PHYSICAL REVIEW B **67**, 134307 (2003)

Microscopic theory of vibronic dynamics in linear polyenes

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(Received 11 February 2003; revised manuscript received 26 February 2003; published 30 April 2003)

We propose an approach to calculate dynamical processes at an ultrafast time scale in molecules in which vibrational and electronic motions are strongly mixed. The relevant electronic orbitals and their interactions are described by a Hubbard model, while electron-phonon interaction terms account for the dependence of the hopping on bond length and the dependence of the equilibrium bond length (atomic radii) on the local charge. The latter term plays a crucial role in the nonadiabatic internal-conversion process of the molecule. The time-resolved photoelectron spectra are in good qualitative agreement with experiments.

DOI: 10.1103/PhysRevB.67.134307 PACS number(s): 71.20.Rv, 71.10.Fd, 78.30.Jw

I. INTRODUCTION

Photoexcitation in polyatomic molecules leads to the rapid mixing of vibrational and electronic motions, inducing charge redistribution and energy flow in the molecule. This nonadiabatic internal conversion is essential in photochemical processes,[1] in photobiological processes, such as those involved in vision,[2] and in molecular electronics.[3]

In recent years, progress in the technology of laser pulses has triggered the development of a new generation of spectroscopies devoted to the investigation of ultrafast phenomena. Beautiful experiments have recently been reported on the study of ultrafast nonadiabatic internal conversion in isolated molecules.[4,5] In particular, time-resolved photoelectron spectroscopy (TRPS) has been used to follow the vibronic dynamics of a linear polyene—specifically, the all-*trans* 2,4,6,8 decatetraene—in a femptosecond time scale.[5]

In this molecule, the electronic ground state is the singlet S_0 ($1^1\,A_g$), which is even under inversion symmetry. The first optically allowed excited state, S_2 ($1^1\,B_u$, odd under inversion), has an energy higher than the first excited ‘‘dark’’ singlet S_1 ($2^1\,A_g$). A short laser pulse (pump) prepares the molecule in a vibrationally hot wave packet involving the state S_2. The packet evolves and its time evolution is probed by photoexciting an electron and analyzing the ensuing spectra at subsequent times.

The analysis of the photoelectron spectra reveals a population of the ‘‘dark’’ band, which increases with time, as a consequence of a nonadiabatic internal conversion between vibrational and electronic excitations. Such a process lasts a few hundred femptoseconds, and is a manifestation of the failure of the adiabatic description.

The aim of any theory in this field is to relate experimental spectroscopic data, such as relaxation times and excitation energies, with the basic microscopic interactions of the system. This task is particularly difficult in the present case. A theory describing the experiments should indeed start from a model which includes both electron-electron correlations as well as electron-phonon interaction, and should treat the latter beyond the adiabatic approximation. So far, to the best of our knowledge, time-dependent photoemission spectra for such nonadiabatic internal-conversion processes have never been calculated on the basis of a microscopic model. Previous theoretical work on the internal-conversion process is based on semiempirical models for the relevant energy surfaces, supplemented by phenomenological couplings between them.[7]

The goal of this work is to describe the whole process behind a TRPS experiment[5] (laser pump followed by a dynamical internal conversion, probed by the ensuing time-dependent photoemission spectra), using a minimal microscopic model in which both electron-electron and electron-phonon interactions are exactly taken into account. Our results show a good qualitative agreement with the experimental findings,[5] and bring insight into the nature of the basic underlying interactions.

The paper is organized as follows. In Sec. II we introduce the model including a detailed description of the role played by each of the interactions considered and explain the theoretical treatment employed to calculate the photoemission spectra. In Sec. III we present the results. Sec. IV contains a summary and the main conclusions of this work.

II. THEORETICAL APPROACH

A. The model

As is usual in the description of graphite, fullerides, and nanotubes, the model we study is based on a formal separation of the hybridized s and p orbitals lying in the plane of the molecule, [see Fig. 1(a)], and the p-π orbitals perpendicular to it. While the former are those with the larger contribution to the chemical bond and vibration dynamics, the latter are those involved in the low-energy excitations of interest to us. A Hubbard Hamiltonian will describe these low-energy electronic degrees of freedom. Its key ingredient is a strong local Coulomb interaction term which is crucial in

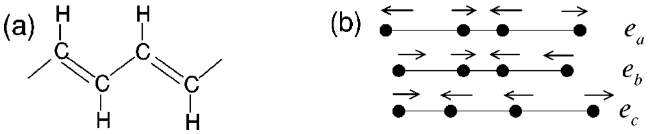

FIG. 1. (a) Scheme of the linear polyene. (b) Scheme of the normal modes of the molecule.

