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Selective excitation of the vibrational-rotational states and dissociation of diatomic molecules by picosecond infrared laser pulses: Modeling for HF in the ground electronic state

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Complete, close to 100%, population transfer between the bound vibrational-rotational states of the HF molecule in the ground electronic state is demonstrated on a picosecond time scale by means of computer simulation within the Schrödinger wave-function formalism. The laser-induced dissociation from selectively prepared moderately high vibrational-rotational states is shown to be very efficient, with the dissociation probability approaching 100%. These processes are controlled by $\sin^2$-shaped linearly polarized picosecond laser pulses in the infrared domain. [S1050-2947(99)05003-9]

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I. INTRODUCTION

State-selective control of molecular dynamics with ultrashort laser pulses, in particular, complete localization of population at a selected energy level on the picosecond and femtosecond time scales is a very promising line in molecular physics and has attracted much interest recently (see, for example, Refs. [1–8] and references therein). Until now, the ultrafast population transfer on the picosecond and femtosecond time scales has been simulated for vibrational [1–7] and vibronic [8] transitions, neglecting molecular rotational motion. Ultrafast selective preparation of the vibrational-rotational states with infrared (IR) laser pulses has not been studied yet. For example, the multiphoton IR excitation and dissociation of the rotating HF molecule has been simulated in Ref. [9] by making use of chirped laser pulses, and in Ref. [10] by making use of the optimal control theory (OCT), but the state selectivity of the process has not been studied therein.

The well-known adiabatic passage approach for the coherent population transfer between the vibrational-rotational states of diatomic molecules in the ground electronic state (see Ref. [11] and references therein) is realized on a nanosecond time scale only and makes use of the the excited electronic state as the intermediate one (the λ-type level configuration).

In this work we develop an alternative approach to multiphoton excitation and dissociation of rotating diatomic molecules. The approach is demonstrated on the picosecond time scale and based on a reasonable choice of the excitation and dissociation pathways solely in the ground electronic state, where use is made of a constructive interference of different excitation routes and state-selective overtone transitions. Firstly, we demonstrate the complete, 100% population transfer between the bound vibrational-rotational states, which makes it possible to prepare a specified state selectively by making use of one or more laser pulses. Secondly, we demonstrate an efficient, close to 100%, dissociation from selectively prepared moderately high vibrational-rotational states. Both the preparation and dissociation are controlled by optimal linearly polarized shaped picosecond IR laser pulses.

Until now, close to 100% dissociation on the picosecond time scale has been simulated only for rotationless models of diatomic molecules [7,12,13], where molecular dipoles are aligned along the electric field axis of a linearly polarized laser pulse. Such an approximation cannot be used when dealing with rotating molecules, and basically new control schemes should be designed to control dissociation with almost 100% probability.

II. MODEL AND TECHNIQUES

As a model system we consider the HF molecule in the ground electronic state. The molecular parameters are adapted from Ref. [10]. Specifically, the potential energy curve is of the Morse form,

$$U(r)=D_e\{\exp[-2\beta_e(r-r_e)]-2\exp[-\beta_e(r-r_e)]\}, \tag{1}$$

where the well depth is $D_e=0.225\,009E_H$, the Morse parameter $\beta_e=1.174\,014a_0^{-1}$, and the equilibrium distance is $r_e=1.732\,516a_0$ (E_H is the Hartree energy and a_0 is the Bohr radius).

Initially, at $t=0$, the HF molecule is assumed to be in the ground vibrational ($v=0$) and ground rotational ($j=0$) state, which implies that an initial temperature is less than about 10 K. Since the linearly polarized laser fields are to be used, the magnetic quantum number $m=0$ is conserved, and the molecule is described by the azimuthally symmetric two-dimensional molecular Hamiltonian

$$\mathcal{H}_{mol}(r,\vartheta)=-\frac{\hbar^2}{2m_r}\frac{\partial^2}{\partial r^2}+U(r)-\frac{\hbar^2}{2m_r r^2}\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\sin\vartheta\frac{\partial}{\partial\vartheta}, \tag{2}$$

where the reduced mass is $m_r=1744.632\,07m_e$ (m_e is the electron rest mass), and ϑ is the angle between the molecular axis and the laser electric-field axis. Interaction with the laser field is treated semiclassically, by the interaction Hamiltonian

$$\mathcal{H}_{int}(r,\vartheta,t)=-\mu(r)\cos\vartheta\,\mathcal{E}(t), \tag{3}$$

where $\mathcal{E}(t)$ is the laser electric-field strength, and the molecular dipole moment function is $\mu(r)=\mu_0 r\exp(-\gamma r^4)$, with $\mu_0=0.454\,141e$ (e is the elementary charge), and $\gamma=0.0064a_0^{-4}$.

