

Quantum engineering in molecules using intense Ti:Sapphire lasers

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Introduction

Engineering the quantum state of a molecule has many interesting and potentially important applications; the control of electron transport and chemical pathways, for example. Impediments to practical implementation include the limits of external control and the effects of noise on the system. The developments in ultrashort intense pulses, such as those created in the Astra facility, can address some of these challenges. In this work we present simulations that lead us to propose an experiment that employs intense Ti:Sapphire lasers to transfer the purity and coherence of their electromagnetic field to the matter field (wavefunction) of the molecule. The aim is to create a novel quantum state of the deuterium molecular ion.

The application of an intense laser, with pulses shorter than the relaxation/dissipation processes in a system, allows quantum manipulation before decoherence destroys the state. Intense infrared lasers have been shown to be effective in the coherent control of dissociation processes^[1] in the simple diatomics. The hydrogen molecule offers an ideal testing ground (for theory and experiment) for these ideas because of its simple structure. However, hydrogen groups and molecules have very rapid vibrations, and hence extremely short pulses are required to engineer these systems. For this reason, the heavier isotopes, with slower vibration, are more practical for experiments.

Coherence in deuterium

Proposals that have been made for coherent control of vibration in the deuterium molecular ion, all have the same underlying principles^[2]. Firstly, an ultrashort intense 'pump pulse', in this case a few-cycle Ti:Sapphire laser pulse (where $\lambda \sim 780$ nm) is used to induce tunnel-ionization of the neutral D_2 target. The application of an intense laser, with pulses shorter than the relaxation/dissipation processes in a system, allows quantum manipulation before decoherence destroys the state. In this process, the transition time (tunneling time) is short in comparison with the optical period, and essentially instantaneous with respect to vibration/rotation. In this article, the ionization from D_2 to D_2^+ will be approximated as a Franck-Condon transition (see^[3,4] for more details and discussion).

The result is that the vibrational wavepacket from the neutral ground-state, $X^1\Sigma_g$, is promoted to the D_2^+ , $1s\sigma_g$ -

potential. The wavepacket is, initially, a coherent (phase-locked) superposition of the vibrational modes of the $1s\sigma_g$ state. However, the different shape, and anharmonicity, of this potential leads to dephasing of the modes and dispersion of the wavepacket within a few vibration cycles. The wavepacket can only regain its original form whenever the phases of the modes match. This quantum 'revival', in the case of deuterium, arises approximately 550 fs after the ionization event. The effect has recently been measured and agrees remarkably well with simulations^[5].

Infrared control pulses

Suppose that a short 'control pulse' can be applied at a time, τ , following ionization by the pump laser, with the aim of altering the wavepacket (see figure 1). A practical approach is to use the same laser employed for the pump process, but at a much lower intensity so as to avoid dissociation or ionization.

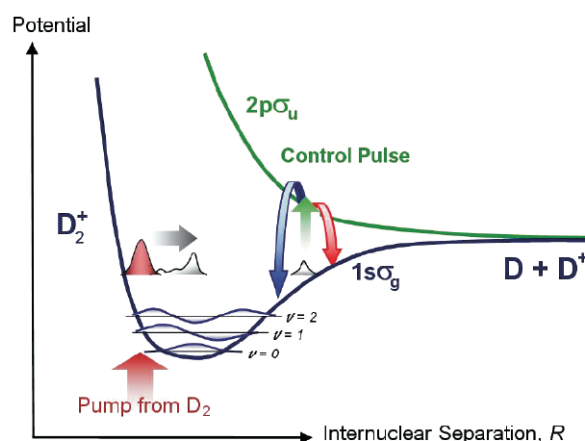


Figure 1. Schematic of intense-field vibrational-control of D_2^+ (not to scale). An ultrashort infrared pump pulse creates the molecular ion ($1s\sigma_g$) wavepacket in a coherent state by dynamic tunnelling ionization. The anharmonicity of the potential allows the modes to dephase and the wavepacket to move and disperse (silver arrow). The application of a secondary, control pulse initiates Raman transitions via the $2p\sigma_u$ virtual levels. The subsequent mode mixing can lead to vibrational cooling (blue arrow) or heating (red arrow).

