

Steps towards vibrational control of D_2^+

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Introduction

In recent years, developments in ultrashort laser technology have lead to the production of coherent Infra-Red pulses with durations as short as a few cycles of the optical field (8/3 fs for 800nm radiation). This has enabled time-resolved studies of some of the fastest modes of molecular motion, such as the vibration of the fundamental hydrogen molecular ions H_2^+ , HD^+ and D_2^+ ^[1-5].

Experimentally, the deuterium molecular ion is the preferred target as it has the same theoretical accessibility as H_2^+ but executes slower nuclear motion (heavier nuclei), making it more accessible for time-resolved studies. In the past two years, experiments at this facility^[3,4] and elsewhere^[2] have demonstrated how a pump-probe arrangement can be used to initiate coherent vibrational motion in D_2^+ and, via fragmentation of the molecule, retrieve excellent temporal resolution of the motion of molecular motion.

The next step in these investigations is to seek control over the molecular dynamics. In last years' annual report^[6], it was shown that two different intense field techniques have been established for controlling the D_2^+ ion. First, it was shown both theoretically and experimentally that control could be exercised over the dissociation pathway of the molecular ion, via the net absorption of either 1 or 2 photons (i.e. the 1ω or 2ω pathways). This was achieved through the specific timing of the probe pulse interaction^[5,6]. Secondly, the more difficult task of exercising state-selective control over the bound vibrational motion was simulated. This method entailed the use of an additional "control pulse" interaction^[7] which acted to couple the two lowest electronic potentials of the D_2^+ system and cause population transfer between the bound vibrational levels. The outcome is a new vibrational distribution which dictates the subsequent motion of the molecule. To this end there have been a number of theoretical investigations which have sought to characterize the different conditions that can affect the new vibrational distribution created^[7-9]. Indeed in an article^[10] by T. Birkeland *et al.* in this years report, and in a recently published article by C. R. Calvert *et al.*^[11], numerical simulations have yielded a fascinating discovery of a plausible 'chessboard' effect that may also be sought in future experimental studies. However to date there has been no direct experimental evidence for state-selective control over the bound nuclear motion.

Control of a coherent D_2^+ vibrational wavepacket

When an intense ultrashort laser pulse interacts with a neutral D_2 target it can result in a tunnel ionization process where some population from the ground electronic state of the neutral molecule is projected to the lowest electronic state of the molecular ion, the bound $1s\sigma_g$ potential; a schematic of this initial wavepacket in D_2^+ is shown in figure 1 (a). For the pulse durations and

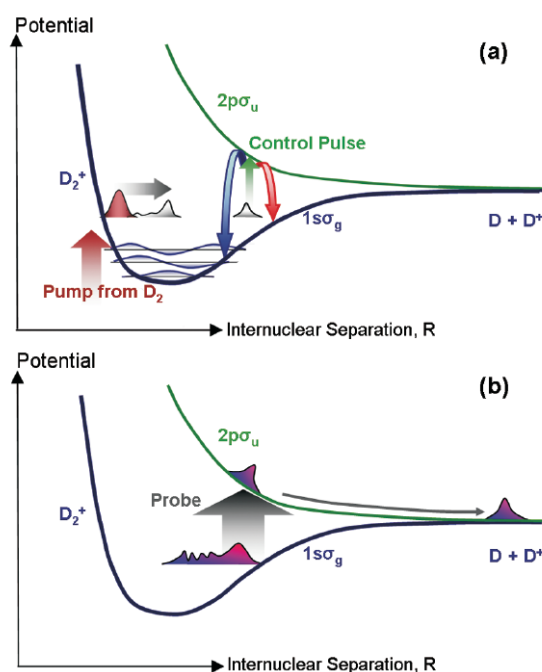


Figure 1. Sketch of pulse interactions with the deuterium molecular ion. (a) Initial creation of bound D_2^+ target via tunnel ionisation from the ground state of D_2 . The initial probability density (shown as red) will then undergo field free motion (silver) across a range of 1 to 5 au. A delayed $1 \times 10^{14} \text{ Wcm}^{-2}$ control pulse (green arrow) changes the vibrational distribution via Raman-type transitions with the $2p\sigma_u$ potential (red and blue arrows). (b) The motion of the modified wavepacket is monitored through photodissociation of the molecule by a $4 \times 10^{14} \text{ Wcm}^{-2}$ probe pulse.

intensities in recent experiments^[3,4] this process was found to be well approximated by a Franck-Condon transition (see^[11] for a more complete discussion), creating a vibrational wavepacket in the molecular ion with a wide distribution of vibrational states.

The anharmonicity of the $1s\sigma_g$ potential means that all vibrational levels evolve at different frequencies, resulting in the wavepacket quickly dephasing within the first 100 fs. After some chosen time delay the control pulse is applied and the laser-induced coupling between the two lowest electronic states of D_2^+ allows for wavepacket transfer between the states while the system is subjected to the laser field. Population transfer between vibrational levels can then take place via Raman-type transitions between the two electronic states so that, following the control interaction, wavepacket population can end up in vibrational levels with either more energy (vibrational heating, red arrow) or with less energy (vibrational cooling, blue arrow).