The laser fields to be used below for state-selective vibrational-rotational excitation and dissociation of HF may be composed of several $\sin^2$-shaped pulses,

$$\mathcal{E}(t)=\sum_n \mathcal{E}_n\sin^2[\pi(t-t_{0n})/t_{pn}]\cos[\omega_n(t-t_{0n})+\varphi_n], \tag{4}$$

where the nth pulse starts at $t=t_{0n}$, its duration is t_{pn}, the pulse amplitude is $\mathcal{E}_n$, and ω_n is the carrier frequency. The phases φ_n proved to be of minor importance, and the results below are presented for $\varphi_n=0$. The $\sin^2$ shape of the laser pulses used here as in Refs. [1,4–8,12] is suitable, but rather arbitrary—similar results can be obtained by using other reasonable, ''bell''-type, shapes of the pulses, for example, Gaussian.

As an absorbing boundary condition at large r use is made of the imaginary optical potential

$$U_{opt}(r)=-iU_0\exp\{(3/2)[1-(r_{max}-r_{opt})^2/(r-r_{opt})^2]\}, \tag{5}$$

if $r\geqslant r_{opt}$, and $U_{opt}(r)=0$ otherwise. With $r_{max}=20.0a_0$ (see below), we set $r_{opt}=12.5a_0$, and $U_0=0.090\,708E_H$.

The quantum dynamics of the molecule is governed by the time-dependent Schrödinger equation

$$(i\hbar)\partial\Psi(r,\vartheta,t)/\partial t=[\mathcal{H}_{mol}(r,\vartheta)+U_{opt}(r)+\mathcal{H}_{int}(r,\vartheta,t]\Psi(r,\vartheta,t). \tag{6}$$

The wave function and the operators of Eq. (6) have been transformed from the (r,ϑ) space to the $(r,x=\cos\vartheta)$ space and represented therein on the 256×24-point grid. The radial part was the 256-point equidistant grid with $r_{min}=0.05a_0$, and $r_{max}=20.0a_0$. The angular grid points were the Gauss-Legendre quadrature points $x_k=\cos(\vartheta_k)$, $k=1,2,\ldots,24$, with the respective weights w_k [14,15]. The time propagation has been accomplished by a split operator method [16]. The time step Δt ranged from 0.1 to 0.9 atu. At each time step, the action of the radial part of the kinetic energy operator on the wave function has been evaluated with the fast Fourier transform procedure, and that of the angular part — by making use of the expansion of the wave function in normalized Legendre polynomials, $P_j(x_k)$, $j=0,1,\ldots,23$, as described in Ref. [15].

The time-dependent wave function $\Psi(t)$, being projected on the vibrational-rotational eigenstates $|v,j\rangle$, yields the time-dependent population

$$P_{v,j}(t)=|\langle j,v|\Psi(t)\rangle|^2. \tag{7}$$

The eigenvalue problem with the molecular Hamiltonian (2) has been solved for the bound states $|v,j\rangle$ with $j=0,1,\ldots,23$ by the Fourier grid Hamiltonian method [17].

III. STATE-SELECTIVE EXCITATION AND DISSOCIATION

As the first target for selective preparation we choose the moderately high vibrational-rotational state $|v=10,j=1\rangle$. Selective preparation of the target state $|10,1\rangle$ from the initial one $|0,0\rangle$ can be achieved by three laser pulses via the intermediate states $|2,1\rangle$ and $|6,1\rangle$ according to the excitation pathway

$$|0,0\rangle\rightarrow(1\text{ photon})\rightarrow|2,1\rangle\rightarrow(2\text{ photons})\rightarrow|6,1\rangle\rightarrow(2\text{ photons})\rightarrow|10,1\rangle. \tag{8}$$

Each of the three steps is to be selectively controlled by a single laser pulse, which should be optimized to yield the 100% population transfer for the respective transition. The optimization procedure used is similar to that described in Refs. [1,4].