explaining the observed structure of the electronic spectrum, namely, the S_1 (dark) excited state lying, in energy, below the S_2 one. Electron-phonon coupling terms are then included, as derived from an expansion of the electron-ion interaction up to first order in the ionic displacements relative to the equilibrium positions.[6]

Specifically, the model reads

$$\begin{aligned}\mathcal{H}=&-\sum_{\sigma=\uparrow,\downarrow}\sum_{i=1}^{L-1}[t_0-g(u_{i+1}-u_i)](f^{\dagger}_{i,\sigma}f_{i+1,\sigma}+\text{H.c.})\\&+U\sum_{i=1}^{L}n_{i\uparrow}n_{i\downarrow}+g'\sum_{i=1}^{L-1}(u_{i+1}-u_i)(q_i+q_{i+1})\\&+\frac{K}{2}\sum_{i=1}^{L-1}\sum(u_i-u_{i+1})^2+\frac{1}{2m}\sum_{i=1}^{L}P_i^2,\end{aligned}\tag{1}$$

where $i=1,\ldots,L$ labels the π orbitals of the C atoms, $f^{\dagger}_{i,\sigma}$ creates an electron with spin σ at site i, $n_{i\sigma}=f^{\dagger}_{i,\sigma}f_{i,\sigma}$, and $q_i=1-n_{i\uparrow}-n_{i\downarrow}$ is the net charge at site i. The hopping matrix element between two nearest-neighbor π orbitals is t_0, and U is the local Coulomb interaction. Finally, u_i are the ionic displacements with respect to the equilibrium positions, and, for simplicity, the vibration dynamics has been assumed to be that of a one-dimensional chain of ions (the CH units) of mass m with a nearest-neighbor harmonic constant K. (This simplification does not affect the essential physics and it would be straightforward to consider any other form of dynamical matrix). Two electron-phonon interactions have been included in Eq. (1), with coupling constants labeled by g and g'. The g term is quite standard and accounts for the fact that the magnitude of electronic nearest-neighbor hopping becomes weaker or stronger as the bond stretches or compresses, respectively. The g' term, with $g'>0$, accounts for the contraction (expansion) of the bond upon removal (addition) of an electron. Such a term is a consequence of the dependence upon the valence charge of the spread of the wave functions (particularly the σ orbitals), a spread which in turn modifies the bond lengths. The adiabatic form of this term has been considered before in a problem of surface segregation of atoms with size mismatch.[8]

The phonon part of the Hamiltonian [last two terms in Eq. (1)] can be diagonalized by introducing the normal-mode coordinates. For the sake of simplicity, and in order to be able to numerically solve *exactly* the Hamiltonian, we consider a molecule with $L=4$ C atoms. The decatetraene molecule measured in Ref. 5 has $L=14$. While this simplification leads to some quantitative difference with respect to the experimental results, it does not affect the conceptual issues related with the understanding of the mechanism of internal conversion. Hence, the vibrational motion of the molecule, for $g=g'=0$, can be described in terms of three normal modes, e_a, e_b, and e_c, oscillating with frequencies

$$\omega_a=\sqrt{(2+\sqrt{2})K/m},$$

$$\omega_b=\sqrt{(2-\sqrt{2})K/m},$$

$$\omega_c=\sqrt{2K/m},\tag{2}$$

as sketched in Fig. 1(b). The mode e_b will not be included, since it describes a uniform dilatation or contraction of the molecule, which should have a small coupling with the electrons in a larger molecule.

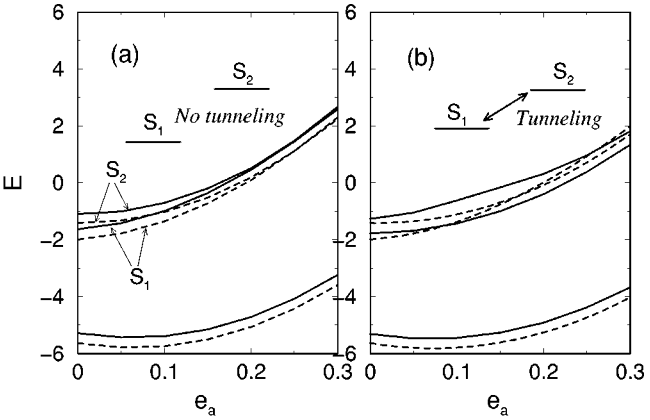

FIG. 2. (a) Cuts of the potential energy surfaces for $g'=0$, with $t_0=2$ eV, $U=4{,}2$ eV, $g=3$ eV/Å, and $K=36$ eV/Å^2. Dashed and solid lines correspond to $e_c=0$ and 0.1, respectively. (b) Same as (a) for $g'=5$ eV/Å.

