths and therefore different intensities. The molecules move only  $1 \mu\text{m}$  during a pulse length of 1 ps. The movement can therefore be considered as frozen on the length scale of the focus diameter. This means the probability for the molecules to be in the focus and the photon fluence they experience are independent of the pulse length. According to FGR, the dissociation results are expected to be equal including saturation effects. Nonlinear optical dissociation probabilities manifest themselves as deviations between measurements recorded at different pulse lengths with equal pulse energies. Pulse lengthening was accomplished by chirping the pulses. No differences showed up between results using lengthened pulses with up or down chirp.

One important experimental result is that the number of fragments from  $\nu = 9$  normalized on the  $H_2^+$ -ion current is almost independent of the laser pulse length, i.e., the intensity, where the pulse energy is held constant

(Figs. 3a–3c). In fact, FGR and LIP predict almost the same dissociation rate for levels just above the crossing (Fig. 2) [10]. The Franck-Condon overlap between the vibrational wave function and the continuum wave function is at its maximum here. In the LIP picture,  $\nu = 9$  lies in the gap between the two light induced potential curves. This yields a transition probability for a wave packet to cross the gap close to unity [10]. Neither trapping nor bond softening should occur. Therefore almost all molecules from  $\nu = 9$  in the focus dissociate also according to LIP.

The dissociation rate of the low vibrational levels ( $\nu = 6, 7$ ) is strongly enhanced in the shorter pulse, i.e., higher intensity measurements (Figs. 3a–3c). This is due to the bond-softening effect, i.e., the lowering of the lower light induced potential barrier leads to a progressive growth of the dissociation probability with increasing intensity. In addition the lower potential well also becomes wider with growing light intensity. Consequently the energetic spacing between vibrational levels decreases. Thus the higher the intensity the lower their eigenvalues. This explains the striking shifts of the fragment energies from  $\nu = 6, 7$  (Figs. 3a–3c) with increasing intensities.

Franck-Condon factors for the vibrational levels above the resonance case  $\nu = 9$  and in the LIP picture above the gap, as for  $\nu = 10, 11$ , are also quite large [10]. Therefore already at intermediate light intensities, the dissociation rate is large here. With the intensity further increasing, molecules tend to follow the adiabatic path and therefore can get trapped in the higher light induced molecular potential. As a consequence, dissociation rates decrease with increasing intensity. This can be observed in our measurements recorded at 0.3 mJ ( $I_0 = 2.5 \times 10^{13}$  W/cm<sup>2</sup>) (Fig. 3a). In the shorter pulse, i.e., higher intensity measurement, we measured a lower number of fragments from  $\nu = 12$  and 13 indicating a smaller dissociation rate than at lower intensity.

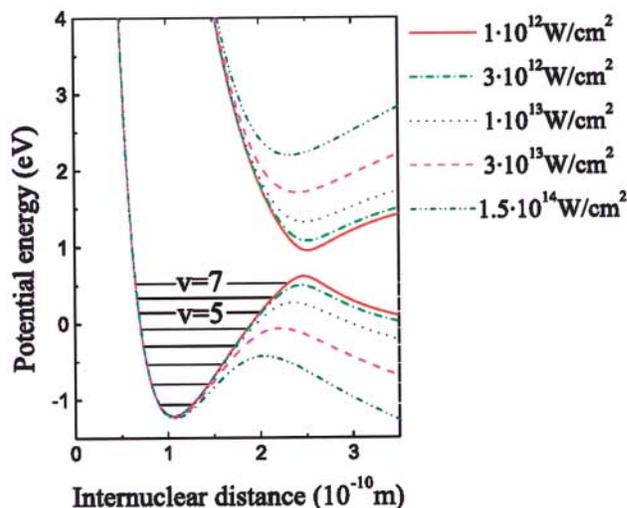
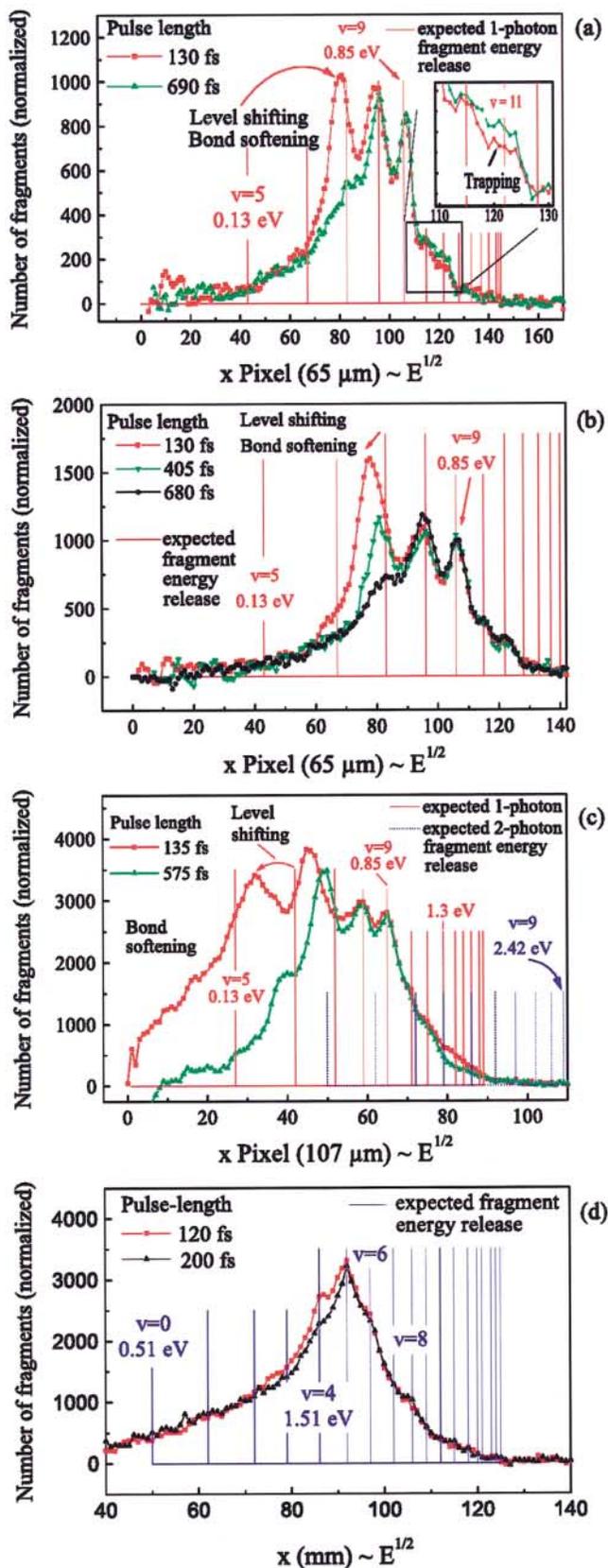


