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FAST TRACK COMMUNICATION

Photodissociation of D_3^+ in an intense, femtosecond laser field

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Abstract

H_3^+ is the simplest triatomic molecule and plays an important role in laboratory and astrophysical plasmas. It is very stable both in terms of its electronic and nuclear degrees of freedom but is difficult to study in depth in the laboratory due to its ionic nature. In this communication, experimental results are presented for the strong field dissociation of the isotopic analogue D_3^+ , using 30 fs, 800 nm laser pulses with intensities up to 10^{16} W cm⁻². By employing a novel experimental set-up, ions were confined in an electrostatic ion trap so that dissociation of the molecule could be studied as it radiatively cools. It was determined that dissociation could only be observed for molecules in ro-vibrational states relatively close to the dissociation limit, while more tightly bound states demonstrated remarkable stability in even the strongest fields.

It has been nearly 100 years since the simplest polyatomic molecule, H_3^+ , was first observed in the laboratory by Thomson (1911). It has since been discovered in the interstellar medium, the auroras of gas giant planets and in supernovae remnants. In these environments, it plays an important chemical role as a proton donor, typically being formed through the exothermic reaction $H_2^+ + H_2 \rightarrow H_3^+ + H$. Given the practical and fundamental importance of this molecule, it is surprising that there is still much to be understood of its structure and dynamics. Due to its three-centre nature, theoretical methods continue to be challenged while traditional spectroscopic measurements typically have to be performed with ion beams of density many orders of magnitude less than a conventional gas target.

An extensive review of the general properties of the molecule was given by McNab (1995). It forms an equilateral triangle in its ground state, while a stable linear form has also been theoretically predicted but is yet to be confirmed

in the laboratory. The equilateral form of H_3^+ is very stable with a binding energy of 4.4 eV. Due to a two-electron closed shell configuration, the vertical excitation energy is about 17.5 eV in its equilibrium geometry (Isla and Alonso 2007), suggesting that excitation is not possible with conventional lasers. However, H_3^+ ion beams can be populated in highly excited ro-vibrational states, making subsequent photo-excitation more accessible. Using a CO₂ laser (tunable from 0.108 to 0.135 eV), Carrington *et al* (1982, 1993) were able to observe thousands of resonant transitions resulting in dissociation into $H_2 + H^+$. This was attributed to transitions between a dense manifold of ro-vibrational states, close to or above the dissociation limit. Dissociation via this channel was also achieved by Alvarez *et al* (2000) through excitation by 1.165 eV photons. Transitions between electronic levels were also observed experimentally by Bae and Cosby (1990) for photon energies from 2.5 to 4.5 eV. Although excitation of the molecule in its ground vibrational state was not possible,

more highly excited ro-vibrational levels were dissociated by one-photon transitions.

The behaviour of the simplest molecule H_2^+ in intense fields has been extensively studied and used as a benchmark for understanding strong field dissociation processes and developing theoretical methods (Williams *et al* 2000, Posthumus 2004, Pavičić *et al* 2005, McKenna *et al* 2008). In contrast, H_3^+ has received considerably less attention due to its additional complexity. Theoretical work has tended to focus on the mechanism of enhanced ionization using a linear geometry to reduce the dimensionality of the problem (Kawata *et al* 2001, Suzuki *et al* 2007). However, these studies are of limited use for comparison with potential experiments. The only theoretical study of the molecule in its equilibrium configuration used time-dependent density functional theory to determine the strong field response for photon energies greater than 5 eV (Isla and Alonso 2007). As yet, there has been no published experimental work on strong field dissociation of H_3^+ , although it should be noted that previous attempts have failed to observe any dissociation signal (Kieess *et al* 2008). The apparent stability of H_3^+ in strong fields has also been confirmed indirectly by a number of studies, in which it was found to be a significant product in short-pulse laser interactions with various hydrocarbons (Hoshina *et al* 2008).

In this report, an experimental study is presented, detailing the interaction of an intense ($>10^{14} \text{ W cm}^{-2}$) femtosecond ($1 \text{ fs} = 10^{-15} \text{ s}$) laser field with a D_3^+ ensemble confined in a linear electrostatic ion trap. In this storage device, the molecular ions were allowed to radiatively cool prior to the laser interaction from which neutral dissociation products were detected and kinetic energy releases were measured. The experimental set-up was previously used to perform the first study of strong field dissociation of vibrationally cold HD^+ (Orr *et al* 2007) and is described in detail in a recent publication (Alexander *et al* 2009). For the present work, D_3^+ ions were produced in an electron cyclotron resonance ion source and accelerated to 1 keV. The D_3^+ isotopologue was used in preference to H_3^+ to avoid contamination of the signal from the dissociation of HD^+ impurities. The D_3^+ beam was pulsed to generate an ion bunch of 5×10^5 ions for each trap cycle, which were introduced to the trap by lowering one of its electrostatic mirrors.

