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Ultrafast coherent control and quantum encoding of molecular vibrations in D$_2^+$ using intense laser pulses

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Abstract. Intense, few-femtosecond pulse technology has enabled studies of the fastest vibrational relaxation processes. The hydrogen group vibrations can be imaged and manipulated using intense infrared pulses. Through numerical simulation, we demonstrate an example of ultrafast coherent control that could be effected with current experimental facilities, and observed using high-resolution time-of-flight spectroscopy. The proposal is a pump-probe-type technique to manipulate the D$_2^+$ ion with ultrashort pulse sequences. The simulations presented show that vibrational selection can be achieved through pulse delay. We find that the vibrational system can be purified to a two-level system thus realizing a vibrational qubit. A novel scheme for the selective transfer of population between these two levels, based on a Raman process and conditioned upon the delay time of a second control-pulse is outlined, and may enable quantum encoding with this system.
1. Introduction

Recent pump-probe experiments [1]–[9] have demonstrated the quantum character of the fastest vibrational motions in nature—the hydrogen stretch modes within a molecule. This has been confirmed with the simplest molecular system of this nature: the H$_2^+$ molecular ion. The larger reduced mass of the isotope D$_2^+$ and, consequently, longer vibrational period ($T_{\text{vib}} \sim 25$ fs) means that few-femtosecond, infrared (IR) pulses can probe the vibrational dynamics of this species. Thus, energy and coherence transfer from the laser to the molecule, and the coupling between the electronic and nuclear motions can be studied [3]–[14]. In this paper, we propose an experiment to manipulate the vibrational state on ultrashort timescales. Controlling the quantum nature of proton/deuteron dynamics could prove of fundamental significance in hydrogen-bonding systems, quantum control of simple chemical processes and possibly in primitive quantum information processing.

The possibility of using molecular vibration to encode quantum information has been, previously, studied. For example, [15, 16] outline how two different, IR-active, vibrational modes of the acetylene (C$_2$H$_2$) molecule may be used to represent a two-qubit system. They demonstrated that it is possible to carry out single- and two-qubit quantum gates by irradiating the molecule with specific laser pulses, designed using optimal control theory (OCT). More recently, the implementation of quantum logic using the vibrational eigenstates of simple diatomic molecules has been considered [17, 18]. These studies have considered a general diatomic system, rather than any specific implementation, and have focussed on how the accuracy of gates is influenced by different physical parameters. In addition, studies of the quantum control of vibrational [19] and rotational [20] wavepackets in simple diatomic molecules have been reported, from a quantum information perspective.

We suggest that the D$_2^+$ molecular ion offers a practical system to test these ideas, and one that is accessible to current experiments. Our simulations indicate that control is possible using a sequence of conventional IR laser pulses, from the same source. The principles of OCT are not invoked at any stage. Instead, we propose that conventional Gaussian pulses can be employed with frequency, intensity, duration and delay time between pulses chosen according to the manipulation desired. It is further proposed that the lowest vibrational states of the D$_2^+$ molecular ion may represent a useful realization of a vibrational qubit. The controlled manipulation of vibrational populations, within this two-level system, that could be adapted to quantum logic operations, is demonstrated.
2. Physical model

The physical processes in intense-field pump-probe experiments [1]–[9] on the deuterium molecule, can be summarized in the following reaction expressions:

\[
\hbar \omega + \text{D}_2(v_0) \rightarrow \text{D}_2^+(\{v\}) + e^-, \quad (1)
\]
\[
m \hbar \omega + \text{D}_2^+(\{v\}) \rightarrow \text{D}^+ + \text{D}(1s), \quad (2)
\]
\[
m' \hbar \omega + \text{D}_2^+(\{v\}) \rightarrow \text{D}^+ + \text{D}^+ + e^-, \quad (3)
\]

