

## Intense-Laser-Field Ionization of Molecular Hydrogen in the Tunneling Regime and Its Effect on the Vibrational Excitation of $\text{H}_2^+$

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(Received 8 August 2003; revised manuscript received 16 January 2004; published 23 April 2004)

$\text{H}_2$  molecules were ionized by Ti:sapphire (45 fs, 800 nm) and Nd-doped yttrium aluminum garnet lasers (6 ns, 1064 nm). The relative populations of the vibrational levels of the  $\text{H}_2^+$  ions were determined and found to be concentrated in the lowest vibrational levels. Tunneling ionization calculations with exact field-modified potential curves reproduce the experimental results. The reason for the departure from conventional Franck-Condon-like distributions is the rapid variation of the ionization rate with internuclear distance.

DOI: 10.1103/PhysRevLett.92.163004

PACS numbers: 33.80.Wz

In recent years substantial progress has been made in the understanding of molecules and clusters in intense-laser fields ( $10^{13}$ – $10^{18}$  W cm $^{-2}$ ) [1]. For diatomic molecules, theory and experiment have demonstrated fundamental processes such as bond softening [2], bond hardening (or vibrational trapping) [3,4], laser induced alignment [5], and enhanced ionization at critical internuclear distances [6]. For the majority of these experiments, the first step is tunneling ionization of neutral molecules. It was often thought, incorrectly, that the vibrational excitation of the molecular ions follows the Franck-Condon principle [7].

For  $\text{H}_2$ , it was either silently or explicitly assumed that the molecules were ionized on the rising edge of the laser pulse in a simple field-ionization process. It appears straightforward to predict the final states: the molecular ion will be in the electronic ground state; the vibrational wave packet will be conserved. The population of the vibrational levels of  $\text{H}_2^+$  should therefore be given by the well-known Franck-Condon factors as computed by Dunn [8]. Accordingly, a broad population distribution is expected, peaking at  $v' = 2$ , but nevertheless with significant population in, for example,  $v' = 8$  and higher levels. However, the interpretation of the earlier-mentioned experiment on bond hardening required that the levels above  $v' = 4$  were not populated [4].

Apparently, the use of the Franck-Condon principle is inaccurate because the rate for tunneling ionization increases sharply with internuclear distance,  $R$  [9,10]. In this Letter we present a substantially improved model and report on a direct and unmistakable measurement of the  $v'$ -population distribution when  $\text{H}_2$  is ionized in the

tunneling regime. Preliminary data were presented at a recent conference [11].

The theoretical model will be detailed in a future paper. We neglect the rotational motion, but consider two limiting cases of alignment: (i) the molecular axis and the  $E$  field of the linearly polarized laser beam are parallel; (ii) they are perpendicular. The  $R$ -dependent ionization rates,  $\Gamma(R)$ , are calculated with the Ammosov-Delone-Krainov tunneling model [12]. For the present experimental parameters, it yields (isotropic) rates that are in excellent agreement with accurate *ab initio* calculations for parallel alignment [13]. The  $R$  dependency originates from the electronic binding energy,  $\Delta E(R)$ , which, for example, is equal to 18.3 eV at  $R = 1a_0$ , but only 14.6 eV at  $R = 2a_0$ . At a laser intensity of  $5 \times 10^{13}$  W cm $^{-2}$ , this difference in binding energy leads to a difference in ionization rate,  $\Gamma$ , of almost 4 orders of magnitude. The variation of the laser intensity during the laser period is taken into account.

The intense-laser field appreciably deforms the vibrational ground state of  $\text{H}_2$ . We use the time-averaged laser-field strength,  $F_{\text{av}} = 2F_0/\pi$  (where  $F_0$  is the peak field strength), to calculate the potential curve and, subsequently, the vibrational ground state. For the in-field potential curve, a fully three-dimensional *ab initio* model is used with explicitly correlated basis functions.

