Manipulation of Bond Hardening in H_2^+ by Chirping of Intense Femtosecond Laser Pulses

L. J. Frasinski,* J. H. Posthumus, J. Plumridge, and K. Codling
J. J. Thomson Physical Laboratory, The University of Reading, Whiteknights, Reading RG6 6AF, United Kingdom

P. F. Taday and A. J. Langley
Central Laser Facility, Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, United Kingdom

(Received 16 April 1999)

Bond hardening of H_2^+ has been observed in the intensity range of 100–200 TW/cm^2 using 792 nm laser pulses. This effect can be understood in terms of a light-induced potential well created at twice the normal (free) equilibrium internuclear distance by an adiabatic mixing of 1- and 3-photon resonances. The trapped population dissociates into H^+ and H when the potential well becomes convex on the trailing edge of the pulse. The dynamics of the nuclear wave packet was manipulated by chirping the pulse duration from 45 to 500 fs and observing a reduction of the kinetic energy release from 0.3 to 0.0 eV. This energy shift is interpreted as a dynamic Raman effect within the laser bandwidth.

PACS numbers: 33.80.Rv, 42.50.Hz

Intuition suggests that a sufficiently strong laser field can weaken molecular bonds and induce dissociation. This mechanism known as *bond softening* [1] is uncontroversial and well understood in H_2^+ (see, for example, Ref. [2]). The opposite effect, also called molecular stabilization, vibrational trapping, creation of light-induced bound states or *bond hardening,* has the same theoretical origin [1], but the history of its experimental verification has been confusing. Two manifestations of bond hardening in H_2^+ near 1-photon [3] and 3-photon [4] resonances were inferred from rather noisy data in the early 1990's. They were received with great interest, as at that time the stabilization of the molecular bond was a candidate for a universal mechanism explaining the invariance of ion kinetic energies with changes of intensity and pulse duration [5,6]. Later, it was established that this invariance is a signature of rapid, sequential ionization at the critical internuclear distance [7–9]. Since then there has been a surprising lack of clear-cut confirmation of the bond hardening effect. With more recent work casting doubt on the existence of light-induced bound states [10,11], the idea of bond hardening has become again only a remote theoretical possibility. Against this trend of scepticism, we present an experimental observation of bond hardening in H_2^+.

In these experiments, chirped pulses from a Ti:sapphire laser were amplified to 10 mJ in energy and compressed to about 50 fs duration at a repetition rate of 10 Hz (see [12] for a recent review of high power ultrafast lasers). The pulse bandwidth had an almost perfect Gaussian shape centered at 792 nm and an extent of 22 nm, full width at half maximum (FWHM). The pulse length was varied by scanning the separation of the two compressor gratings and introducing some uncompensated chirp. The linearly polarized beam, 5 mm in diameter, was focused in an ultrahigh vacuum chamber using an $f/4$ parabolic mirror to give a peak intensity of the order of 10^{14} W/cm^2. Hydrogen gas was introduced into the vacuum chamber via simple effusion, raising the ambient pressure to about 10^{-6} torr. At this pressure and intensity no space charge effects were observed. Following the process of multiphoton ionization of H_2, an external electric field directed "forward" and "backward" fragment ions into a vertical, 13-cm-long drift tube. Ions were detected by microchannel plates with a 10-mm circular restriction in front to improve the energy and angular resolutions. The ion time-of-flight (TOF) spectrum and pulse energy were recorded at each laser shot by a digital oscilloscope and stored in a computer.

Figure 1 shows ion TOF spectra recorded at several pulse lengths. For each grating separation the peak intensity was adjusted to about 150 TW/cm^2, i.e., below saturation of any ion channel [13]. At each laser pulse the ion signal and the pulse energy were stored, but ion signals from only a narrow energy window were selected for the TOF plots. The position of the window was

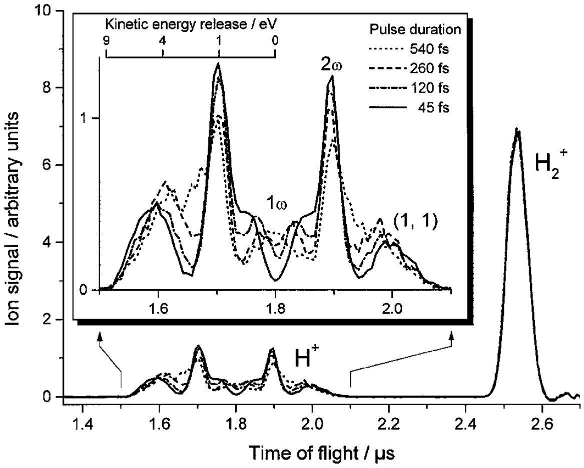

FIG. 1. Bond hardening manifests itself as a shift in the low-energy proton peak labeled 1ω, from 0.0 to 0.3 eV of kinetic energy release when the laser pulse is shortened from 540 to 45 fs. The inset shows details of the proton peaks.