1. The role played by the different interactions

In order to show that the Hamiltonian (1) represents the minimal model containing the relevant ingredients to describe the essential physics, we discuss first each interaction term within the adiabatic picture.

a. Role of U. The role of electron-electron correlations in the excitation spectrum of polyenes has been already discussed.[10,11] It suffices here to say that in the noninteracting limit $(U=0)$, the optically allowed S_2 state would have a lower energy than the dark S_1 state, while a Coulomb repulsion $(U/t_0)\gtrsim 1.7$ leads to the observed ordering of both singlet excitations. Given the reasonable estimate of $t_0=2$ eV for the electronic hopping,[9] we find that the value of U that best fits the data on decatetraene is $U=4.2$ eV.

b. Role of g. The electron-phonon interaction g is a standard ingredient of the Pariser-Parr-Pople-Pierls (PPPP) model,[10,11] crucial in explaining dimerization effects. The coupling between the electrons and the e_a mode (the dimerization mode) leads to different equilibrium lengths for C-C and C=C bonds, alternating short and long bonds. From experimental data on the typical frequency of the dimerization mode[12] we took $\omega_a=0.2$ eV (which implies $K=36$ eV/Å^2 and $\omega_c=0.15$ eV). A value for $g=3$ eV/Å is then calculated by fitting the experimentally observed difference in bond lengths.[13] With all the parameters so determined, and setting for the time being $g'=0$, one can study the Born-Oppenheimer (BO) surfaces corresponding to the three lowest-energy singlets S_0, S_1, and S_2, as functions of the normal-mode coordinates e_a and e_c [see Fig. 2(a)]. The position of the minimum of the S_0 (ground-state) BO surface, occurring at a finite $e_a>0$, reflects the previously mentioned dimerization effect. It is also evident from Fig. 2(b) that the electron-phonon interaction introduces anharmonicities in the BO energy surfaces leading to the occurrence of level crossings in the excited states, known as conical intersections.[6] The S_2 singlet is odd under space inversion while the S_1 is even. The conical intersection between both states is a central feature of the physics we want to describe. Note that the e_a mode is even under inversion, while e_c is odd. Then, on general symmetry grounds, the coupling between the electrons and the e_c mode would be expected to produce a nonvanishing matrix element between the S_1 and the S_2 states, leading to an *avoided crossing* between the corresponding bands, with a gap proportional to the effective tunneling amplitude.[6] As a consequence of that mixing, the adiabatic description in terms of uncoupled BO surfaces would lose meaning, and the quantum nature of the phonons should be included explicitly. However, in the absence of the g' term, the Hamiltonian possesses a subtle electronic symmetry (particle hole) which leads to the vanishing of the interband tunneling matrix element, even for $e_c \neq 0$, as explained below. The particle-hole symmetry $P_{p\text{-}h}$ is defined as the invariance of $\mathcal{H}$ (when $g'=0$, and up to an inessential chemical-potential shift) under the transformation $f^{\dagger}_{i,\sigma} \rightarrow (-1)^i f_{i,-\sigma}$. Taking into account that the electronic states in polyenes correspond to half-filled configurations (the number of π electrons $N=L$) and that this subspace is left invariant by $P_{p\text{-}h}$, the eigenstates of $\mathcal{H}$ within this sector can be classified as even or odd according to $P_{p\text{-}h}$.[10] Detailed analysis reveals that S_1 is even under $P_{p\text{-}h}$, while S_2 is odd. As a consequence, the interaction term g alone cannot produce the interband coupling leading to the nonadiabatic internal conversion observed in these molecules.