The first step in the excitation pathway (8) is the overtone R-transition $|0,0\rangle\rightarrow|2,1\rangle$, while the other two steps are the ''forbidden'' Q-type transitions

$$|v,j\rangle\rightarrow(2\text{ photons})\rightarrow|v+4,j\rangle. \tag{9}$$

The idea is that each of these forbidden transitions is to be accomplished via two excitation routes, involving two sequential one-photon transitions: the $(R+P)$ route,

$$|v,j\rangle\overset{R}{\rightarrow}|v+2,j+1\rangle\overset{P}{\rightarrow}|v+4,j\rangle, \tag{10}$$

and the $(P+R)$ route,

$$|v,j\rangle\overset{P}{\rightarrow}|v+2,j-1\rangle\overset{R}{\rightarrow}|v+4,j\rangle, \tag{11}$$

which can interfere constructively providing the complete population transfer. The proposed control scheme is somewhat similar to that of Shapiro and Brumer [18], where two independent excitation routes are controlled by two laser fields. On the contrary, in our case, the two routes (10) and (11) are to be controlled by a single laser pulse.

The population dynamics controlled by three optimal nonoverlapping 1-ps laser pulses is shown in Fig. 1(a), where the initial, intermediate, and target states are indicated explicitly, and curve ''others'' gives the overall population of all other bound states. The sequence of three optimal laser pulses is shown in Fig. 1(b). It is seen that each pulse provides complete population transfer for the respective transition. The final population of the target state at the end of the third pulse is $P_{10,1}(t=3\text{ ps})=0.9966$. The time-dependent rotational energy of HF is presented in Fig. 1(c). It demonstrates the oscillatory behavior during each laser pulse and takes, with a very good accuracy, the value of the first rotational quantum of the intermediate and target states at the end of the respective pulse. This serves as an additional demonstra-

