Revival of a rotational wavepacket initiated by ultrafast impulsive alignment

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Introduction

Presented here is a study of the revival of a rotational wavepacket in deuterium observed in a pump-probe experiment, which demonstrates impulsive alignment of the molecule to the laser field polarization direction. The polarization angle of the ultrafast pump pulse was rotated, causing impulsive alignment of the molecule to this axis. While cooling translational degrees of freedom in atoms has been demonstrated (from magneto-optic traps[1] to Bose-Einstein Condensates[2]), and optical lattices can be generated to introduce regular crystal-like structure into a large number of atoms, such manipulation is rather more difficult with molecules. The complex level structure reflects extensive nuclear and electronic degrees of freedom. However, following original suggestions of Friedrich and Herschbach[3], and Seideman[4] two methods have been demonstrated[5] to spatially align an ensemble of molecules using linearly polarized laser fields.

Adiabatic alignment occurs when a laser pulse much longer than the rotational period of the molecule is used. The molecule can adiabatically adjust to the changing potential energy created by the interaction of the anisotropy of the molecular polarizability with the electric field vector of the laser. The long laser pulse causes the molecules to align their most polarizable axis along the laser polarization direction and can generate a high degree of uniformity of laser-molecule alignment. However, the molecules adibatically adjust to the laser field, so alignment only exists while the laser pulse is 'on', typically pico- to nanoseconds, which will non-perturbatively distort the molecules under observation.

The alternative method, 'impulsive alignment' creates a superposition of rotational eigenstates that continue to evolve long after the initial interaction. In the present work, a linearly polarized few-cycle pulse (FCP) is employed to produce the impulse, which is far shorter than the natural rotational period of the molecule under investigation. The FCP coherently imparts angular momentum while the molecules remain essentially stationary. This rotational 'kick' towards the polarisation direction produced by the FCP transfers significant population from the rotational *J*-states populated at room temperature to higher lying *J*-states. As the molecules are free to rotate after the pulse has gone, this alignment is short-lived as the phases of the eigenstates continue to evolve.

As we have recently demonstrated for a coherent superposition of vibrational states[6] an analogous coherent superposition of rotational states can 'revive' or rephase some time after the initial impulse. The full revival of this rotational wave packet occurs at integer multiples of the rotational period $T_o = h/2B_o$ where B_o is the rotational constant. Further periodic rephasing occurs at a half and a quarter of the rotational period.

While the revival of rotational wave packets has been thoroughly investigated in CS_2, O_2, N_2[7], and I_2[8] by a number of groups, the rotational period of these molecules is such that a 40-60 fs pulse can resolve the rotational motion. These heavier molecules have rotational periods of the order of picoseconds, e.g. for N_2 $t = 8.462$ps, which diabtically align to the laser pulse. In the present work, we investigate the rotational behaviour of the deuterium molecule which has a natural period of 550fs. It is therefore necessary to employ a FCP to resolve the rotational dynamics of an ensemble of such molecules. By investigating both the rotational and vibrational dynamics of a diatomic molecule we hope to be able to precisely manipulate larger systems.

Experimental Configuration

The laser used was a Ti:Sapphire ($\lambda = 800$ nm, 1 KHz) at Astra TA1 of the CLF. Using an argon filled hollow fibre, pulses are spectrally broadened then compressed via a set of 10 chirped mirrors (see ref[6] for further details). The pump and probe pulses were produced by passing the beam through a Mach-Zehnder type interferometer. The two beams were identical and colinear. One arm of the interferometer incorporated a Newport translation stage, interfaced to our data acquisition system which enabled the high resolution (~1/3 fs) variable time delay. A SHG autocorrelator was used to measure a pulse length of 13fs arriving at the interaction region. The focused intensities of the pump and probe beams were 0.6 PWcm^{-2} and 0.8 PWcm^{-2} respectively, estimated by measuring the ionization of xenon[9].

The beams entered a time-of-flight mass spectrometer (Wiley McLaren configuration), where they are focused into the interaction region using a reflective f/5 optic. D_2 gas is present as a diffuse target, as are molecular ions (D_2^+) and ionic fragmentation products (D^+), all generated by the focused laser pulses. The D_2^+ ions are generated

thermally (≈1/40 eV), thus reveal little about the rotational state of the ensemble. However, photodissociation (D^+ + D) is highly sensitive to the orientation of the internuclear axis. By extracting the energetic photodissociation fragments through a 250 micron aperture, a precise gauge of the degree of alignment of the ensemble is obtained. Therefore, by rotating the polarization of the pump pulse with respect to the vertically polarized probe pulse for a range of pump-probe delays, we are able to map the rotational wavepacket set up in deuterium by a 13fs pulse.
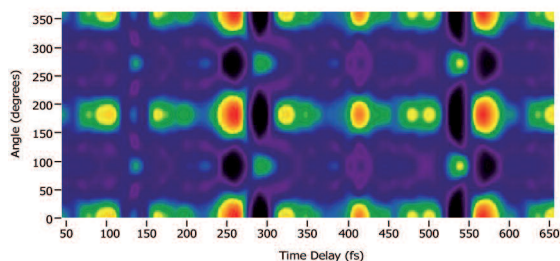

Figure 1. "Quantum carpet" simulation for deuterium. The probability distribution of the rotational wavepacket is represented as a colour map - black lowest, blue mid, red highest. Clearly apparent are the rotational revivals for alignment angles 0-360° as a function of time delay. Full revival occurs at 550 fs, and half revival at 270fs.

