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Nonperturbative quantum control via the nonresonant dynamic Stark effect

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The nonresonant dynamic Stark effect (NRDSE) is investigated as a general tool for quantum control in the intermediate field strength regime (nonperturbative but nonionizing). We illustrate this scheme for the case of nonadiabatic molecular photodissociation at an avoided crossing. Using the NRDSE exclusively, both the electronic branching ratio and predissociation lifetime may be controlled. Infrared control pulses are used to modify the field-free dynamical evolution during traversal of the avoided crossing, thus controlling the nonadiabatic branching ratio. Predissociation lifetimes may be either increased or decreased using properly timed short infrared pulses to modify phase differences between the diabatic wave packets. In contrast with the limiting cases of perturbative control (interference between transitions) and strong field control with ionizing laser fields, control via the NRDSE may be thought of as reversibly modifying the effective Hamiltonian during system propagation.

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The ability to generate precise, strong electric fields is an important outcome of modern laser science. As electric forces underlie essentially all of molecular and solid state physics, this ability has consequences for the control of quantum processes. A range of quantum control schemes have been investigated [1]. Methods analogous to Young's double slit experiments use quantum interference between two or more pathways to a target state [2]. These often perturbative control schemes can be compared with the strong resonant methods that are useful for the transfer of population in few level systems [3]. An alternate approach utilizing adaptive learning algorithms that optimize target state yield by shaping strong laser fields has also proven effective [4]. Other techniques also rely on dipole couplings to control dissociation rates and position localization. These include bond hardening and softening [5], adiabatic passage by light-induced potentials [6], and suppression of spontaneous decay using series of short kicks [7]. In intermediate strength (nonperturbative but nonionizing) nonresonant laser fields, two limiting cases for exerting control exist: the dipole coupling regime and the Raman regime [8]. Only in the latter case do the field-induced modifications follow the envelope of the laser field, leading to the general idea of reversibly modifying an effective Hamiltonian during propagation. This is in stark contrast to many control techniques that emphasize selectivity through careful state preparation. Here, as an illustration of this general approach, we investigate the intermediate field quantum control of molecular predissociation using schemes that utilize exclusively the Raman-coupled nonresonant dynamic Stark effect (NRDSE).

The Hamiltonian for a charged quantum system in the presence of an optical field $\mathbf{E}(t)=\mathbf{e}E_0(t)\cos(\omega t)$ is $H=H_0-\mathbf{d}\cdot\mathbf{E}$, where $\mathbf{e}$ is the polarization vector, $E_0(t)$ is the pulse envelope, H_0 is the field-free Hamiltonian with eigenstates ψ_i and energies ω_i, and $\mathbf{d}$ is the dipole operator. Often states can be divided into two sets: states that participate in the dynamics directly, and nonessential states that are nonresonant for one-photon or Raman transitions. Furthermore, nature often furnishes systems that have eigenstates that form bands as, for example, in a molecule, a set of quantum wells, a hyperfine manifold, or a Stark or Zeeman split manifold. The dynamics of such systems can often be represented by an effective Hamiltonian where the nonessential state dynamics have been adiabatically eliminated by "integrating out" their motion and introducing their influence as a polarizability. Formally, the optical interaction $-\mathbf{d}\cdot\mathbf{E}$ may then be replaced with the effective perturbation $V_{jk}^{eff}=V_{jk}^{d}+V_{jk}^{R}$ and the equation of motion for the wave function $\psi(t)=\Sigma_i c_i(t)e^{-i\omega_i t}\psi_i$ becomes $i\dot{c}_j=\Sigma_k V_{jk}^{eff}c_k e^{-i\omega_{kj}t}$, where $V_{jk}^{d}=-\mathbf{d}_{jk}\cdot\mathbf{e}\,E_0(t)\cos(\omega t)$, $V_{jk}^{R}=-\frac{1}{4}E_0^2(t)\alpha_{jk}(\omega)$, and the dynamic polarizability is given by

$$\alpha_{jk}(\omega)\equiv\sum_{p,\pm}\frac{\mathbf{d}_{jp}\cdot\mathbf{e}\;\mathbf{d}_{pk}\cdot\mathbf{e}}{\omega_{kp}\pm\omega}$$

[9]. Above, the indices j, k refer to the essential states, p refers to the nonessential states, and i refers to all states. When the intraband dipole moments are large and the dipole detunings small, V_{jk}^{d} will dominate the effective Hamiltonian. By contrast, V_{jk}^{R} dominates when the interband dipole moments are large and the Raman detunings are small. In the dipole case, the system response attempts to follow the instantaneous electric field. In the Raman case, the field envelope is followed.

