Quantum revivals in ultrashort intense field dissociation of molecular ions

D S Murphy, C R Calvert, J McKenna, I D Williams and J F McCann

School of Mathematics and Physics, Queen’s University of Belfast, Belfast BT7 1NN, N.I.
E-mail: domhnall.murphy@qub.ac.uk

Abstract. Ultrashort (< 15 fs) high intensity (10^{14} – 10^{16} W cm^{-2}) laser pulses have provided novel methods for investigation of the dynamics of simple molecular ions such as H^{+}2 and D^{+}2. In this paper we report on simulations carried out for the D^{+}2 molecular ion, within the Born-Oppenheimer and two-state approximations. These simulations allow one to investigate the dissociation dynamics of the D^{+}2 molecular ion when subjected to such ultrashort, intense laser pulses. In particular, these simulations are compared to the results from recent pump-probe experiments, in which, the nuclear vibrational motion of D^{+}2 has been imaged. Simulations suggest that the nature of the dissociation process, be it 1- or 2-photon, may be influenced by the tuning of the pump-probe delay time.

1. Introduction
The interactions of intense, short laser pulses with matter have strong similarities with highly charged ion interactions. Both topics are concerned with quantum dynamics involving intense dynamic fields. Simple diatomic molecular ions, such as D^{+}2 and H^{+}2, provide an ideal test bed for the detailed study of quantum principles. The simplicity of these molecular systems make them particularly attractive for theoretical study [1, 2, 3, 4]. Likewise, this theoretical endeavour has been matched by a continual experimental effort to explore and understand these fundamental molecular systems [5, 6, 7].

Laser technology has advanced rapidly in the past decades, since its inception in the 1960s. Today, experimentalists routinely utilize ultrashort laser pulses (duration < 15 fs) and high intensities, frequently in the range 10^{14} – 10^{18} W cm^{-2} (equivalent to ~ 10^{10} V m^{-1}). Continual advancement means that we are currently on the threshold of attosecond (10^{-18} s) pulse technology [7], whilst the advent of free electron lasers promises to make the highest intensities more widely accessible. At such high intensities, dissociation and ionization processes occur readily. At the same time, the use of ultrashort femtosecond pulses allows one to probe the molecular dynamics on a timescale that is comparable to that of molecular vibrations (~ 25 fs for D^{+}2). The advent of control, at this level, will surely lead to a host of different applications relating to quantum control of chemical interactions, and within the exciting field of quantum information [8].

In this study we have employed wavepacket simulations in an effort to gain insight into the dissociation dynamics of the D^{+}2 molecular ion when subjected to such intense, ultrashort laser pulses. In particular, we have tried to interpret the results obtained in recent pump-probe experiments carried out on this molecular ion (W. A. Bryan et al, Manuscript in preparation), and shown in Fig. 2.
2. Theory and Numerical Model

In the experiments of interest one begins with a sample of neutral D$_2$ molecules. The initial 'pump' pulse, produced by a Ti:Sapphire laser ($\lambda \sim 790$ nm), leads to ionization of the D$_2$ molecule:

$$m\hbar \omega + D_2 \rightarrow D_2^+ + e^-.$$  \hspace{1cm} (1)

As this ionization process is highly non-linear in the field intensity, it is assumed that ionization occurs almost instantaneously, at the peak of the pump pulse, in a Franck-Condon-like process [7], indicated by the broken vertical arrow in Fig. 1. The situation is simplified as the D$_2^+$ molecular ion has only a single electronic level that is capable of supporting bound molecular states, that is the 1s$\sigma_g$ state (see Fig. 1). Furthermore, for low-frequency light, this lowest electronic level, along with the next lowest level (2p$\sigma_u$), are sufficiently well isolated from higher lying levels, such that it is reasonable to assume that the molecular ion will be restricted to these two lowest electronic levels - this is the two-state approximation.

![Figure 1](image.png)

**Figure 1.** Relevant electronic energy levels of the D$_2^+$ molecular ion - 1s$\sigma_g$ (——) and 2p$\sigma_u$ (—·—). The energy-shifted D$_2$ ground state (– – –) is included for reference.

Application of a second ('probe') laser pulse may lead to the dissociation (2) or dissociative ionization (3) of the D$_2^+$ molecular ion:

$$m\hbar \omega + D_2^+ \rightarrow D^+ + D (1s) ,$$

$$m'\hbar \omega + D_2^+ \rightarrow D^+ + D^+ + e^- .$$  \hspace{1cm} (2) \hspace{1cm} (3)

Employing the usual Born-Oppenheimer treatment for molecular systems, along with the two-state approximation, noted above, and neglecting rotational motion, the equations governing the nuclear motion of this system are given, in atomic units (au), by

$$-\frac{1}{2\mu} \frac{\partial^2 F_{g,u}}{\partial R^2} + E_{g,u} (R) F_{g,u} + \Omega (R,t) F_{u,g} = \frac{i}{\hbar} \frac{\partial}{\partial t} F_{g,u} .$$  \hspace{1cm} (4)

Here $\mu$ is the reduced mass of the two deuteron nuclei, $F_{g,u} (R,t)$ represent the time-dependent nuclear wavefunctions upon the 1s$\sigma_g$ and 2p$\sigma_u$ curves, respectively, and $E_{g,u} (R)$ represent the corresponding potentials (see Fig. 1). The term, $\Omega (R,t) = -\mathcal{E}_0 (t) \cdot d(R)$, represents the coupling between the electronic levels that is effected by the applied laser pulse (the 'probe'). Here $\mathcal{E}_0(t)$ is the E-field of the applied pulse, which is taken to have a Gaussian envelope with FWHM 15 fs, and $d(R)$ is the dipole coupling between the two electronic levels of interest [2].

