



Rotational aspects of short-pulse population transfer in diatomic molecules

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Received 5 January 2004; in final form 12 May 2004

Abstract

A fully-selective population transfer scheme for diatomic molecules using short-duration (<ns) laser pulses is developed via the concept of light-induced potentials. It explicitly takes rotational degrees of freedom into account. We apply it to a specific Na₂ transition from the lowest ro-vibronic state to a single ro-vibronic state of a doubly excited electronic state via an intermediate electronic state. The process insures total selective population transfer with pulses short compared to the molecule rotation time. However, an estimate of the multiphoton ionization rate using time-dependent density functional theory suggests that ionization may significantly adversely affect the transfer.

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1. Introduction

The use of long pulse duration laser light for adiabatic population transfer in atoms and molecules is now a well-established method for fully and selectively moving population in molecules from one ro-vibronic state to another [1–3]. For short-duration optical pulses (that need to be used for processes involving excited states which decay quickly), the concept of light-induced adiabatic potentials was suggested by Garraway and Suominen [4] in order to completely and selectively transfer population from one molecular vibronic state to another. A generalization of this concept using chirped pulses was developed so that lower intensity ultra-short pulses could be used for vibronic population transfer [5]. A variety of pulse sequences and configurational schemes have been studied [5–8]. However, rotational degrees of freedom of the molecules were not considered in the short-pulse studies (see however [9] which considers rotational motion upon

applying unchirped ps infrared pulses to HF molecules). It may be expected that for intense optical pulses with pulse durations short compared with the rotation time of the molecule, selectively of ro-vibronic states may be infeasible due to the ‘mushrooming’ of the rotational levels populated by an intense light pulse and the non-adiabaticity within the rotational manifold of levels. Here, we show that, despite this expectation, fully-selective population transfer from the ground ro-vibronic level of a diatomic molecule to a single ro-vibronic level of an excited electronic state is possible with pulses of duration even well below the rotation time of the molecule. We explicitly consider the Na₂ three-electronic-level model studied in [4–7] involving transitions from the lowest vibrational level of the ground electronic state to the lowest vibrational level of a third electronic state via allowed optical transitions from the ground and third electronic states to a second (intermediate) electronic state, $X^1\Sigma_g^+ \rightarrow A^1\Sigma_u^+ \rightarrow 2^1\Pi_g$. The molecular rotation time of Na₂ are 170, 240, and 410 ps for the initial ($X^1\Sigma_g^+$), intermediate ($A^1\Sigma_u^+$), and final ($2^1\Pi_g$) electronic state, respectively, yet we succeed in fully selective population transfer using pulses even for pulses as short as 50 ps.

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2. Methods

Our objective is to totally move the population from the ground ro-vibronic state of the $X^1\Sigma_g^+$ manifold, with a minimum in the potential at 5.8 Bohr, to a single ro-vibronic state within the rotational manifold of the $2^1\Pi_g$ electronic state, with a minimum in the potential at 9.0 Bohr, by optically coupling these manifolds to the intermediate ro-vibronic manifold $2^1\Pi_g$, with a minimum in the potential at 6.8 Bohr. The electromagnetic field consists of short-duration light pulses that are linearly polarized along a space-fixed z -axis and have frequencies centered at ω_1 and ω_2 , which are roughly resonant with the $X^1\Sigma_g^+ - A^1\Sigma_u^+$ and $A^1\Sigma_u^+ - 2^1\Pi_g$ transitions, respectively. The light pulses have a Gaussian temporal amplitude and chirps that vary with time (see below). Using a basis of states $\{|e\rangle|J\Omega M\rangle|\psi_{eJ\Omega M}(R, t)\rangle\}$, we numerically solve the time-dependent Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t} \psi_j(R, t) = \sum_k H_{jk}(R, t) \psi_k(R, t), \quad (1)$$

for the wave packets $\{\psi_j(R, t)\}$ labeled by $j = eJ\Omega M$. The Hamiltonian for the optically-dressed molecule is

$$\mathbf{H} = \frac{\hbar^2}{2m} \frac{\partial^2}{\partial R^2} \mathbf{1} + \mathbf{V}(R, t), \quad (2)$$