A Ti:Sapphire laser producing 30 fs, 4 mJ linearly polarized pulses at a central wavelength of 800 nm (1 kHz repetition rate) was crossed with the trapped D_3^+ ions. In this communication, the laser propagation direction is defined as the z -axis while the x -axis is parallel to the trap axis and hence the direction of the ion trajectories. A 25 cm focal length lens was used to focus the pulses and could be translated along the z -axis to vary the interaction intensity, allowing lower intensities to be probed for larger overlap volumes. At focus ($z = 0$), a maximum interaction intensity of $10^{16} \text{ W cm}^{-2}$ was achieved, which reduced to approximately 10^{15} and $10^{14} \text{ W cm}^{-2}$ at $z = 3 \text{ mm}$ and $z = 9 \text{ mm}$, respectively.

A channel electron multiplier located at a distance $x = 0.55 \text{ m}$ from the interaction point, was used to detect neutral products of the laser-induced dissociation. This allowed the break-up kinematics to be determined although contributions

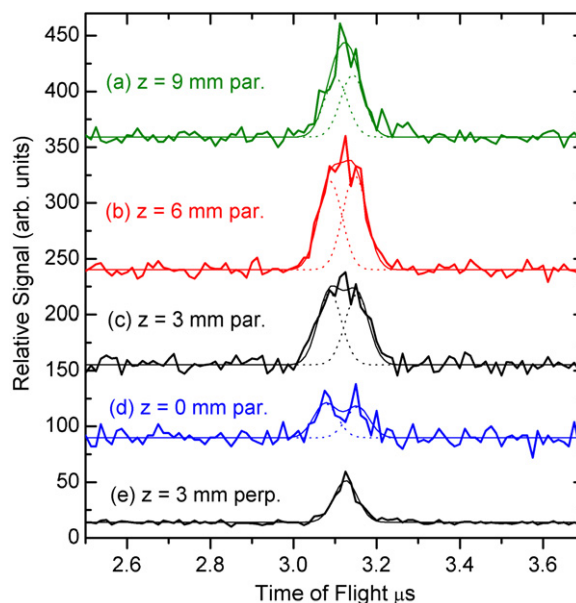


Figure 1. Time of flight of laser-induced neutral dissociation products from ions trapped for up to 0.5 ms. Plot (e) displays the signal obtained with the lens at $z = 3 \text{ mm}$ and the laser polarization perpendicular to the time of flight axis with a single Gaussian peak fitted to it (thin line). Plots (a)–(d) correspond to signal from different positions of the focusing lens as marked on the graph with the polarization parallel. Two Gaussians (dotted lines) and their sum (thin line) have been fitted to each (see text for more details). The baselines of (a)–(e) have been shifted for clarity.

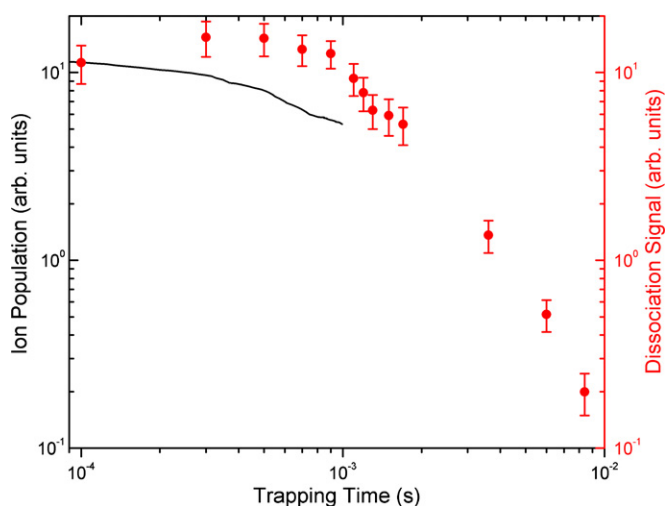
from D and D_2 neutrals could not be directly separated. Figure 1 shows time of flight spectra obtained at different z positions due to dissociation of ions which were trapped for up to 0.5 ms. Spectra (a)–(d) correspond to the laser polarization orientated parallel to the time of flight axis (x), while spectrum (e) was acquired with the laser polarization perpendicular to this axis. With the polarization perpendicular, the data can be fitted with a single Gaussian whose width is determined solely by the initial energy spread associated with the injected ions (about 35 eV). In all the plots where the polarization is parallel, the peak is broader demonstrating that neutral fragments are given momentum parallel and anti-parallel to the x -axis in the centre of mass frame. This suggests that dissociation along the laser polarization is preferred and that the dipole coupling is also greatest along this axis.