The Hamiltonian for the system is represented upon a finite-difference grid with both electronic states represented over the interval 0.1-20 au, with a mesh of $N \approx 500$ finite-difference points. The wavepacket propagation is achieved by an eighth-order Taylor series propagator with a time step of $\Delta t = 0.01$ au.
3. Results from Simulations

3.1. Vibrational Revival

The experimental results in Fig. 2 relate to a pump-probe experiment, as outlined above, where the delay time between pump and probe pulses is varied. The figure shows the deuteron (D\(^+\)) dissociation spectrum obtained for varying delay times. The low energy band is attributed to the process of photodissociation (2), whilst the higher energy features arise from the secondary ionization of D\(_2\^+\), a process known as Coulomb explosion (3). Concentrating on the lower energy band, one can clearly see that the dissociation signal initially shows an oscillatory behaviour which dies away after \(\sim 100\) fs only to revive once again after \(\sim 500\) fs. This revival can be attributed to the dephasing and subsequent rephasing of the nuclear wavepacket as it oscillates in the 1s\(\sigma_g\) potential [4, 6].

![Figure 2.](image)

Integrated this photodissociation signal (lower band) over energy, gives the ion yield at each delay time. The integrated yield is plotted in Fig. 3 along with the results of our numerical simulation.

![Figure 3.](image)

3.2. Energy Spectra of Dissociating Deuterons

Extending the finite-difference grid, and allowing the simulation to propagate over a longer period of time, allows one to isolate and analyse that fraction of the nuclear wavepacket that is dissociating, and to determine the associated kinetic energy spectrum of the D\(^+\) fragments produced during the process of photodissociation. Fig. 4 shows the kinetic energy spectrum for two different values of the pump-probe delay time, namely 625 and 635 fs. Of the calculations considered by the authors, these particular values of delay time offer two of the most contrasting dissociation spectra, for two very similar delay times. One can notice clear differences in these two spectra. In particular, for a delay of 625 fs the dissociation yield arises, almost completely, via a net two-photon process. The distribution, in this instance, mirrors the initial Franck-Condon distribution of the wavepacket with the peak at \(\sim 0.5\) eV correlating to the \(\nu = 3\)
vibrational level of $D^+_2$, under absorption of two photons. By contrast, for a delay of 635 fs, dissociation is a mixture of one- and two-photon processes. It, therefore, appears that with adequate control of laser parameters, including intensity and pulse duration, one may exert a degree of control over the actual nature of the dissociation process (be it one- or two-photon dissociation) through varying the pump-probe delay time.

Figure 4. Kinetic energy spectra for the $D^+$ fragments arising through photodissociation. Spectra have been obtained for two different pump-probe delay times: 625 fs (left) and 635 fs (right). Note that, by changing the delay time one may affect the nature of the dissociation process, switching from 2-photon dissociation (625 fs) to a mixture of 1- and 2-photon dissociation (635 fs).

4. Remarks
In this study the theoretical model has been successfully employed in the simulation of quantum revivals. It has been verified that the dissociation signal exhibits a revival structure which may be attributed to the the dephasing and subsequent rephasing of the evolving nuclear wavepacket. Extending these wavepacket simulations allows one to investigate the kinetic energy spectrum of the dissociating products. Our numerical simulations suggest that the character of the dissociation process (i.e. one-photon or two-photon dissociation) is, also, affected by the delay time between pump and probe pulses. This allows one to exert a degree of control over the dissociation process by altering the delay time. For the example shown, it is seen that one can achieve a clean switch to an, almost exclusively, two-photon process.

Acknowledgments
The authors would like to thank W. A. Bryan et al for making their experimental data available, prior to publication. The experiments were undertaken with the financial support of the Engineering and Physical Sciences Research Council (UK). DSM, CRC and JMK would like to acknowledge funding from the Department for Employment and Learning (NI); DSM also thanks the Sorella Trust (NI) for its support.

References
[1] Sharp T E 1971 Atomic Data 2 119
[2] Bates D R 1951 J. Chem Phys. 19 1122
[3] Kawata I, Kono H and Fujimura Y 1999 J. Chem. Phys. 110 11152
[4] Feuerstein B and Thumm U 2003 Phys. Rev. A 67 063408
[5] Williams I D et al 2000 J. Phys. B : At. Mol. Opt. Phys. 33 2743
[6] McKenna J et al 2006 J. Mod. Opt. to be published
[7] Niikura H, Legare F, Hasbani R, Bandrauk A D, Ivanov M Y, Villeneuve D M and Corkum P B 2003 Nature 417 917
[8] Shapiro E A, Spanner M and Ivanov M Y 2003 Phys. Rev. Lett. 91 237901
Lee K F, Villeneuve D M, Corkum P B and Shapiro E A 2004 Phys. Rev. Lett. 93 233601