Imaging quantum vibrations on an ultrashort timescale: the deuterium molecular ion

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Abstract. The vibrational wavepacket revival of a basic quantum system is demonstrated experimentally. Using few-cycle laser pulse technology, pump and probe imaging of the vibrational motion of D₂⁺ molecules is conducted, and together with a quantum-mechanical simulation of the excited wavepacket motion, the vibrational revival phenomenon has been characterised. The simulation shows good correlation with the temporal motion and structural features obtained from the data, relaying fundamental information on this diatomic system.

1. Introduction

Time-resolved momentum imaging of the dynamics of small molecules using coherent optical sources is now within reach of short pulse laser science [1, 2, 3]. This area shows great promise for the control of molecular motion by an intense few-cycle laser field [4, 5, 6]. While a major drive for contemporary physics is to harness these techniques to control the reaction dynamics of large chemical and biological molecules [7], there is first a need to demonstrate the feasibility on smaller, more manageable and predictable systems.

The innovative idea of using coherently excited nuclear wavepackets (rotational [8, 9, 10, 11] and vibrational [4, 5, 6]) to image and control simple molecules has recently been implemented. Enforcing such control in a systematic manner may prove revolutionary for quantum chaos [11] and information studies [9]. It has other potentially exciting applications too, particularly for molecular bond energy transfer within larger systems [9]. The quantum nature of rotational wavepackets has successfully been imaged and control has been demonstrated for some small molecules (O₂ [9] and N₂ [10, 11]). Vibrational manipulation proves more difficult due to the faster motion of this degree of freedom although the feasibility of these experiments has been demonstrated for D₂⁺ [6] and HD⁺ [12].

We report here on an experiment on a target of D₂ molecules where few-cycle pump and probe laser pulses are used to coherently excite a superposition of D₂⁺ vibrational eigenstates and subsequently image their quantum revival [13] at later time. This motion is simulated with a quantum-mechanical model, illustrating the interference between different vibrational levels, eigenstates of the system.
Figure 1. (Colour online) Experimental imaging of the vibrational revival structure of coherently excited D$_2^+$ molecules as a function of pump-probe delay time. The signal is detected through the low-energy photodissociation (a), and high-energy Coulomb explosion (b), fragmentation of the molecules. The 2D projection onto the side plane is the integrated yield of the signal, for a given delay time, across the energy band. The colour represents the depth of the surface plot as indicated by the surface yield axis.

2. Experimental Method
The experiments were performed at the CCLRC Rutherford Appleton Laboratory laser facility (UK). This facility hosts a Femtolasers femtopower compact pro Ti:Sapphire laser system (central wavelength, $\lambda = 800$ nm) employing chirped pulse amplification with a multipass amplifier to deliver 30 fs, 0.8 mJ pulses at 1 kHz repetition rate. These pulses were further compressed to 10 fs duration by spectrally broadening them ($\Delta \lambda = 120$ nm) through self-phase modulation in a 1 m long argon-filled hollow core fibre and recompressing them temporally via reflection off 10 multilayered chirped mirrors, compensating for additional dispersive optics. Pump and probe laser pulses were obtained by a single pass through a Mach-Zehnder interferometer enabling variable delay of the temporal overlap with sub-femtosecond (300 as) resolution. A thin quartz half waveplate was used to orientate the polarization direction of the pump pulse orthogonal to the detection axis of the time-of-flight mass spectrometer (TOFMS) while that of the probe pulse was maintained parallel to this direction.

The TOFMS chamber housed an $f = 50$ mm spherical mirror which focussed the pulses onto a gas target of spectrally-pure D$_2$ molecules. The gas pressure in the system was maintained low to avoid space-charge effects. The ionization and fragmentation products from the interaction were extracted by a weak DC $E$-field (20 V cm$^{-1}$) through a small aperture of diameter 250 $\mu$m to selectively define the peak intensity region and avoid intensity averaging effects. The TOFMS, operated using Wiley-McLaren conditions for high energy resolution of products, contained a micro-channel plate detector system, the signal from which was collected using a fast digital storage oscillation. Each spectral data point is an average of the signal from 2000 laser shots. On-target pump and probe pulses had duration 13 fs measured by online intensity autocorrelation and calibrated using interferometric methods [14] with a xenon gas target. The intensities were determined as 0.8 PW cm$^{-2}$ and 0.6 PW cm$^{-2}$ respectively.
3. Results and Discussion