For the calculation of the potential curve of  $\text{H}_2^+$ , we use the same methodology with one-electron basis functions. For parallel alignment, the laser field induces a strong coupling between the electronic ground state and the first excited state, which is antibonding. In strong fields, the potential curve can support only a limited number of

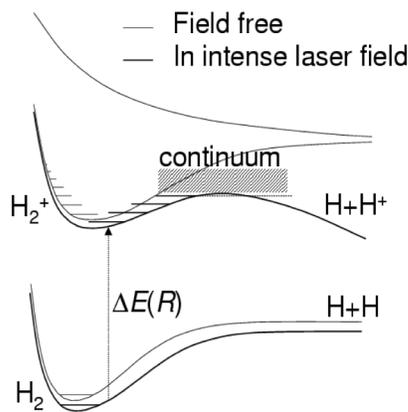


FIG. 1. Field-induced modifications to the potential curves and the vibrational levels for parallel alignment. Not drawn to scale.

quasibound vibrational levels. The dissociation probability of the quasibound levels is usually negligible.

The field-induced modifications to the potential curves and the vibrational levels for parallel alignment are illustrated schematically in Fig. 1. The transition rates to the individual field-modified vibrational levels of  $H_2^+$  are given by

$$\Gamma(v') = \left| \int \Gamma^{1/2}(R) \chi_{v'}(R) \chi_0(R) dR \right|^2, \quad (1)$$

where  $\chi_{v'}(R)$  and  $\chi_0(R)$  are the vibrational wave functions of  $H_2^+$  and  $H_2$ . Typical vibrational distributions, for both parallel and perpendicular alignment, are presented in Figs. 2(a)–2(d). At the lowest intensity, there is practically no dissociation. The distributions for the two kinds of alignment shown in Fig. 2(a) are therefore very similar. At the higher intensities, the “parallel” and “perpendicular” distributions are again similar for the lowest vibrational levels, but there exists a certain threshold above which the parallel aligned molecules all dissociate and are therefore absent in the figure.

For example, for  $I = 5.4 \times 10^{13} \text{ W cm}^{-2}$  the highest quasibound level for parallel alignment is  $v' = 3$ . While the white bars for perpendicular alignment thus all add up to nearly 100% (the bound vibrational levels alone do not form a complete basis), the dark bars add up to 99%, 95%, 83%, and 67% for the intensities shown in Figs. 2(a)–2(d). For comparison, Fig. 2(e) shows the values for  $v' = 0$  to 10 of the vibrational excitation of  $H_2^+$  that was measured by von Busch and Dunn after ionization of  $H_2$  with 100 eV electrons [14].

For the experimental study of tunneling ionization of  $H_2$ , we have used the Ti:sapphire laser (45 fs, 800 nm, and 700 mJ at 1 kHz) at the CEA Saclay Laser-Matter Interaction Center (SLIC) European Facility. The beam is focused in high vacuum with a spherical lens of focal distance 250 mm. The beam profile and the  $M^2$  factor, which characterizes the difference with an ideal