The control of branching ratios in molecular photodissociation has become a benchmark for the investigation of control schemes. We therefore investigate control at an avoided crossing, focusing exclusively on the Raman dominated case. Some early quantum control studies [10] investigated avoided crossing electronic branching ratios in IBr photodissociation, a system of continuing interest [11,12]. The IBr avoided crossing, depicted in Fig. 1, will be the focus of this study, but the principles discussed are general. We demonstrate that predissociation branching ratio control and predissociation lifetime enhancement or reduction are out-

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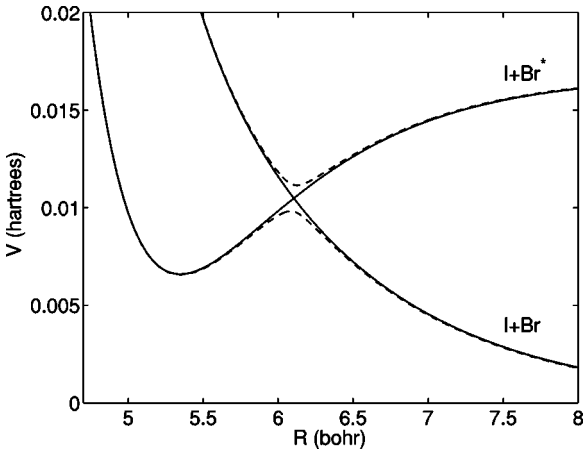

FIG. 1. Nonadiabatic wave packet dynamics in IBr. The diabats (solid lines) are the quasibound $V_1 = B(^3\Pi_{O^+})$ and the repulsive $V_2 = Y(O^+)$. The dashed lines are the adiabats which avoid each other. At the photoexcitation energies considered here, the I+Br channel alone may be open, or both the I+Br and the I+Br* exit channels may be open.

comes of our approach Branching ratio control is achieved by applying NRDSE shifts either during photoexcitation or during times when the excited state wave packet traverses the avoided crossing. Lifetime control is achieved by the application of short infrared pulses that modify the relative phase shift between the diabatic wave packets, producing either constructive or destructive interference in the product channel. For IBr, NRDSE pulses in the near to short wavelength infrared would be appropriate: typically 1–3 μm.

We investigate the nonadiabatically coupled vibrational motion on the molecular electronic surfaces $V_1 = B(^3\Pi_{O^+})$ and $V_2 = Y(O^+)$ in the presence of a Raman-coupled NRDSE control field using the diabatic representation. Excitation from the ground state $V_0 = X(^1\Sigma_0^+)$ is achieved with a visible dipole transition $V_{01}(t)$

$$H_d = T + \begin{bmatrix} V_0(R) & V_{01}(t) & 0 \\ V_{10}(t) & V_1(R) + V_{11}^R(t) & V_{12} \\ 0 & V_{12} & V_2(R) + V_{22}^R(t) \end{bmatrix}. \tag{1}$$

In general, the diagonal dynamic Stark level shifts V_{ii}^R may be time and position dependent; here, in the lowest order approximation, they are taken as position independent variables that follow the intensity envelope. Owing to the freedom to scale the zero point energy, there are only two free differential polarizabilities to consider. We investigate only a differential polarizability α between the excited states: $V_{11}^R = -V_{22}^R = -\frac{1}{4}\alpha E_0^2(t)$. Unfortunately, the calculation of excited state polarizabilities is nontrivial so only rough estimates of the field strengths required are available. A system with $\alpha = 10$ Å^3 receives a 0.01-eV shift in a 7×10^{11} W/cm^2 field. It is therefore reasonable to assume surface shifts of a few hundredths of an eV to be available. The off-diagonal term V_{12} is the nonadiabatic coupling parameter (here, spin-orbit induced) and neglects any dipole coupling owing to the differing spin multiplicities of the diabats. The physical origin of the differential polarizability is that one diabat is dissociative while the other is bound.

