

Stopping a Vibrational Wave Packet with Laser-Induced Dipole Forces

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Intense near-infrared laser pulses can generate laser-induced dipole forces that are strong enough to influence or control vibrational motion of a small molecule. Generally, the force acts to pull the molecule apart. Our numerical simulations show that, by applying the laser-induced dipole force at an appropriate time within one vibrational period, the wave packet motion of H_2^+ or D_2^+ can be accelerated or decelerated. Using the wave packet formed by the rapid ionization of H_2 or D_2 , we also show that it is possible to move the vibrational population almost entirely to the $\nu = 0$ state. Coherent cooling of the molecular vibrational motion can be achieved.

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Static or oscillating electric fields shift the energy levels of any electronic quantum system. The gradient along an internal coordinate R of the Stark shift V generates an internal laser-induced dipole force, $F = \partial V / \partial R$ [1]. When the laser intensity approaches $\sim 10^{14}$ W/cm², dipole forces can become comparable with the molecular binding forces. We show that vibrational motion can be accelerated or decelerated (or even stopped) by applying the laser-induced dipole force at an appropriate time within a vibrational period. Since the laser-induced dipole force generally has a positive value [1], it acts to pull the molecule apart. If the bond is stretching when the force is applied, then the vibrational energy increases. On the other hand, if the bond is shrinking when the force is applied, energy is removed.

We demonstrate these processes by numerical calculations of vibrational wave packet motion, using the simplest molecule, H_2^+ or D_2^+ . We suppose that two short laser pulses are used: one creates the vibrational wave packet and the other controls it. By changing the delay time between them, we add or subtract energy, ~ 0.3 eV. As a practical application, a 10 fs control pulse applied at a delay time of $\sim \frac{3}{4}$ of the vibrational period following ionization yields D_2^+ with $\sim 50\%$ of population in the ground vibrational state.

Selective bond breaking or controlling chemical reactions has long been a goal of the field of coherent control [2]. Coherent control has been established in atomic [3,4] and solid-state physics [5]. These experiments, performed in the perturbation limit, are based on the interferences between different excitation paths.

Even in strong laser fields, where many pathways must contribute to the final state, controllability survives. However, it is less useful to think of interfering pathways in a strong laser field. Instead, concentrating on the laser-induced dipole force can provide physical insight. Often called molecular optics, intense laser pulses align [6,7], focus in space [8], or spin molecules [9]. Recently, it has been demonstrated that combining wave packet motion with laser-induced dipole force can squeeze rotational

wave packets [10] and improve the degree of molecular alignment [11]. We extend the concept of wave packet molecular optics to the control of the internal (vibrational) motion.

Our work is also related to optimal control experiments [12]. In these experiments, phase and amplitude modulated pulses, controlled by a self-learning loop, selectively break a specific bond of even relatively complex molecules [12,13]. Although we control the wave packet motion in a deterministic way, the interaction between wave packet motion and the laser-induced dipole force may be one of the mechanisms responsible for control in learning loop experiments.

Like nonadiabatic (dynamic) alignment [7], our method is a highly multiphoton *impulsive* Raman process. Impulsive Raman processes have been demonstrated in solid-state physics [14]. Generally, such Raman processes couple together different vibrational levels, allowing a population to move up or down, but with no selectivity for a particular direction. However, selective population transfer is possible [15,16]. We exploit the well-defined phase relationship between vibrational eigenstates that is characteristic of a localized wave packet, together with a Raman pulse that is shorter than a vibrational period, to either accelerate or decelerate the wave packet.

Figure 1 shows the potential energy surfaces of $\text{D}_2^+(X\Sigma_g^+)$ and $\text{D}_2^+(A\Sigma_u^+)$ in field-free (solid lines) and field-modified (dotted lines) conditions. We assume that an initial laser pulse creates a well-defined vibrational wave packet on $\text{D}_2^+(X\Sigma_g^+)$ by tunnel ionization of D_2 [17–19], shown schematically in Fig. 1. The vibrational wave packet first propagates on the lower surface. After a delay, Δt , the second (control) pulse is applied. The laser field couples the two electronic surfaces and thereby produces the Stark shift that separates the potential energy surfaces.