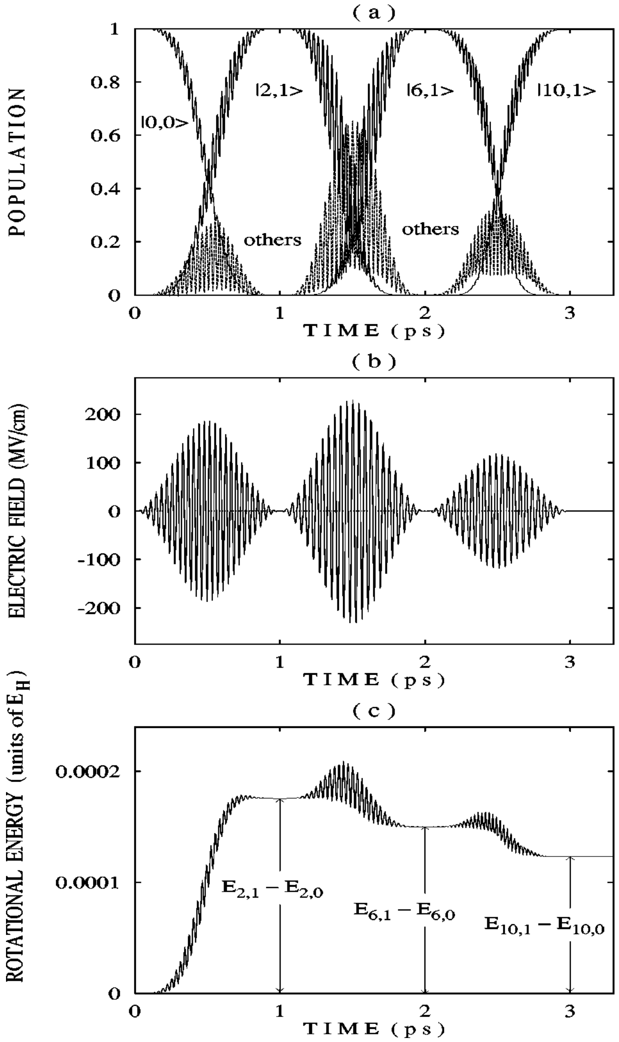

FIG. 1. Complete population transfer from the initial vibrational-rotational state $|v=0,j=0\rangle$ to the target state $|v=10,j=1\rangle$ of HF controlled by three nonoverlapping 1-ps laser pulses. (a) Population dynamics. (b) Optimal laser field: $\mathcal{E}_1^{opt}=186.66$ MV/cm, $\omega_1^{opt}=7795.52$ cm^{-1}, $\mathcal{E}_2^{opt}=233.46$ MV/cm, $\omega_2^{opt}=6710.88$ cm^{-1}, $\mathcal{E}_3^{opt}=119.81$ MV/cm, and $\omega_3^{opt}=5323.80$ cm^{-1}. (c) Time-dependent rotational energy of the HF molecule during selective preparation of vibrational-rotational state $|v=10,j=1\rangle$.

tion of a very high state selectivity of the process, even at the smallest rotational sublevel spacing corresponding to $j=1$.

Both shorter (0.5 ps) and longer (2 ps) laser pulses have been used in our simulations. The 2 ps-pulses provide even a better state selectivity, while the 0.5 ps pulses, which require stronger optimal laser fields, decrease the state selectivity by approximately 2–3% for excitation pathway (8). Excitation pathway (8) can also be controlled by overlapping laser pulses, which reduce the overall time of the process and provide almost the same population transfer to the target state of the isolated molecule if the overlaps are not too large, for example, not much larger than half of the pulse duration (see also Ref. [4]). Note that overlapping laser pulses may provide much better population transfer than the nonoverlapping pulses if the molecule is coupled to a thermal environment (similarly to overlapping pulses used previously to control dissipative quantum dynamics of rotationless models of OH [5,6]).

An evident extension of the excitation pathway (8) makes it possible to selectively prepare higher vibrational-rotational states. The problem of selective preparation of the topmost states, close to the dissociation threshold, will be considered in a separate work. Now, we assume that the HF molecule is selectively prepared in the moderately high state $|v=10,j=1\rangle$, as described above, and consider its laser-induced dissociation from this state.

The dissociation yield is defined by the integrated outgoing flux at $r=r_{opt}$,

$$D(t)=\frac{\hbar}{m_r}\mathrm{Im}\left(\int_0^t dt'\int_{-1}^{1}dx\Psi^*(r_{opt},x,t')\times\partial\Psi(r_{opt},x,t')/\partial r\right). \tag{12}$$

Our approach to the laser-controlled dissociation is as follows. Starting from selectively prepared state $|10,1\rangle$, we choose state $|17,2\rangle$ as a higher intermediate state that, being pumped in three-photon resonance, is spaced by less than one-photon energy from the continuum. The dissociation is to be controlled by a single 1-ps laser pulse, according to the dissociation pathway

$$|10,1\rangle\rightarrow(3\ \text{photons})\rightarrow|17,2\rangle\rightarrow(1\ \text{photon})\rightarrow\text{``continuum.''} \tag{13}$$

The intermediate state $|17,2\rangle$ is accessible from the initial one $|10,1\rangle$ via three interfering excitation routes, involving three sequential one-photon transitions: the $(P+R+R)$ route,

$$|10,1\rangle\xrightarrow{P}|12,0\rangle\xrightarrow{R}|14,1\rangle\xrightarrow{R}|17,2\rangle, \tag{14}$$

the $(R+P+R)$ route,

$$|10,1\rangle\xrightarrow{R}|12,2\rangle\xrightarrow{P}|14,1\rangle\xrightarrow{R}|17,2\rangle, \tag{15}$$

and the $(R+R+P)$ route,

$$|10,1\rangle\xrightarrow{R}|12,2\rangle\xrightarrow{R}|14,3\rangle\xrightarrow{P}|17,2\rangle. \tag{16}$$

The intermediate state $|17,2\rangle$ should not be prepared selectively but serves to enhance the overall dissociation process. We set the laser carrier frequency to the exact three-photon resonance, $\omega_{res}=(E_{17,2}-E_{10,1})/3\hbar$, and calculate the dissociation yield at the end of the pulse as a function of the pulse amplitude for three pulse durations: $t_p=0.5$, 1, and 2 ps. The results presented in Fig. 2(a) show that the dissociation yield may approach 100%, which is basically a matter of the laser field strength used. Note that while the resonant laser frequency used, $\omega_{res}=3998.389$ cm^{-1}, is a reasonable initial guess, it is still not optimal for every field strength. An additional optimization of the frequency at a given laser field strength makes it possible to further increase the dissociation yield (details will be reported elsewhere).