where $\mathbf{1}$ is the unit matrix, and $\mathbf{V}(R, t)$ is the potential energy matrix, including the Rabi frequency coupling by the chirped time-dependent light fields. After making the rotating-wave approximation, an excellent approximation for the ps pulse durations and 10^{11} W/cm² intensities used here [1–3,10], the off-diagonal matrix elements of the Hamiltonian, $V_{eJ\Omega M, e'J'\Omega'M'}(R, t)$, are given in terms of the Rabi frequencies which couple the ro-vibronic molecular states, $V_{eJ\Omega M, e'J'\Omega'M'}(R, t) = \hbar \tilde{\Omega}_{eJ\Omega M, e'J'\Omega'M'}(R, t)/2$, where the Rabi frequencies can be evaluated as follows [11]:

$$\begin{aligned} \tilde{\Omega}_{eJ\Omega M, e'J'\Omega'M'}(R, t) &= \frac{2A_{ee'}(t)}{\hbar} \sum_q \mu_q^{ee'}(R) \\ &\times \sqrt{(2J'+1)(2J+1)} (-1)^{q+M-\Omega} \\ &\times \begin{pmatrix} J & 1 & J' \\ -M & 0 & M' \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ -\Omega & -q & \Omega' \end{pmatrix}. \end{aligned} \quad (3)$$

Here, $A_{ee'}(t)$ is the complex chirped slowly varying envelope of the field nearly resonant with the ee' transition, $\mu_q^{ee'}(R)$ is the transition dipole moment for the ee' transition [11], and standard notation is used for the Wigner 3-J symbols in Eq. (3). For any given transition, q is fully determined and takes on the single value $q = \Omega - \Omega'$; this component of the transition dipole moment thereby fully determines the off-diagonal matrix element for the ee' radiative transition. The diagonal elements of $\mathbf{V}(R, t)$ take the form,

$$V_{eJ\Omega M, eJ\Omega M}(R) = U_e(R) + \frac{B_e(J(J+1) - \Omega^2)}{R^2} + \hbar\Delta_e, \quad (4)$$

where $U_e(R)$ is the Born–Oppenheimer (BO) potential curve for state $e(X^1\Sigma_g^+, A^1\Sigma_u^+, 2^1\Pi_g)$, Δ_e is the detuning of the appropriate laser from resonance with the molecular transition involving state e , and B_e is the rotational constant of state e . The laser chirps can be incorporated into the diagonal matrix elements of $\mathbf{V}(R, t)$ by making a phase transformation on the wave function vector. Hence, the off-diagonal elements of the resulting potential energy matrix become the absolute values of the Rabi frequencies, and the Hamiltonian matrix is real-symmetric [5,12–15]. An explicit description of this transformation is given in Eqs.(5) and (6) of [5].

The time-dependent Schrödinger equation is solved using a split-step Fast-Fourier transform method. The propagator can be written in terms of the potential and kinetic energy operators as

$$e^{-i(T+V)\Delta t/\hbar} \approx e^{-\frac{iV\Delta t}{\hbar}} e^{-\frac{iT\Delta t}{\hbar}} e^{-\frac{iV\Delta t}{\hbar}}, \quad (5)$$

where the diagonal \mathbf{V}_D and off-diagonal \mathbf{V}_{OD} parts of the potential matrix \mathbf{V} are separately treated:

$$\exp\left(\frac{-i\mathbf{V}\Delta t}{\hbar}\right) = \exp\left(\frac{-i\mathbf{V}_D\Delta t}{\hbar}\right) \sum_n \frac{(-i\mathbf{V}_{OD}\Delta t/(2\hbar))^n}{n!}. \quad (6)$$

The first term on the right-hand side (RHS) of Eq. (6) is diagonal and is propagated in exponentiated form. To simplify the calculations we make the commonly used R -centroid approximation in calculating the bound–bound transition dipole moments, evaluating the electronic transition dipole moments in the off-diagonal potential \mathbf{V}_{OD} at the R -centroid of the transition for the lowest vibrational states of the electronic surfaces. We then use the Taylor series expansion of the exponential of the off-diagonal operator, incorporating a sufficient number of terms in the expansion to insure unitarity. This procedure is adequate since Δt is small; it is more efficient than diagonalization of $\mathbf{V}_{OD}(t)$.