We calculate the vibrational wave packet motion of D_2^+ using the time-dependent adiabatic model [20–23]. (The Floquet approximation, conventionally used for describing bond-softening dissociation [24], is not valid for a

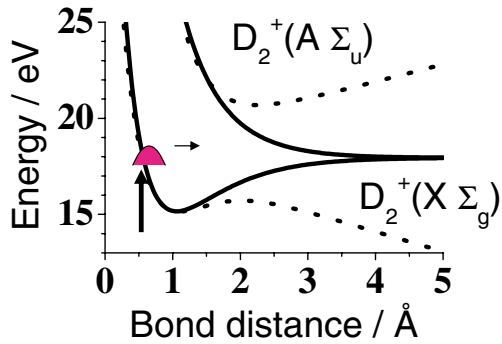


FIG. 1 (color online). The lowest two potential energy surfaces of D_2^+ in field-free conditions (solid lines) and with an electric field (dotted lines). We suppose that the two laser pulses are used. The first ionizes D_2 and launches the vibrational wave packet on $D_2^+(X\Sigma_g)$ [17–19]. The second laser pulse couples the two electronic surfaces and generates the laser-induced dipole force. Depending on the delay time (Δt) between the two pulses, the energy of the vibrational wave packet can be increased or decreased.

few-cycle pulse.) The two-state adiabatic model [23] agrees with a complete 3D numerical solution for few-cycle pulses. We solve the time-dependent Schrödinger equation using a split operator method [22]:

$$i\hbar \begin{pmatrix} dX_1/dt \\ dX_2/dt \end{pmatrix} = \left[\begin{pmatrix} T & 0 \\ 0 & T \end{pmatrix} + \begin{pmatrix} V_1 & \Omega \\ \Omega & V_2 \end{pmatrix} \right] \begin{pmatrix} X_1 \\ X_2 \end{pmatrix}. \quad (1)$$

Here, $X_{i=1,2}$ describe the vibrational wave packets propagating on the lower (V_1) and upper (V_2) surfaces, T is the kinetic energy operator, $\Omega = -\langle \phi_2 | \mu E(t) | \phi_1 \rangle = -\langle \phi_1 | \mu E(t) | \phi_2 \rangle$ is the transition matrix element [20], and $\phi_{1,2}$ are the electronic wave functions under field-free conditions. The energy eigenstates of the interaction matrix in a static field are shown as dotted lines in Fig. 1.

The magnitude of the Stark shift for the ground state is given by $V(R; t) = -\Delta w + \sqrt{(\Delta w)^2 + \Omega^2}$, where $\Delta w(R) = (V_2 - V_1)/2$ and Ω is given by $\frac{1}{2}R|E(t)|$ [20]. At relatively small laser fields, the value of Ω is smaller than that of Δw , resulting in $V \sim \frac{1}{2}\alpha E(t)^2$ where $\alpha = 2\langle \phi_2 | \mu | \phi_1 \rangle \langle \phi_1 | \mu | \phi_2 \rangle / (V_2 - V_1)$ is the polarizability. When the laser field becomes intense ($>10^{14}$ W/cm²) and at larger bond distances, Ω becomes larger than Δw , and the value of Stark shift (V) approaches $\sim \frac{1}{2}R|E(t)|$. Thus, the induced dipole forces are constant with R and take a positive value. Typically, for bond distances larger than ~ 1.5 Å in H_2^+ and at a laser intensity of $\sim 10^{14}$ W/cm², the dipole force reaches ~ 0.5 eV/Å. The same approach is applicable to other diatomic molecules like N_2 or Ar_2 [25], when the laser-induced dipole moment is represented by a charge transfer transition [26].

If the vibrational wave packet reaches the outer classical turning point when the laser field is present, the wave packet may dissociate [19]. At bond distances larger than

~ 2.5 Å, the laser-induced transition between lower and upper electronic surfaces becomes significant [20]. At >4 Å, the transition probability between these two surfaces becomes unity [20]. At these distances, the laser-induced dipole force on the upper surface has the same magnitude as the lower surface, but in the opposite direction. Thus, the net laser-induced forces cancel. Dissociation degrades the controllability. However, we can minimize this effect using a sufficiently short control pulse [27]. For example, the dissociation yield is only 10% for a 12 fs laser pulse. If the laser field is off when the wave packet reaches the outer turning point, bond-softening dissociation does not occur [19].