where \(\{n, m, m'\}\) are photon numbers. The pump process (1), illustrated in figure 1(a), strips an electron from the neutral \(\text{D}_2\). For infrared light, this ionization event is highly nonlinear in the field intensity and highly nonresonant in the photon frequency. It proceeds via a tunnelling mechanism, occurring almost instantaneously on the optical cycle and vibrational timescales. Consequently, the molecule orientation is approximately fixed and a Franck–Condon distribution of the \(\text{D}_2^+\) vibrational manifold, \(\{v\}\), is formed. The validity of the Franck–Condon approximation for this ionization event, (1), has not been fully established [21, 22], however, the temporal agreement observed between the current theoretical model and experimentally observed revivals [7, 8, 23, 24] support this conjecture. Following ionization, a second pulse can be applied leading to photodissociation, (2), and/or secondary ionization, (3), of the \(\text{D}_2^+\). In the present scheme, this second pulse plays the role of a ‘control’ pulse. The initial ionization step, (1), is strongly enhanced when the molecular axis is aligned parallel with the polarization axis of the pump pulse. The second pulse is chosen to be linearly-polarized along the same axis as the pump laser polarization. Provided the delay is short with respect to the rotational period \((T_{rot} \sim 350 \text{ fs})\), the orientation of the molecular ion will remain approximately parallel to the polarization direction of the second (control) pulse, and the dissociation fragments will be, predominantly, ejected along the laser polarization direction [7, 8]. Under such conditions, the nuclear dynamics can be effectively modelled as a one-dimensional (1D) system.

In the present scheme, the control pulse is intense, but not sufficiently strong to cause secondary ionization, equation (3). In practical terms this means that control pulse intensities lower than \(10^{15} \text{ W cm}^{-2}\) are considered. Furthermore the electronic dynamics, leading to dissociation, are considered within a two-state model, which is appropriate for IR light at high intensity (figure 1). Under such a two-state approximation one only considers the effect of the two lowest electronic levels (\(1s\sigma_g^+\) and \(2p\sigma_u^-\)—see figure 1(b)), with remaining levels sufficiently higher in energy as to be considered inaccessible [25, 26].

The equations governing the motion of this system are 1D and given, in atomic units (au), by

\[
-\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} F_{g,u}(R, t) + U_{g,u}(R) F_{g,u}(R, t) + \Omega(R, t) F_{g,u}(R, t) = i \frac{\partial}{\partial t} F_{g,u}(R, t). \quad (4)
\]

Here, \(\mu\) is the reduced mass of the deuterons, \(R\) represents the internuclear separation, and \(t\) the time. \(F_{g,u}(R, t)\) represent the time-dependent nuclear wavefunctions for the molecular ion, in
Figure 1. Energy levels for the $\text{D}_2/\text{D}_2^+$ system. (a) The nuclear wavepacket for the neutral $\text{D}_2$ molecule, in the $(1s\sigma_g)^2$ electronic state (dot-dashed line), makes a vertical transition, indicated by the broken vertical arrow, to the $1s\sigma_g$ electronic level of the $\text{D}_2^+$ molecular ion (full line). (b) The oscillating wavepacket (illustrated schematically) can be probed or manipulated by coupling to the $2p\sigma_u$ electronic level (broken line), leading to Raman transitions and/or dissociation.

the $1s\sigma_g$ and $2p\sigma_u$ electronic states, respectively. The potential curves are denoted by $U_g(R)$ and $U_u(R)$ (see figure 1, [27]). The term, $\Omega(R, t) = -\epsilon(t) \times d(R)$, represents the induced-dipole coupling. The dipole moment is denoted by $d(R)$ [28], while the control pulses have Gaussian envelopes with full width at half maximum (FWHM) equal to $t_w$, i.e.: $\epsilon(t) = E_0 \exp\left[-(4\ln2/t_w^2)(t - t_d)^2\right]\cos(\omega t)$. Here $t_d$ is the delay time between the centre of the control pulse being considered and the initial ionization step (1). The angular frequency of the applied field is $\omega$, and corresponds to a wavelength of $\lambda = 790$ nm. The laser intensity is denoted by $I$ and follows from the amplitude of the applied field, $E_0$.

The coupled differential equations, (4), are solved using a finite-difference scheme in $R$ for the Hamiltonian, and an eighth-order Taylor series method for the evolution operator [24, 29]. The initial conditions are (i) $F_u(R, 0) = 0$ and (ii) the spatial distribution $F_g(R, 0)$ given by the ground vibrational eigenfunction ($v_0$) of the $\text{D}_2$ $(1s\sigma_g)^2$ electronic potential, as shown in figure 1(a), and in keeping with the Franck–Condon approximation.

