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Adiabatic climbing of vibrational ladders using Raman transitions with a chirped pump laser

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We present detailed calculations of a new scheme for the adiabatic transfer of population in molecular vibrational ladders and for controlling chemical reactions: Raman chirped adiabatic passage. The scheme makes use of far-off-resonant Raman transitions with one chirped and one monochromatic laser pulse. We show that this method can be used to climb vibrational ladders in molecular systems and, with sufficiently large chirping, can vibrationally dissociate diatomic molecules.

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Laser control of molecular reactions is a problem of fundamental importance. One of the simplest reactions involves breaking of a specific bond in a complex molecule by making use of its unique vibrational frequency and exciting it until it dissociates. However, four effects tend to frustrate this process: (1) anharmonicity in the vibrational potential well, (2) small efficiencies for dissociation, (3) availability of convenient lasers at vibrational frequencies, and (4) intervibrational redistribution of energy between bonds in the molecule. All of these issues have been individually addressed to varying degrees by many authors but have not yet been solved simultaneously. The main goal of this paper is to introduce the Raman chirped adiabatic passage (RCAP) technique and to investigate theoretically the possibility of using this technique to climb molecular vibrational ladders. We show that this method adiabatically moves population up through the vibrational levels in diatomic molecules, leading to rapid and efficient dissociation of the molecular bond while avoiding the first three problems discussed above. However, since in this paper we have studied the excitation of only one vibrational ladder, the problem of intervibrational redistribution of energy remains to be studied, separately.

Adiabatic passage is the simplest way to transfer population in a multilevel system with efficiencies approaching 100%. During the past decade various schemes of population transfer within multilevel systems have been investigated [1–18]. Much attention has been devoted to inversion in a λ configuration using stimulated Raman adiabatic passage (STIRAP) [1–6]. However, STIRAP cannot be used for climbing a vibrational ladder because exact tuning to the two-photon resonance is required. This cannot be maintained along the ladder with a single pair of laser frequencies due to the potential anharmonicity.

Alternatively, schemes using a frequency chirped pulse have been investigated to move population in multilevel ladder systems [7–17]. Recently, adiabatic population transfer was demonstrated experimentally in three electronic states of Rb [13,14], for inverting the population between two vibrational states of two different electronic surfaces of I_2 [15] and in a long ladder of circular Rydberg states [16]. The possibility of climbing vibrational ladders using chirped infrared laser pulses adapted to the molecular anharmonicity has been investigated theoretically [7–11]. So far, this method has not been tried experimentally, mainly because of the lack of strongly chirped intense laser pulses in the frequency region 2000–4000 cm^{-1}.

Combining these two approaches offers the alternative RCAP. Using Raman transitions avoids the problem of requiring lasers in the midinfrared, as only the difference frequency is important. In addition, using one chirped laser to produce the adiabatic transition avoids the problems with the STIRAP technique. The possibility of achieving an inversion in three-level λ systems by sweeping through the two-photon resonance was mentioned in Refs. [1,2], but to our knowledge no quantitative analysis has yet been done for this case.

In this paper, we first show that chirping of a pump laser with a simultaneously applied monochromatic Stokes laser inverts the λ system efficiently in the regime where both lasers are far from the one-photon resonances but are swept through the two-photon resonance for the transition between the lower levels. Next, we show that this technique can be used to climb vibrational ladders in two specific cases, H_2 and H_2^+, although the technique is quite general.

RCAP has the following advantages: (1) as with most adiabatic schemes, the exact tuning to transition frequencies is not required, only sufficiently slow sweeping through resonances is necessary to achieve near 100% efficiencies. Furthermore, the anharmonicity of the molecular bond can be followed; (2) considerable control over the excitation can be achieved by simply stopping the chirp at a specific frequency; (3) the laser frequencies can be chosen in the near infrared, where short-pulse laser technology is very well developed; (4) the dissociation can be driven quickly, possibly before the vibrational energy has a chance to redistribute to other molecular bonds; (5) this scheme can be applied to both homonuclear and heteronuclear bonds, unlike previous methods based on chirped lasers in the midinfrared [7–11,17]; (6) sufficiently large chirping leads to a breaking of the bond in such a way that the kinetic energy of the fragments is very low; (7) this method does not suffer from the bottleneck of previous (infrared) schemes [10,17] resulting from the weak coupling between upper vibrational states caused by the decaying dipole moment function at large R.