Now, returning to the wave packet motion, we show how the delay between when the wave packet is created and when the second laser pulse is applied influences the vibrational energy of the wave packet. We calculate the time evolution of the energy expectation value for the D_2^+ vibrational wave packet moving on the lower surface, $\langle E \rangle = \langle X_1 | H | X_1 \rangle / \langle X_1 | X_1 \rangle$, where H is the Hamiltonian of Eq. (1). At the laser intensity (2×10^{14} W/cm², 800 nm) and pulse duration (~ 12 fs) examined here, a small fraction of the wave packet ($<10\%$) dissociates. To remove the contribution of the dissociating part, we include only the wave packet remaining on the bounded potential after the pulse is over, i.e., for $R < 3$ Å. Note that the wave packet moving on upper surface inevitably dissociates after the laser pulse.

Figure 2(a) plots the final energy $\langle E \rangle$ after the laser pulse is over as a function of the delay time. Two pulse durations are shown: 12 fs (solid line) and 18 fs (dotted line). With both control pulse durations, the dependence is similar. We normalize $\langle E \rangle$ to be zero for the case of no control pulse. The vibrational wave packet gains its maximum energy at $\Delta t = 6$ fs, which corresponds to $\sim \frac{1}{4}$ of the $T_v = 25$ fs vibrational period of D_2^+ , whereas the laser field extracts energy most effectively at $\Delta t = 20$ fs ($\sim \frac{3}{4}T_v$). The result agrees with the following qualitative description: if the molecule is stretching (0–12 fs) when the control laser field is applied, the wave packet motion is accelerated, whereas when the molecule is shrinking, the wave packet is decelerated.

At $\Delta t = 20$ fs ($\Delta t \sim \frac{3}{4}T_v$), the expectation values for the final kinetic energy is ~ 0.13 eV and the potential energy is ~ 15.45 eV, relative to the neutral ground state. These are close to the energies of the $D_2^+(\Sigma_g, v=0)$ state. Thus the wave packet is almost stopped. Figure 2(b) shows the square of the vibrational wave packet obtained for $\Delta t = 20$ fs after the control pulse (solid line). Compared to the field-free condition (dotted line), the vibrational wave packet is more localized, centered at ~ 1.15 Å with a width of ~ 0.2 Å.

We show that the decrease in the vibrational energy is not due to dissociation, but instead to coherent population transfer between vibrational levels. We calculate the time evolution of the population for each vibrational eigenstate

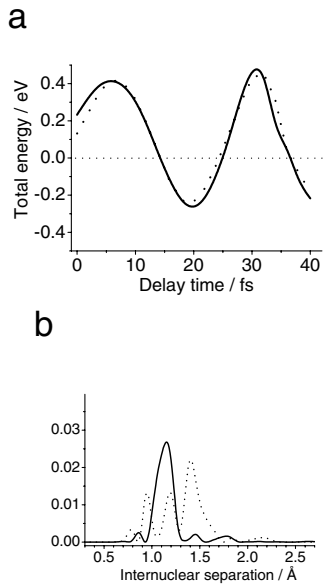


FIG. 2. (a) is a plot of the expectation value of the total energy $\langle E \rangle$ of the wave packet shown as a function of the delay time between when the vibrational wave packet is launched and when the control pulse is applied. We take the value of $\langle E \rangle$ after the laser pulse is over. We examine two different laser pulse durations, 12 fs (solid line) and 18 fs (dotted line). The laser intensity is 2×10^{14} W/cm². Depending on the phase of the vibrational motion, the vibrational wave packet is accelerated ($\sim \frac{1}{4}$ of the vibrational period, T_v) or decelerated ($\sim \frac{3}{4}T_v$). The solid line in (b) shows the vibrational wave packet when the control pulse is applied at $\Delta t \sim 20$ fs, where the energy is mostly removed. Compared to the field-free case (dotted line), the vibrational wave packet is more localized in space.

of $D_2^+(\Sigma_g)$, $P_v(t) = |\langle X_v | X_1(t) \rangle|^2$, where X_v is the eigenfunction of each vibrational level in field-free conditions. Figure 3 shows the case at $\Delta t \sim \frac{3}{4}T_v$. The pulse duration is 18 fs, and the intensity is 2×10^{14} W/cm² (800 nm). At $t = 0$, the population is distributed over the vibrational eigenstates from $v = 0$ to ~ 9 . When the control pulse is applied, the population transfers primarily to the lowest vibrational state. The energy of the wave packet is removed through the potential energy, and thus the wave packet is *coherently* cooled. If the laser field is applied at $\Delta t \sim \frac{1}{4}T_v$, the population transfers preferentially to higher eigenstates (not shown).

