

Dissipative State Selective Vibrational Excitation in Picolinic Acid *N*-oxide

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This paper investigates the effect of Redfield relaxation on the control of state selective excitation in a two-dimensional model system. The model potential, tailored to DFT data for picolinic acid *N*-oxide, comprises the proton transfer and the heavy atom coordinate. The present study shows that selective excitation of the O–H stretching mode can be achieved by simple analytical pulses satisfying the π pulse condition. The efficiency of the preparation is tested against the instability of pulse characteristics.

Key words: laser control, proton transfer, pulse shaping, Redfield relaxation.

INTRODUCTION

The problem of active control over light-matter interaction has been of considerable interest during the past ten years. In the most general terms laser control of a chemical reaction implies a strategy that best drives a given molecular system from a well defined initial state to a specific target state. This goal could be achieved by applying appropriately shaped sequence of laser pulses, short on a vibrational time scale.¹ In particular ultrafast laser sources in the infrared (IR) spectral range have opened the possibility of controlling reactions such as bond breaking during photodissociation or isomerisation reactions. Having these techniques at hand one may also wish to excite the molecule in a desired vibrational state along a specific bond.^{2,3} The rea-

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son for this is that molecular samples whose population resides almost completely in a particular excited states provide a ideal ground for studying intramolecular vibrational redistribution processes.⁴ On the other hand a selectively excited sample can be highly reactive intermediate in a chemical reaction. If the target state is a low vibrational state the population inversion can be achieved by applying the two-level system theory.⁵ Then the π -pulse criterion specifies the area of the pulse needed for complete population transfer. Applying the same methodology high vibrational states can be selectively excited using a sequence of overlapping IR pulses.⁶ Alternatively Chelkowski and Bandrauk developed the so called ladder-climbing strategy in which optically chirped pulses successfully overcome the anharmonicity of the molecular potential.^{7,8} From the experimental side, Maas and co-workers reported state selective excitation of the NO molecule by linearly chirped IR laser pulses.^{9,10}

In spite of the large amount of theoretical work done controlling the outcome of a chemical reaction in condensed phase is still an open problem. There are several issues that have to be addressed before laser control in condensed phase can be realized. A careful balance between pulse intensity and duration has to be achieved. While intense laser fields can overcome the problem of small transition dipole moments between the initial and the target state (typical situation in a polyatomic molecule) they induces side effects like deformation of the potential energy surface, ionization of the molecule and multiphoton transitions. Better selectivity can be obtained using longer and less intense laser pulses, but if the duration of the pulse is longer than the characteristic time for intramolecular vibrational relaxation (IVR) the state selectivity is destroyed.¹¹ The development of robust laser control strategies for multilevel systems that will take into account energy redistribution processes is therefore in the focus of theoretical interest. As the solution of the time dependent Schrödinger equation is limited by computational difficulties to systems with only few degrees of freedom (DOF) the system-bath idea has been frequently employed. The density matrix theory is one such approach in which few selected molecular degrees of freedom evolve in contact with a quantum environment.¹² In the Markovian (memoryless) approximation it has been used to study the influence of external fields on the dynamics of radiatively coupled potential energy surfaces¹³ as well as for selective excitation of the O–H stretching vibration.¹⁴ Recently we used density matrix theory in the state representation (Redfield theory) to study laser driven proton transfer in asymmetric model potentials¹⁵ and to investigate the influence of relaxation on time resolved infrared spectra.¹⁶ In order to satisfy the weak system-bath coupling approximation we included the strongly coupled heavy atom mode into the exactly treated system dynamics. Extensions of the same approach has been reported by Cina

and Ungar¹⁷ where they discussed the impact of different system-bath couplings (bilinear *versus* quadratic and correlated *versus* noncorellated) on the time resolved fluorescence signal.

In the present contribution we are concerned with laser control of the O–H stretching vibration in a two-dimensional model proton transfer system subject to energy and phase relaxation. The molecular system of our choice, picolinic acid *N*-oxide (PANO) has been identified as a medium strong hydrogen bonding system having a strongly asymmetric potential energy function with a minimum placed near the carboxylic oxygen atom.^{18,19} Our aim is to excite the molecule in a particular vibrational state and explore the robustness of the selected laser control scheme in a dissipative environment. Our intention is moreover to find laser field parameters that best cope with energy and phase relaxation within the dissipative dynamical calculation.

The rest of the paper is laid out as follows. In the next section (Theoretical model) we briefly review the density matrix theory in the Redfield formalism. The model Hamiltonian is then presented (the second subsection). In the following, third, section we present the numerical results of state selective excitation in a two-dimensional model of PANO in a coherent and dissipative environment. The paper is summarized in the last section.