3. State-selective control of vibration

3.1. Selective population of vibrational states

In previous work, the possibility of vibrational cooling has been demonstrated [12, 13]. If the laser pulse is sufficiently short, the laser-induced dipole force can be applied as the molecule expands or contracts, adding or removing energy from the system. In this section, we briefly review these principles. We extend the ideas to study the coherence of this process and the application in a practical scheme. Finally, we carry out a study on further coherent manipulations, of the ‘cooled’ system, through the use of an additional control pulse. In our simulations, pulses are considered to have duration $t_w = 14$ fs and wavelength, $\lambda = 790$ nm, corresponding to current Ti:Sapphire lasers [7, 8, 29]. Figure 2 illustrates the vibrational
Figure 2. Vibrational population and probability density in $D_2^+$ for different delay times of the control pulse: $t_d = 20$ fs (left figure) and $t_d = 30$ fs (right figure). The pulses considered are Gaussian, of duration $t_w = 14$ fs (FWHM), wavelength $\lambda = 790$ nm and intensity $I = 2 \times 10^{14}$ W cm$^{-2}$. For $t_d = 20$ fs (left figure) the population becomes concentrated in the lower levels ($v = 0$ and 1). For $t_d = 30$ fs (right figure) the lower level populations are diminished, and the upper levels (e.g. $v = 11$) are increased. The colour density plots illustrate the time evolution of the probability density associated with the wavepacket, with colour scale running from red (high probability) to blue (low probability). These colour plots show the dissociation process (i.e. population escaping to large $R$) and the contrast in the vibrational amplitude after application of the two differently-timed pulses. For $t_d = 20$ fs one can also notice the periodic structures at small $R$ (dark red patches), indicating the oscillation of a localized wavepacket.
The application of an ultrashort, high-intensity pulse can cause, either, (a) cooling or (b) heating of the vibrational wavepacket motion. Application of the pulse as the wavepacket is moving in towards small separation, $R$, (i.e. as molecule is contracting) means that the proportion of the wavepacket promoted on to the repulsive $2p\sigma_u$ potential will be moving against a potential gradient and will, thereby, lose energy. In contrast, for a pulse applied as the molecule is expanding, the wavepacket gains energy.

It was suggested [12] that the cooling process could be attributed to the laser-induced (AC Stark effect) modification of the adiabatic potential curve. An alternative interpretation of the cooling mechanism based on a coherent process of curve jumping is suggested by the picture presented in figure 3(a). Dispersion (dephasing) will occur if $t_d > 100\text{ fs}$, but for shorter times the wavepacket is localized (quasiclassical) [3, 8, 10, 24]. If the control pulse is applied as the wavepacket is moving inwards (contraction), then a proportion of the wavepacket is transferred on to the upper, $2p\sigma_u$, potential. This fraction of the wavepacket is forced up a potential gradient, thereby losing energy, before being returned to the $1s\sigma_g$ potential, resulting in cooling. The slowing of vibrational motion on the $2p\sigma_u$ curve is due to the reduced shielding in this electronic state, leading to a slowing in the contraction of the molecular ion. An equivalent interpretation of vibrational heating is given in figure 3(b). The probe pulse is applied as the localized wavepacket is moving outwards (expansion). The wavepacket is promoted on to the repulsive $2p\sigma_u$ curve, whereon it accelerates before the field couples it back to the $1s\sigma_g$ state. In this case the reduction in shielding, associated with the promotion to the upper $2p\sigma_u$ level, allows the nuclei to repel each other further, imparting energy to the expansion. The success of this process relies upon the motion of the wavepacket being, essentially, ‘unidirectional’ for the duration of the pulse. For this reason, pulse duration must be considerably shorter than the vibrational period of the wavepacket ($\sim 25\text{ fs}$ for $D^+_2$). As such, this process is crucially dependent upon the use of ultrashort pulse technology.

Figures 2 and 3 have shown that the time delay of the control pulse ($t_d$) is the fundamental parameter controlling the cooling or heating effect. By carrying out similar simulations, for a range of delay times of this control pulse, some interesting effects have been observed. The results of this analysis are plotted in figure 4. Through appropriate choice of delay times, the selective population of different vibrational levels is made possible, and this appears to be particularly efficient for the lower vibrational modes. For example, applying our control
Figure 4. (A) Final vibrational state populations in the lowest vibrational levels \((v = 0 - 3)\), after application of the control pulse, for varying delay times. Control pulse is of duration \(t_w = 14\) fs, intensity \(I = 2 \times 10^{14}\) W cm\(^{-2}\) and wavelength \(\lambda = 790\) nm. The final population of the lowest vibrational eigenstates can be controlled through variation the time delay. Panels (B)–(D) are colour density plots indicating the wavepacket dynamics for three specific cases. The probability density, associated with the wavepacket, is represented by a colour scale running from red (high probability) to blue (low probability). Panel (B) indicates the wavepacket evolution with no pulse applied. Panels (C) and (D) indicate the wavepacket evolution for the specific delay times highlighted in (A), corresponding to vibrational population predominantly in the \(v = 0\) and 1 levels (C), and the \(v = 1\) and 2 levels (D). In both these cases the colour density plots illustrate clear beating patterns.