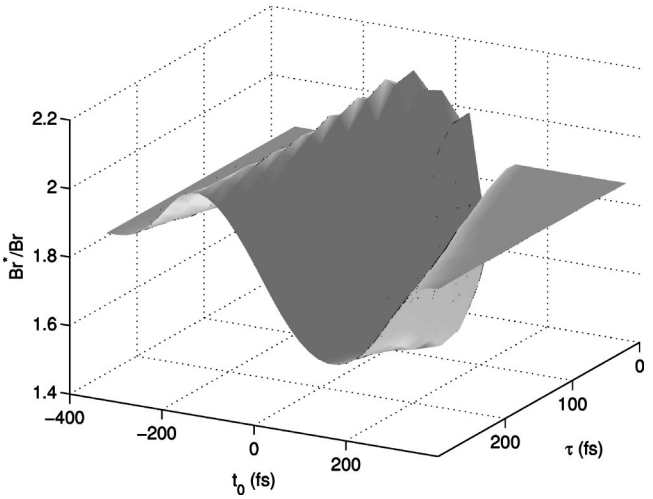

FIG. 2. The nonadiabatic Br*/Br branching ratio control surface via Raman-coupled NRDSE. The ratio of the flux out both channels Br*/Br is plotted as a function of two control parameters: t_0 and τ. By adjusting the timing t_0 of the control pulse with respect to the excitation pulse (at $t_0 = 0$) and by adjusting the control pulse duration τ, channel selectivity is clearly obtained.

The numerical simulations were performed using the split-operator technique [13]. The diabatic representation was used for the excited states and the evaluation of the 2×2 potential matrix exponential was performed analytically. The electronic potentials V_i and the nonadiabatic coupling V_{12} used were those suggested by Guo [14]. Pulse durations quoted in the text are approximate Gaussian full width at half maximum values.[1]

We first consider control over the Br*/Br photodissociation branching ratio. The simple Landau-Zener hopping formula

$$P = \exp\left[\frac{-2\pi V_{12}^2}{v\partial_R(V_{11}(R) - V_{22}(R))}\right]$$

gives the probability for a wave packet of velocity v hopping across adiabats [15]. Within the range of applicability of the hopping formula, the terms in the exponent are available for control via NRDSE. For example, application of a NRDSE control pulse either during photoexcitation or during the subsequent propagation of the wave packet can result in branching ratio control. Both the timing of the NRDSE pulse and its duration are important variables. We consider preparation of a wave packet on V_1 from V_0 with a 50-fs, 540-nm pulse. In Fig. 2 we show the Br*/Br branching ratio control surface as a function of: (i) the time of application t_0 of the NRDSE

[1]The quoted pulse durations τ are the Gaussian full width at half maximum values. However, the simulations use cosine-squared pulse envelopes based on the approximation about $t=0$ that $e^{-(t/\tau)^2 4\ln(2)} \approx \cos^2[(t/\tau)\sqrt{4\ln(2)}]$. Therefore the area under the pulse envelope is $[\pi/4\sqrt{\ln(2)}]\tau$.

pulse; and (ii) the duration τ of the NRDSE pulse. The peak amplitude of the NRDSE interaction is 0.002 hartrees $=0.054$ eV. If, during excitation, the control field lowers the V_1 surface, higher energy resonances are effectively made accessible. Following extinction of the control, the resulting increased wave-packet velocity at the crossing yields a more diabatic behavior. The result can be understood classically from the energy conservation of a particle traveling on V_1 whose velocity at the crossing point is increased due to the initial potential energy NRDSE shift. By contrast, if during traversal of the crossing the diabats are shifted relative to each other, the slope difference is changed and the velocity is reduced as the particle must travel farther up the potential, thus leading to the opposite effect. The observed branching ratio control is quite significant, with a peak-to-peak fractional change of roughly 40%. The classical model (using the peak NRDSE shift) shows a fractional change of 52%, a discrepancy that can be attributed to localization effects. Note that low contrast in a nonperturbative scheme may result in a larger net population transfer than a perturbative scheme with higher contrast. This is because perturbative methods can typically only transfer small amounts of population.