0031-9007/99/83(18)/3625(4)$15.00

slightly adjusted to give the same height of the H_2^+ peak and highlight amplitude changes in the H^+ peaks. The lowest energy channel, 1ω, involves dissociation of H_2^+ via 1-photon absorption. The next channel, 2ω, is a similar process but involves absorption of three photons and an emission of one of them. The $(1,1)$ channel is the Coulomb explosion of two protons following H_2^+ ionization. This peak shifts to higher kinetic energies with pulse shortening, because shorter rise time initiates Coulomb explosion at a smaller internuclear distance. A similar dynamic shift is observed in the 1ω peak, but the details are quite different; bond hardening is involved.

Potential energy curves for H_2^+ dressed in the photon field are shown in Fig. 2, which was adapted from [2] by adjusting the photon wavelength to 792 nm. It is sufficient to consider only the two lowest molecular ion states: the attractive $1s\sigma_g$ and repulsive $2p\sigma_u$ states. Since the system, H_2^+ and photons, must be considered as a whole, the molecular curves must be repeated at all discrete energies of the photon field. Zero energy is set at some arbitrarily large number of photons and the states are labeled with $n\omega$, where n is the number of photons absorbed. Because of selection rules, the photon interaction couples only half of the states, alternating between $1s\sigma_g$ and $2p\sigma_u$ for even and odd n. These diabatic states, shown in Fig. 2 as solid lines, describe the system correctly at low laser intensity. When the intensity increases, the curve crossings become anticrossings and a widening of the energy gap between the upper and lower branches of the new, adiabatic states (broken lines) occurs.

On the lower branch the electronic charge oscillates in phase with the laser field, decreasing the energy of the system; on the upper branch these oscillations are in antiphase. At the center of the gap almost the entire electronic charge oscillates between the two protons. As the system moves away from resonance, the amount of oscillating charge diminishes, in sympathy with the reduced mixing of the $1s\sigma_g$ and $2p\sigma_u$ states. At the 1ω crossing the charge oscillates with the laser frequency; at the 3ω crossing the charge oscillations are 3 times faster. Strictly speaking, this adiabatic picture is valid only for a slowly evolving system. Nevertheless, it allows us to understand the dynamics of H_2^+ on a time scale only an order of magnitude slower than the oscillations of the laser field.

In Fig. 3 the process of bond hardening is illustrated with the relevant potential curves copied from Fig. 2. The ionization of the neutral molecule starts at about $50\ \mathrm{TW/cm^2}$ on the leading edge of the laser pulse creating a wave packet composed of a few of the lowest vibrational states of H_2^+. The interesting part of this wave packet has an energy just below the 1ω dissociation limit [see Fig. 3(a)]. It crosses the potential well in about 10 fs and arrives at the 3ω gap while the gap is still rather small. The Landau-Zener transition probability (see [14] for a convenient formula) tells us that most of the wave packet crosses the gap diabatically. The wave packet slows down in the shallow part of the potential well, turns back, and arrives again at the 3ω crossing, when the gap is much wider and the probability of a diabatic crossing is small. Now the wave packet is trapped in the

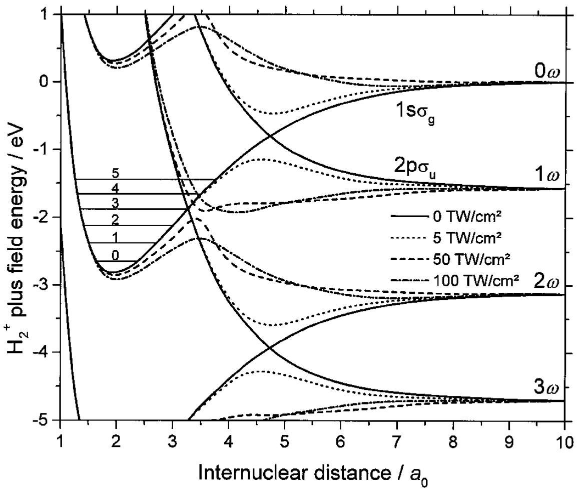

FIG. 2. Molecular potential energy curves of H_2^+ dressed in a photon field of 792 nm wavelength. With increasing laser intensity curve crossings become anticrossings. A nuclear wave packet with kinetic energy corresponding to the 3rd and 4th vibrational levels of a free molecule can be trapped in the potential well created by intensities of $100-200\ \mathrm{TW/cm^2}$ at $4a_0$.