The slowly varying envelope of the fields are taken to be of the form

$$A_{ee'}(t) = A_{0ee'} \exp\left[-\frac{(t-t_{ee'})^2}{2\sigma_{ee'}^2} - i \int^t dt' (\omega_{ee'}(t') - \omega_{ee'})\right], \quad (7)$$

the instantaneous chirped frequency $\omega_{ee'}(t)$ is taken to have the form

$$\omega_{ee'}(t) = \omega_{ee'} + \delta\omega_{ee'} \left(\frac{1}{\pi} \arctan \frac{(t - T_{ee'})}{\tau_{ee'}}\right), \quad (8)$$

where $\delta\omega_{ee'}$ is the amplitude of the non-linear chirp, $T_{ee'}$ is the temporal center of the chirp, and $\tau_{ee'}$ is the chirp width [5]. We use Gaussian pulses whose intensities are centered at $t = 0$ (i.e., there is no time-delay between

pulses), central frequencies $\omega_1/2\pi = 14020$ and $\omega_2/2\pi = 16180$ cm^{-1} , respectively, and equal pulse widths (i.e., $\sigma_{A\Pi} = \sigma_{XA}$). The chirp amplitude parameters are taken as $\delta\omega_{XA} = 5.67 \times 10^{13}$, $\delta\omega_{A\Pi} = 3.67 \times 10^{13}$ s^{-1} , and the chirp widths as $\tau_{XA} = \tau_{A\Pi} = 38.70$ ps, and $T_{A\Pi} = T_{XA} = 0$. The peak chirp rates correspond to a peak rate of change of energy of 0.223 and -0.144 Hartree/ns for the dressed X and Π states, respectively. The pulse intensities are of order 10^{11} W/cm^2 .

In order to insure adiabaticity with respect to the electronic and vibrational degrees of freedom in the transitions we use the concept of adiabatic following of light-induced potentials to determine the pulse parameters as discussed in [4,5]. The general idea is that, were the rotational degrees of freedom adiabatic, population would go directly from the initial $|X^1\Sigma_g^+, v=0, J=0, \Omega=0, M=0\rangle$ state to the final $|2^1\Pi_g, v=0, J=2, \Omega=1, M=0\rangle$ state without populating other rotational and vibrational states in these electronic manifolds. The rotational manifold of the ground electronic state that participates in the optical dynamics, $|X, J, \Omega=0, M=0\rangle |\psi_{X,J00}(R, t)\rangle$ (with $J = 0, 2, 4, \dots$), is chirped up in frequency (by the optical dressing with an up-chirped laser pulse) and the manifold of the target electronic state $|\Pi, J, \Omega=1, M=0\rangle |\psi_{\Pi,J10}(R, t)\rangle$ (with $J = 2, 4, 6, \dots$) is chirped down in frequency (by the dressing with a down-chirped laser). These two manifolds cross near $t = 0$, the time at which the Rabi frequencies for the two transitions are both peaked. The intermediate electronic state manifold $|A, J, \Omega=0, M=0\rangle |\psi_{A,J00}(R, t)\rangle$ (with $J = 1, 3, 5, \dots$) is blue detuned with respect to the crossing point between the ground and target electronic manifolds (see Fig. 1). This pulse sequence results in an adiabatic light-induced potential surface that is softened in the interaction region near the crossing point due to the repulsive interaction with the blue detuned intermediate surface. As shown in Fig. 1, a softening of the adiabatic surface barrier results with increasing Rabi frequency. The initial wave packet has all the population in the $|X, 000\rangle |\psi_{X,000}(R, t)\rangle$ component wave packet. This component is coupled only to the $|A, 100\rangle |\psi_{A,100}(R, t)\rangle$ component wave packet, which in turn is coupled to $|\Pi, 200\rangle |\psi_{\Pi,210}(R, t)\rangle$ and the $|X, 000\rangle |\psi_{X,200}(R, t)\rangle$ component wave packet, etc. With our choice of laser polarizations, $\Delta M = 0$ and hence $M = 0$ for all states involved in the process. Q branch transitions vanish since $\begin{pmatrix} J & 1 & J \\ 0 & 0 & 0 \end{pmatrix}$ vanishes.

