

Intense-field dissociation of electrostatically trapped D_3^+ ions

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Introduction

The behaviour of fundamental molecules in intense laser fields has been an area of extensive study over the past two decades^[1]. Due to the increasing availability of Ti:Sapphire systems (such as Astra-Artemis at the CLF) experimenters can now routinely avail of short pulses (< 50 fs) of IR radiation at intensities >10¹⁴ W cm⁻². As such, a wealth of studies has provided significant insight into molecular ionisation and fragmentation processes in strong laser fields.

Naturally, the prototype for such studies has been the fundamental molecular ion H_2^+ and its isotopologues HD^+ and D_2^+ . When irradiated by these intense fs pulses, the resultant molecular dynamics are best understood in terms of the strong electric field mediated by the high photon flux, leading to highly non-linear phenomena such as bond-softening, charge-resonance enhanced ionisation and electron re-scattering. Although the behaviour of H_2^+ in intense fields continues to yield subtle surprises and new phenomena^[2,3], the ionisation and dissociation channels have been sufficiently characterised to enable temporally resolved studies of wavepacket dynamics^[4-7] and control of electron localisation^[8]. One key factor in understanding the energetics in the dissociation of the hydrogen molecular ion has been the ability to isolate, and study, a vibrationally cold target. This has recently been demonstrated at the CLF^[2,9] where a linear electrostatic device^[10] provided a means for storing HD^+ ions for up to a few seconds and enabling fs studies of a vibrationally pure ($v = 0$) diatomic target.

With these most fundamental diatomics so extensively studied and understood^[1], it is of interest to consider the simplest polyatomic molecule, H_3^+ . To date, there has been surprisingly little success in studying this system (or the isotope D_3^+) with intense fs pulses. More explicitly, prior to 2009 there have been no published reports of experimentally observed strong-field dissociation of H_3^+ , and it is worth noting that previous attempts by the authors and elsewhere^[11] have been unsuccessful.

In its ground state, H_3^+ forms an equilateral triangle and occupies a very stable potential well with a

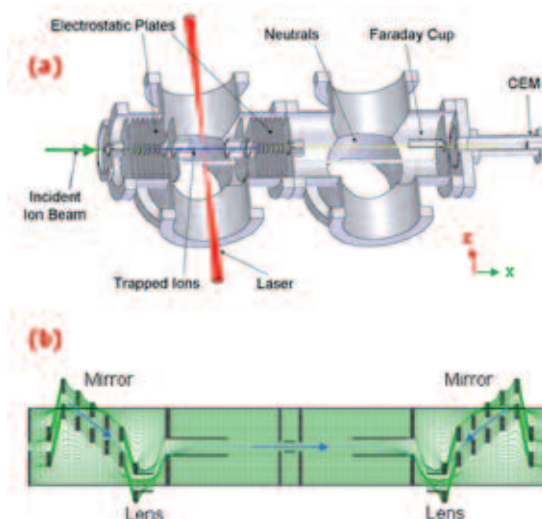


Figure 1. Linear electrostatic storage device used to prepare a D_3^+ target for intense-field studies. (a) cut-away of the device (b) potential surface experienced by a positive ion in the trapping region. Low-energy (1 keV) ions were confined in the electrostatic cavity, where electrostatic plates provide axial confinement (mirrors) and radial confinement (lens). Neutrals from the laser interaction will escape the trapping region and be detected at the channel electron multiplier (CEM).

binding energy of 4.4 eV. In its equilibrium geometry the first excited state is about 17.5 eV above the ground state and such a transition is inaccessible for conventional lasers. This provides some insight to the stability of H_3^+ in intense laser fields (photon energies of ~ 1.5 eV), which is further confirmed by experimental studies where H_3^+ was found as a stable by-product in intense field studies of hydrocarbons^[12]. Although H_3^+ is clearly very stable in its ground-state configuration, it is important to note that H_3^+ ion beams can be created in a range of highly excited ro-vibrational states. This makes subsequent photo-excitation more accessible (for more details see the discussion^[13] and references therein).