c. Role of g'. For this reason, the additional interaction g', which breaks particle-hole symmetry, is *essential* for the internal conversion in our model. Figure 2(b) shows the BO energy surfaces when g' is included. Notice that the ground-state energy surface is practically unaffected by this interaction. This is due to the fact that the on-site Coulomb repulsion inhibits charge fluctuations in the ground state, thus making the g' term, involving the net charges q_i, ineffective. On the contrary, charge fluctuations are important in the excited states, and couple to the phonon modes through the g' term: As a consequence of the quantum tunneling for $e_c \neq 0$ due to g', the two relevant potential-energy surfaces show now an avoided crossing [Fig. 2(b)], instead of intersecting [Fig. 2(a)]. A rough estimate for the strength of g' can be obtained from its effect on a C_2 dimer. By fitting experimental data for the bond lengths of C_2 (1.2425 Å) and of C_2^- (1.2682 Å) with our model, we get $g' \approx 3.95$ eV/Å.[14] Similar values are obtained using data of ionic radii. For instance, a rough estimate based on the ionic radii of C^{+4} and C^{-4} ions (0.15 and 2.60 Å, respectively[15]), leads to $g' \approx 10$ eV/Å. We found that $g' \approx 5$ eV/Å leads to reasonable values for the effective interband coupling and for the position of the conical intersection.

B. Time-resolved photoelectron spectra

As discussed above, in order to describe the internal-conversion effects observed in TRPS experiments, the adiabatic picture must be abandoned and the classical normal coordinates must be quantized as

$$e_a = \sqrt{\frac{\hbar}{2m\omega_a}}(a + a^{\dagger}),$$

$$e_c = \sqrt{\frac{\hbar}{2m\omega_c}}(c + c^{\dagger}). \tag{3}$$

The resulting Hamiltonian $\mathcal{H}$ can be numerically diagonalized by introducing a cutoff in the number of phonons n_a and n_c. We found that keeping states with up to $n_a = n_c = 10$ was enough to obtain accurate results for the excitations within the energy window of interest.

The laser pump is simulated by acting at $t=0$ on the ground state $|\phi_0\rangle$ with the following operator:

$$\hat{O} = \sum_m G_m |\phi_m\rangle\langle\phi_m|\hat{E}, \tag{4}$$

where $|\phi_m\rangle$ denote the exact eigenstates of $\mathcal{H}$, and the effect of the laser electric field is represented by the dipole operator $\hat{E} = \Sigma_i R_i q_i$, where R_i is the position of the C atom i for $u_i = 0$. The pump pulse is assumed to have a Gaussian shape in time. The Fourier transform of its envelope determines the excitation amplitudes

$$G_m \sim \exp[-(\epsilon_m - \overline{\epsilon})^2/2\sigma_p^2], \tag{5}$$

where $\epsilon_m = E_m - E_0$ are the excitation energies relative to the ground state E_0, while $\overline{\epsilon}$ and σ_p are parameters defining the mean excitation energy and the half width of the pump pulse. The Schrödinger time evolution of the prepared wave packet is then given by

$$|\psi(t)\rangle = \exp(-i\mathcal{H}t/\hbar)\hat{O}|\phi_0\rangle. \tag{6}$$

In order to describe in detail the TRPS-experimental probe of the dynamics, we must calculate time-dependent photoelectron spectra. Within the sudden approximation, the photoelectron spectrum at time t is essentially a measure of the following spectral function:[16]

$$\rho_t(\omega) = \sum_{i,\sigma} \sum_m |\langle\phi'_m|f_{i,\sigma}|\psi(t)\rangle|^2 \delta(\omega - E'_m), \tag{7}$$

where E'_m and $|\phi'_m\rangle$ denote the eigenenergies and eigenstates of $\mathcal{H}$ upon removal of a valence electron, i.e., within the sector with $N = L - 1$ particles.

III. RESULTS

A qualitative picture of the resulting dynamics can be obtained from

$$P_o(t) = \langle\psi(t)|P_o|\psi(t)\rangle, \tag{8}$$

where P_o is defined as the projector of the eigenstates of $\mathcal{H}$ on the subspace of electronic states with odd parity under space inversion.