3. Numerical simulations

For pulse durations that are much longer than the rotation time of the molecule (i.e., $\sigma \gg \tau_{\text{rot}} = 500$ ps), we expect this scheme to obey the adiabatic theorem so that the population will remain on the lowest adiabatic

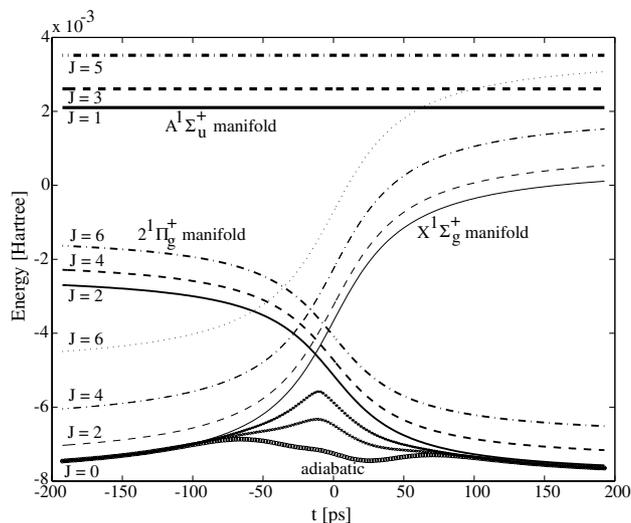


Fig. 1. Minimum with respect to R of the diabatic time-dependent potentials, $\min_R V_{ii}(R, t)$, and the lowest adiabatic potential, $\min_R V_{\alpha=1, \beta=1}(R, t)$, for three different values of peak Rabi frequency (the three curves at the bottom of the figure), for $\hbar\Omega_{XA} = \hbar\Omega_{A\Pi} = 6.0 \times 10^{-3}$ (filled circles – highest of the three curves), 8.0×10^{-3} (crosses – middle curve), 10.0×10^{-3} Hartree (1320, 1760, and 2200 cm^{-1} , respectively) (unfilled circles – lowest curve). The up-chirped curves are for the $X^1\Sigma_g^+$ state, the down-chirped curves are for the $2^1\Pi_g$ state and the unchirped curves are for the $A^1\Sigma_u^+$ state. The rotational constants are taken to be 100 times larger than in reality so that the curves can be seen on this scale.

light-induced surface throughout the whole process, and the probability for being on the target ro-vibrational state at the final time should be close to unity, $P_{\Pi,210}(T_f) \rightarrow 1$. In Fig. 2 we show the lowest adiabatic light-induced surface potential as a function of R and t . The adiabatic surface coincides with the up-chirped ground electronic state as $t \rightarrow -\infty$, whereas for $t \rightarrow \infty$ it coincides with the down-chirped terminal electronic state. While adiabatic propagation on such a surface ensues for long pulse durations, coupling between adiabatic surfaces with different J is expected for pulse durations shorter than the rotation time due to the near degeneracy of rotational states with different J . It is convenient to consider basis states $|e, \pm\rangle = |e\rangle \frac{1}{\sqrt{2}} (|000\rangle \pm |200\rangle)$. In this basis, solely the $|X, +\rangle$ state is coupled while the $|X, -\rangle$ state is dark (uncoupled) and therefore does not participate in the process. We shall find that our scheme is highly selective in reaching the target ro-vibronic state because basically only one level ($|X, +\rangle$) is coupled in the process.

We calculate the dynamics of the system for pulse durations well below the rotation time. Fig. 3a–c shows the probability of being in states $|e, J\Omega\rangle$ as a function of time during the optical process for 50 ps pulses and peak Rabi frequencies $\hbar\Omega_{XA} = \hbar\Omega_{A\Pi} = 6 \times 10^{-3}$ Hartree (1320 cm^{-1}), which corresponds to intensities of 7.86×10^{10} and 1.69×10^{11} W/cm^2 , respectively. The probabilities are calculated by integrating the absolute

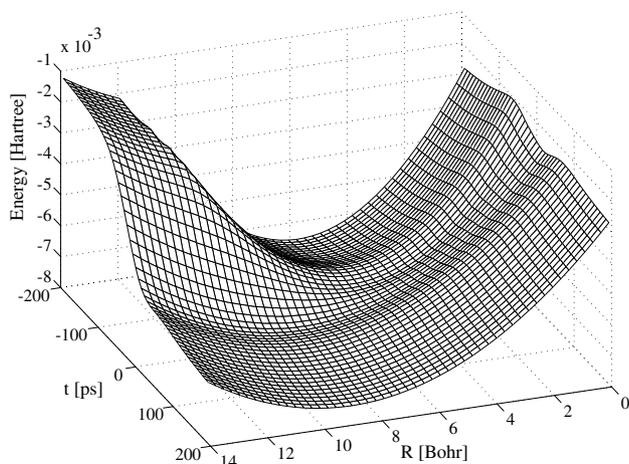


Fig. 2. Lowest adiabatic light-induced potential surface versus t and R . A manifold of nearly degenerate such surfaces that differ by rotational energy differences exist.