In this report, we will demonstrate how fragmentation of D_3^+ ions in intense laser fields has recently been observed and reported for the first time^[13] using our linear electrostatic storage device, where a pulsed beam of ions can be stored for a chosen time delay prior to laser-interaction.

Experiment

The experimental study was carried out at the Astra-Artemis facility, where intense fs pulses interacted with a D_3^+ ensemble confined in a linear electrostatic ion trap. The molecular ions were stored for a chosen time prior to the laser interaction, from which neutral dissociation products were detected and kinetic energy releases measured.

The experimental set-up was previously used to perform the first study of strong field dissociation of vibrationally cold HD^+ ^[2] and is described in detail in a recent publication^[10]. In brief, the ions are produced in an electron cyclotron resonance (ECR) ion source and a bending magnet is used to select the desired mass/charge ratio from the ions created. The D_3^+ isotopologue was chosen in preference to H_3^+ , as the latter would contain contamination of the beam from HD^+ impurities. The D_3^+ beam was accelerated to 1 keV to provide a continuous current of 30 nA and pulsed to generate an ion bunch of 5×10^5 ions for each trap cycle, which was introduced to the trap by lowering one of its electrostatic mirrors.

The electrostatic trapping region is analogous to a laser cavity, comprising two mirrors (each consisting of 4 plates) to provide axial confinement and two (einzel) lenses to provide radial confinement. We use a lens potential of opposite polarity to the ion charge to increase the stable phase space of trapped ions and thus improve the trapping efficiency^[10]. The D_3^+ ions were trapped and interrogated with the laser at a series of delay times. The neutral fragments from laser-induced dissociation will escape the electrostatic cavity and are detected at the channel electron multiplier (CEM).

The Ti:Sapphire laser at Astra-Artemis provided 30 fs, 4 mJ linearly polarised pulses at a central wavelength of 800 nm and 1 kHz repetition rate. The pulses were focussed down onto the D_3^+ ensemble in the field-free region of the trap, via a 250 mm focal length lens. The direction of laser propagation (z-axis in Figure 1) was aligned perpendicular to the direction of ion propagation within the trap (x-axis). The focussing lens was translated along the z-axis to vary the interaction intensity with the D_3^+ ensemble, allowing lower intensities to be probed for larger overlap volumes.

Results

Using this ‘Z-scan’ technique, a time-of-flight spectrum was obtained at each z position and the corresponding data has been plotted in Figure 2. The focal position was varied in 3 mm steps from $z = -9$ mm to $z = +9$ mm. At focus ($z = 0$), a maximum interaction intensity of 10^{16} W cm⁻² was achieved, which reduced to approximately 10^{15} and 10^{14} W cm⁻² (on-axis) at $z = 3$ mm and $z = 9$ mm respectively. As a rough guide, in the figure a sketch is given of the laser focus profile. The data was obtained for the first 500 μ s of trapping, corresponding to vibrationally ‘hot’ ions which may further decay if trapped for longer times.

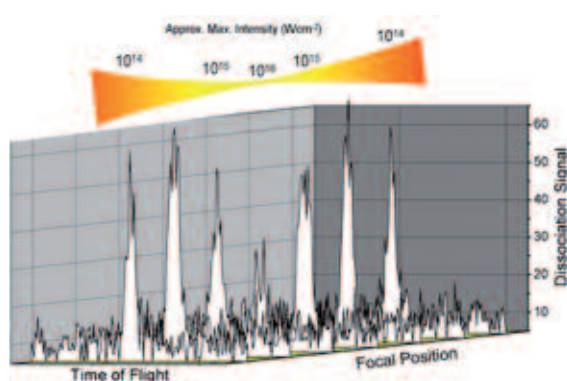


Figure 2. Z-scan of D_3^+ dissociation in intense fs pulses. The yield from neutral fragments is found as a function of the laser focus z-position. The focal position was varied from $z = -9$ mm to $z = +9$ mm, in steps of 3 mm. The ToF spectra are centred around 3.1 μ s, from the time of laser interaction.