THEORETICAL MODEL

Dissipative Dynamics

In spite of its apparent simplicity proton transfer reactions are characterized by a complex dynamics. The main cause of this complexity lays in the fact that the motion of the light particle is coupled to the motion of the remaining nuclear DOF.^{20,21,22} A proper treatment of proton transfer reactions therefore requires multidimensional quantum dynamics. Unfortunately the rapid rise of the required number of basic function with increasing system dimensionality limits the full quantum treatment of the dynamics to systems with only few degrees of freedom. Thus considerable attention has been paid to the development of approximative method.^{23–26} Density matrix theory is an appropriate method for studying the dynamics of the quantum system coupled to a fluctuation macroscopic environment.^{27,28,12} In the following we will briefly review the density matrix theory in the Markovian limit¹² *i.e.* we suppose that the decay of the bath correlation function is rapid compared with the system relaxation rate. The bath carries therefore no memory of the past states of the system. In this approach the dynamics of the system is described by the reduced density operator $\hat{\rho}_s(t)$ which is obtained by aver-

aging the statistical operator of the relevant system plus the environment $\hat{\rho}_{\text{tot}}(t)$ with respect to the statistical description of the environment

$$\hat{\rho}_{\text{s}}(t) = \text{Tr}_{\text{b}} \hat{\rho}_{\text{tot}}(t) \quad (1)$$

where the trace has been taken over the complete set of states of the environment. For quantitative considerations the equation of motion of the reduced density operator has to be recast into a specific representation. Since we are interested in applying density matrix theory to the study of selective vibrational excitation in a dissipative environment, the representation of the reduced density operator in terms of eigenstates of the relevant system is the most suitable. Using the set $\{|m\rangle\}$ of molecular eigenstates obtained as the solution of the stationary Schrödinger equation

$$\hat{H}_{\text{s}} \phi_m = E_m \phi_m \quad (2)$$

the reduced density operator can be expressed as

$$\hat{\rho}_{\text{s}} = \sum_{m,n} \rho_{mn} |m\rangle \langle n| \quad (3)$$

where ρ_{mn} are the elements of the density matrix.

Providing the coupling between the system and the bath is sufficiently weak one can use the Redfield theory to derive the equation of motion for the elements of the density matrix. The starting point is the partition of the total Hamiltonian into three parts:

$$\hat{H}_{\text{tot}} = \hat{H}_{\text{s}}(\vec{r}) + \hat{H}_{\text{b}}(\vec{Q}) + \hat{H}_{\text{s-b}}(\vec{r}, \vec{Q}) \quad (4)$$

a system Hamiltonian \hat{H}_{s} , a bath Hamiltonian \hat{H}_{b} , and a system-bath coupling Hamiltonian $\hat{H}_{\text{s-b}}(\vec{r}, \vec{Q})$ that depends on both the system coordinates \vec{r} and bath coordinates \vec{Q} . Following the reaction surface Hamiltonian approach of Miller and co-workers the reaction coordinates are the system. The locally harmonic vibrations, orthogonal to the reaction surface as well as the possible solvent modes constitute the bath. In the derivation of Redfield equation we assume that the coupling of the system's DOF to the environmental DOF bath can be factorized as

$$\hat{H}_{\text{s-b}}(\vec{r}, \vec{Q}) = \hat{S}(\vec{r}) \hat{B}(\vec{Q}) \quad (5)$$

The system-bath coupling can be put in the form of Eq. (5) by expanding the coupling potential in a Taylor series around an appropriate system equilibrium configuration $(\vec{r}_{\text{e}}, 0)$.

$$\hat{H}_{\text{s-b}} \approx \sum_a \left[\sum_i \frac{\partial^2 V(\vec{r}_e, 0)}{\partial r_i \partial Q_a} (r_i - r_{e,i}) + \frac{1}{2} \sum_{i,j} \frac{\partial^3 V(\vec{r}_e, 0)}{\partial r_i \partial r_j \partial Q_a} (r_i - r_{e,i})(r_j - r_{e,j}) \right] Q_a \quad (6)$$

In the numerical application we will make some severe approximations: we will treat the coupling derivatives in Eq. (6) as parameters (see next section) and truncate the expansion on the bilinear and quadratic term.

Under these conditions the equations for the matrix elements of the reduced density operator can be written as

$$\frac{d\rho_{mn}}{dt} = -i\omega_{mn}\rho_{mn} - \sum_{kl} R_{mnkl}\rho_{kl} \quad (7)$$

where $\omega_{mn} = (E_m - E_n) / \hbar$ are the transition frequencies between different eigenstates of the system Hamiltonian H_s . The dissipative dynamics is accounted for in the Redfield relaxation tensor \mathbf{R} given by

$$R_{mnkl} = \delta_{ln} \sum_a \Gamma_{maak}(\omega_{ka}) + \delta_{km} \sum_a \Gamma_{naal}(\omega_{la}) - \Gamma_{kmnl}(\omega_{ln}) - \Gamma_{lnmk}(\omega_{km}) \quad (8)$$

where Γ_{klmn} are the elements of the damping matrix. In the framework of the discussed approximations the elements of the damping matrix are given by

$$\Gamma_{klmn} = S_{k,l} S_{m,n} [1 + n(\omega)] J(\omega) \quad (9)$$

where $S_{m,n}$ are the matrix elements of the system part of the system-bath Hamiltonian *i.e.* the quantity in square brackets in Eq. (6) and $n(\omega) = 1 / [\exp(\hbar\omega / k_B T) - 1]$ is the Bose-Einstein distribution function. The bath enters the dynamics *via* its spectral density $J(\omega)$. As experimental data on the frequency dependence of the spectral density are hardly obtainable we will use a model function having a broad distribution of frequencies which is tailored to the particular system at hands (see next section)

