Above threshold dissociation of vibrationally cold HD+ molecules

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Introduction

The behaviour of H_2^+, HD^+ and D_2^+ in intense, femtosecond laser fields has been the focus of extensive theoretical and experimental study as they provide a fundamental understanding of how molecules interact with short intense light sources. This is essential if the potential of these laser systems to influence chemical processes is to be realized. Experimental and theoretical work has revealed a variety of mechanisms influencing molecular dissociation such as bond softening, bond hardening and zero-photon dissociation (see reviews [1,2]). Despite this attention, H_2^+ continues to yield surprises such as how coherent nuclear wavepackets can be formed, imaged and controlled using ultrashort pulses, as has recently been demonstrated recently at the Central Laser Facility [3].

When atoms are exposed to sufficiently intense infra-red fields, absorption of many photons is required for ionization. However, as the emitted electron still experiences the laser field and the coulomb potential of the ion, it may absorb additional photons in a process known as above threshold ionization. The analogous process in molecular dissociation is above threshold dissociation (ATD). This has proved more difficult to observe experimentally in the H_2^+ model system. This is primarily caused by the range of vibrational states in which the molecular ion is initially formed. Each of these states may dissociate through different mechanisms with rates which may vary by many orders of magnitude.

Experiment

To advance experimental work in this field requires the initial target molecular ion to be prepared in a well defined quantum state rather than in, for instance, a Franck-Condon distribution produced from a plasma discharge ion source. We have achieved this using a novel linear electrostatic ion trap to confine the ions, allowing for radiative relaxation into the ground vibrational state. As H_2^+ and D_2^+ have no permanent electric dipole moment, their vibrational populations are essentially frozen. However, HD^+ does possess a small electric dipole moment resulting in a lifetime of about 60 ms for a $\upsilon = 1$ to $\upsilon = 0$ transition [4]. Using an initial Franck-Condon distribution for the vibrational levels [5] and the theoretical transition rates, 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.

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 [6]. 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. A cut-way of the interaction region is shown in Figure 1. With suitable potentials applied to the mirrors and lenses, stable trajectories are attained for ions injected close to the axis. 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. Pulses from the Astra TA1 laser operating at 800nm, 0.5 mJ, 40 fs, and a repetition rate of 1 kHz were focussed 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 (Figure 1).
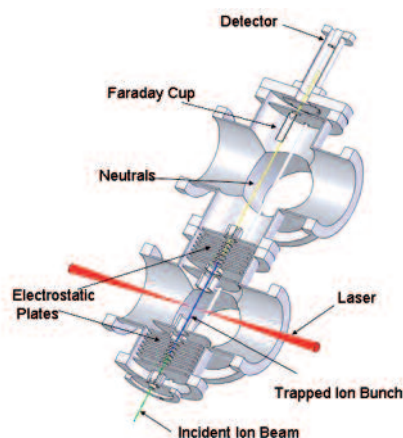

Figure 1. Schematic of the experimental interaction region cut-away along the ion beam axis.

Results

A time of flight spectrum obtained for dissociation of HD^+ ions trapped for less than 10 ms, at a relatively weak laser intensity of 5×10^{12} Wcm^{-2} is shown in Figure 2. At this time interval, 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 $\upsilon = 10$. This produces two main peaks due to release of D fragments in
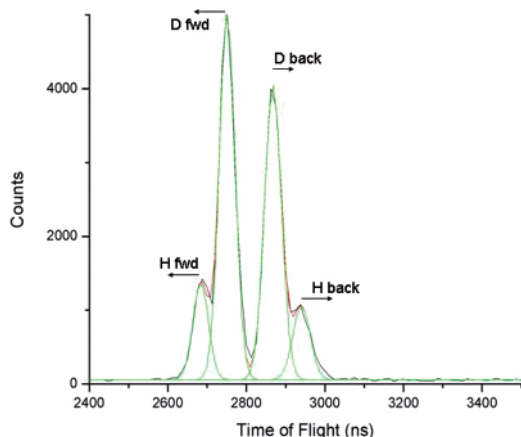
Figure 2. Time of flight spectrum obtained for dissociation of 1 keV HD$^+$ ions trapped for less than 10 ms. The forward (fwd) and backward (bwd) contributions of the H and D neutral fragments are marked.