We now consider control of the predissociation lifetime (i.e., when only the lower I+Br channel is open). One may elect to describe this dissociation process in two conventional ways: (i) the coupling of the V_1 states to the V_2 states causes an irreversible decay; or (ii) the initial excitation populates a set of incoming scattering states that are correlated to certain free states at the end of the process. In the latter case, the incoming solutions $|n\rangle$ satisfy $(H-E_n+i0^+)|n\rangle=0$, where H is the 1-2 portion of (1), less the Raman terms

$$V_R \equiv \begin{bmatrix} V_{11}^R & 0 \\ 0 & V_{22}^R \end{bmatrix}.$$

The incoming state is composed of both electronic states

$$|n\rangle = \begin{pmatrix} |n(1)\rangle \\ |n(2)\rangle \end{pmatrix},$$

with n representing the energy E_n and any necessary quantum numbers. If, during the application of a very short and strong NRDSE control field, the field-free Hamiltonian can be momentarily neglected, the evolution of the system is governed by $i\partial_t\Psi=V_R\Psi$ and the unitary evolution of this period is given by

$$U_R \equiv e^{-i\int V_R dt}.$$

The effect is that there is an extraordinary phase change

$$\int V_R dt \equiv \begin{bmatrix} \phi & 0 \\ 0 & -\phi \end{bmatrix}$$

that is accumulated between the two electronic components of each eigenfunction.

While the eigenstates may have orthonormal relations $\langle n|m\rangle=\langle n(1)|m(1)\rangle+\langle n(2)|m(2)\rangle=\delta_{m,n}$, the same cannot be said of the individual electronic components $|n(i)\rangle$: $\langle n(i)|m(i)\rangle\neq\delta_{m,n}$. Thus, the relative phase shift transports in-states out of the initial set of eigenfunctions. As a concrete example, consider the projection onto the longest lived in-state $|\ell\rangle$ following a phase shift $|\ell\rangle\rightarrow|\ell'\rangle \equiv U_R|\ell\rangle$: $\langle\ell|\ell'\rangle=e^{-i\phi}\langle\ell(1)|\ell(1)\rangle+e^{i\phi}\langle\ell(2)|\ell(2)\rangle$. By a judicious choice of ϕ the two different electronic states can be used to interfere with each other. The inner product is minimized for a π pulse: $2\phi=\pi$, with the remaining population being projected onto shorter lived states. The contrast is highest if there is equal population in both electronic states. In general, constructive or destructive interference can be produced in a chosen product space P (i.e., $|P|\Psi(t)\rangle|$ can be extremized as desired). Note that this NRDSE π pulse differs from the usual dipole π pulse in that the transfer matrix is

$$U_R = \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} \text{ not } \begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix}.$$

Since the Raman-induced force $-\partial_x V_R=0$, there is no conventional application of force. However, the Raman coupling can still impart an impulse to the system. Its origin comes indirectly from the coupling between levels and can be observed in the adiabatic potentials $A_{1,2}=\frac{1}{2}(V_1+V_{11}^R+V_2+V_{22}^R)\pm\frac{1}{2}\sqrt{(V_1+V_{11}^R-V_2-V_{22}^R)^2+4V_{12}^2}$, whose spatial derivatives do depend on the Raman coupling. As the duration of the phase kick is increased and the intensity decreased, the kinetic and potential terms of the Hamiltonian can no longer be neglected and the phase shift becomes more of a potential kick.