It can be seen that as the interaction intensity increases, there is a tendency towards an increase in break-up velocities. In order to characterize the fragmentation dynamics at each z position, two Gaussian peaks of 57 ns width (which corresponds to the instrumental width from (e)) were fitted to this data to model neutral emission towards and away from the detector. For each plot, the separations of these fitted peaks along with the total integrated signal are given in table 1.

Figure 2 shows how the integrated dissociation signal (circles) changes in the first 10 ms of confinement. The ion population in the trap is also plotted, as measured by the image charge induced by the ion bunch on a pick-up ring at the centre of the trap. The population is only displayed to 1 ms, as accurate measurements could not be made for longer

Table 1. Results from the fitting of two Gaussian peaks to the time of flight spectra shown in figure 1. The peak separation is used to calculate the total kinetic energy release ΔE for two possible dissociation channels.

z position (mm)	Maximum on-axis intensity (W cm^{-2})	Integrated signal (relative units)	Peak separation (ns)	ΔE (eV) $\text{D}_2 + \text{D}^+$	ΔE (eV) $\text{D}_2^+ + \text{D}$
0	10^{16}	7.4 ± 2.3	77 ± 8	0.31	0.08
3	10^{15}	14.6 ± 2.9	64 ± 6	0.21	0.05
6	3×10^{14}	18.8 ± 2.4	59 ± 6	0.18	0.045
9	10^{14}	14.6 ± 2.2	40 ± 5	0.08	0.02

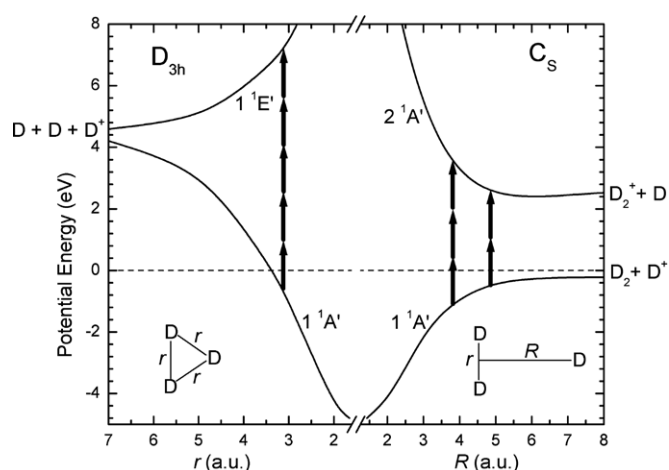
**Figure 2.** Variation of ion population (line), and laser-induced dissociation signal (circles) as a function of time in the trap.

(This figure is in colour only in the electronic version)

trapping times, due to bunch dispersion. In this interval up to 1 ms, the dissociation signal remains steady or even increases slightly, with the ratio of the signal to the overall ion population increasing by around a factor of 2. This is followed by a drop of two orders of magnitude to 10 ms with no observed signal beyond this.

For H_3^+ , the first few states corresponding to the vibrational bending mode have lifetimes of less than 10 ms, while the breathing mode is infrared inactive and decays via mode-mixing transitions with lifetimes of up to a second (Dinelli *et al* 1992). When compared with our results, these timescales suggest that the strong field dissociation is limited to excited states well above the lower vibrational states of D_3^+ . It appears that the population of states contributing to the signal initially increases due to fast radiative decay from even more highly excited states, but once the states themselves are radiatively depleted there is no signal from lower levels.