In the present contribution we are interested in the interaction of a intense electromagnetic field and the molecular system. Within the semiclassical dipole approximation the field-matter Hamiltonian reads

$$H_F(t) = -d(\vec{r}) E(t) \quad (10)$$

where $d(\vec{r})$ is the dipole operator of the molecule along the reactions coordinates. When the electromagnetic field is included in the dissipative dynamics the following form of the Redfield equations is obtained

$$\frac{d\rho_{mn}}{dt} = i\omega_{mn}\rho_{mn} + i\varepsilon(t) \sum_k (d_{kn}\rho_{mk} - d_{mk}\rho_{kn}) - \sum_{kl} R_{mnkl}\rho_{kl} \quad (11)$$

in which $d_{mn} = \langle \psi_m | \hat{d} | \psi_n \rangle$ are the matrix elements of the dipole operator. From the numerical solution of the Redfield equations the time evolution of the density matrix is obtained. The diagonal elements of ρ are the occupation probabilities of various vibrational levels while the non diagonal elements of the density matrix represent the coherences.

Model Hamiltonian

The model system under consideration, picolinic acid *N*-oxide (see inset in Figure 1), has been extensively studied, both experimentally and theoretically.¹⁸ The choice of this molecule has been motivated by the increasing interest in the dynamics of low and medium barrier proton transfer systems. Particularly their role as transition state stabilizer in enzymatic reactions (in the hydrolysis of peptide bonds) has been the subject of controversial discussions in the past.^{29,30,31}

In Ref. 19 a two-dimensional model potential for PANO has been constructed based on medium high quantum chemical calculations (B3LYP/6-31G(d)).

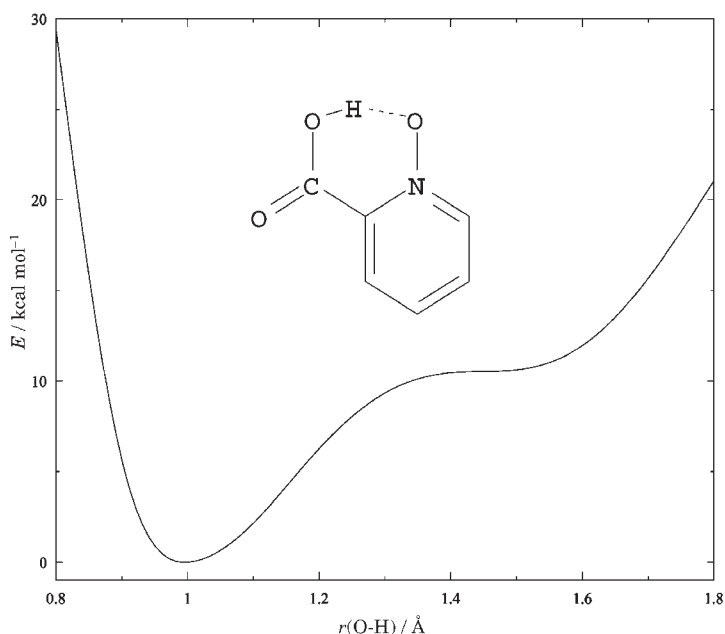


Figure 1. Potential energy curve along the minimum energy path for PANO obtained at the B3LYP/6-31G(d) level.

In total 165 single points calculations have been performed corresponding to different O–O and O–H distances. The model potential fitted to the quantum chemical results reads

$$V(x,q) = V_x(x) + V_q(q) + S_{xq}(x,q) \quad (12)$$

where $V_x(x)$ is the potential energy for the proton motion along the proton transfer coordinate x , $V_q(q)$ is the potential energy for the heavy atom mode and $S_{xq}(x,q)$ is the coupling function between the two modes.

In the proton transfer direction the characteristic shelf behavior of the potential (see Figure 1) is most easily reproduced by a fourth-order polynomial function of the form

$$V_x(x) = \frac{k_1}{2}x^2 + \frac{k_2}{2}(x - x_2^0)^4 + \delta \quad (13)$$

In Table I we list the optimal values of all fitting parameters. Note that in Eq. (13) the origin of the coordinate system has been placed at the minimum of the potential.