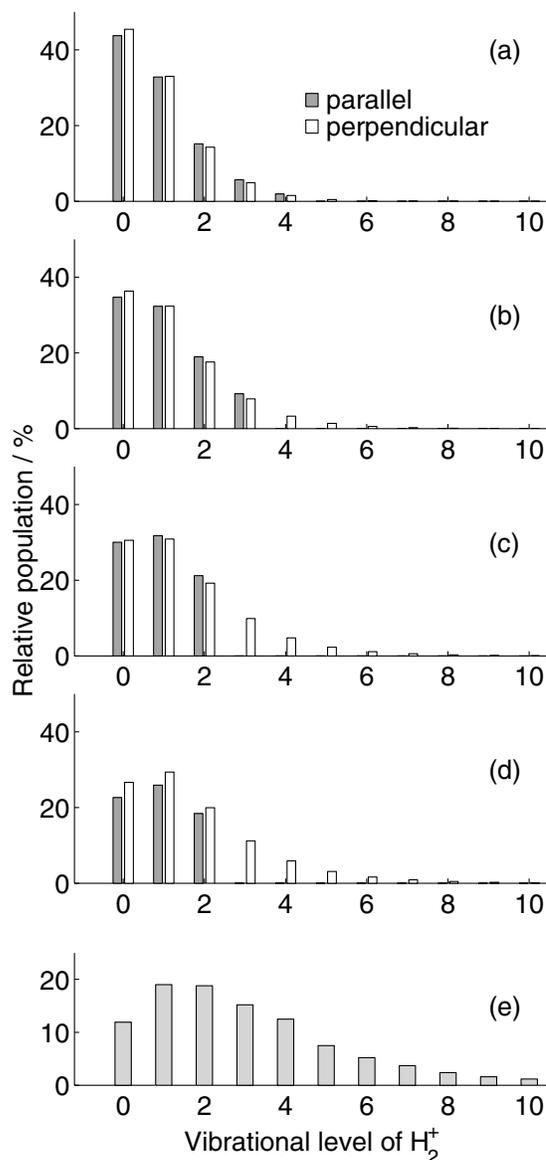


FIG. 2. (a)–(d) Theoretically predicted vibrational excitation of  $H_2^+$  produced by tunneling ionization of  $H_2$  in intense laser fields. Calculations for molecules aligned parallel and perpendicular to the laser  $E$  field are presented. The laser intensities are  $3.5 \times 10^{13} \text{ W cm}^{-2}$  (a),  $5.4 \times 10^{13} \text{ W cm}^{-2}$  (b),  $7.8 \times 10^{13} \text{ W cm}^{-2}$  (c), and  $1.06 \times 10^{14} \text{ W cm}^{-2}$  (d). (e) The vibrational excitation of  $H_2^+$  produced by electron impact ionization of  $H_2$  as measured by von Busch and Dunn [14].

Gaussian laser beam, were measured. The laser intensity is calculated with good accuracy ( $\pm 20\%$ ). Hydrogen gas is introduced through a thin needle (inner diameter = 0.3 mm) a couple of mm above the focus. Ionization is observed for intensities of  $3 \times 10^{13} \text{ W cm}^{-2}$  and higher. The Keldysh parameter [15] is approximately one. The ionization process is therefore in the tunneling regime. A seeded Nd-doped yttrium aluminum garnet laser (Nd:YAG) (Continuum NY81C, 6 ns, 1064 nm, and 1 J at 10 Hz) was also used.

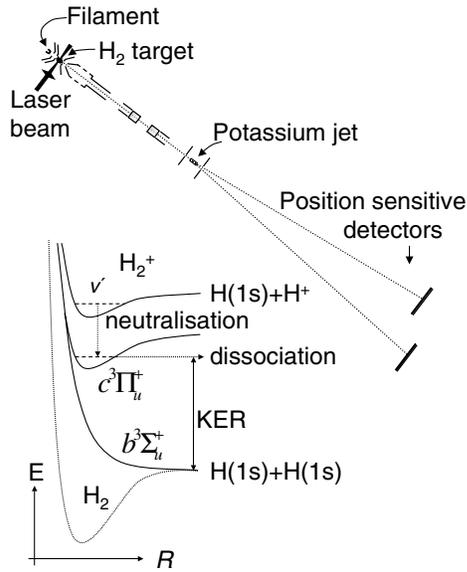


FIG. 3. A schematic top view of the experimental setup. The potential curve diagram illustrates the physics of the neutralization and subsequent predissociation processes.

The transportable experimental setup from Louvain-la-Neuve is shown schematically in Fig. 3. The  $\text{H}_2^+$  ions are accelerated to 4 keV and collimated before passing through an effusive jet of K atoms, where they are neutralized with an efficiency of approximately 1%. The electron capture from the K atoms happens to be into a small band of excited states of  $\text{H}_2$ , the  $c^3\Pi_u^+$  state being one of them. Because of its Rydberg character, the vibrational excitation of the molecular core is practically conserved. However, the  $c^3\Pi_u^+$  state is unstable and predissociates along the repulsive curve of the  $b^3\Sigma_u^+$  state. The kinetic energy release (KER) is directly related to the level of vibrational excitation of the  $c^3\Pi_u^+$  state and therefore also to the original vibrational level of  $\text{H}_2^+$ . The technique was developed by de Bruijn and Los [16]. The KER is determined from coincidence measurements of the neutral fragments of the predissociation process with two position-sensitive detectors.