Quantum chess board

For our simulations we suppose that the control pulse has a Gaussian envelope with full-width half-maximum, $W=5$ fs, and with an intermediate intensity, $I \sim 5 \times 10^{13}$ W cm⁻². We consider a single variable parameter, the control pulse delay, τ . In figure 2 we present the results of our simulations. The vibrational populations before and after the application of the control pulse are shown for a range of delay times: $0 \leq \tau \leq 600$ fs.

The colour density in Figure 2(a) represents the final population of the vibrational states with respect to the delay time. We highlight distributions corresponding to $\tau = 293$ fs and $\tau = 306$ fs as bar charts in figure 2(c) and 2(d), respectively. The initial probability distribution is shown in figure 2(b) for reference.

For short delays ($\tau < 50$ fs) the anharmonic correction is small, and dephasing is not significant. It appears that the control pulse spreads the population evenly with only slight enhancements and deficits. In the region $\tau = 100$ fs, enhancement is concentrated in a specific level (e.g. $v = 4$ at $\tau = 100$ fs). These effects are repeated close to the wavepacket revival ($\tau = 550$ fs), in a periodic pattern. The most striking feature of figure 2(a) is the alternating light and dark squares, suggestive of a ‘chessboard’, centred around $\tau = 300$ fs.

The origin of this feature is that, at a fractional revival time, the even and odd vibrational subsets will be in phase with each other separately. When a pulse is applied at this instant, the partial coherence can be exploited to produce strong interference effects.

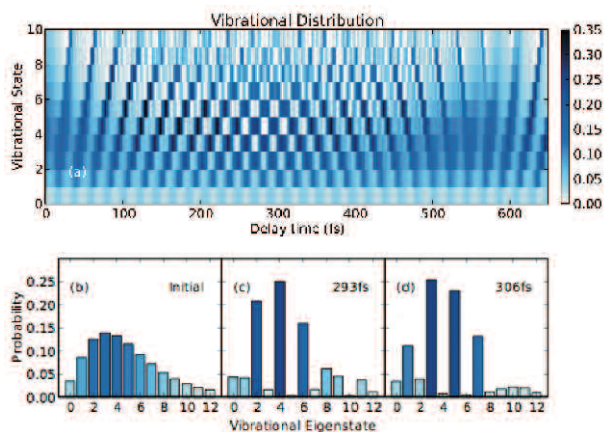


Figure 2. Vibrational redistribution following an ultrashort control pulse: $\lambda = 790$ nm, $W = 5$ fs, $I = 5 \times 10^{13}$ W cm⁻² for a range of delay times, τ . (a) The Colour density represents the relative population of each level. (b) Initial probability distribution. The ‘chessboard’ pattern (centred around the fractional-revival $\tau \sim 300$ fs) shows an interference pattern in which even- or odd-numbered states are annihilated. For $\tau = 293$ fs and $\tau = 306$ fs, individual plots (cuts through the colour-map) are shown in (c) and (d).

Discussion and conclusions

The action of the control pulse creates a Raman coupling of the vibrational levels with propensity rules $v \rightarrow v, v \pm 1$, favouring a dynamic Stark shift of the parent state ($v \rightarrow v$) and in-phase coupling to the nearest neighbour states. A simple model for the process is explained in more detail, along with a discussion of the numerical techniques for the wavepacket calculations, in the extended report^[4].

If destructive interference occurs for even v , then constructive interference will be observed for odd v . Conversely this process alternates after half a vibrational cycle, giving rise to the light and dark patterns in figure 2 as the even and odd states are enhanced and annihilated.

Experimentally, the effect might be best observed by the probe pulse creating a dissociative ionization process, with a spectral analysis of the deuteron energies. Certainly the experiment we describe is feasible at the limit of current technologies, and would make an interesting, albeit difficult challenge, for a laboratory study in the next few years.

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