Above Threshold Dissociation of Vibrationally Cold HD^+ Molecules

P. A. Orr, I. D. Williams, and J. B. Greenwood*
School of Maths and Physics, Queen's University Belfast, Belfast BT7 1NN, United Kingdom

I. C. E. Turcu and W. A. Bryan
Central Laser Facility, CCLRC Rutherford Appleton Laboratory, Didcot, OX11 0QX, United Kingdom

J. Pedregosa-Gutierrez
National Centre for Plasma Science and Technology, School of Physical Sciences, Dublin City University, Dublin, Ireland

C. W. Walter
Department of Physics and Astronomy, Denison University, Granville, Ohio 43023, USA

(Received 17 November 2006; published 19 April 2007)

The experimental study of molecular dissociation of ${H_2}^+$ by intense laser pulses is complicated by the fact that the ions are initially produced in a wide range of vibrational states, each of which responds differently to the laser field. An electrostatic storage device has been used to radiatively cool HD^+ ions enabling the observation of above threshold dissociation from the ground vibrational state by 40 fs laser pulses at 800 nm. At the highest intensities used, dissociation through the absorption of at least four photons is found to be the dominant process.

DOI: 10.1103/PhysRevLett.98.163001 PACS numbers: 33.80.Wz, 39.90.+d

It has been recognized that intense femtosecond laser pulses have the potential to influence molecular systems in a way that is beneficial to fields such as quantum control chemistry [1] and the formation of molecular Bose-Einstein condensates [2]. For these applications to be realized, a fundamental understanding of how molecules interact with short intense light sources is essential. Naturally, the simplest molecules, ${H_2}^+$ and its isotopologues, have been the focus of intense theoretical and experimental study. This work has revealed a variety of mechanisms influencing molecular dissociation such as bond softening, bond hardening, zero-photon dissociation, and above threshold dissociation (see reviews [3,4]). The predominance of one of these mechanisms over the others is sensitive to wavelength, intensity, pulse length, and the vibrational state of the molecule. Despite this attention, ${H_2}^+$ continues to yield surprises and has been used recently to demonstrate how coherent nuclear wave packets can be formed, imaged, and controlled using ultrashort pulses [5].

In the above threshold dissociation (ATD) process, analogous to above threshold ionization, more photons are absorbed than are required to overcome the bond energy. Theoretically, ATD has been predicted to be the dominant dissociation mechanism for a wide range of intensities [6]. In a number of early experiments a small proportion of the dissociation products possessed higher kinetic energy releases which were attributed to ATD [7,8]. More recent work, which has been performed predominantly at 800 nm, has however failed to show any evidence for ATD despite continuing theoretical work that has predicted dissociation by 4 photons to be dominant for ground state ions [9].

The main reason for this anomaly is almost certainly due to the initial vibrational distribution found in experimental ${H_2}^+$ targets. Each of these levels will dissociate with a different energy release and their dissociation rates may differ by many orders of magnitude. There is no way of being absolutely sure what part of a spectrum arises from a particular vibrational level. With very high resolution, it is possible to identify contributions from individual energy levels [10], but even at moderate intensities overlap of additional processes and Stark shifting of the levels makes assignments uncertain.

There are two experimental methods for preparing ${H_2}^+$ ions, which result in different population distributions. An H_2 gas target can be used so that ${H_2}^+$ is produced by ionization on the leading edge of the laser pulse. This has been shown to predominantly populate lower vibrational levels and is sensitive to intensity and wavelength [11,12]. As a high intensity is required for this initial ionization, the ${H_2}^+$ is "born" into a strong field. Alternatively, an ${H_2}^+$ ion beam can be produced, typically in an electron discharge source, and then crossed with the focused laser beam [10,13–15]. As the ionization is caused by high energy electron impact, a wide range of vibrational levels are populated in a Franck-Condon distribution [16,17]. This method benefits from having the ionization and dissociation processes clearly separated, and as the dissociation products are traveling at keV energies, the neutral fragment from dissociation can be detected.

Because of the different vibrational populations of these techniques, the kinetic energy release spectra at 800 nm look very different. For the ion beam experiments, a low energy dissociation peak due to one photon bond softening

© 2007 The American Physical Society

of high vibrational levels is dominant. This mechanism is also present in the gas target studies, but a higher energy peak arising from two photon dissociation of lower vibrational levels is also apparent [13,18,19]. This peak is sometimes erroneously referred to as ATD even though two photons is the minimum number needed for dissociation of these vibrational levels. A third peak at energy releases in the range 3–10 eV is due to Coulomb explosion following ionization. If steps are not taken to separate the ionization and dissociation contributions, any high energy ATD that is present in the spectrum may be obscured by or confused with ionization.