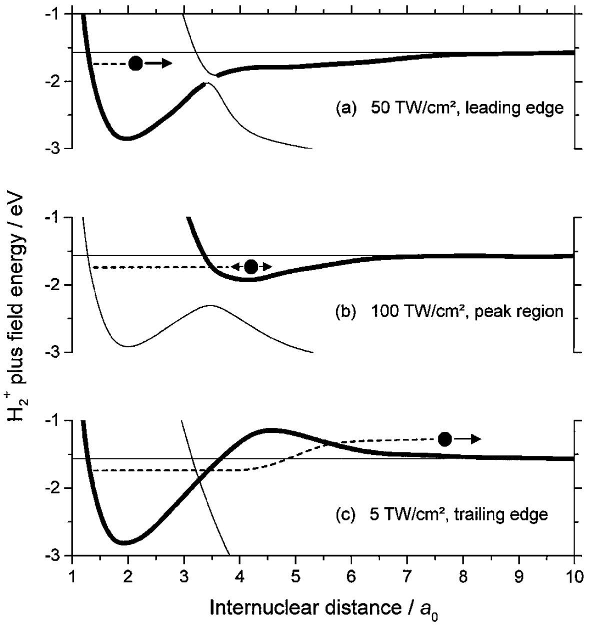

FIG. 3. The dynamics of bond hardening. H_2^+ is created on the leading edge of the laser pulse and the wave packet jumps the anticrossing gap (a). As the intensity increases, the gap widens and the wave packet is trapped (b). Falling intensity flexes the well upwards and the wave packet is released (c). The kinetic energy release depends on the speed of the intensity fall.

laser-induced adiabatic state [see Fig. 3(b)], essentially completing the process of bond hardening.

Of particular interest is the decay of the bond-hardened state. As the intensity falls on the trailing edge of the laser pulse, the shape of this state changes from concave to convex [see Fig. 3(c)]; it now becomes the bottom part of the 1ω anticrossing. In this process the trapped wave packet is lifted up and about a half of it falls back into the $1s\sigma_g$ well, but the other half spills out to the 1ω dissociation limit. Clearly, the faster the intensity fall time, the higher the wave packet is lifted and the larger is the kinetic energy it gains. This dynamic process is responsible for the shift of the 1ω peak shown in Fig. 1.

Chirping laser pulses change the wavelength at the leading and trailing edges of the pulse. To test if this wavelength variation affects the 1ω peak, the grating separation was scanned to give a chirp variation from positive to negative. The recorded TOF spectra shown in Fig. 4 are symmetrical with respect to the zero-chirp grating separation. To test further for a possible wavelength effect, a slit selecting only a part of the optical spectrum was inserted in the compressor and several TOF spectra were recorded at various wavelengths. It was found that only the reduced bandwidth and not the central wavelength affected the kinetic energy of the 1ω peak. These tests show that chirped pulses are just as good as bandwidth-limited ones for manipulating the dynamics of bond hardening.

Reducing the pulse intensity to well below the saturation level does not shift the position of the 1ω peak. This suggests an absence of dynamic effects near the peak of intensity and indicates that the wave packet is released from the bond-hardened state on the *trailing* edge of the laser pulse. Such intensity independence of the 1ω peak contrasts with the behavior of the $(1,1)$ peak. Here dissociation of H_2^+ on the *leading* edge [13] is followed by further ionization and Coulomb explosion, with the kinetic energy release being affected by the magnitude of the peak intensity.

The threshold for population trapping in the bond-hardened state is experimentally estimated to be about $100\ \mathrm{TW/cm^2}$. This population trapping is expected to cease above $200\ \mathrm{TW/cm^2}$ due to increasing probability of ionization [13] rather than shallowness of the bound state. Even if the state cannot support any vibrational levels at high intensity, the spreading of the wave packet is too slow to disperse the population before the intensity drops again.

It is interesting to note the complex *electron* dynamics of the bond-hardened state, which is the result of the combined mixing of the $1s\sigma_g$ and $2p\sigma_u$ states at 1ω and 3ω frequencies. At large internuclear distances the electron charge oscillates in phase with the laser field and the attractive force of the bond comes from the diminishing of these oscillations with increasing internuclear distance. At small distances the charge oscillations become 3 times faster and in antiphase, but the repulsive force on the nuclei is dominated by the antibonding nature of the $2p\sigma_u$ state.