The strongly coupled O–O stretching mode has been modeled by the Morse potential function

$$V_q(q) = D(1 - e^{\alpha(q - q_0)})^2 \quad (14)$$

while the coupling function

$$S_{xq}(x,q) = axq + bx^2q + cxq^2 \quad (15)$$

TABLE I

Optimal values of the fitting parameters for the two-dimensional model potential, Eqs. (13), (14) and (15)

Fitting parameters / a.u.					
$V_x(x)$	k_1	k_2	x_1^0	x_2^0	δ
	-0.078	0.082	1.11	0.98	0.018
$V_q(q)$	D	α	q_0		
	0.07	0.56	-0.11		
$S_{xq}(x,q)$	a	b	c		
	0.008	-0.014	0.025		

contains the physics of the interaction between the two modes. Thus the total molecular Hamiltonian reads

$$H_M = \frac{p_x^2}{2\mu_x} + \frac{p_q^2}{2\mu_q} + V(x, q) \quad (16)$$

where $\mu_x = 1.05$ and $\mu_q = 16.0$ are the reduced masses for the motion along the proton transfer and heavy atom coordinate, respectively.

Since our aim is to study state selective vibrational excitation in PANO the form of the dipole operator $d(x, q)$ entering the interaction Hamiltonian Eq. (10) has to be specified. In Ref. 19 a model dipole operator has been obtained by fitting the following rational function

$$(a_1 + b_1x + c_1x^2 + d_1x^3)q + \frac{(a_2 + b_2x + c_2x^2 + d_2x^3 + e_2x^4)}{(a_3 + b_3x + c_3x^2 + d_3x^3 + e_3x^4)} \quad (17)$$

to the quantum chemical data in the range $0.8 \leq x \leq 1.8 \text{ \AA}$, $2.35 \leq q \leq 3.10 \text{ \AA}$. Outside this region the dipole function is taken to be constant. The model function takes into account the sharp change of the total dipole moment from 2.34 D to 3.7 D when going from the CO side to the NO side. All fitting parameters in atomic units are given in Table II.

Finally we have to define the coupling between both system coordinates and the bath *i.e.* the so far neglected intramolecular degrees of freedom as well as possible solvent modes. We will investigate two forms of system-bath coupling: the standard bilinear form

$$\hat{H}_{s-b} = \sum_i (c_{i,x}x + c_{i,q}q)Q_{i,b} \quad (18)$$

where $c_{i,x}$ ($c_{i,q}$) are the coupling parameter between the i -th bath mode and the proton transfer (heavy atom) coordinate. For simplicity we will put $c_{i,x} =$

TABLE II

Optimal values of the fitting parameters for the two-dimensional dipole moment function, Eq. (17)

$d(x, q)$	Fitting parameters / a.u.				
	a	b	c	d	e
Coef. 1	-0.54	-0.53	-0.12	0.98	
Coef. 2	-1.36	0.207	0.66	0.34	0.55
Coef. 3	0.53	-0.09	0.17	0.16	0.12

$c_{i,q} = c_i$. The quadratic term in the expansion of the system-bath coupling will also be investigated

$$\hat{H}_{\text{s-b}} = \sum_i (c_{i,x}x + c_{i,q}q + c'_{i,xq}xq)Q_{i,b} \quad (19)$$

The ratio of quadratic to linear coupling, c'/c is set to 4 \AA^{-1} . For the spectral density, $J(\omega)$, we will assume

$$J(\omega) = g \frac{\omega}{\omega_c} e^{-|\omega|/\omega_c} \quad (20)$$

where the factor g contains the coupling strengths c_i . For PANO we assume $J(\omega)$ to have a maximum at the frequency $\omega_c = 1100 \text{ cm}^{-1}$ which correspond to the C–O stretching vibration.³²

NUMERICAL RESULTS

In this section we consider the preparation of selected excited vibrational states of the PANO molecule. The stationary Schrödinger equation (2) has been solved for the Hamiltonian given in Eq. (16) using the Fourier grid Hamiltonian method.³³ The probability distribution of some selected eigenstates of PANO along with the two-dimensional model potential surface are shown in Figure 2. Of particular interest for laser control of vibrational excitation are the states delocalized along the proton transfer direction: the ϕ_7 state and the states ϕ_9 and ϕ_{10} laying close to the plateau region having a significant localization of the probability density on the *N*-oxide side of the potential. In our previous study¹⁹ we proposed two pathways for laser controlled excitation of the ϕ_{10} eigenstate: the $\phi_0 \rightarrow \phi_7 \rightarrow \phi_{10}$ and the $\phi_0 \rightarrow \phi_9 \rightarrow \phi_{10}$ pathway. As the efficiency of a particular pathway strongly depends on the controllability of the intermediate states we focus here on the preparation of these two states. In particular is our intention to investigate the robustness of such preparation *i.e.* how the efficiency of state selective preparation decreases with changes in the laser field intensity or/and pulse duration. The field parameters for a complete population inversion in a dissipation-free environment are obtained from the so-called π pulse criteria. We know from the theory of the two-level systems that for resonant pulses the transition amplitudes are function of the pulse area defined by

$$\sigma(t) = d/\hbar \int_0^t s(t') dt' \quad (21)$$

where d is the transition dipole moment and $s(t)$ is the slowly varying field amplitude. The population inversion occurs when the time integral of the