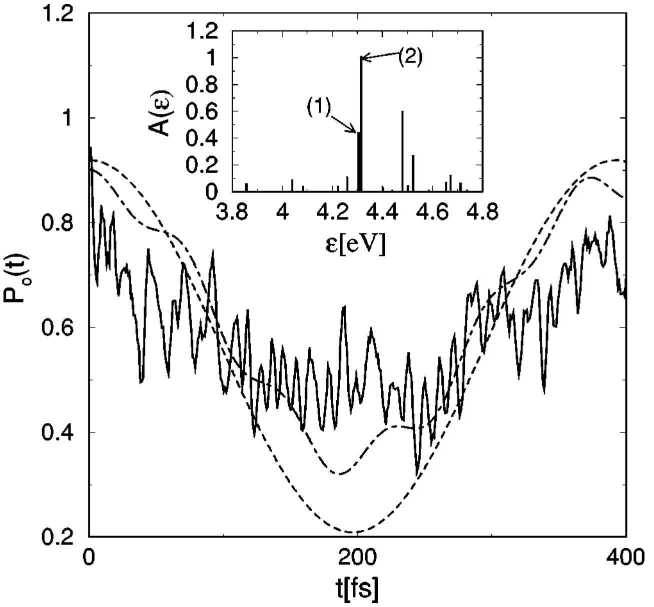

FIG. 3. Evolution of the projector $P_o(t)$ for $\overline{\epsilon}=4.3$ eV, and $\sigma_p=2$ eV (solid line) and 0.04 eV (dot-dashed line). The dashed line is the result for a wave packet consisting only of the two states (1) and (2) indicated in the inset. Inset: Spectrum of the wave packet for a Gaussian pulse with $\overline{\epsilon}=4.3$ eV and $\sigma_p=2$ eV. Other parameters are as in Fig. 2(a).

The evolution of $P_o(t)$ as a function of time is shown in Fig. 3. The first energies of the singlet excitation (with predominantly S_1 and S_2 character) are ~ 3.74 eV and ~ 4.31 eV, respectively. The spectral density profile of the initial wave packet ($t=0$, that is, immediately after the laser pulse),

$$A(\epsilon)=\sum_m |\langle \phi_m|\psi(0)\rangle|^2\delta(\epsilon-\epsilon_m), \tag{9}$$

is shown in the inset of Fig. 3 for a pulse with $\sigma_p=2$ eV and $\overline{\epsilon}=4.3$ eV. Both these parameters, as well as the energy gap between the two lowest-energy excited singlets, are very close to the experimental conditions of Ref. 5. The results for $P_o(t)$ in Fig. 3 show that, on top of a fast oscillatory component, there is a slower internal-conversion component which lasts approximately 243 fs. This process is dominated by the evolution of the two excited states labeled by (1) and (2) in the inset of Fig. 3. The excitation energies of these states are $\epsilon_1=4.304$ eV and $\epsilon_2=4.315$ eV, respectively. State (1) has predominantly S_1 (even) character ($\langle \phi_1|P_o|\phi_1\rangle\sim 0.4$), while state (2) has predominantly S_2 (odd) character ($\langle \phi_2|P_o|\phi_2\rangle\sim 0.74$). Both states have approximately the same small mean value of excited e_a phonons, $\langle n_a\rangle<1$, which leads us to identify them as the quantum counterparts of the semiclassical states at the conical intersections. The evolution of a wave packet composed of just these two states is indicated with a dashed line in Fig. 3. This behavior suggests that the relevant time scale in the evolution of $|\psi(t)\rangle$ is set by $\sim\hbar/(\epsilon_2-\epsilon_1)$.