So far, we have demonstrated that a single laser pulse can control wave packet motion. As long as the vibrational wave packet remains localized, we can apply further laser pulses to enhance the motion. For instance, if control pulses are applied at $\Delta t = 6, 28,$ and 78 fs, we find that the wave packet successively gains energy, leading to molecular dissociation. The delay time for applying the second and third control pulses is empirically determined because of the anharmonicity of the potential energy of D_2^+ . The dissociation yield reaches $\sim 53\%$. (It does not reach 100% due to wave packet spread.) Because of the pulse separation increases, it corresponds to a highly

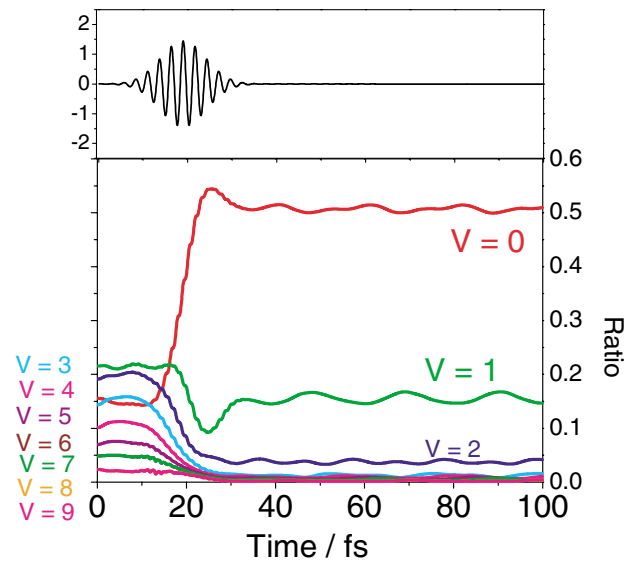


FIG. 3 (color online). The time evolution of the population of the vibrational eigenstates when the control laser pulse, whose pulse duration is 18 fs and intensity is 2×10^{14} W/cm² at 800 nm, is applied at $\Delta t \sim 3/4$ of the vibrational period. After the laser pulse is over, the population transfers primarily to $v = 0$. The population is normalized to be unity at $t = 0$. About 25% of the population is dissociated. The upper panel shows the control laser pulse.

multiphoton chirped Raman transition in a frequency domain picture [16].

In general, the underlying mechanism of coherent control is the interferences between two or more excitation pathways leading to the same final state [2]. By creating a wave packet, we arrange a well-defined phase between a set of vibrational states. As the wave packet moves, the relative phase between adjacent vibrational levels evolves by $\phi_{n,n+1} = (\omega_{n+1} - \omega_n)t$, where n is the vibrational quantum number and ω_n is the energy of that level. During a $\frac{1}{2}$ vibrational period, the phase changes by $\Delta\phi_{n,n+1} \sim \pi$. Our results show that, depending on $\Delta\phi_{n,n+1}$, the nonradiative transitions between vibrational levels is selective with respect to excitation or deexcitation. In the case of $\pi/2 < \Delta\phi_{n,n+1} < \pi$ the laser field causes excitation, whereas in the case of $\pi < \Delta\phi_{n,n+1} < 3/2\pi$ it causes deexcitation. In the frequency domain picture, the highly multiphoton Raman process optically connects the vibrational levels through many pathways. However, even in that case, the phase relationship between eigenstates remains important.

In conclusion, by combining coherent wave packet motion with carefully timed laser-induced dipole forces, the vibrational wave packet and the laser field can exchange energy in either direction. With current laser technology [28] it is practical to exercise control over the fastest vibrational motion, e.g., a C-H stretch. We have used D_2^+ as an example. Experiment [27] shows that a sub-8 fs pulse can produce a well-defined wave

packet in D_2^+ . We have shown how they can be controlled using a delayed laser pulse. The population of the vibrational states can be measured using standard spectroscopic techniques [29] or even by using an intense picosecond laser pulse [30].

Our approach may be applicable to the control of specific vibrational motion in large molecules. A triatomic molecule is an interesting case. Imagine an aligned molecule undergoing an asymmetric oscillation. The internal laser-induced dipole force, appropriately timed, will extract energy from one bond and add it to the other. Such localization implies that we excite a coherent superposition of symmetric and antisymmetric modes. Another example of a larger molecule is C_{60} . In C_{60} many electrons contribute to the dipole force [31]. Finally, recall that control occurs on a time scale shorter than a vibrational period. The *timed* laser-induced dipole force will influence the targeted bond before intramolecular vibrational relaxation becomes significant.

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