A pulse with \(t_d = 25\) fs leads to population being predominantly transferred into the \(v = 2\) level. Two interesting cases are highlighted in figure 4 and denoted by the letters C and D. Point C, corresponding to \(t_d \sim 18\) fs, produces an even division of population between \(v = 0\) and \(v = 1\), with some residual bound population (\(\sim 30\%\)) in the higher levels. In a similar way, one may obtain an even superposition of \(v = 1\) and 2, corresponding to point D, with only \(\sim 20\%\) of the bound population in other levels. In all cases, a fraction of the population will dissociate, resulting in a reduction in the sum total of the bound state populations (i.e. sum total of bound state populations <1).

The prospect of confining the population to a small subset of quantum levels is ideal for quantum manipulation. Isolating two or three vibrational levels, provides a quantum system with femtosecond switching time. In the next section, we demonstrate a technique for implementing operations on such a system.

We note, in the current theoretical model, no account is taken of the duration of the initial pump pulse, nor the rotation of the molecular axis. It is expected that inclusion of both of these effects will lead to a reduction in the effects demonstrated in this section and the subsequent section. Nonetheless, it is anticipated that, providing a sufficiently short pump pulse is utilized and delay times are restricted to \(t_d \ll T_{rot}\), then these effects should still be observable, although, possibly, with some attenuation. It is also noted that the two-state model,
upon which these simulations are based, will not take account of any dissociative ionization events, equation (3), that arise as a consequence of the control pulse. It is to be expected that any experimental realization of these principles will lead to some degree of dissociative ionization of the $D_2^+$ and, again, this process may lead to an attenuation of the effects demonstrated. However, for appropriately chosen intensity of the control pulse ($<10^{13}$ W cm$^{-2}$) the probability of dissociative ionization can be significantly reduced, meaning that the competition of these ionization processes should only result in a small effect.

### 3.2. Single qubit operations

Suppose the cooling mechanism has isolated the system into two eigenstates, analogous to a spin-1/2 qubit (point C in figure 4(A)). We show that this system in turn can be manipulated by the same IR pulses used in the initial stages. Let us consider level populations, the diagonal elements of the density matrix, $\rho_{00}$ and $\rho_{11}$. An IR laser pulse can be used to couple the states via a Raman process. Figure 5 shows how both $\rho_{00}$ and $\rho_{11}$ vary during a three-pulse sequence. Again, the first pulse ionizes the $D_2$ neutral, forming a Franck–Condon distribution of the $D_2^+$ vibrational levels, equation (1). The first control-pulse then produces the two-level system, with the delay time corresponding to point C in figure 4(A). This leads to an equal-weighting of $v = 0$ and 1, with some residual population in the higher levels. The second control pulse is chosen with duration $t_w = 20$ fs and intensity $I = 5 \times 10^{13}$ W cm$^{-2}$. The bandwidth of this pulse is of the order of the energy level splitting of the levels, thereby enhancing the Raman transition. For a pulse with $t_w = 20$ fs, the equivalent bandwidth is $\delta \omega = 4\sqrt{2\ln 2/\omega_0} \sim 0.005$ au, compared with the energy difference $\sim 0.0072$ au. Figure 5(a) shows the effect of applying this second control-pulse at $t_0 \sim 64$ fs. In this case, the majority of the population moves to the $v = 0$ vibrational level, almost exclusively from the $v = 1$ level. While the applied field causes population transfer between the higher vibrational levels at the same time, the two lowest levels appear to be quite well isolated. In contrast, figure 5(b) illustrates the effect of applying this second control-pulse at $t_0 \sim 74$ fs, leading to transfer from $v = 0$ to 1. Again, there is negligible depletion of the $v = \{0, 1\}$ subspace. The effect of this delay (of our second control-pulse) is to permit the controlled dephasing of the $v = 0$ and 1 vibrational levels, thereby, allowing one to control the relative population of these two vibrational states by varying the delay time at which this second, Raman-type pulse is applied.