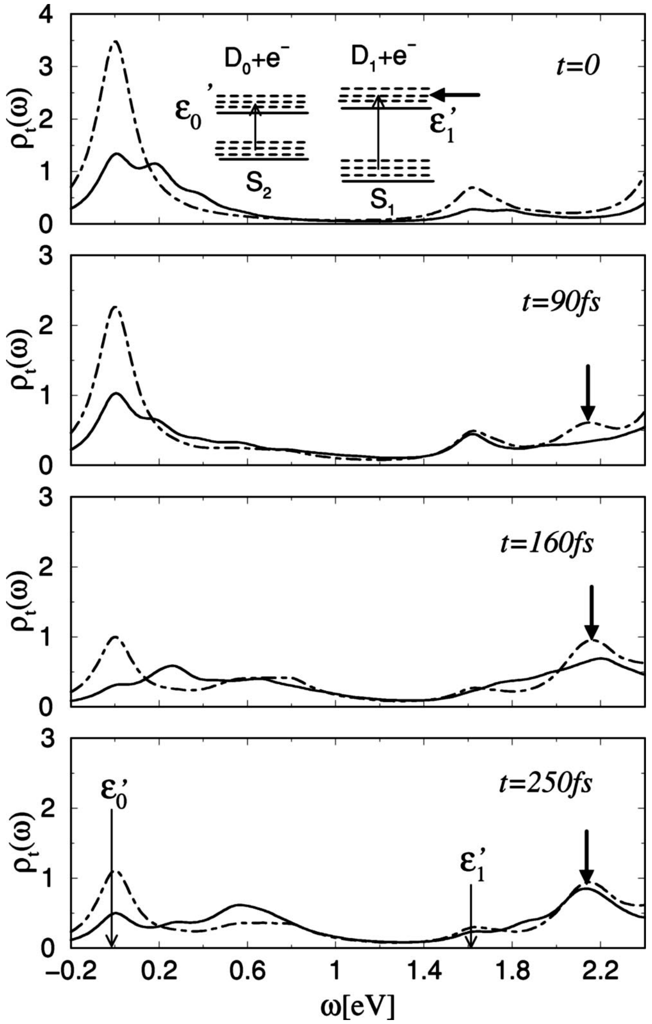

FIG. 4. Evolution of the photoelectron spectra for the parameters of Fig. 2. A scheme of the photoelectron channels and corresponding levels is shown in the upper panel. The origin of energies is set at $\epsilon_0'=0$ eV. The solid arrow indicates the "hot" group with a dominant D_1 electronic component. The state with lowest energy of this set has $\epsilon_1'\sim 1.61$ eV.

Results for the time evolution of $\rho_t(\epsilon)$ are shown in Fig. 4, where an artificial broadening of the delta functions has been introduced by replacing $\delta(\omega-E_m')$ with a Lorentzian. The most salient feature of Fig. 4 is the transfer of spectral weight, as a function of time, from a group of states close in energy to the ground state of the system with $N=L-1$ electrons (a doublet, which is obtained by photoexciting S_2, and is indicated with D_0 in the scheme of Fig. 4), to a group of states at a higher energy. The latter states are identified as vibrationally hot states related to a doublet, which are obtained by photoexciting S_1 (see D_1 in the scheme of Fig. 4). The arrow in the lowest panel of Fig. 4 indicates the position of the lowest-energy state of such a band. The behavior of the photoelectron spectra as a function of time is in qualitative agreement with the experimental results of TRPS. Quantitative differences, such as the larger energy gap between the relevant photoelectron spectral features which we find in our simulation [~ 2 eV in our case, to be compared with the experimental result of ~1.2 eV (Ref. 5)] should be likely ascribed to the smaller size of the molecule we consider in our simulation.

IV. SUMMARY AND CONCLUSIONS

In summary, we have shown that the model Hamiltonian in Eq. (1) contains all the basic ingredients necessary to explain the essential features of the dynamics of linear polyenes, notably, electron-electron correlations and electron-phonon interactions treated in a nonadiabatic (fully quantum) framework. With such a model, we have described the various features of a time-resolved photoemission spectroscopy experiment, obtaining a good picture of the underlying physics. We remark that, although the ground-state properties as well as the structure of the electronic excited states are properly described by the standard PPPP model,[10,11] the proper treatment of the observed nonadiabatic internal conversion, related to tunneling between coupled Born-Oppenheimer states, requires the inclusion of usually neglected electron-phonon interactions, such as the g' term we have considered, which break a residual particle-hole symmetry of the Hamiltonian.

On the technical side, we remark that exact diagonalization techniques are useful theoretical tools for the study of these effects, as shown by the reasonable agreement of our simulations with the behavior reported in Ref. 5. A closer quantitative comparison between theory and experiment would probably require relaxing some of the simplifications of our model, to describe in a more detailed way the actual decatetraene molecule. Extensions of our study to more realistic cases are, in principle, feasible either by larger computational effort[17] or through alternative techniques. Recent work on dynamical density-matrix renormalization group methods[18] and advances on real time dynamical quantum Monte Carlo[19] calculations seem promising. Our results should serve to test approximations for calculations in larger molecules.

In addition, dissipative effects due to the coupling of the molecule with the external world, not included in our model, could also play a role. The detailed investigation of these effects is left to future studies. However, one might anticipate the result of such a coupling to the environment on the basis of previous studies found in the literature. In particular, as reviewed in Ref. 20, when a quantum two-level system is coupled to a bath of bosonic modes, the internal oscillations with time tend to be damped, and might be even suppressed, eventually, if the coupling is too strong. The basic quantum-mechanical ingredient of a tunneling between two otherwise unconnected states, however, is the crucial ingredient to observe a conversion between the two states.

ACKNOWLEDGMENTS

We thank P. Bolcatto for useful discussions. This work was sponsored by PICTs Contract No. 03-06343 of ANPCyT, Argentina. L.A. and A.A.A. acknowledge support from CONICET. Part of the numerical work was done at the Max Planck Institut PKS. G.E.S. acknowledges support by MIUR under Project COFIN.

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