To determine the mechanisms contributing to the observed signal, the electronic states of D_3^+ associated with these dissociation limits must be considered. Figure 3 shows calculations by Talbi and Saxon (1988) of the potential energies associated with the ground and first excited states in isosceles (C_s symmetry) and equilateral (D_{3h}) triangle geometries. For the C_s geometry, the coordinate R is the separation of one nucleus from the mid-point of the other two, which are a distance r apart. For each R , the value of r is chosen to minimize the potential energy. As a result, for the

**Figure 3.** Electronic potential energy curves of the ground and first excited states for D_{3h} and C_s geometries (from Talbi and Saxon 1988). Possible multi-photon transitions at 800 nm (1.55 eV) are plotted as vertical arrows.

ground electronic state $1^1A'$, r changes from 1.65 a.u. at the minimum to 1.4 a.u. (corresponding to the D_2 ground state) at the dissociation limit.

The zero energy in figure 3 corresponds to the $\text{D}_2 + \text{D}^+$ dissociation limit with D_2 in its ground vibrational state. Ground and first excited states for D_{3h} and C_s symmetries are plotted on the left and right of the figure. For a C_s geometry, two- or three-photon transitions ($1^1A' - 2^1A'$) are possible from ro-vibrational states 0.5 and 1.1 eV below the dissociation limit, respectively. In a D_{3h} geometry, a five-photon transition ($1^1A' - 1^1E'$) is the lowest order excitation process from a bound ro-vibrational state. It should be noted that for dissociation on the $1^1E'$ or $2^1A'$ curves, photon re-emission is also possible. For example, a three-photon transition ($1^1A' - 2^1A'$) could be followed by re-emission of two photons when R approaches 4.8 a.u., returning to the $1^1A'$ ground state with sufficient kinetic energy to dissociate.

Table 2 shows the total kinetic energy released in the centre of mass (ΔE) for mechanisms open to detection since they produce a neutral product. As all the results demonstrate very low kinetic energy release, this would tend to rule out contributions from channel (4) even if distortion of the potential curves due to the strong field are considered. In contrast, the two-photon excitation channel (1) gives the appropriate ΔE and in agreement with our findings possesses a transition dipole moment along R . Modelling of the overlap between the laser focus and trapped ions indicates that the variation of the total signal observed with z in figure 1 and

Table 2. Possible dissociation mechanisms with corresponding total kinetic energy release ΔE (eV) in the weak field regime where the potential energy curves are minimally distorted.

Dissociation channel	Photon coupling	Net photons absorbed	Products	ΔE (eV)
(1) $1^1A' - 2^1A'$	2	2	$D_2^+ + D$	<0.1
(2) $1^1A' - 2^1A'$	3	3	$D_2^+ + D$	1.0
(3) $1^1A' - 2^1A' - 1^1A'$	3	1	$D_2 + D^+$	0.4
(4) $1^1A' - 1^1E'$	5	5	$D + D + D^+$	2.8
(5) $D_3^+(1^1A') - D_3^{2+}$	>17	>11	$D + D^+ + D^+ + e^-$	~9

table 1 is consistent with an intensity squared (two-photon coupling) dissociation rate.

At the maximum intensity, contributions to the signal from the dissociative ionization channel (5) are also possible. While more photons are required for a transition to a dissociative state, this does not need to be resonant with an integer number of photons as the ionized electron takes away the excess energy. Therefore, this channel is open to a larger number of ro-vibrational states. Although dissociative ionization will release a large amount of kinetic energy, this will be predominately given to the charged fragments, leaving the neutral D with a small kinetic energy in the centre of mass.

To summarize, the first strong field dissociation of D_3^+ or any of its isotopologues has been performed using a novel apparatus which enables the molecule to be studied as it radiatively cools. For up to 1 ms of ion confinement, it was observed that the molecular dissociation rate remained fairly constant despite the fact that ion population was decreasing. The signal then dropped dramatically to the extent that none was observed beyond 10 ms. This shows that, as previously unsuccessful studies have suggested, this molecule is very stable in a strong field and only relatively highly excited ro-vibrational levels of the ground electronic state can dissociate. For most of the interaction intensities studied, the kinetic energy release from the dissociation was found to be very small, increasing to some extent as the intensity reached the maximum of 10^{16} W cm⁻². From consideration of calculated electronic potential energy curves, this was found to be consistent with a two-photon transition between the ground and the first excited state in a C_s geometry, from ro-vibrationally excited states about 0.5 eV below the dissociation limit. This results in $D_2^+ + D$ fragments being released with a total kinetic energy of 0.1 eV or less. At the highest intensities studied, additional contributions from higher order transitions between these states or from dissociative ionization yielding $D + D^+ + D^+$ may also play a significant role, as evident from the recent measurements of Ben-Itzhak *et al* (2008).

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