Our experimental arrangement utilizes an ion beam approach in conjunction with an electrostatic ion storage device to trap ions for half a second. As $H_2{}^+$ and $D_2{}^+$ have no permanent electric dipole moment, their vibrational populations are frozen on these time scales. However, HD^+ does possess a small electric dipole moment resulting in a lifetime of about 60 ms for a $v = 1$ to $v = 0$ transition [20]. Using an initial Franck-Condon distribution for the vibrational levels [17] and the theoretical transition rates [20], we have determined that for a confinement time of 300 ms, 96.5% of the ions are in their vibrational ground state, increasing to 99.9% at 500 ms.

2 keV HD^+ ions produced from the source were mass selected with a bending magnet and steered into the ion storage device. This region was pumped to a base pressure of a few 10^{-10} mbar which rose to nearly 10^{-9} mbar during operation of the ion source. The device behaves as an electrostatic analog of a laser cavity and is similar to one developed at the Weizmann Institute [21]. At each end, four aperture plates with steadily increasing voltages are used as a planar mirror for axial reflection together with a single lens which provides radial confinement. With suitable potentials applied to the mirrors and lenses, stable trajectories are attained for ions injected close to the axis. Bunches of around 2×10^6 HD^+ ions were initially injected into the device by pulsing the high voltages applied to the entrance mirror plates. An ion would subsequently be lost if found on an unstable trajectory due to its initial conditions or from ion-ion or ion-background gas elastic collisions. Around 5%–6% of these initially injected ions survive for 500 ms.

In the field-free central region of the device, ions possess a 2 keV energy with trajectories close to the central axis. Pulses from a Ti:sapphire laser operating at 800 nm, 0.5 mJ, 40 fs, and a repetition rate of 1 kHz were focused into this region to interact with the ions. The laser was polarized linearly along the axis. Neutral H and D produced from dissociation were ejected, and their time of flight to a channel electron multiplier was measured. For a 1 eV total (center of mass) release energy, D products fell within the detector's solid angle if the angle between the internuclear axis and time of flight axis was less than about 20° which reduces to 10° for a kinetic energy release of 4 eV.

Time of flight spectra were acquired over 10 ms trapping time intervals up to 500 ms. Spectra obtained from dissociation of HD^+ ions for trapping times between 10–20 ms and 300–500 ms are shown in Fig. 1. For 10–20 ms, all the vibrational levels are still significantly populated and there is a single dominant component to the signal corresponding to one photon dissociation of vibrational levels around $v = 10$. This produces two main peaks due to release of D fragments in the forward and backward directions with two outer shoulders due to the H fragments. As all the products have laboratory velocities close to the initial beam velocity, the D products are more efficiently detected than H due to their greater laboratory kinetic energy. The H and D peaks are poorly separated as the ion kinetic energy distribution from the source is large. Peak widths of 30 ns full width half maximum indicate that the energy spread in the primary beam was 60 eV at 2 keV. For the 300–500 ms data which correspond to a ground vibrational state HD^+ population, a higher energy release is indicated by a larger peak separation.

The forward and backward contributions for 300–500 ms data have been folded into one to improve the statistics in Fig. 2. One spectrum was obtained with the laser focused onto the ions at a maximum intensity of 10^{15} W cm^{-2} [Fig. 2(b)], while for the other a larger volume of ions was irradiated by a lower intensity of 5×10^{12} W cm^{-2} [Fig. 2(a)] using an off-focus beam. These spectra contain both H and D fragments, but D dominates. At the top of the graphs, the expected positions of these fragments due to absorption of integer numbers of photons for both H and D are displayed. For the lower intensity [Fig. 2(a)], there is a low energy release corresponding to absorption of 2 photons. In contrast, at the higher intensity [Fig. 2(b)], the largest peak is due to the release of D