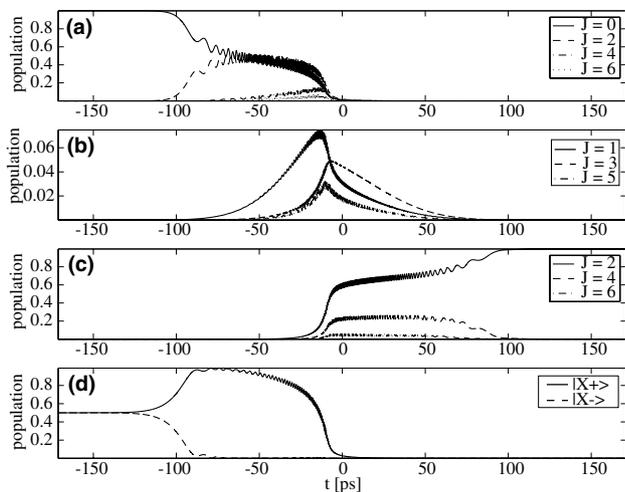


Fig. 3. Probability of the ro-vibrational states versus time. (a) Population of the $X^1\Sigma_g^+$ state for $J = 0, 2, 4$ ($J = 6$ is too small to be seen). (b) Population of the $A^1\Sigma_u^+$ state for $J = 1, 3, 5$. (c) Population of the $2^1\Pi_g$ state for $J = 2, 4, 6$. (d) Population of the $X^1\Sigma_g^+ | \pm \rangle = X^1\Sigma_g^+ \frac{1}{\sqrt{2}} (|000\rangle \pm |200\rangle)$ states.

value squared of the wave packet on the state over the internuclear coordinate. In this simulation we took $J = 0, 2, 4, 6$ states in the $X^1\Sigma_g^+$ manifold, $J = 1, 3, 5$ in the $A^1\Sigma_u^+$ manifold, and $J = 2, 4, 6$ in the $2^1\Pi_g$ manifold. The time-dependence of $\max_R \{ |\psi_{\Pi,210}(R, t)|^2 \}$ (not shown in the figure) looks just like the time-dependence of the population up to a multiplicative constant. The stationary behavior of $\max_R \{ |\psi_{\Pi,210}(R, t)|^2 \}$ as $T \rightarrow -\infty$ and the $T \rightarrow \infty$ form of the wave packet show that the final state contains only the ground vibrational level of the Π state. As shown in Fig. 3a, the dynamics within the rotational manifold of states within the ground electronic state manifold is nonadiabatic, as expected for such short-pulses, nevertheless, full selec-

tivity is achieved for the target ro-vibrational state. In the lowest panel of Fig. 3d we show the population versus time for the $|X, +\rangle$ and $|X, -\rangle$ states. The two almost degenerate $J = 0$ and $J = 2$ levels are strongly coupled so that for times when the Rabi frequencies are large, the relevant states of the system are the $|+\rangle$ and $|-\rangle$ states. The energy difference between the $|+\rangle$ and $|-\rangle$ states is enhanced as the coupling is increased. These states are equally populated at the beginning of the process, but the total population moves adiabatically to the $|+\rangle$ state which has lower energy. It can be shown that for exactly degenerate states the $|-\rangle$ state is a dark state and the population on it remains constant through the whole process. However, in our case, the two states are not exactly degenerate and there is complete transfer of the population to the $|+\rangle$ state which, in turn, couples solely to the $|\Pi, 210\rangle$ rotational state. Population on the A state develops and then disappears as the population is transferred to the Π state. The population on the higher rotational levels of the Π state eventually transfer to the lowest rotational level. We investigated the behavior of the system under a large range of pulse durations, intensities and chirps parameters. In contradistinction to the long-pulse Stirap process which shows monotonic growth of population in the desired state as a function of increasing Rabi frequencies [1–3], here the Rabi frequency (intensity) dependence is non-monotonic, and 99.9% probability is achieved for the desired ro-vibrational state only for a narrow range of Rabi frequencies around the optimal. The selectivity and full population transfer is also rather sensitive to the laser chirp rates, but rather robust to small changes in the time-delay between pulses, detuning, and increase in pulse width duration.