Upon interaction of the first (pump) laser pulse with a D\(_2\) neutral molecule, ionization excites the newly formed D\(_2^+\) molecular ion into a Franck-Condon distribution of its classical vibrational levels. Any dissociation from this first pulse goes undetected as its polarization direction lies perpendicular to the detection axis. These vibrational levels are quantized eigenstates of this simple diatomic system. A laser pulse of duration shorter than the vibrational period of the molecule (20 fs for D\(_2^+\) \(v = 0\) level), as used here, will excite these states coherently and initially in phase with one another. The resultant nuclear wavepacket, a superposition of these states, is hence created as a well defined structure localized at small internuclear separation, \(R\), reflecting the equilibrium distance of the neutral molecule. As time progresses the states of differing vibrational period, due to the anharmonicity of the D\(_2^+\) potential well, dephase with respect to one another, and the regular structure of the wavepacket breaks up. Using the probe pulse in this experiment, the localization of the wavepacket is measured by imaging it at relatively large \(R\). This is done through two channels: (i) photodissociation, when the molecule is near the outer turning point of its bond separation, resulting in low energy D + D\(^+\) fragments, and (ii) Coulomb explosion, imaging the wavepacket across a range of \(R\) with the appearance energy of the high energy D\(^+\) + D\(^+\) fragments reflecting the bond distance at the time of breakup \((E_{\text{frag}} \propto 1/R)\) [15].

Presented in figure 1 are experimental results from the direct imaging of the D\(_2^+\) bound nuclear vibrational wavepacket. The results from (a) photodissociation, and (b) Coulomb explosion imaging, are recorded with a delay between the pump and probe laser pulses in the range 400 – 700 fs. One can see from the data a slow build up in the oscillation of the D\(^+\) yield which dissipates again after 600 fs. This indicates an increasing localization of the vibrational wavepacket as the oscillation builds up which then recedes as it becomes delocalized once more. This oscillation corresponds to the first quantum revival of the D\(_2^+\) system where the different vibrational levels get into phase with each other as before, reconstructing the original wavepacket created at time \(t = 0\). Later revivals may be found at multiple times of the revival period. The period of the individual oscillations correspond to the vibrational period for the system, of
the order of 20 - 25 fs as the lowest states are the most highly populated (Franck-Condon distribution).

In figure 2 the motion of the wavepacket is simulated. Here, a coherent superposition of $D_2^+$ vibrational eigenstates, which may be described by the Fourier expansion:

$$\Psi(R,t) = \sum_v a_v \psi_v \exp^{-iE_v t/\hbar},$$

is plotted ($|\Psi(R,t)|^2$) as a function of time. In equation (1), $v$ is the vibrational quantum number of the excited eigenstates $\psi_v$, $E_v$ the eigenvalues of these states, $t$ their time evolution, and $a_v$ the overlap integral of each state with the $D_2 v = 0$ state.

In figure 2(a), at short times, the structured movement of the wavepacket is clearly visible as it oscillates across the potential well while simultaneously dephasing and becoming irregularly spread. Figure 2(b) shows the same wavepacket at a later time relating to the first revival as imaged experimentally. The re-creation of a well-defined wavepacket at a time of 580 fs is prominent reproducing well the time dependence observed by the experiment. Furthermore the structural features of the simulated revival mirror those of the imaged revival extremely well with the asymmetry in its buildup and dephasing fully predicted.

4. Conclusion
Using an extremely powerful pump and probe imaging technique, the quantum revival of a $D_2^+$ wavepacket has been imaged with high resolution. This revival structure gives fundamental information on the $D_2^+$ molecular ion, characteristic of the period and population of its coherently excited vibrational states. This work also illustrates the current capacity of short pulse laser science to image the smallest and fastest vibrating molecular systems, albeit a hydrogenic isotope.

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