Energy conservation deserves a brief comment. The dashed trajectory in Fig. 3(c) indicates that the H_2^+ ion gains a fraction of a photon energy in the bond-hardened state. This can be explained by absorption of photons from the high-energy end of the spectrum and re-emission at the low-energy end, a dynamic Raman effect within the laser bandwidth (45 meV FWHM).

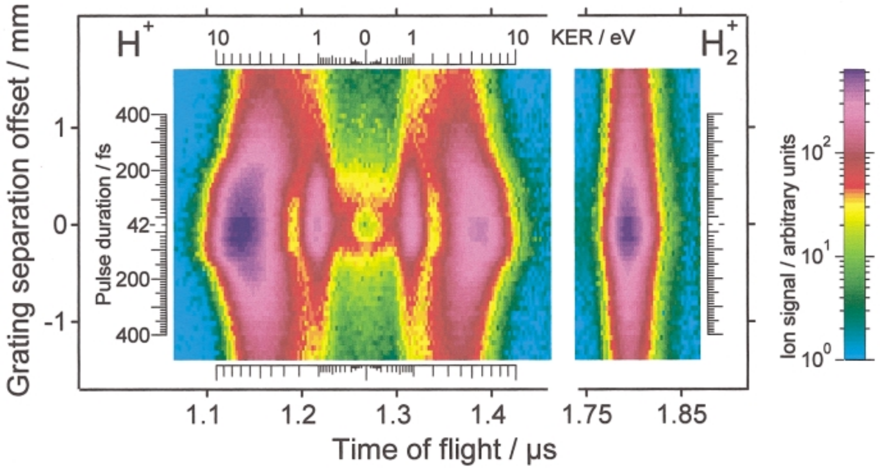

FIG. 4 (color). The variation of ion TOF spectra with grating separation offset, s, shows the dynamic Raman effect as a round "crater" in the middle of the proton peaks. The variation of the pulse duration (FWHM) with s is given by $\Delta t/\mathrm{fs} = \sqrt{42^2 + (350s/\mathrm{mm})^2}$. The kinetic energy release is quadratic with the TOF difference. The symmetry of the crater with respect to the $s = 0$ position (the shortest pulse) shows that the dynamics of the bond hardening is independent of the chirp direction. (The small asymmetry of the Coulomb-explosion peak is probably due to imperfect compensation of the fourth order dispersion in the compressor [12], which affects the pulse shape differently for positive and negative chirp.)

TABLE I. Experimental and theoretical kinetic energy release from the bond-hardened state (1ω peak). The mechanism of Fig. 1 suggests that the fall time of the pulse, rather than its duration or rise time, determines the proton kinetic energy.

Pulse duration FWHM (fs)	Rise and fall time τ (fs)	Kinetic energy release (eV)
540	324	≤0.01 ± 0.01[a]
260	156	0.09 ± 0.03[a]
150	78	0.20 ± 0.05[b]
120	72	0.13 ± 0.03[a]
45	27	0.30 ± 0.05[a]
58	20	0.35 ± 0.1[c]
37	10	0.7 ± 0.1[c]
28	5	1.0 ± 0.1[c]

[a] Experiment, this work, Gaussian pulses: $I = I_0 \exp(-t^2/\tau^2)$.
[b] Theory [2], $\sin^2$ pulses, τ estimated by fitting a Gaussian.
[c] Theory [15], rectangular pulses with Gaussian rise and fall time.

The interpretation of the shift in the 1ω peak in terms of the bond-hardening process depicted in Fig. 3 is supported by previous theoretical work. Figure 19(b) in Ref. [2] shows the evolution of a wave packet exposed to a pulse of 150 fs duration, 150 TW/cm^2 peak intensity, and 780 nm wavelength. The simulation starts from the $v = 4$ vibrational level of H_2^+. As the intensity increases, one half of the population escapes with high kinetic energy to the 2ω dissociation limit, whereas the other half gets trapped at an internuclear distance of between 4 and 5 a_0 for about 100 fs. When the intensity falls, about half of the trapped population is released with energy of 0.2 eV to the 1ω limit. It is remarkable that this population is lifted from just below the dissociation limit, providing a theoretical basis for the dynamic Raman effect. The calculated proton energy spectrum [Fig. 20(b) of [2]] clearly shows the 1ω and 2ω peaks we observe in Fig. 1.