We prove the validity of our method by ionizing the  $\text{H}_2$  molecules with 100 eV electrons. The KER spectrum is presented in Fig. 4(a). A detailed analysis [17] showed that the peak areas correspond closely to the well-established distribution measured by von Busch and Dunn [14]; see Fig. 2(e).

In the actual experiment on tunneling ionization,  $\text{H}_2$  molecules were ionized with the Ti:sapphire laser under otherwise identical experimental conditions. Intensities range between  $3 \times 10^{13}$  and  $4 \times 10^{14} \text{ W cm}^{-2}$ . Figures 4(b)–4(d) show three typical KER spectra measured with the Ti:sapphire laser. The dissociation fractions, i.e., the amount of protons divided by the sum of protons and  $\text{H}_2^+$  particles, were measured close to the interaction region. They are <1%, 5%, and 25%.

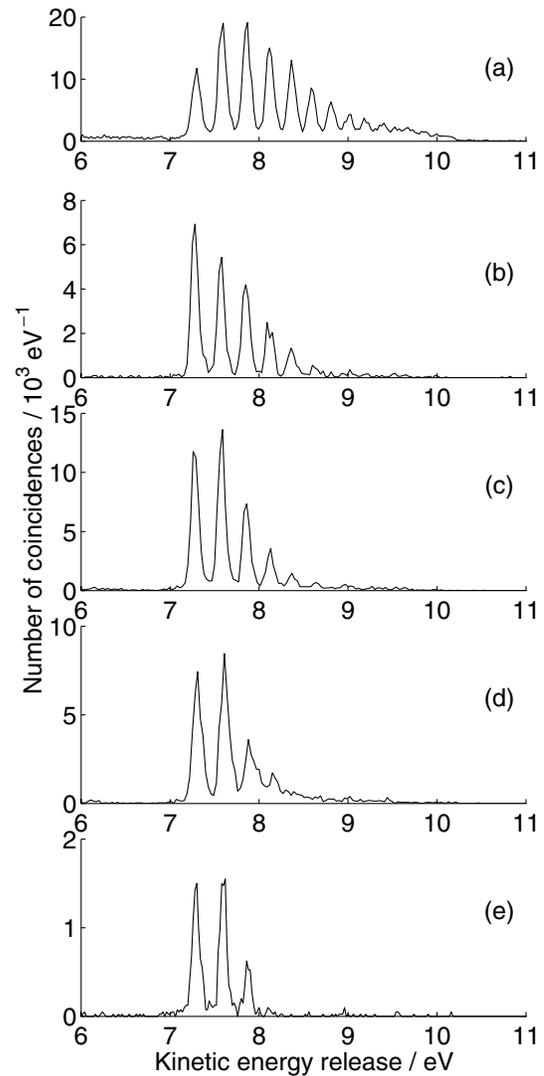


FIG. 4. (a) Kinetic energy release spectrum for the case in which  $\text{H}_2^+$  was produced by ionizing  $\text{H}_2$  with electrons of approximately 100 eV. The spectrum may be compared to the bar diagram of Fig. 2(e). (b)–(e) Kinetic energy release spectra showing the vibrational excitation of  $\text{H}_2^+$  ions produced by tunneling ionization in intense laser fields. Spectra (b)–(d) were taken with a 45 fs, 800 nm Ti:sapphire laser. The laser intensities are  $3 \times 10^{13} \text{ W cm}^{-2}$  (b),  $4.8 \times 10^{13} \text{ W cm}^{-2}$  (c), and  $1.5 \times 10^{14} \text{ W cm}^{-2}$  (d). Spectrum (e) was taken with a Nd:YAG (6 ns, 1064 nm) at an intensity of  $1 \times 10^{14} \text{ W cm}^{-2}$ .

Spectrum (e) was taken with a Nd:YAG laser (6 ns, 1064 nm) at an intensity of  $1 \times 10^{14} \text{ W cm}^{-2}$ . The dissociation fraction is 50%.