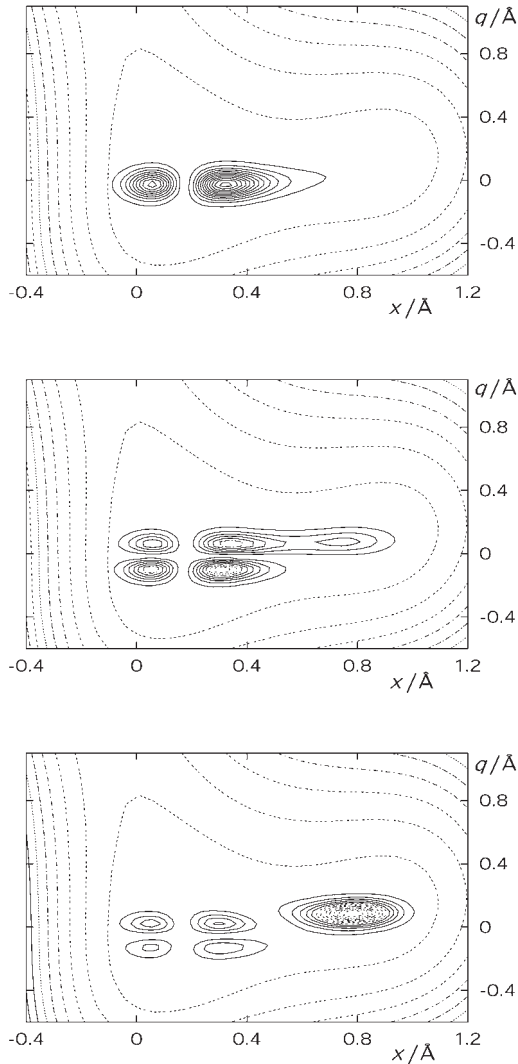


Figure 2. The two-dimensional potential energy surface, Eq. (12), is shown together with the density plots for some of the vibrational (v) eigenstates of the system Hamiltonian H_s . From top to bottom we have $v = 7, 9, 10$.

Rabi frequency (the pulse area) is equal to π or any odd-multiple of π . A longer pulse with area 2π or any even-multiple of π will return the population to the initial state.

In the following we will use Gaussian shaped IR pump pulses of resonant frequency ω_p and pulse duration t_p

$$E(t) = E_{0,p} \left(\frac{2}{\pi \Delta_p^2} \right)^{1/2} \exp[-2(t-t_p)^2 / \Delta_p^2] \cos(\omega_p t) \quad (22)$$

with the width $\Delta_p = t_p/4$. In order to induce a complete population transfer to the target states with pulses of duration around 700 fs the π -pulse procedure requires the field amplitudes of $E_{0,p} = 0.00155 E_h/ea_0$ for the ϕ_7 state and $E_{0,p} = 0.00774 E_h/ea_0$ for the ϕ_9 state.

In the numerical simulation we start with the system in thermal equilibrium at 300 K (the first seven states have occupation probabilities higher than 10^{-5}) and consider first the population dynamics in the dissipation free case and then the dissipative dynamics for moderate ($g = 8 \times 10^{-5}$ in Eq. 20) and for stronger system-bath coupling ($g = 3 \times 10^{-4}$). In order to take into account the temperature of the system we specify the yield of the preparation Y as

$$Y = \frac{P_t}{P_i} \quad (23)$$

where P_i is the total thermal equilibrium population of the initial state and P_t is the total thermal equilibrium population of the target state at the end of the pulse.

The laser induced dynamics of all states involved in the preparation of the ϕ_7 state are shown in Figure 3 (upper panel). As expected, the population dynamics in the dissipation-free case (solid line) indicates that the ϕ_7 state can be prepared with high efficiency. The yield of the preparation is $Y = 0.92$. Moreover being the laser pulse in resonance also with the $\phi_1 \rightarrow \phi_9$ transition it induces an almost complete population inversion between these two states (see inset in Figure 3). The populations of the other states are not significantly affected by the laser pulse. Apparently the multi-level system at hand behaves as a sequence of two-level systems. Using the same pulse parameters we calculated the occupation probability of the ϕ_7 state under dissipative conditions. The population dynamics can be seen in Figure 3 (dashed line). At the end of the pulse we have a diminished, but still very high population of the ϕ_7 state ($Y = 0.88$) as well as of the ϕ_9 state. In the case of faster dissipation (dotted line in Figure 3) the level of control of the ϕ_7 is still appreciable ($Y = 0.81$) if the pulse duration is taken as reference. Of course, after the pulse is switched off the system relaxes back to equilibrium. The relaxation is much faster than in the previous case and it is reached after few tens of picoseconds.