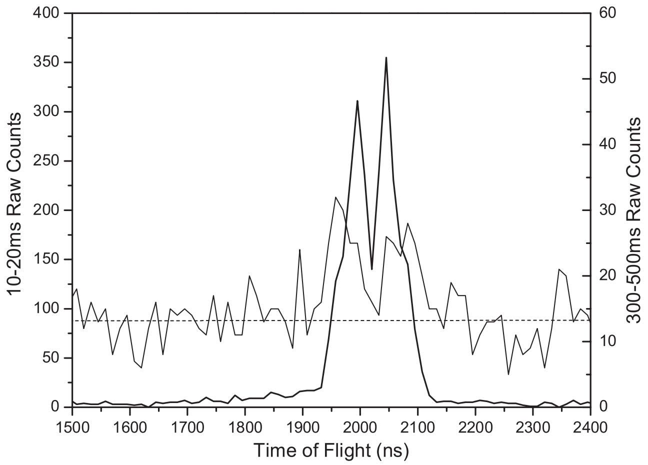

FIG. 1. Raw time of flight spectra for dissociation of HD^+ by 800 nm, 40 fs, 10^{15} W cm^{-2} laser pulses for times 10–20 ms (thick line) and 300–500 ms (thin line) after its formation. The dashed horizontal line indicates the average background level for the 300–500 ms data.

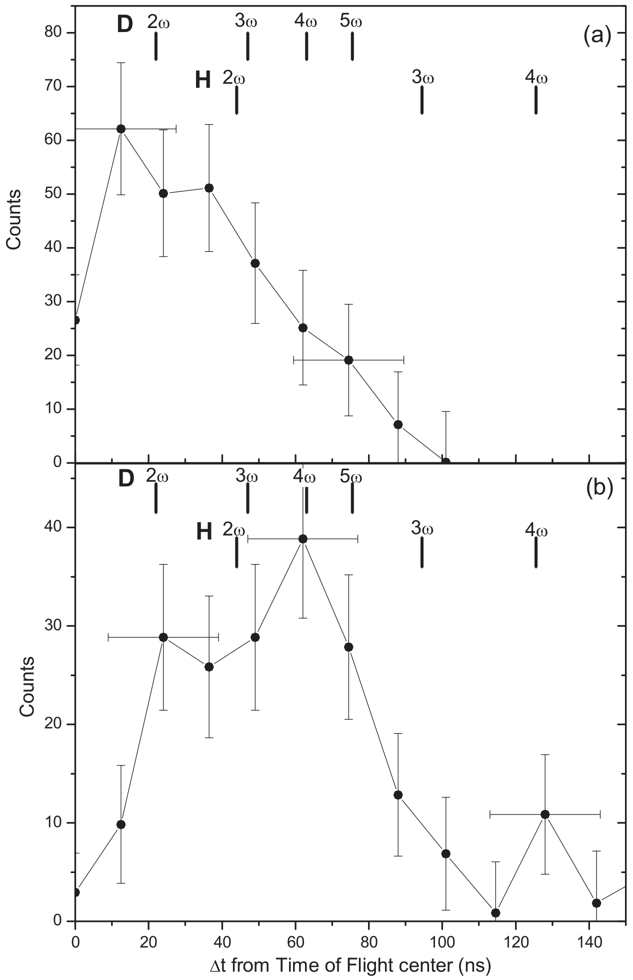

FIG. 2. Center of mass frame time of flight spectra in the interval 300–500 ms after the ions have been trapped for off-focus, (a) 5×10^{12} W cm^{-2}, and on-focus, (b) up to 10^{15} W cm^{-2}, interactions. Forward and backward components have been summed to improve statistics. Vertical error bars indicate statistical uncertainties at the one sigma level while horizontal error bars indicate the effect of the ion energy spread on the spectrum. Lines between points are drawn to guide the eye. Vertical lines mark the expected positions of D and H fragments due to absorption of an integer number of photons by molecules in an unperturbed ground vibrational state. These correspond to total kinetic energy releases in the center of mass frame of: $2\omega - 0.43$ eV, $3\omega - 1.98$ eV, $4\omega - 3.53$ eV, $5\omega - 5.08$ eV.

fragments following absorption of 4 or 5 photons. The equivalent contribution from H fragments can be seen as a small peak at 130 ns.

Theoretical calculations for dissociation of H_2^+ without ionization effects have been made under similar laser conditions by Peng *et al.* [9] who performed direct integration of the time dependent Schrödinger equation using a two state model with the internuclear axis fixed along the laser polarization direction. They predicted that for intensities up to 5×10^{12} W cm^{-2} dissociation from the ground vibrational state would occur via a 2 photon dissociation process, while for intensities in the range $(0.5\text{–}1.0)\times 10^{14}$ W cm^{-2} a 4 photon ATD process would dominate. However, there are few theoretical studies of HD^+ even though the difference in symmetry compared to H_2^+ and D_2^+ introduces some interesting differences. If we consider the dressed field approach [22] to the laser interaction with HD^+, the light field-molecule system can be represented by the field-free potential energy curves of the ground $1s\sigma_g$ and first excited state $2p\sigma_u$, dressed by a large number of photons, with states separated by one photon energy. This forms a series of diabatic curves shown in Fig. 3. For H_2^+, due to parity considerations, coupling only occurs between curves differing in odd numbers of photons. There is no such restriction for HD^+ as its wave function is not symmetric about the internuclear midpoint. As the electric field of the laser increases, strong mixing of the two states leads to a large number of avoided crossings in the adiabatic limit. This disparity between H_2^+ and HD^+ is discussed by Datta *et al.* [23] who demonstrate different dissociation processes between the two at a wavelength of 330 nm.