Suppose the delay time of this second control-pulse is varied. The results of our calculations are summarized in figure 6. This figure shows the absolute population in the lowest vibrational levels ($v = 0–4$) that results from the application of the three-pulse sequence, exemplified in figure 5, with the delay time of this second control-pulse allowed to vary. The $x$-axis represents the delay time of the second control-pulse (relative to the initial ionization step, equation (1)); all other pulse parameters remain fixed. In each case the initial cooling pulse is used to move the system into an equal superposition of the $v = 0$ and 1 levels, corresponding to point C in figure 4(A). Appropriate choices of the delay time can effectively engineer the relative population of $v = 0$ and 1 levels.

Interestingly, the contrast seen in figure 6 can be improved by considering a Raman pulse composed of different frequency components. This suggests that adjusting other pulse parameters could optimize the process of population transfer. For instance, consider a pulse composed of two frequencies, namely $(\omega_0 + \Delta)$ and $(\omega_0 - \Delta)$, where $\Delta$ is given by the energy level spacing of the $v = 0$ and 1 levels. The results are shown in figure 7. In this instance, the
Figure 5. Population of lowest vibrational levels when subjected to a three-pulse sequence (as described in the text) comprised of an ionizing pulse (not illustrated), which gives rise to a Franck–Condon distribution, and two consecutive controlling pulses (illustrated in upper panel). Initial cooling pulse chosen with delay time corresponding to point C in figure 4(A). Second control-pulse of same wavelength as first ($\lambda = 790$ nm), with duration 20 fs and intensity $I = 5 \times 10^{13}$ W cm$^{-2}$. Considering effect of applying second control-pulse at a delay time of $\sim 64$ fs (a) and $\sim 74$ fs (b), after the initial ionizing pulse. In both cases, upper panel illustrates the E-field associated with the control-pulse sequence.

Figure 6. Absolute population of lowest vibrational eigenstates ($v = 0$–4) at the end of the three-pulse sequence described in the text. Initial control pulse cools the system into an even superposition of $v = 0$ and $v = 1$ vibrational levels, corresponding to point C in figure 4(A). By varying the delay time of the second control-pulse, one is able to control the relative population of the $v = 0$ and $v = 1$ vibrational levels.
Figure 7. As in figure 6, except with second control-pulse composed of two constituent frequencies \((\omega + \Delta, \omega - \Delta)\) with a Gaussian envelope. Varying delay time of this second pulse, allows one to control the relative population of \(v = 0\) and 1, with greater contrast than seen in figure 6.

particular choice of frequencies gives rise to an increased contrast in the transfer of population between the two levels.

4. Conclusions

The goal of ultrafast coherent control is close at hand with the developments in ultrashort-pulse lasers. Imaging of the fastest molecular vibrations (i.e. those of the hydrogen groups) is possible. Our calculations indicate that it should also prove possible to effect coherent control of the vibrational levels and, potentially, employ these methods for quantum encoding. In this paper, the \(D_2^+\) molecular ion was chosen as this is relevant to current experiments. It is possible to create cold vibrational modes through the application of an ultrashort IR control pulse. The populations of the low vibrational levels are controlled by the pulse delay. It was shown that up to \(\sim 70\%\) of population can be transferred into the two lowest levels. Transitions and manipulations between the \(v = 0\) and 1 states can be effected by further IR pulses from the same Ti:Sapphire source. Optimization of certain pulse parameters may lead to improved fidelity in the operations presented here. Such rigorous optimization of these operations, with respect to the pulse parameters used, has not been considered in the present work. Instead, the purpose has been to outline the principle involved, to explore the role of the key control parameters (i.e. the delay times of the individual control pulses) and the feasibility of an experiment based upon currently available techniques.

It is acknowledged that pump pulse duration, rotational effects and the competition of dissociative ionization channels, which have not been included in the simple model used here, will lead to some attenuation of the effects demonstrated. However, it is believed that, using current ultrashort pulses (< 10 fs), appropriately chosen field intensities and for sufficiently short delay times, it should be possible to realize this type of coherent vibrational state control. As well as being potentially useful in the field of quantum information, this technique could also
be invaluable in the general field of quantum control, including the exciting area of quantum control of simple chemical processes.

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References

[27] Sharp T E 1971 Atomic Data 2 119
Corrigendum added 5 September 2007

In the right panel of figure 2 (relating to $t_d = 30$ fs), the vertical axis of the upper line-plot should run from 0 to 0.2 rather than 0 to 0.4, as indicated.