FIG. 2 (color). Dressed potentials of  $H_2^+$  at a wavelength of 785 nm.



In Fig. 3b the sensitivity of the trapping effect towards intensity is demonstrated: three measurements recorded at 0.5 mJ with three different pulse lengths, i.e., intensities are compared. The ones with 130 and 680 fs show no significant deviations of the number of fragments from high vibrational levels whereas at 405 fs the number of fragments from  $v = 11$  is lower. This can be explained in the following way: with further increasing light intensity, as in the case of 130 fs, the minimum of the upper light induced potential well rises above the energy of some vibrational quantum numbers making them nonbonding. As a consequence, trapping is no longer observed. Other possible reasons for the destruction of the trapping are rotational excitations at higher intensities [11].

If the rise time of the pulse is longer, e.g., 680 fs in Fig. 3b, the molecules are exposed to lower intensities for a rather long time. Therefore, they follow the diabatic path for a long time until the intensity is high enough for the trapping mechanism to become efficient [12]. As a result, the measurements recorded with 0.5 mJ at pulse lengths of 130 and 680 fs and the number of fragments of the concerned levels are equal because the trapping no longer takes place for the two reasons mentioned above (see Fig. 3b). However, in the measurement recorded with the same pulse energy at an intermediate pulse length of 405 fs some trapping seems to persist.

In Fig. 3c our highest intensity measurements ( $1.5 \times 10^{14}$  W/cm<sup>2</sup>) are shown. A higher number of fragments shows up in the higher intensity measurement in the fragment energy release range between 1.3 and 1.5 eV (see Fig. 3c). Here, the nonlinear process involved is three-photon absorption followed by one-photon emission, resulting in net two-photon absorption. Similar to the one-photon channel, here the fragment energy releases from  $v = 4, 5$  are shifted down. We do not detect as many fragments due to two-photon absorption as in experiments starting from neutral H<sub>2</sub> at comparable laser intensities (Fig. 3c) [2]. Since our population distribution of the vibrational levels of H<sub>2</sub><sup>+</sup> does not differ much from that expected after ionization of H<sub>2</sub> by a laser pulse, the reason for this has to be sought in the additional ionization process in the H<sub>2</sub> experiments.

In the H<sub>2</sub> experiments H<sub>2</sub><sup>+</sup> is created only where the intensity is high enough for the multiphoton ionization. In that intensity region also multiphoton dissociation should occur then with a higher relative probability than in our experiment on H<sub>2</sub><sup>+</sup>. The same argument leads to the higher relative yield of one-photon fragments on H<sub>2</sub> experiments

FIG. 3 (color). Cut through the two-dimensional momentum projection of fragments at  $y = 0$ . The intensities given are maximum intensities in the focus in the respective short pulse measurements. (a)–(c)  $\lambda = 785$  nm: (a)  $E_{\text{pulse}} = 0.3$  mJ,  $I_0 = 2.5 \times 10^{13}$  W/cm<sup>2</sup>; (b)  $E_{\text{pulse}} = 0.5$  mJ,  $I_0 = 4.2 \times 10^{13}$  W/cm<sup>2</sup>; (c)  $E_{\text{pulse}} = 1.0$  mJ,  $I_0 = 1.5 \times 10^{14}$  W/cm<sup>2</sup>; (d)  $\lambda = 392$  nm,  $E_{\text{pulse}} = 0.2$  mJ,  $I_0 = 6 \times 10^{13}$  W/cm<sup>2</sup>.