The above considered approach, where use is made of forbidden Q-type transitions [see Eqs. (8)–(11)], makes it possible to excite a diatomic molecule vibrationally and keep its rotational energy corresponding to a fixed j [for example,

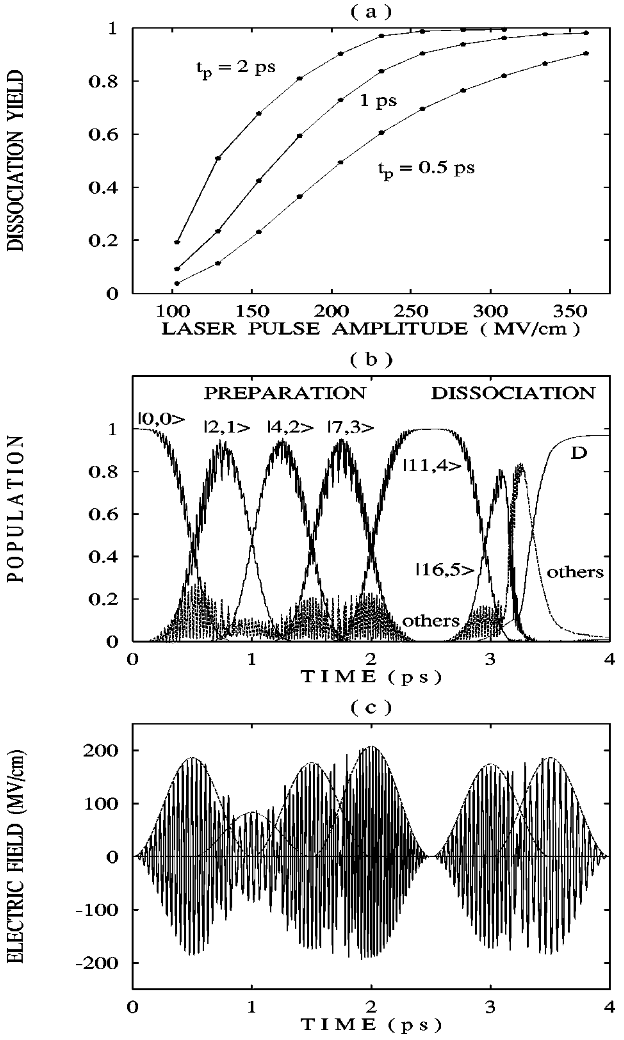

FIG. 2. Laser-controlled dissociation of HF. (a) Dissociation from state $|10,1\rangle$ by single laser pulses. (b) Selective preparation of state $|11,4\rangle$ controlled by four overlapping 1-ps laser pulses, followed by dissociation controlled by two overlapping 1-ps pulses (the 0.5-ps overlaps are used). (c) Optimal laser field: $\mathcal{E}_1^{opt}=186.66$ MV/cm, $\omega_1^{opt}=7795.52$ cm^{-1}, $\mathcal{E}_2^{opt}=83.30$ MV/cm, $\omega_2^{opt}=7129.41$ cm^{-1}, $\mathcal{E}_3^{opt}=176.89$ MV/cm, $\omega_3^{opt}=9373.32$ cm^{-1}, $\mathcal{E}_4^{opt}=207.74$ MV/cm, $\omega_4^{opt}=10029.33$ cm^{-1}, $\mathcal{E}_5^{opt}=174.32$ MV/cm, $\omega_5^{opt}=8557.75$ cm^{-1}, $\mathcal{E}_6^{opt}=186.66$ MV/cm, and $\omega_6^{opt}=902.98$ cm^{-1}.