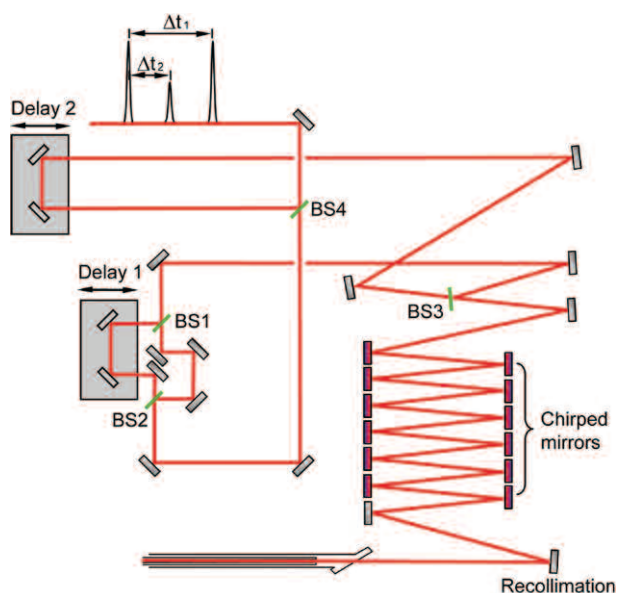


Figure 2. Schematic of three pulse interferometer for pump-control-probe experiments. Delay 1 was used to temporally separate the pump and probe pulses while delay 2 varied the time between the pump and control pulses for each experiment. Beam splitters (BS 1-4) were carefully chosen so that the experimental parameters closely matched previous theoretical simulations.

Changes in the vibrational distribution are highly dependent on the position of the wavepacket during the control interaction and hence on the timing of the control pulse^[7-11], thus this has been the main variable investigated in numerical simulations and has been shown to create drastic changes in the motion of the wavepacket within the bound potential.

Experimental arrangement

The experiment was carried out using the Astra TA 1 laser system. Transform-limited 30 femtosecond pulses produced by a Ti:Sapphire oscillator were spectrally broadened through self-phase modulation in an Argon-

filled hollow fiber and recompressed via a chirped mirror compression system to their transform limit of approximately 10 fs. Previously these pulses were split in two and separated temporally using a Mach-Zehnder interferometer, with sub-fs resolution^[12,13], but the requirement for a third pulse meant that a dual Mach-Zehnder arrangement was required as shown in figure 2. The beam splitters were carefully chosen to give pulses with peak intensities of $4 \times 10^{14} \text{ Wcm}^{-2}$ for the pump, $1 \times 10^{14} \text{ Wcm}^{-2}$ for the control and $4 \times 10^{14} \text{ Wcm}^{-2}$ for the probe pulse. The three pulses were then aligned into a time-of-flight mass spectrometer (TOFMS) and reflection focused (via an $f/5$ spherical mirror) onto a D_2 gas target under ultrahigh vacuum conditions.

The pulses were all linearly polarized, with the polarization vectors of the probe and control pulses aligned parallel to the detection axis of the TOFMS, and the pump pulse was aligned perpendicular to the detection axis. This ensured that dissociating fragments caused by the pump pulse were not detected. The remaining bound wavepacket was then subjected to a control pulse at fixed delay times, ranging from 18 to 40 fs after the original pump interaction. The effect of the control pulse on the wavepacket motion was monitored through the photodissociation (PD) of the molecule, as sketched in Figure 1 (b), which was induced by the probe pulse across a range of delay times. The charged products created by PD were extracted by a weak electric field (2000 Vm^{-1}) with their energy determined by their time-of-flight to a micro channel plate detector recorded on a fast digital storage oscilloscope.

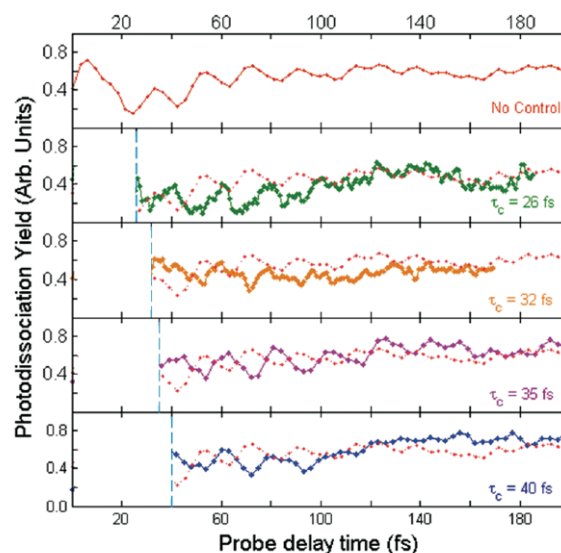


Figure 3. PD deuteron yields for pump-control-probe experiments with control pulse delays, $\tau_c = 26, 32, 35$ and 40 fs. For comparison, the experimental ion yield for a pump-probe investigation (i.e. no control) is also shown and superimposed on each control plot (dashed red).