To illustrate the phase kicks, a 10-fs infrared control pulse is used to alter the decay lifetime[2] as a function of the control amplitude V and the control pulse timing t_0. In Fig. 3 we show the Raman-coupled NRDSE lifetime control surface. At $t_0=0$ a 50-fs pulse centerd at 569 nm is used to create a wave packet at energies where only the $Y(0^+)$ I+Br channel is open. The deep minimum in Fig. 3 corresponds to an acceleration of decay. There are also maxima on this surface that are higher than the field-free $V=0$ case, illustrating the suppression of decay. As a function of intensity, the onset of the minimum occurs close to the intensity expected for a NRDSE π pulse: $V=4\sqrt{\ln(2)}/\tau=0.008$ hartrees $=0.22$ eV. The small deviation from this point is attributed to an unbalanced population in the two electronic levels, kinetic and potential coupling, and the superposition of resonances. As a function of temporal position t_0, the minimum corresponds to a maximum in the population on V_2, which is always lower than that on V_1: i.e., the control has the greatest contrast when the populations on the electronic surfaces are similar.

Experimentally, in systems with small polarizabilities, extremely large field strengths would be required in order to induce large level shifts. Unfortunately, since NRDSE control pulses with reduced intensity will likely be necessary in order to avoid large field destructive processes such as multiphoton ionization, one would naively expect the phase shift approximation to fail if pulse durations are extended and

[2]Our measure of "lifetime" is the quasibound population remaining at a long time delay (6 ps).

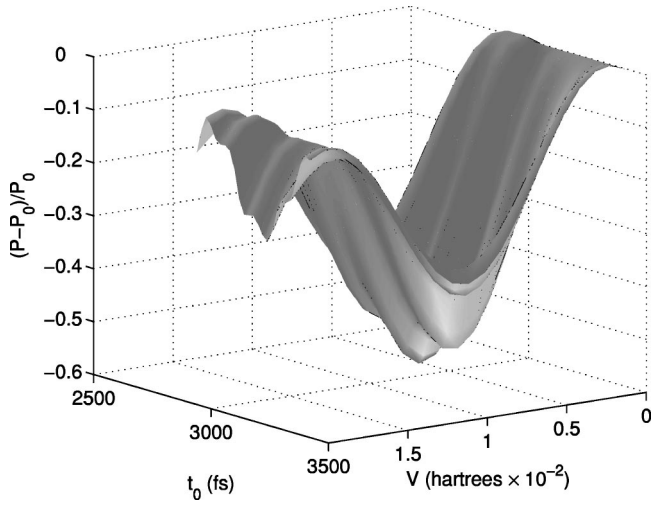

FIG. 3. Control over decay lifetimes using short NRDSE pulses. The survival probability P at 6 ps resulting from a 10-fs NRDSE pulse at t_0 having peak amplitude $V=-2V_{11}^R=2V_{22}^R$, is compared to the field-free survival probability P_0 remaining at 6 ps. The deep minimum corresponds to a π pulse.

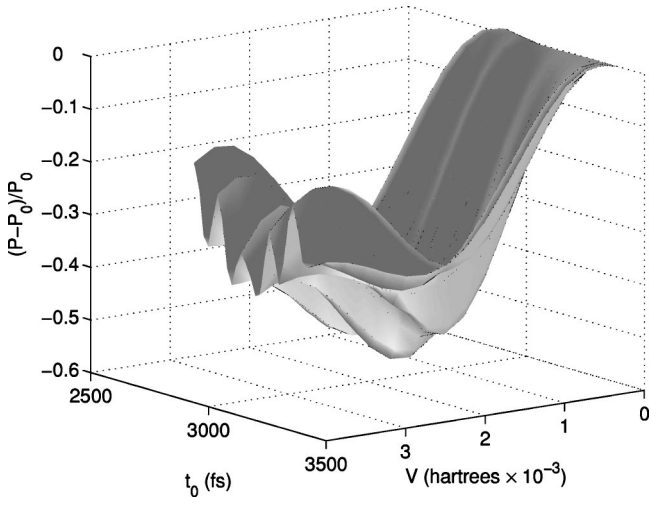

FIG. 4. Control over decay lifetimes using longer NRDSE pulses. As in Fig. 3, but with 50-fs NRDSE pulses. The deep minimum still corresponds to a π pulse despite the much longer pulse duration.