As a second example we consider the state selective preparation of the ϕ_9 state. Due to the smallness of the transition dipole momentum the field intensity required for the population inversion is quite high ($E_{0,p} = 0.00774$ a.u.) when compared to the one needed for the $\phi_0 \rightarrow \phi_7$ transition ($E_{0,p} = 0.00155$ a.u.). In Figure 3 (lower panel) we show the population dynamics in the dis-

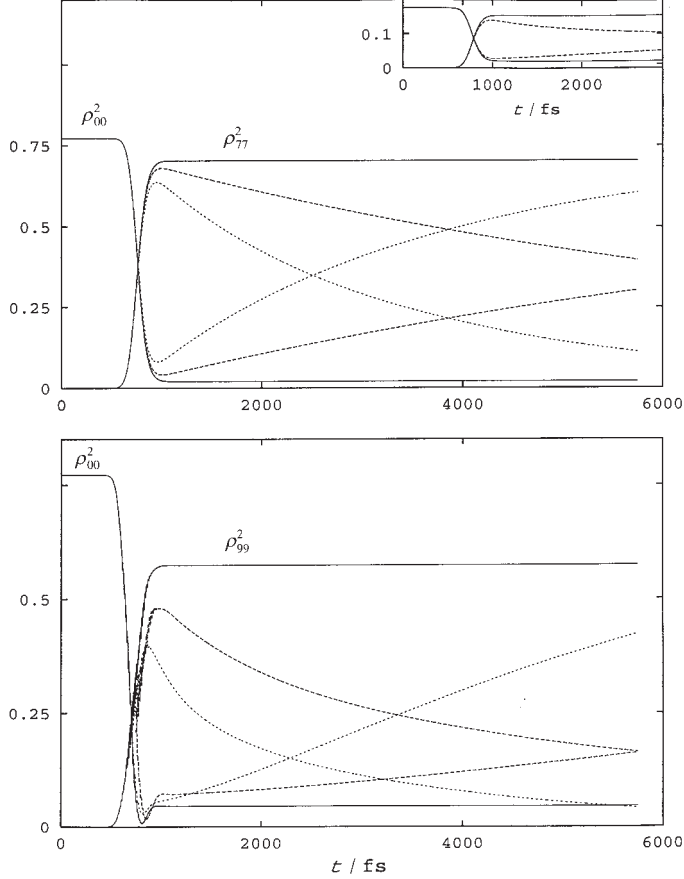


Figure 3. Upper panel: Population dynamics of the ϕ_0 and ϕ_7 state for the driving pulse of Eq. (22) with $E_{0,p} = 0.00155 E_h/ea_0$, $t_p = 700$ fs (solid: non-dissipative dynamics; dashed: dissipative dynamics with $g = 8 \times 10^{-5}$; dissipative dynamics with $g = 3 \times 10^{-4}$) Inset: The population dynamics of the ϕ_1 and ϕ_9 state for the driving pulse which is tuned in resonance with the $\phi_0 \rightarrow \phi_7$ transition. (solid: non-dissipative dynamics; dashed: dissipative dynamics with $g = 8 \times 10^{-5}$). Lower panel: Population dynamics of the ϕ_0 and ϕ_9 state for the driving pulse which is tuned in resonance with the $\phi_0 \rightarrow \phi_9$ transition. $E_{0,p} = 0.00774 E_h/ea_0$, $t_p = 700$ fs.

sipation free case (solid line). Although an almost complete depopulation of the ground state is present, a complete population switch between the initial and target state does not take place. The yield of the preparation is $Y = 0.75$, a value which is significantly lower than that for the ϕ_7 state. Apparently the high intensity field required for the population switch induces multiphoton transitions in the system. Higher vibrational states get therefore significantly populated during the excitation of the ϕ_9 . Upon inclusion of energy

and phase relaxation the yield of the reaction decreases to $Y = 0.62$ and $Y = 0.51$ in the weak and strong coupling limit, respectively. This lower level of controllability indicates that the two level system theory can be efficiently applied only to states coupled by a large transition dipole momentum.