When the D_3^+ target was positioned at the focus of the laser, a noticeable dip is seen in the dissociation signal. This may initially seem surprising, as the highest intensity is experienced at this point. However, even if the dissociation probability is saturated at this intensity, the small overlap volume between the laser focus and the ion beam will place a limit on the magnitude of the signal. When the focal position is at $z = \pm 6$ mm, there is a noticeable peak in the dissociation yield. Although the intensity has decreased at this point (compared to smaller z values), the volume has significantly increased. At $z = \pm 9$ mm, even though the overlap volume increases further, the signal begins to drop due to a decrease in intensity. By modelling the overlap of the focussed laser with the ion beam, the trend of the data has been found to be consistent with a multi-photon process of 2 or 3 photons.

The energetics of the dissociation process can also be deduced from the time-of-flight spectra, and this has been addressed in more detail elsewhere^[13]. Each spectra has a ToF profile with the width providing a measure of the energy release from the dissociation process. This is particularly evident at $z = 0$ in Figure 2, where two distinct peaks can be observed. The small separation between these ‘forward’ and ‘backward’ peaks implies a low energy release, and from Gaussian fitting to the ToF spectra the energy release upon dissociation is found to be small (< 0.2 eV). In the Z-scan data, the highest energy release is found at $z = 0$ and for higher z values (lower intensities) the energy release is found to decrease^[13]. This Z-scan data was taken over the first 500 μ s of trapping time, and provides a useful insight into the energetics of the dissociation process and the number of photons involved.

In a recent article^[13], the dissociation signal has also been studied as a function of trapping time. For interactions occurring during the first millisecond of trapping, the dissociation signal was found to remain relatively steady. Given the inevitable decrease in the number of trapped ions, this is suggestive of an increase in the dissociation probability. This was followed by a dramatic drop of two orders of magnitude between 1 and 10 ms with no observed signal beyond this.

For H_3^+ , the first few states corresponding to the vibrational bending mode have lifetimes less than 10 ms, while the breathing mode is infrared inactive and decays via mode-mixing transitions with lifetimes of up to a second^[14]. When compared with our results^[13], 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 of even more highly excited states, but once they themselves are radiatively depleted there is no signal from lower levels.

Conclusion

The first strong field dissociation of D_3^+ (or any of its isotopologues) has been performed. This work has been described in a recent publication^[13] and the technique (utilising the electrostatic storage device) has recently been described in detail in a special edition article^[10]. For most of the interaction intensities studied, the kinetic energy release from the dissociation was found to be very small and consistent with a 2-photon process. For up to 1 ms of ion confinement, it has been found that the molecular dissociation rate remains fairly constant despite the fact that ion population was decreasing^[13]. The signal then drops 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.

Acknowledgements

JD Alexander acknowledges funding from the European Social Fund. O Kelly and CR Calvert acknowledge funding from the Leverhulme trust. RB King and L Graham acknowledge funding from the Department for Employment and Learning (NI) and GRAJ Nemeth acknowledges funding from the STFC.

References

1. J. H. Posthumus, *Rep. Prog. Phys.*, **67**, 623 (2004).
2. P. A. Orr *et al.*, *Phys. Rev. Lett.* **98**, 163001 (2007).
3. T. Nubbemeyer *et al.*, *Phys. Rev. Lett.* **101**, 233001 (2008).
4. A. Rudenko *et al.*, *Chem. Phys.* **329**, 193 (2006).
5. J. McKenna *et al.*, *J. Mod. Opt.* **54**, 1127.
6. Th. Ergler *et al.*, *Phys. Rev. Lett.* **97**, 193001 (2006).
7. B. Feuerstein *et al.*, *Phys. Rev. Lett.* **99**, 153002 (2007).
8. M. F. Kling *et al.*, *Science* **312**, 246 (2006).
9. P. A. Orr *et al.*, CLF Annual Report p64 (2006/07).
10. J. D. Alexander *et al.*, *J. Phys. B.* **42**, 154027 (2009).
11. A. Kiess *et al.*, *Phys. Rev. A* **77**, 053401 (2008)
12. K. Hoshina *et al.*, *J. Chem. Phys.* **129**, 104302 (2008).
13. J. D. Alexander *et al.*, *J. Phys. B.* **42**, 141004 (2009).
14. B. Dinelli *et al.*, *J. Mol. Spectrosc.* **153**, 778 (1998).