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 energy, the D products are more efficiently detected than H due to their greater laboratory kinetic energy.

This signal reduces dramatically in strength as the ions are trapped for longer due to the finite lifetime of the ions in the trap and fact that as the ions become colder they become more resistant to the field induced dissociation. For trapping times greater than 300 ms (i.e. all ions in their ground vibrational state), the signal is barely distinguishable from background. However, when exposed to the highest intensity (up to 10^{15} Wcm^{-2}) the ions are observed to dissociate much more readily.

Discussion

Figure 3 shows the centre of mass time of flight spectrum of vibrationally cold ions for low (a) and high (b) intensities, with the forward and backward peaks folded about the mid-point to improve the statistics. At the top of the graphs, the expected positions of fragments due to absorption of an integer numbers of photons for both H and D is displayed. For the lower intensity (a), there is a low energy release corresponding to absorption of 2 photons. In contrast, at the higher intensity (b), the largest peak is due to the release of D fragments following absorption of 4 photons.

These results are consistent with theoretical calculations of dissociation of ground state H_2^+ made under similar laser conditions by Peng *et al.* [7] 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} Wcm^{-2} dissociation from the ground vibrational state would occur via a 2 photon dissociation process, while for intensities in the range (0.5-1.0) $\times 10^{14}$ Wcm^{-2} a 4 photon ATD process would dominate. The ATD mechanism appears to arise from the coupling of the ground electronic and vibrational state with the dissociative first excited state via 5 photons. As the molecule dissociates, one photon is then re-emitted to give net absorption of 4 photons.
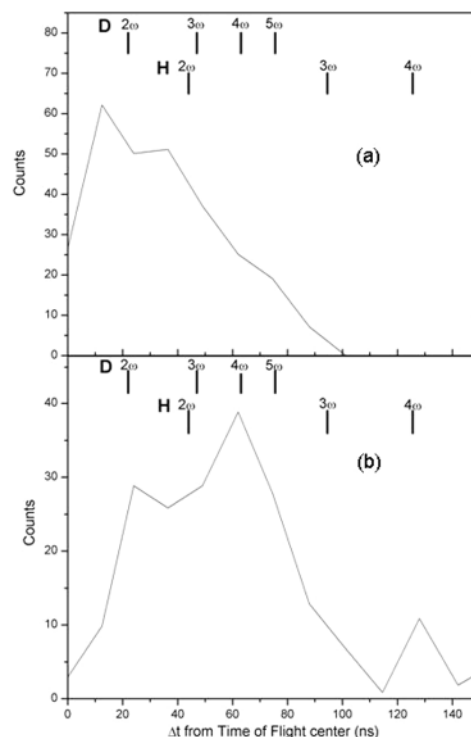

Figure 3. Center of mass frame time of flight spectra in the interval 300-500 ms after the ions have been trapped for off-focus, (a) 5×10^{12} Wcm^{-2}, and on-focus, (b) up to 10^{15} Wcm^{-2}, interactions. Vertical lines mark the expected positions of D and H fragments due to absorption of an integer number of photons by molecules in an unperturbed ground vibrational state. These correspond to total kinetic energy releases in the centre of mass of: 2ω - 0.43 eV, 3ω - 1.98 eV, 4ω - 3.53 eV, 5ω - 5.08 eV.

Conclusions

We have demonstrated the use of an electrostatic ion beam trap in the study of molecular dissociation by intense, femtosecond laser fields. By trapping the ions for sufficiently long periods, an ion target in a well defined quantum state can be achieved and by detecting the time of flight of the neutrals produced, the energetics of the dissociation can be elucidated.

This result provides the first clear demonstration of molecular above threshold dissociation. It also shows that in this case, unlike above threshold ionization where the absorption of extra photons becomes less likely as the order increases, absorption of additional photons in ATD is the dominant process.

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