In the following we switch attention to the robustness of the π -pulse scheme. In order to simplify this task we shall fix the pulse frequency at the resonance value and vary the field intensity as well as the pulse duration. In Figure 4

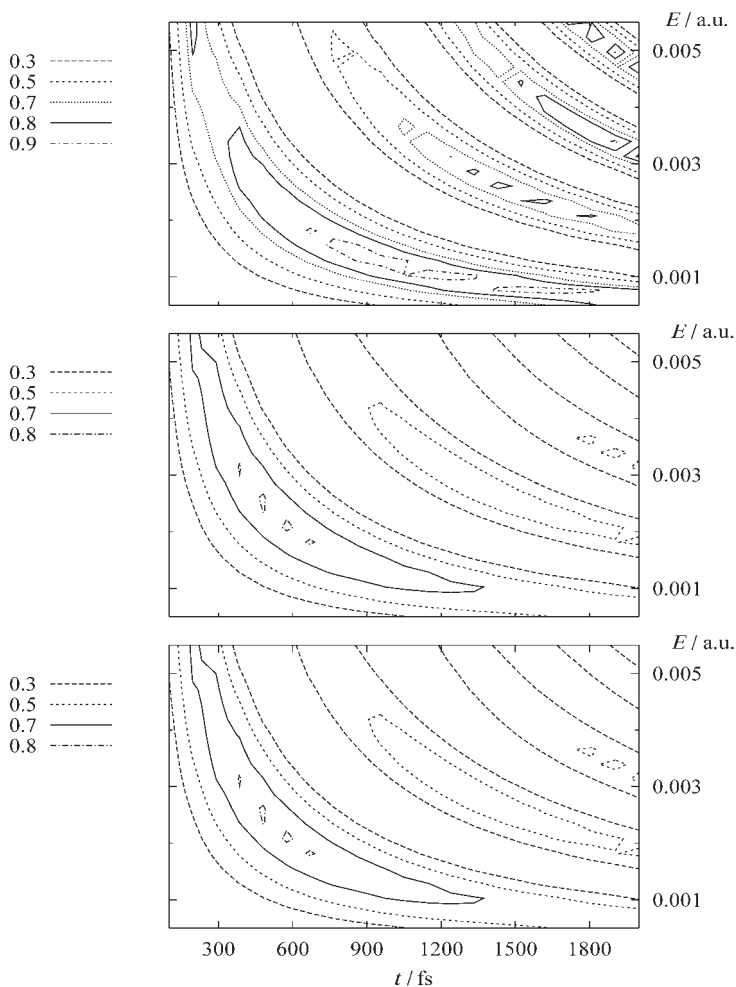


Figure 4. The preparation efficiency of the ϕ_7 state against the instability of the pulse characteristics under non-dissipative conditions (upper panel), strong dissipation with bilinear system-bath coupling (middle panel), strong dissipation with quadratic system-bath coupling (lower panel).

(upper panel) we first show the yield of the $\phi_0 \rightarrow \phi_7$ reaction in a dissipation-free environment. Apparently the reaction yield is larger than $Y = 0.8$ (solid line) for a range of parameters satisfying only approximately the π pulse condition. In addition a second area of control can be seen at higher field intensity as a result of undamped Rabi oscillations ($\sigma(t) = 3\pi, 5\pi$ in Eq. 21). Next we consider the efficiency of the preparation against the instability of the pulse characteristics under strong dissipative condition ($g = 3 \times 10^{-4}$). In

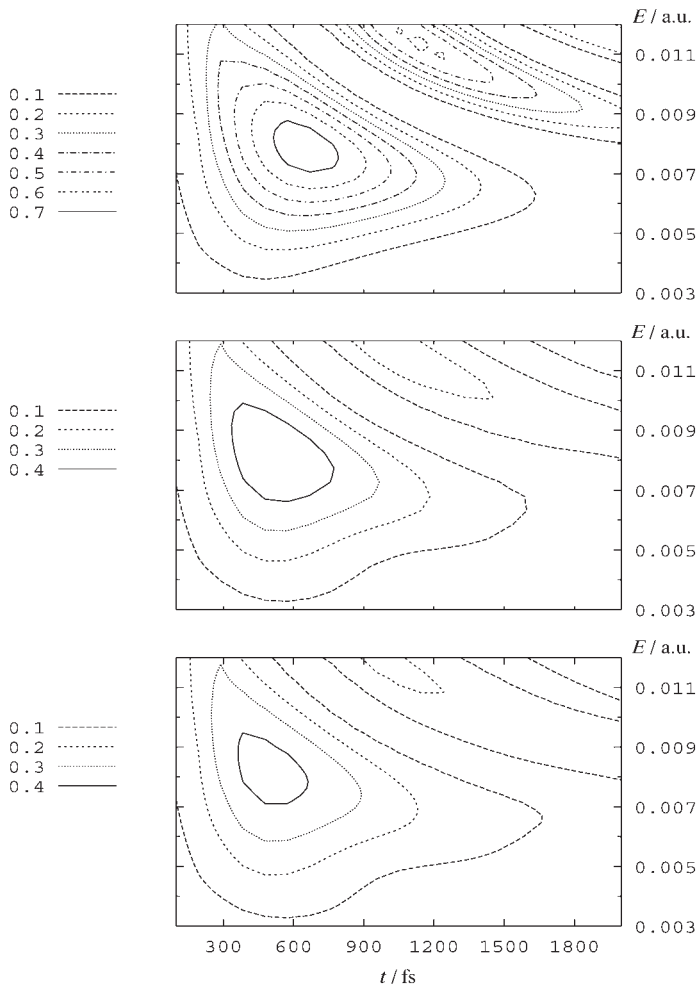


Figure 5. The ϕ_9 state preparation efficiency against the instability of the pulse characteristics under non-dissipative conditions (upper panel), strong dissipation with bilinear system-bath coupling (middle panel), strong dissipation with quadratic system-bath coupling (lower panel).