[4] from low vibrational levels, e.g.,  $v = 5$  compared to  $v = 9$ , where we detected the most fragments.

Additionally, we carried out experiments with frequency-doubled femtosecond pulses at 392 nm. Here the crossing lies between  $v = 5$  and  $v = 6$ . Qualitatively we observe the same effects as at 785 nm (see Fig. 3d).

In order to obtain the angular distributions of the fragments of the vibrational levels above the crossing, we extract the distributions on a circle of the recorded momentum projection. They are found to be close to a  $\cos^2$ -distribution at pulse energies  $\leq 0.7$  mJ. The effective intensity the molecules experience is proportional to the  $\cos^2$  of the angle between the laser polarization and the internuclear axis. Therefore this confirms the observation we have already made concerning the energetic fragment distribution, that the dissociation rate grows nearly linearly with the intensity for high vibrational levels. The slightly broader distribution in the measurement recorded at 1.0 mJ (Fig. 4a) reflects the saturation of the photodissociation for vibrational levels in the vicinity of the avoided crossing (see Fig. 4a).

The fragment angular distributions of the low energetic fragments were obtained by subtracting the  $\cos^2$ -fragment distribution of the high energetic fragments from the total measured distribution. They turn out to be much narrower

than  $\cos^2$  (Fig. 4). This underlines the strong progressive nonlinear dependence of the photodissociation probability on the intensity for vibrational levels below the crossing. Thus, for a fragment energy release of 0.16 eV, which is attributed to  $v = 6$ , the angular distribution is slightly narrower than the one for 0.36 eV ( $v = 7$ ). This can also be explained in terms of the nonlinear dissociation probability as predicted here by LIP theory: the closer the shifted levels to the gap between the two light induced potential curves the higher their dissociation probability. Since the  $v = 7$  level is closer to the gap than the  $v = 6$ , the dissociation takes place for lower effective intensities, i.e., greater angles to the laser polarization for  $v = 7$  than for  $v = 6$ . This qualitatively explains the widths observed in Fig. 4a.

Experimentally we have found equally narrow energetic angular distributions in measurements carried out with approximately the same spatial intensity distribution but different pulse lengths (see Fig. 4b). This means that the angular distribution does not crucially depend on the time the molecules interact with the laser field. The pulse length of 405 fs is comparable to one  $J = 1$  rotational cycle of the  $\text{H}_2^+$  molecule, the most populated rotational state here. This seems to indicate that, at least up to intensities in the  $10^{13}$  W/cm<sup>2</sup> region used here, the alignment of the molecules does not play an important role for the angular distribution of the photofragments. However further investigations, e.g., using shorter pulses and double pulse experiments are necessary to finally clarify if alignment of the mother molecules plays a role.

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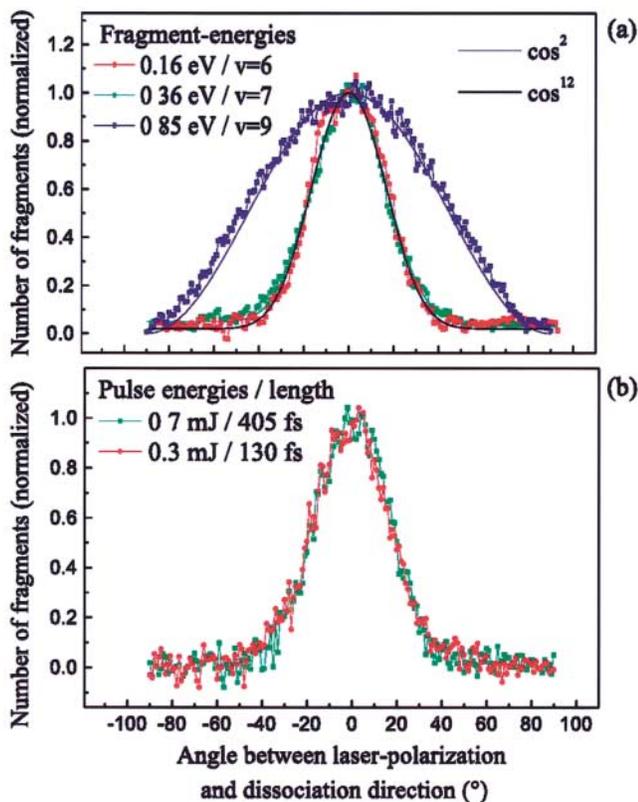


FIG. 4 (color). Angular distributions of the photofragments from measurements (a) for various fragment energy releases [measurement in Fig. 1(a)], (b) with pulse energies of 0.7 and 0.3 mJ and at pulse lengths of 405 and 130 fs, respectively, from  $v = 6$ .

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