We played with a toy model to show that full selective population transfer can also be achieved for the case when the final electronic state is $^1\Sigma_g$, rather than the $^1\Pi_g$ state as considered above. The model used an identical potential curve for the final $^1\Sigma_g$ state to that used for the final Π state above. Total selective population transfer can be obtained using similar pulses to those used above.

4. Multiphoton ionization

In order to estimate the multiphoton ionization that might occur during our population transfer process, we carried out a study using time-dependent density-functional theory which can determine the above threshold ionization of molecules in the presence of intense laser pulses [16–18]. Our study used 25 and 50 fs duration unchirped and chirped far-off-resonance pulses, since longer pulses are prohibitively time consuming, with detunings and peak intensities corresponding to the pulses used here. The pulses used in this study were of

the same form as the pulses described above, except that their temporal duration is about 1000 times shorter. We found the calculated averaged ionization rate is on the order of 10^{10} s^{-1} for these pulses, independent of pulse duration. If we assume that the amount of ionization for longer pulses of the same peak intensity is also proportional to pulse duration, our results suggest that multiphoton ionization might be significant for the 10^{11} W/cm^2 peak intensity, 50 ps pulses used in our calculations. We also checked the effect of chirp on the multiphoton ionization by using linearly chirped pulses with the same chirp rates as the two pulses used in our population transfer scheme, corresponding to 0.223 and $-0.144 \text{ Hartree/ns}$, and, not surprisingly, found completely negligible changes in the multiphoton ionization rate due to chirp. Moreover, we checked the effect of chirp on the multiphoton ionization by using linearly chirped pulses with the same chirp *range* as the two pulses used in our population transfer scheme, corresponding to 0.223 and $-0.144 \text{ Hartree/ps}$, and found that this fast chirp increases the multiphoton ionization rate less than 10%. The present calculation can only assess the vertical ionization rate from the initial nuclear configuration. For the control process described in this Letter, the ionization rate may change substantially when the nuclei move to new positions. Despite this, it is possible to deduce from the present calculation that multiphoton ionization may pose a problem, and it could deleteriously affect the process proposed. An independent indication that this might be the case can be inferred from experiments reported in [19], although these experiments were carried out in a different wavelength range and pulse duration than used in our population transfer scheme. Further details of our study of multiphoton ionization will be published elsewhere [20].

5. Summary and conclusion

In summary, complete selective population transfer in a diatomic molecule from the ground ro-vibronic state to a specific final excited ro-vibronic state has been obtained in our numerical calculations with chirped optical pulses of duration shorter than the molecular rotation time. Non-chirped pulses lead to mushrooming of the number of rotational levels populated, as does the use of chirps of opposite sign to those used here. Previous suggestions for short-pulse adiabatic population transfer in molecules excluded rotational degree of freedom from consideration. Inclusion of rotational degrees of free-

dom significantly changes the nature of the dynamics for short intense light pulses, since the rotational degrees of freedom are not able to respond adiabatically. Nevertheless, we showed that even when the rotational degrees of freedom are included, complete population transfer is still possible for the ro-vibronic process considered here. Our method can be viewed as a robust generalization of the vibrational-rotational state selective population transfer discussed in [9] to the ro-vibronic case. However, for our electronic process, time-dependent density-functional theory calculations of the ionization rate indicate that for the short intense pulses used, multiphoton ionization could be a significant deleterious effect. Our time-dependent density-functional technique can be employed quite generally for optimal-control population transfer schemes for estimating multiphoton ionization in the domain of ultrashort laser pulses. Experiments are needed to test these ideas and to determine in practice the degree of population transfer and multiphoton ionization in the adiabatic following process suggested here.

Useful conversations with Carl J. Williams are gratefully acknowledged. This work was supported in part by grants from the Israel Science Foundation for a Center of Excellence (Grant No. 8006/03), by the Binational (US–Israel) Science Foundation under Grant No. 2002147, and by the GIF under Grant No. 699.

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