Let us consider the following three-level system, which simulates the couplings of two adjacent vibrational levels,

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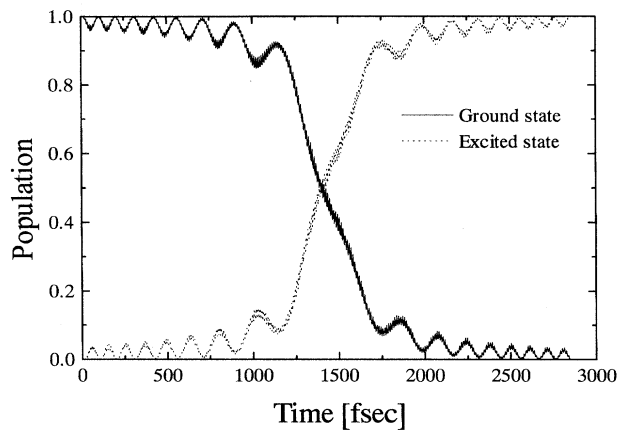

FIG. 1. Ground and first excited-state populations in the three-level system. The fast oscillations result from the beat frequency between the pump and Stokes lasers.

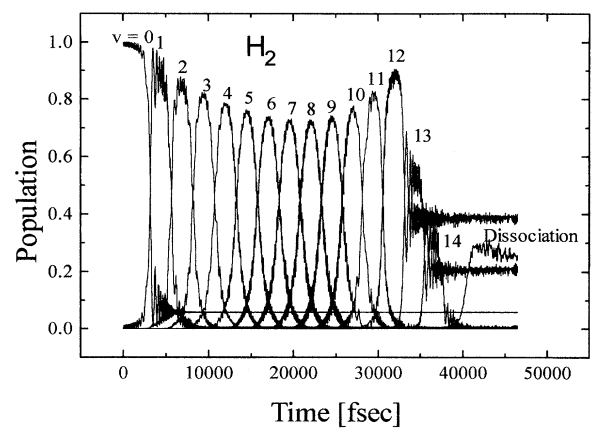

FIG. 2. Population of the vibrational levels of the ground state of H_2 and the dissociated fraction.

E_1 and E_2, of a molecular ground-state surface with levels in the upper electronic surfaces, E_3. In our three-level simulation we chose $E_1=0$, $E_2=0.3577$ eV (the energy spacing between the two lowest vibrational energy levels of HCl [19]) and $E_3=10$ eV (three upper surfaces of HCl that are strongly coupled with the ground surface are 8, 10, and 11 eV above the ground state [20]). In order to stimulate a practical laser configuration, the Stokes laser wavelength is constant and equal to 1064 nm (neodymium-doped yttrium aluminum garnet laser), while the pump laser is centered at the wavelength necessary for the two-photon resonance between states E_1 and E_2, 814.1 nm (Ti:sapphire laser), and linearly chirped from 3% below to 3% above this wavelength. The chirp rate c_r is 3.181×10^{-5} eV/fsec, and the electric field is given by

$$E(t)=U(t)E_o[\sin(\omega_i t-(c_r/2)t^2)+\sin(\omega_s t)], \qquad (1)$$

where $E_o=0.010\,68$ a.u., ω_i is the initial pump-laser frequency, and ω_S is the Stokes laser frequency. $U(t)$ describes pulse turn-on and turn-off: a $\sin^2[\pi(t/2)t_r]$ rise and fall with $t_r=17.7$ fsec and a constant intensity portion of 1700 fsec.

Figure 1 shows the population of the two lower levels as a function of time. The long period oscillations show that the transition is not strictly adiabatic, although the population transfer is virtually complete. Nonadiabaticity results from too fast a chirp, too sudden a turn-on, or starting too close to resonance, all of which can lead to oscillations or incomplete population transfer. These results agree with estimates from simple three-level calculations using the rotating-wave approximation (RWA) (although the RWA was not used in our simulations). If the Rabi frequencies Ω_s and Ω_p of each laser ($\Omega_p=E_o p_{13}$, $\Omega_s=E_o p_{23}$, where p_{ij} is the effective dipole moment and taken to be 1 in these calculations) is much smaller than Δ, where Δ is the detuning from the upper level, then at the two-photon resonance the three-level system has the following dressed-state energies: 0, $-\Omega_{\rm eff}$, and Δ, where $\Omega_{\rm eff}=(\Omega_p^2+\Omega_s^2/(4\Delta)$ is the effective Rabi frequency for the two-photon transition. Using the analogous conditions for an adiabatic transitions in two-level systems [11] we should have $\Delta\omega_p\gg\Omega_{\rm eff}$, where $\Delta\omega_p$ is the initial detuning of the chirped pulse, so that the states are initially unmixed, and $c_r\ll\Omega_{\rm eff}^2$ for the chirp rate. In our case, $\Omega_s=\Omega_p=0.2909$ eV, $\Delta=8.477$ eV, $\Omega_{\rm eff}=4.99\times10^{-3}$ eV, and $\Delta\omega_p=45.70\times10^{-3}$ eV, so the first condition above is well satisfied. In atomic units, $c_r=2.83\times10^{-8}$ and $\Omega_{\rm eff}^2=3.347\times10^{-8}$ a.u., so the second condition is only marginally satisfied.