The dynamic shift of the 1ω peak has been revealed in simulations at 532 nm using a range of pulse duration [15]. The authors call this mechanism "below threshold dissociation" (BTD) and attribute it to nonadiabatic effects on the *rising* edge of the laser pulse, which contrasts with our interpretation suggesting that the steepness of the *falling* edge matters here. (Clearly, experiments or simulations that vary only the rise or fall time of the laser pulses can shed more light on this problem.) Table I compares the experimental and theoretical results. The consistent variation of the 1ω energy with pulse rise and fall time suggests that the same physics is responsible for the BTD process and dynamic the Raman effect.

A lower range of vibrational levels of H_2^+ seems to be populated than expected from the Franck-Condon overlap with the ground state of H_2 (see, for example, Fig. 3 of [16]). This indicates that bond softening also takes place in the neutral molecule and the first ionization occurs at a relaxed internuclear distance. The $v = 0$ level is expected to be highly populated, but its tunneling probability through the bond-softened barrier is small (see Fig. 2). Higher vibrational levels dissociate with increasing efficiency through the 3-photon gap to the 2ω limit. Trapping in the bond-hardened state is expected to start at $v = 3$ and be quite efficient at $v = 4$. The population of $v \geq 5$ levels, which are above the 1ω dissociation limit, is probably negligible. We therefore believe that almost all population of the 1ω peak shown in Fig. 1 is lifted from *below* the dissociation limit by the dynamic process depicted in Fig. 3(c).

With hindsight we suggest that peaks B in Fig. 2 of Ref. [11] are a signature of the bond-hardened state, despite the authors' claim that their experimental conditions cannot populate such states. This state is the same one allegedly observed much earlier [4], but it turns out that it is populated without the initial molecular wave packet bouncing back and can be observed in the low-energy 1ω channel rather than the energetic $(1,1)$ channel (see Figs. 2 and 3 of [4]).

We are pleased to acknowledge the Engineering and Physical Sciences Research Council (U.K.) for their financial support.

---

*Email address: L.J.Frasinski@reading.ac.uk

[1] A. D. Bandrauk and M. L. Sink, J. Chem. Phys. **74**, 1110 (1981).
[2] A. Giusti-Suzor, F. H. Mies, L. F. DiMauro, E. Charron, and B. Yang, J. Phys. B **28**, 309 (1995).
[3] S. W. Allendorf and A. Szöke, Phys. Rev. A **44**, 518 (1991).
[4] A. Zavriyev, P. H. Bucksbaum, J. Squier, and F. Saline, Phys. Rev. Lett. **70**, 1077 (1993).
[5] K. Codling and L. J. Frasinski, J. Phys. B **26**, 783 (1993).
[6] M. Schmidt, D. Normand, and C. Cornaggia, Phys. Rev. A **50**, 5037 (1994).
[7] J. H. Posthumus, L. J. Frasinski, A. J. Giles, and K. Codling, J. Phys. B **28**, L349 (1995).
[8] T. Seideman, M. Yu. Ivanov, and P. B. Corkum, Phys. Rev. Lett. **75**, 2819 (1995).
[9] T. Zuo and A. D. Bandrauk, Phys. Rev. A **52**, R2511 (1995).
[10] T. D. G. Walsh, F. A. Ilkov, and S. L. Chin, J. Phys. B **30**, 2167 (1997).
[11] G. N. Gibson, M. Li, C. Guo, and J. Neira, Phys. Rev. Lett. **79**, 2022 (1997).
[12] S. Backus, C. G. Durfee III, M. M. Murmane, and H. C. Kapteyn, Rev. Sci. Instrum. **69**, 1207 (1998).
[13] J. H. Posthumus, J. Plumridge, P. F. Taday, J. H. Sanderson, A. J. Langley, K. Codling, and W. A. Bryan, J. Phys. B **32**, L93 (1999).
[14] A. Zavriyev and P. H. Bucksbaum, in *Molecules in Laser Fields*, edited by A. D. Bandrauk (Marcel Dekker Inc., New York, 1994).
[15] R. Numico, A. Keller, and O. Atabek, Phys. Rev. A **56**, 772 (1997).
[16] T. D. G. Walsh, F. A. Ilkov, S. L. Chin, F. Châteauneuf, T. T. Nguyen-Dang, S. Chelkowski, A. D. Bandrauk, and O. Atabek, Phys. Rev. A **58**, 3922 (1998).