$j=1$ as in Fig. 1(a)]. In order to prepare vibrational-rotational states with higher j one can use sequential R-transitions. The example given in Fig. 2(b) demonstrates selective preparation of the moderately high target state $|v=11,j=4\rangle$, followed by the laser-induced dissociation. The preparation stage is accomplished by four overlapping 1-ps laser pulses with the 0.5-ps overlaps of the pulses. The excitation pathway involves four sequential one-photon R transitions:

$$|0,0\rangle \overset{R}{\rightarrow} |2,1\rangle \overset{R}{\rightarrow} |4,2\rangle \overset{R}{\rightarrow} |7,3\rangle \overset{R}{\rightarrow} |11,4\rangle. \tag{17}$$

The final population of the target state at the end of the fourth laser pulse is $P_{11,4}(t=2.5\ \text{ps})=0.9991$. The dissociation from selectively prepared state $|11,4\rangle$ is accomplished by two 1-ps laser pulses with the 0.5-ps overlap. The dissociation pathway is chosen as follows:

$$|11,4\rangle \rightarrow (1\ \text{photon}) \rightarrow |16,5\rangle \rightarrow (4\ \text{photons})$$
$$\rightarrow |22,5\rangle \rightarrow (1\ \text{photon}) \rightarrow \text{continuum}. \tag{18}$$

Pathway (18) is based on those used in this work previously. The first step is the overtone R transition $|11,4\rangle \rightarrow |16,5\rangle$. The second step is the "forbidden" Q-type four-photon transition $|16,5\rangle \rightarrow |22,5\rangle$, which is accomplished via six interfering excitation routes from state $|16,5\rangle$ to state $|22,5\rangle$, with the latter, being spaced by less than one-photon energy from the continuum, serving to enhance the dissociation process. The optimal laser field controlling both the preparation and dissociation stages is shown in Fig. 2(c) together with the $\sin^2$-shaped envelopes of the overlapping pulses. The final dissociation yield is $D(t=4\ \text{ps})=0.9698$.

As already mentioned earlier, our control schemes are quite flexible with respect to the overlaps of the the laser pulses, when dealing with the isolated molecule. The 0.5-ps overlaps used in the preparation and dissociation stages (17) and (18) are close to the maximum that still provides almost complete population transfer. Similar dissociation yields (more than 96%) have been obtained with nonoverlapping pulses and with overlapping preparation and dissociation stages.

IV. DISCUSSION

The OCT-designed superposition of five subpicosecond IR laser pulses used in Ref. [10] provided the maximal dissociation yield of only 25% for the same model of HF as used in the present work. A brief comparison of our approach with that of Ref. [10] is in order. Rabitz and coworkers [10] have used a superposition of five single-frequency Gaussian pulses with identical fixed amplitudes and widths. The phases of the pulses have been set to zero. With the overall duration of the global laser field being limited to 1.6 ps, the time centers of the five pulses (timings) and their carrier frequencies have been optimized to maximize the dissociation yield. On the contrary, in our approach the timings of the laser pulses are quite flexible for the isolated molecule, while their amplitudes and carrier frequencies are optimized to yield the complete population transfer at every stage of the process. The shorter duration of the global laser field (1.6 ps) used in Ref. [10] seems not to be the main reason of a comparatively small dissociation yield. We have performed several simulations with the 0.5-ps laser pulses for pathways (17) and (18), thus reducing our time scale to 2 ps, and dissociation yields of about 87% have been calculated. On the other hand, since all optimal laser pulses designed in our work have different amplitudes, one can assume that the identity of amplitudes of all laser pulses used in Ref. [10] was probably a too strong constraint.

The problem of whether complete dissociation of rotating diatomic molecules can also be achieved with chirped laser pulses requires a more detailed investigation. Here we only note that the optimal sequences of laser pulses designed in this work for complete dissociation of rotating HF can also be treated as global laser fields with a stepwise chirping. Both envelopes and time-dependent instantaneous frequencies of these global fields are substantially different from those used in Ref. [9] where dissociation yields of less than 15% only have been calculated for the rotating HF molecule.

In conclusion, the results of this work show that, similarly to the rotating HF molecule studied here, an optimal choice of the state-selective excitation and dissociation pathways makes it possible to achieve ultrafast selective preparation of prespecified vibrational-rotational states and dissociation of diatomic molecules with almost 100% probability. Experimental realization of the proposed control schemes becomes feasible with modern laser techniques [19,20].

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