To a very good approximation, the area underneath the peak at 7.3 eV is proportional to the population of the  $v' = 0$  level in the  $\text{H}_2^+$  molecules, the peak at 7.6 eV to that of the  $v' = 1$  level, and so on. Since the peaks are equally wide, the spectra may be compared directly to the bar diagrams of Fig. 2. Starting with the spectrum of Fig. 4(b) at  $3 \times 10^{13} \text{ W cm}^{-2}$ , we note the good resemblance with the theoretical values at  $3.5 \times 10^{13} \text{ W cm}^{-2}$

shown in Fig. 2(a). The maximum is at  $\nu' = 0$ , and the population for  $\nu' > 5$  is negligible. Also, the theoretical dissociation fractions of zero for perpendicular alignment and 1% for parallel alignment are consistent with the measured value of  $<1\%$ . Since the dissociation fraction is virtually zero, the spectrum represents the true vibrational excitation of the  $\text{H}_2^+$  ions after tunneling ionization.

The spectrum of Fig. 4(c) at  $4.8 \times 10^{13} \text{ W cm}^{-2}$  has a dissociation fraction of 5%. The parallel version of the theoretical spectrum of Fig. 2(b) at  $5.4 \times 10^{13} \text{ W cm}^{-2}$  also has a dissociation fraction of 5%. On the other hand, it peaks at  $\nu' = 0$ , whereas the experimental spectrum peaks at  $\nu' = 1$ , i.e., more like the theoretical spectrum of Fig. 2(c) at  $7.8 \times 10^{13} \text{ W cm}^{-2}$ . For perpendicular alignment there is practically no dissociation. The white bars reveal that the theoretical spectrum becomes broader with increasing intensity; i.e., it becomes more and more Franck-Condon-like. For parallel alignment this process is reflected in the shift of the maximum from  $\nu' = 0$  to  $\nu' = 1$ . Nevertheless, the parallel spectra become narrower because the threshold for dissociation is shifting. The experimental spectra clearly reproduce these two trends.

For the experimental spectrum of Fig. 4(d) at  $1.5 \times 10^{14} \text{ W cm}^{-2}$ , the dissociation fraction is 25%. This is somewhat less than the 33% calculated for parallel alignment at  $1.06 \times 10^{14} \text{ W cm}^{-2}$ . Comparing the distributions, we also note that the sharp cutoff due to dissociation, which is predicted for parallel alignment, is not reproduced experimentally. Earlier experiments have shown that hydrogen molecules align in sub-100 fs laser pulses [5]. The present experimental spectra at 45 fs suggest that the alignment is not perfect. Naturally, the theoretical model also has its limitations by assuming time-averaged potentials, etc.

For the Nd:YAG (6 ns pulses) we present one spectrum; see Fig. 4(e). Another spectrum at  $6 \times 10^{13} \text{ W cm}^{-2}$  was similar. Because of the low repetition rate and long pulse length, the dynamic range is very limited. With the Ti:sapphire laser, the variation of the spectra can be observed over quite a range of laser intensities. Nevertheless, the spectra taken with the two types of laser are comparable. For the long pulses it appears that the dissociation of the highest quasibound vibrational levels is more important and that the cutoff is therefore sharper.

In conclusion, we have demonstrated that tunneling ionization of  $\text{H}_2$  does not follow the Franck-Condon principle. By analyzing the population of the vibrational levels of  $\text{H}_2^+$ , we find that, predominantly, the lowest levels  $\nu' = 0-4$  are populated, consistent with the experiment on bond hardening [4]. The theoretical spectra are in rather good agreement with the data. One may expect that intense laser-molecule interactions are generally affected by the described mechanism and that interpretations of

earlier experiments in this field may sometimes have to be reconsidered.

This work was supported by the Belgian National Fund for Scientific Research (FNRS), the Special Research Fund (FSR), and by the European Community-Access to Research Infrastructure Action of Improving Human Potential Program under the Contract No. HPRI-CT-2002-00191. A.S. acknowledges support by the Stifterverband für die Deutsche Wissenschaft and the Deutsche Forschungsgemeinschaft DFG (Project No. SA 936/2-1).

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