There are two issues to be considered in generalizing the three-level results from above to a multilevel ladder system. Let $\Delta\omega_{\rm anh}$ be the frequency difference due to the molecular anharmonicity between vibrational transitions: $\Delta\omega_{\rm anh}=E(v+1)-E(v)-[E(v+2)-E(v+1)]$. For the Morse oscillator, $\Delta\omega_{\rm anh}$ is independent of the vibrational level. If $\Delta\omega_{\rm anh}\gg\Omega_{\rm eff}$, then the individual transitions in the ladder are decoupled from one another and the population will move stepwise through the vibrational states. If $\Delta\omega_{\rm anh}\ll\Omega_{\rm eff}$, then the states all become mixed. $\Delta\omega_{\rm anh}$ also determines, using the adiabatic conditions above, how much time Δt must be allocated for each step, $\Delta v=1$, in the vibrational ladder (steps with $\Delta v>1$ are forbidden by selection rules for nonresonant Raman transitions [19]): $\Delta t=\Delta\omega_{\rm anh}/c_r\gg\Delta\omega_{\rm anh}/\Omega_{\rm eff}^2$.

We have solved numerically the time-dependent Schrodinger equation for two coupled nuclear wave functions for the ground and excited electronic surfaces $\chi_1(R,t)$ and $\chi_2(R,t)$. With $\chi=[\chi_1,\chi_2]$, we have

$$\left[i\hbar\frac{\partial}{\partial t}+\frac{\hbar^2}{2m}\frac{\partial^2}{\partial^2 R}\right]\chi(R,t)=\begin{bmatrix}V_1(R) & V_{12}(R,t)\\ V_{12}(R,t) & V_2(R)\end{bmatrix}\chi(R,t), \qquad (2)$$

where $V_1(R)$ and $V_2(R)$ are the unperturbed potentials of H_2 of H_2^+, and $V_{12}(R,t)=\mu(R)E(t)$, where $\mu(R)$ is the dipole function and $E(t)$ is given by Eq. (1). This was solved using the second-order split-operator method, as discussed in Refs. [21–23].

Two typical molecular situations were studied: the upper surface has bound states (H_2) and the upper surface is repulsive (the Σ_u surface of H_2^+). The potential functions were chosen as Morse potentials (for the bound surfaces): $V_i(R)=D_i\{1-\exp[-a_i(R-R_i)]\}^2+C_i$, where $i=1$, (2) for the lower (upper) surface. D_i and a_i were chosen so that the resulting Morse potential had the same vibrational constants,

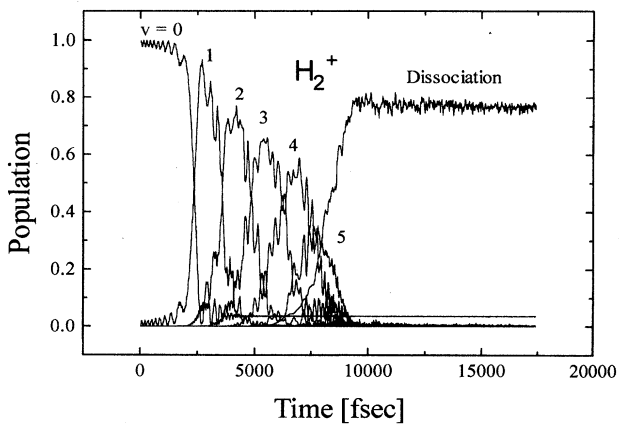

FIG. 3. Population of the vibrational levels of the ground state of H_2^+ and the dissociated fraction.

ω_e and $\omega_e x_e$, [19] as the actual states. The value of $\Omega_{\rm eff}$ can be evaluated without doing the full calculation from the following approximate expression, valid for large detunings [24]:

$$\Omega_{\rm eff}=E_pE_s\langle v'|\mu(R)^2/[V_1(R)-V_2(R)]|v\rangle, \qquad (3)$$

where E_p and E_s are the electric fields of the pump and Stokes lasers, respectively. v and v' indicate the initial and final vibrational levels.