For HD^+ to absorb 4 or 5 photons, the ground vibrational state has to couple to the $2p\sigma_u$ state dressed by 5 or 6 photons (Fig. 3). As the nuclei move along one of these dissociating curves, they may reemit photons due to

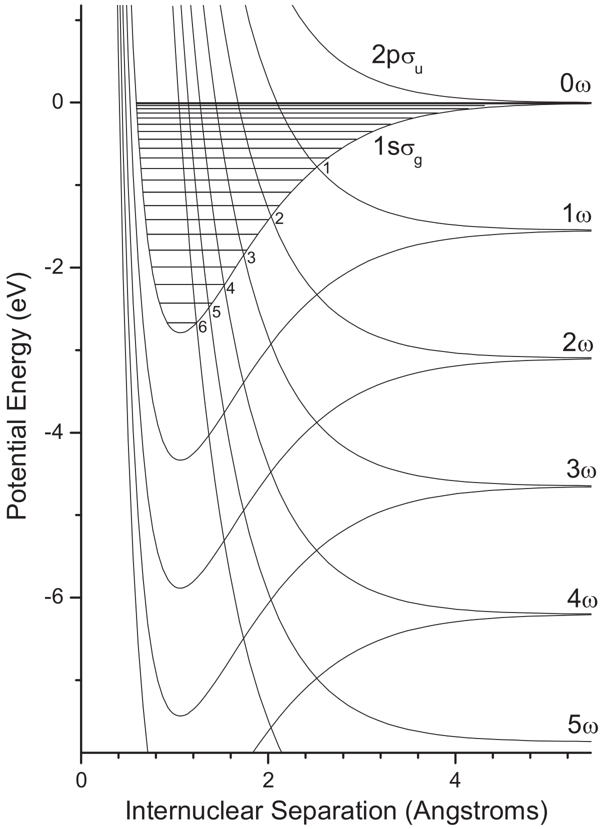

FIG. 3. Diabatic dressed state potential energy curves for HD^+ at 800 nm. Horizontal lines indicate the vibrational energy levels of the electronic ground state.

avoided crossings (e.g., dissociation on the 5 photon curve followed by emission of 1 photon at 2.5 Å). However, the initial coupling to the ground vibrational state will only occur at higher intensities, as seen from the differences between Figs. 2(a) and 2(b). Although the number of counts for the lower intensity data is comparable to the high intensity results, this actually corresponds to a considerably lower signal rate given that a much larger volume of ions was being irradiated. Our observation of a two photon process at low intensity agrees with the predictions of Peng *et al.* [9], with dissociation through tunneling to the 3 photon curve followed by one photon emission being the probable mechanism.

In conclusion, using a linear electrostatic ion storage device, we have dissociated ground state HD^+ ions using 40 fs, 800 nm laser pulses with a maximum intensity of 10^{15} W cm^{-2}. Under these conditions the molecule dissociates primarily by absorption of at least 4 photons. This is conclusive experimental evidence for above threshold dissociation in HD^+. In contrast to previous experimental work in ${H_2}^+$ which suggested that ATD provides a minor contribution, our results show that high energy release can be the dominant dissociation process. This is of significance for the use of femtosecond lasers in chemical control, as more energetic fragments produce different reaction rates. In the future, this technique could enable studies of carrier-envelope phase effects in the control of dissociation of the ground state of HD^+ [24] as has been recently demonstrated for double ionization of H_2 [25].

This work has been supported by the Engineering and Physical Sciences Research Council (UK), the Higher Education Authority (Rep. of Ireland), and the International Research Centre for Experimental Physics at Queen's University Belfast. The experiment was carried out at the ASTRA laser facility, Rutherford Appleton Laboratory (UK).