intensities are reduced. However, Fig. 4 demonstrates the interesting fact that a 50-fs pulse can still be used to introduce phase kicks. In this case, the π shift occurs at 0.0016 hartrees=0.044 eV and the only penalty is a loss of contrast. The features of the control surfaces are fairly broad, which means the control schemes are fairly robust with respect to fluctuations in the control fields. However, the Raman potentials depend on molecular orientation and these control schemes would therefore benefit from the simultaneous use of a field-free alignment technique [8,16] or a selective probing technique. We will report elsewhere that the implementation of multiple NRDSE control pulses (the simplest example of pulse shaping) can be used to compound these effects, enhancing the control.

The Raman-coupled NRDSE applied to quantum dynamical systems corresponds to the modification of the field-free effective Hamiltonian during propagation. It differs from perturbative control scenarios where the propagator always remains the field-free one. It also differs from strong (ionizing) field control scenarios where many electronic states are mixed in the field. In the nonresonant intermediate field strength regime discussed here, there are no unwanted (real) electronic transitions and, therefore, the effective Hamiltonian modified by the control field returns to the field-free one after the control pulse is over. This type of control applies to all material systems where the Raman coupling dominates. We have illustrated control at an avoided crossing in IBr, but we believe that the control schemes discussed here will translate readily to both larger molecules and mesoscopic systems.

[1] M. Shapiro and P. W. Brumer, *Principles of the Quantum Control of Molecular Processes*, (Wiley, New York, 2003); S. A. Rice and M. Zhao, *Optical Control of Molecular Dynamics*, (Wiley, New York, 2000).

[2] P. Brumer and M. Shapiro, Annu. Rev. Phys. Chem. **43**, 257 (1992) and references therein; R. J. Gordon and S. A. Rice, *ibid.* **48**, 601 (1997) and references therein.

[3] K. Bergmann *et al.*, Rev. Mod. Phys. **70**, 1003 (1998); J. Oreg *et al.*, Phys. Rev. A **29**, 690 (1984).

[4] R. S. Judson and H. Rabitz, Phys. Rev. Lett. **68**, 1500 (1992); A. Assion *et al.*, Science **282**, 919 (1998); R. J. Levis *et al.*, *ibid.* **292**, 709 (2001).

[5] A. Zavriyev *et al.*, Phys. Rev. A **42**, 5500 (1990); L. J. Frasinski *et al.*, Phys. Rev. Lett. **83**, 3625 (1999); T. F. George *et al.*, Faraday Discuss. Chem. Soc. **62**, 246 (1977).

[6] B. M. Garraway and K.-A. Suominen, Phys. Rev. Lett. **80**, 932 (1998).

[7] E. Frishman and M. Shapiro, Phys. Rev. Lett. **87**, 253001 (2001).

[8] J. G. Underwood *et al.*, Phys. Rev. Lett. **90**, 223001 (2003).

[9] B. W. Shore, *The Theory of Coherent Atomic Excitation* (Wiley, New York, 1990), Vols. I and II.

[10] C. K. Chan *et al.*, J. Chem. Phys. **94**, 2688 (1991); I. Levy *et al.*, *ibid.* **93**, 2493 (1990).

[11] M. Shapiro *et al.*, J. Chem. Phys. **110**, 2465 (1999).

[12] A. N. Hussain and G. Roberts, J. Chem. Phys. **110**, 2474 (1999).

[13] M. D. Feit *et al.*, J. Comput. Phys. **47**, 412–433 (1982).

[14] H. Guo, J. Chem. Phys. **99**, 1985 (1992).

[15] L. D. Landau, Phys. Z. Sowjetunion **2**, 46 (1932); C. Zener, Proc. R. Soc. London, Ser. A **137**, 696 (1932).

[16] H. Stapelfeldt and T. Seidman, Rev. Mod. Phys. **75**, 543 (2003); J. J. Larsen *et al.*, Phys. Rev. Lett. **83**, 1123 (1999).