Preliminary results

By integrating over the PD energy band (0.5-2.0 eV) a measure of the absolute dissociation yield was acquired. As PD is more probable at large internuclear separations, (R), this method provides information on the wavepacket

position within the bound potential and its corresponding dephasing as it evolves in time. Shown in figure 3 are the integrated photodissociation deuteron yields for a conventional pump-probe experiment (i.e. with the control-pulse path blocked), as well as experiments with control investigations, where the control pulse interacts with the system at specific delay times τ_c . The observed oscillating structure in each of the figures is the result of the wavepacket moving between small and large R. The amplitude of the oscillations gradually decreases as the wavepacket components dephase; the time with which this takes place depends strongly on the vibrational levels populated and their relative populations. Superimposed on each of the control plots is the time at which the peak of the control pulse is expected to interact with the system (vertical blue line) and the original pump-probe signal when there was no control interaction (dashed red) for comparison.

Preliminary analysis

It is quite evident that the structure within the dephasing region for each control delay has distinct differences to the ion yield structure observed when there is no control interaction. Differences are observed in the number of peaks recorded, their temporal position and their relative amplitude for each control delay. As each data point is averaged over 500 individual pump-control probe interactions, it is unlikely that this is the result of statistical processes.

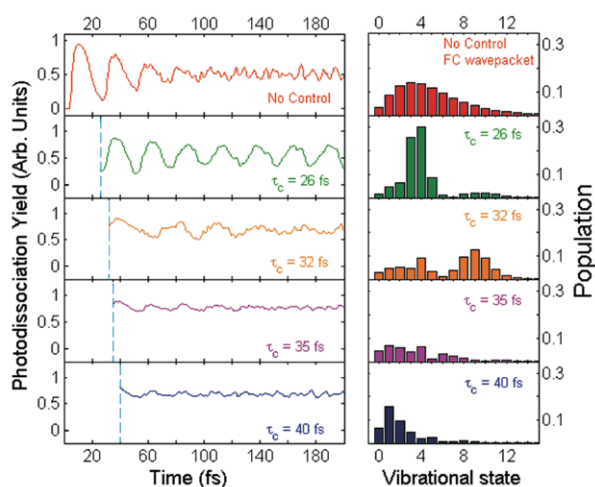


Figure 4. (Right) Predicted vibrational distributions following a $1 \times 10^{14} \text{ Wcm}^{-2}$ control interaction at delay time τ_c . (Left) The subsequent wavepacket motion was modelled and the photodissociation yield simulated across a 200 fs range for comparison with experiment in Figure 3.

Figure 4 displays the structure expected in the photodissociation yield, for simulations carried out over the same range of control delays as used in the experiment. The corresponding vibrational distributions from the model are also shown in the figure. One key control delay time is 26 fs where the wavepacket appears to be primarily distributed between the $v = 3$ and $v = 4$ vibrational levels, this results in a wavepacket that oscillates back and forth across the $1s\sigma_g$ surface at the beat frequency between these

eigenstates^[3], i.e. with a 24 fs period. Therefore the probe pulse enforces an enhanced PD sampling of this oscillating wavepacket when it is near its outer turning point and the PD yield correspondingly displays a periodic modulation of 24 fs. There is minimal dephasing here as these two states are so dominant in the wavepacket and the oscillations are observed well beyond 200 fs.

A quantitative comparison of the experiment and simulation will require a more detailed analysis. In particular, given the experimental uncertainty in the actual control pulse intensity and the well-known volume effect, careful modelling of the simulation parameters will be necessary. This work is ongoing.

Future work

While comparison of the dephasing region can provide preliminary evidence for the achievement of quantum control a definitive measure of the changes in the vibration distribution is more desirable. Therefore an improvement to the current method would be to extend the probe scans to larger delay times which would allow for the implementation of Fourier analysis to determine the dominant vibrational beats present in the wavepacket^[2,3], and hence provide an indication of the states which are populated.

With higher intensity probe pulses, direct observation of the changes in the $1s\sigma_g$ wavepacket motion could be achieved through Coulomb explosion imaging^[1,2]. This method of imaging involves ionizing the remaining binding electron from the molecule causing the two nucleons to repel each other through Coulomb repulsion. The kinetic energy that the deuterons have following the ionisation is dependent on their separation at the time of the ionizing event and hence provides an indication of their R-distribution.

Furthermore the effect of the CEP relationship and the control pulse duration could also be considered. It may be that pulses with shorter durations and with their CEP locked would be beneficial in future control investigations.

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