---

*Corresponding author.
Email address: j.greenwood@qub.ac.uk

[1] T. Brixner and G. Gerber, Chem. Phys. Chem. **4**, 418 (2003).
[2] B.L. Brown, A.J. Dicks, and I.A. Walmsley, Opt. Commun. **264**, 278 (2006).
[3] A. Giusti-Suzor, F.H. Mies, L.F. DiMauro, E. Charron, and B. Yang, J. Phys. B **28**, 309 (1995).
[4] J.H. Posthumus, Rep. Prog. Phys. **67**, 623 (2004).
[5] J. Mckenna, W.A. Bryan, C.R. Calvert, E.M.L. English, J. Wood, D.S. Murphy, I.C.E. Turcu, J.M. Smith, K.G. Ertel, O. Chekhlov, E.J. Divall, J.F. McCann, W.R. Newell, and I.D. Williams, J. Mod. Opt. (to be published).
[6] A. Giusti-Suzor, X. He, O. Atabek, and F.H. Mies, Phys. Rev. Lett. **64**, 515 (1990).
[7] P.H. Bucksbaum, A. Zavriyev, H.G. Muller, and D.W. Schumacher, Phys. Rev. Lett. **64**, 1883 (1990).
[8] B. Yang, M. Saeed, L.F. DiMauro, A. Zavriyev, and P.H. Bucksbaum, Phys. Rev. A **44**, R1458 (1991).
[9] L. Y. Peng, I. D. Williams, and J. F. McCann, J. Phys. B **38**, 1727 (2005).
[10] D. Pavičić, T. W. Hänsch and H. Figger, Phys. Rev. A **72**, 053413 (2005).
[11] X. Urbain, B. Fabre, E.M. Staicu-Casagrande, N. De Ruette, V.M. Andrianarijiaona, J. Jureta, J.H. Posthumus, A. Saenz, E. Baldit, and C. Cornaggia, Phys. Rev. Lett. **92**, 163004 (2004).
[12] A. Requate, A. Becker, and F.H.M. Faisal, Phys. Rev. A **73**, 033406 (2006).
[13] I.D. Williams, P. McKenna, B. Srigengan, I.M.G. Johnston, W.A. Bryan, J.H. Sanderson, A. El Zein, T.R.J. Goodworth, W.R. Newell, P.F. Taday, and A.J. Langley, J. Phys. B **33**, 2743 (2000).
[14] P.Q. Wang, A.M. Sayler, K.D. Carnes, J.F. Xia, M.A. Smith, B.D. Esry, and I. Ben-Itzhak, J. Phys. B **38**, L251 (2005).
[15] I. Ben-Itzhak, P.Q. Wang, J. Xia, A.M. Sayler, M.A. Smith, K.D. Carnes, and B.D. Esry, Phys. Rev. Lett. **95**, 073002 (2005).
[16] G.H. Dunn, J. Chem. Phys. **44**, 2592 (1966).
[17] Z. Amitay, A. Baer, M. Dahan, J. Levin, Z.Vager, D. Zajfman, L. Knoll, M. Lange, D. Schwalm, R. Wester, A. Wolf, I.F. Schneider, and A. Suzor-Weiner, Phys. Rev. A **60**, 3769 (1999).
[18] T.D.G. Walsh, F.A. Ilkov, and S.L. Chin, J. Phys. B **30**, 2167 (1997).
[19] C. Trump, H. Rottke, M. Wittmann, G. Korn, W. Sandner, M. Lein, and V. Engel, Phys. Rev. A **62**, 063402 (2000).
[20] Z. Amitay, D. Zajfman, and P. Forck, Phys. Rev. A **50**, 2304 (1994).
[21] M. Dahan, R. Fishman, O. Heber, M. Rappaport, N. Altstein, D. Zajfman, and W.J. van der Zande, Rev. Sci. Instrum. **69**, 76 (1998); D. Zajfman, O. Heber, L. Vejby-Christensen, I. BenItzhak, M. Rappaport, R. Fishman, and M. Dahan, Phys. Rev. A **55**, R1577 (1997).
[22] R.J. Glauber, Phys. Rev., **131**, 2766 (1963).
[23] A. Datta, S. Saha, and S.S. Bhattacharyya, J. Phys. B **30**, 5737 (1997).
[24] V. Roudnev, B.D. Esry, and I. Ben-Itzhak, Phys. Rev. Lett. **93**, 163601 (2004).
[25] M.F. Kling, C. Siedschlag, A.J. Verhoef, J.I. Khan, M. Schultze, T. Uphues, Y. Ni, M. Uiberacker, M. Drescher, F. Krausz, and M.J.J. Vrakking, Science **312**, 246 (2006).