Simulation of Rotational Wavepacket Dynamics

A numerical simulation was performed by considering a linear molecule exposed to a nonresonant linearly polarized laser field[5]

$$\vec{E}(t) = \hat{\varepsilon} E_0 f(t) \cos \omega t$$

where $\hat{\varepsilon}$ is a unit vector along the pump polarization direction. E_0 is the field amplitude, $f(t)$ is the pulse envelope, and ω is the laser frequency. The laser pulse shape is modelled using a $sech^2$, with a pulse duration of 12fs. The molecule is described as a rigid rotor with eigenstates denoted by quantum numbers J and M in the absence of the laser field. As the impulsive alignment of the molecule occurs over a short time, the time-dependent interaction potential generates a broad superposition of rotational eigenstates in the molecule

$$\Phi(R,t) = \sum_J a_J \phi_J e^{-iE_J t/\hbar}$$

where ϕ_J are the eigenfunctions for the rotational J-states. These eigenfunctions are a series of spherical harmonics. Rotational J-states each have a different period, and will revive when all states are back in phase. This occurs at multiples of the rotational period of the molecule $T_o = h/2B_o$ where B_o is the rotational constant.

The evolution of the rotational wavepacket in time for all polarization angles is shown as a so called "quantum carpet" in figure 1. Rich rotational structure is observed around 550fs (full revival) and 270fs (half revival) as adjacent minima and maxima of wavepacket amplitude squared, i.e. probability. At 0° and 180°, quarter and three-quarter revivals are present in the simulation as a minimum at 140fs and a maximum at 410fs respectively.

Interestingly, around the half and full revivals the phase of the preferred axis of the ensemble changes from 0° to 90° within 50fs. Such rapid dynamics are unresolvable with 40-60fs pulses, justifying our choice of pulse duration.

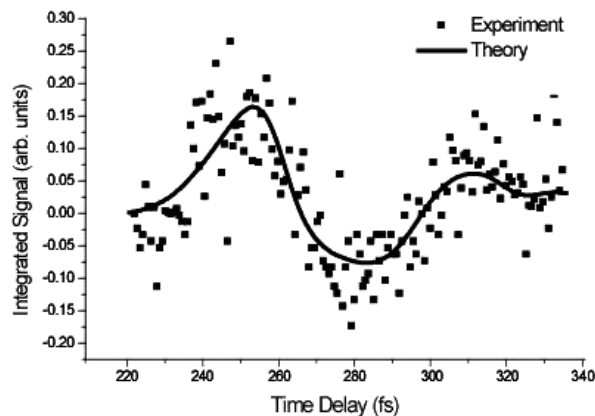### Experimental Realisation of Rotational Revivals

Figure 2. A half-period revival of D^+ ion signal for a pump pulse with vertical polarization (0°).

Experimental data were recorded around the half revival for a series of angles between 0° and 90°. The half revival was used for clarity, as vibrational revival structure is also observed at the time of the full revival[6]. A background subtraction was performed on the data, normalizing the isotropic regions to 1.

Figure 2 shows good agreement between the theory and experimental data taken with a 0° pump polarization angle. The theory curve is a slice taken from the quantum carpet in figure 1. The peak and trough structure are characteristic of a rotational half revival at 270fs delay time. This revival is shown in figure 3, demonstrating the change in structure as the polarization angle changes. A series of pump probe scans were taken to produce this experimental data, each with a different pump pulse polarization angle. The resulting scans are plotted together, shown with the corresponding theory from figure 1.
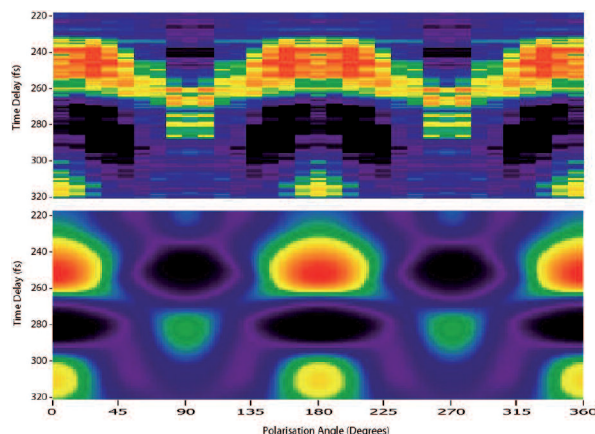

Figure 3. Theory (bottom) and experiment (0°-90° reflected) showing a rotational half revival around 270fs. Pump pulse polarization angle is along the x-axis for both maps.

In order to show how the alignment of the molecules changes with pump pulse angle, a series of polar plots are shown in figure 4. At 250fs, the molecules are aligned

along the axis of detection, and at 280fs they are aligned perpendicular to this axis. A good agreement can be seen between theory and experiment.
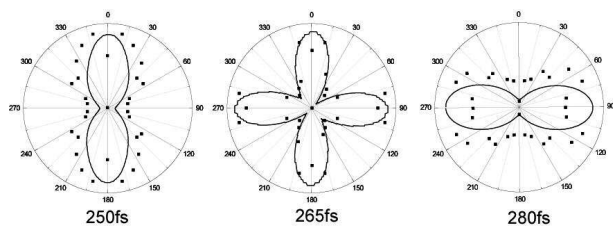

Figure 4. The polar plots show D$^+$ angular distribution at delay times within the revival. Experimental data is shown as points, and theory as a line. The axis of detection lies along θ = 0. Molecules are aligned at 250fs and antialigned at 280fs.

Conclusion

A pump and probe experiment using few cycle pulses has demonstrated molecular alignment through the observation of a rotational revival. The experimental results mapping the rotational wavepacket shown here are in good agreement with calculated quantum mechanical simulations. The ability to produce field free ensembles of aligned molecules will be advantageous for applications such as surface scattering research[10].

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