the presence of competing relaxation processes (Figure 4, middle panel) the high yield area with $Y \geq 0.7$ (solid line) is reduced and shifted towards shorter and more intense pulses. Note that in the numerical simulation we employ the standard bilinear expansion of the system-bath coupling (Eq. 18). The best controllability is obtained for the field intensity $E = 0.00155$ a.u. and laser pulse duration in the range of 400–700 fs ($t_p = 700$ fs in Figure 3). As expected the area in which the population inversion occurs as a consequence of higher Rabi oscillations is significantly reduced. The inclusion of the quadratic form of the system-bath coupling (Figure 4, lower panel) with normalized coupling strength¹⁷ results in a marginal reduction of the control area.

Let us now investigate the π -pulse strategy for selective population of the ϕ_9 state. In Figure 5 we show how the yield of the reaction depends on the pulse parameters in a non dissipative environment. The high yield area with $Y \geq 0.7$ (solid line) is quite reduced and localized in a small region with field intensity between $E_p = 0.007$ – 0.008 a.u. and duration of $t_p = 550$ – 650 fs. State selective excitation in the weak coupling limit is therefore very much dependent on the balance between pulse duration and intensity. Upon inclusion of the bilinearly coupled bath (middle panel) the yield is decreased to only $Y \geq 0.4$ (solid line). Compared to the preparation of the ϕ_7 state here the difference in the reaction yield between relaxation with linear or quadratic (lower panel) coupling is more pronounced. The reason for this can be found in a more efficient mixing of the proton transfer coordinate and the heavy atom mode. Since the target state ϕ_9 is delocalized in the proton transfer direction as well as in the heavy atom coordinate its relaxation dynamic is more affected by the coupling term $\propto xqQ_i$. While the quadratic coupling does not effect significantly the $\phi_9 \rightarrow \phi_1 \rightarrow \phi_0$ relaxation pathway it makes more effective the relaxation through the $\phi_9 \rightarrow \phi_7 \rightarrow \phi_0$ pathway.

However our most important point is that for strongly coupled states small deviations of the laser field parameters from the π -pulse condition do not affect dramatically the yield of the reaction. Thus even in the case of fast dissipation a population inversion between states coupled by a large dipole moment should be possible.

SUMMARY

We have investigated state selective vibrational excitation under dissipative conditions in a two dimensional model system tailored to treat hydrogen bond in picolinic acid N-oxide. Special attention has been paid to the robustness of the laser control strategy. The model potential energy surface as well as the transition dipole moment have been adapted to medium high level DFT calculations. The influence of a dissipative environment was modeled

using multilevel Redfield theory. We assume a Markovian bath coupled to a two dimensional system and explore the impact of the bilinear and quadratic coupling terms on the efficiency of state selective excitation. The present study shows that efficient excitation of the O–H stretching mode can be achieved by simple analytical pulses satisfying the π pulse condition. The efficiency of this process strongly depends on the value of the transition dipole momentum between the initial and target state. The study confirms the robustness of the π -pulse criteria for selective vibrational excitation and shows that population inversion between strongly coupled states can occur for quite large range of laser field parameters. In the weak coupling limit, we have shown that population transfer to such states is very difficult. Besides the well know problem of multiphoton transitions, the main obstacle in the realization of the population inversion is the reduced area of pulse parameters for which such inversion takes place. Moreover our results show that the inclusion of the quadratic term in the expansion of the system-bath coupling Hamiltonian results in a even faster relaxation of states having mixed excitation.

At present, within the multilevel Redfield theory, we neglect the field influence on the relaxation rates. We also disregard the coupling of the bending and stretching mode of the OH fragment. Our future work will focus on overcoming these limitations. The method of choice is density matrix evolution theory, an appropriate tool for coupling a number of classical degrees of freedom to a quantum system.

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SAŽETAK

Disipativna pobuda ciljanih vibracijskih stanja u N-oksidu pikolinske kiseline

Nada Došlić i Jernej Stare

U radu se istražuje utjecaj relaksacije Redfieldova tipa na mogućnost kontrole populacijske dinamike u modelnom dvodimenzijском potencijalu. Modelni potencijal, dobiven na temelju DFT podataka za N-oksid pikolinske kiseline, sastoji se od koordinate koja opisuje prijenos protona i od koordinate teških atoma. Pokazano je da je oblikovanim laserskim pulsevima čija je površina jednaka π , moguće selektivno pobuditi istežanje O–H u sustavu. Efikasnost kontrole testirana je s obzirom na nestabilnost pulsa.