The lower and upper surfaces in H_2 are the $X\ ^1\Sigma_g^+$ and $B\ ^1\Sigma_g^+$ states, respectively, and $\mu(R)$ was taken from Ref. [25]. In the calculations, the chirp rate is $c_r=1.058\times10^{-8}$ a.u., the laser intensity $I=10^{13}$ W/cm^2, the pump-laser wavelength is 1.06 μm and the initial wavelength of the Stokes laser 723.2 nm, placing it 2% above the first two-photon resonant transition. Figure 2 shows the populations of the first 15 vibrational levels in H_2, as well as the dissociated fraction as a function of time through the pulse. Clean stepwise behavior up the vibrational ladder is strikingly evident. From Eq. (3), $\Omega_{\rm eff}=4\times10^{-3}$ eV. Thus, $\Omega_{\rm eff}<\Delta\omega_{\rm anh}$, implying that the levels are fairly well decoupled, as can be seen in Fig. 2. $\Omega_{\rm eff}^2=2.2\times10^{-8}$ a.u. is larger than c_r, and so the transitions should be adiabatic, as is confirmed by the smooth nature of the peaks in Fig. 2. Furthermore, significant dissociation is found at the end of the pulse.

The lower surface of H_2^+ is the $X\ ^2\Sigma_g^+$ state, while the upper surface is repulsive and was taken from Table I-D in Ref. [26]. $\mu(R)$ is taken to be $eR/2$. In this case, the chirp rate is $c_r=2.234\times10^{-8}$ a.u., the laser intensity is $I=4\times10^{12}$ W/cm^2, the pump-laser wavelength is 1064 nm, and the initial wavelength of the Stokes laser is 846.1 nm, again placing it 2% above the first two-photon resonant transition. Figure 3 shows the results of the calculation for H_2^+. Again, stepwise climbing of the vibrational ladder is evident, but only up to about $v=5$. At this point, three-photon transitions from $v=5$ to the repulsive Σ_u state are possible with the pump laser, driving the molecule to dissociation well before the top of the vibrational ladder is reached.

Two issues need to be addressed to evaluate the usefulness and practicality of RCAP: what is the minimum pulse duration and total chirp required for efficient dissociation. The total chirp, C_t, required depends only on the molecular system through $C_t=\Delta\omega_{\rm anh}v_{\rm diss}$, where $v_{\rm diss}$ is the vibrational level where dissociation begins to occur. Above, we saw that $v_{\rm diss}=12$ for H_2 and 5 for H_2^+. In the case of H_2, $C_t\sim2400$ cm^{-1}, which corresponds to a pulse length of 3.5 fsec for a transform-limited pulse. This short of a pulse is still beyond state-of-the-art laser technology, and thus, RCAP could not be successfully applied. However, for molecules with a smaller anharmonicity a more reasonable chirp is required. For example, in HCl, $\Delta\omega_{\rm anh}=105$ cm^{-1}. Taking $v_{\rm diss}=10$ gives $C_t=1050$ cm^{-1}, corresponding to a virtual pulse of 10 fsec. Pulses with a duration of 11 fsec have been reported recently [27].

The total pulse duration required to achieve dissociation is given by $T_{\rm diss}=\Delta\omega_{\rm anh}v_{\rm diss}/c_r$. However, the chirp rate is constrained by $\Omega_{\rm eff}$ through the adiabatic condition discussed above. $\Omega_{\rm eff}$, in turn, is determined by three contributions: (1) the dipole moment of the molecule, (2) the laser intensity as I^2, and (3) the detuning from the upper levels as Δ^{-1}. Again, taking the example of HCl and $\Omega_{\rm eff}$ estimated for H_2, HCl could be dissociated in about 1.1 psec. This fast time scale is on the order of, and may avoid, intervibrational redistribution. The laser intensity cannot be significantly increased due to multiphoton ionization. However, the detuning can be reduced somewhat from about 8 to maybe 2–3 eV through the use of ultraviolet lasers. This would increase $\Omega_{\rm eff}$ by about 3 and allow the chirp rate to be increased by a factor of 10.

Since $\Omega_{\rm eff}$ is proportional to $1/\Delta(R)$, where $\Delta(R)=V_2(R)-V_1(R)-\omega_p+\omega_s$, the effective coupling will grow during the excitation process. Therefore, one can expect that parabolic chirping, instead of linear, can give faster excitation. Furthermore, in our calculations, only the two nearest surfaces were included, while most molecules have strong couplings with more upper surfaces. Since all of these couplings are nonresonant, one can expect that they will add up to give a larger effective coupling.

Raman chirped adiabatic passage is a robust and efficient way to transfer population up a molecular vibrational ladder, leading to fast excitation and dissociation of the molecular bond in a diatomic molecule. While selective bond breaking with our method in a polyatomic molecule remains to be demonstrated, the state-selective excitation within triatomic molecules exhibiting distinct anharmonic ladders, similar to that discussed in Ref. [28] for the HOD molecule, should easily be achieved with our scheme.

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