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Theoretical study of the absorption and nonradiative deactivation of 1-nitronaphthalene in the low-lying singlet and triplet excited states including methanol and ethanol solvent effects

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The photophysics of the 1-nitronaphthalene molecular system, after the absorption transition to the first singlet excited state, is theoretically studied for investigating the ultrafast multiplicity change to the triplet manifold. The consecutive transient absorption spectra experimentally observed in this molecular system are also studied. To identify the electronic states involved in the nonradiative decay, the minimum energy path of the first singlet excited state is obtained using the complete active space self-consistent field//configurational second-order perturbation approach. A near degeneracy region was found between the first singlet and the second triplet excited states with large spin-orbit coupling between them. The intersystem crossing rate was also evaluated. To support the proposed deactivation model the transient absorption spectra observed in the experiments were also considered. For this, computer simulations using sequential quantum mechanic-molecular mechanic methodology was used to consider the solvent effect in the ground and excited states for proper comparison with the experimental results. The absorption transitions from the second triplet excited state in the relaxed geometry permit to describe the transient absorption band experimentally observed around 200 fs after the absorption transition. This indicates that the T_2 electronic state is populated through the intersystem crossing presented here. The two transient absorption bands experimentally observed between 2 and 45 ps after the absorption transition are described here as the $T_1 \rightarrow T_3$ and $T_1 \rightarrow T_5$ transitions, supporting that the intermediate triplet state (T_2) decays by internal conversion to T_1. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4738757]

I. INTRODUCTION

The photophysics of the 1-nitronaphthalene molecule is deserving particular experimental attention in the recent years. Previous studies on nitroaromatic compounds have indicated that when the NO_2 group is directly bonded to aromatic polycyclic compounds, they experience a fast multiplicity change after the absorption transition to the first singlet excited state and conclude in a phosphorescent triplet state.[1–5] Although these compounds have been considered nonfluorescent, their emission spectrum from the first singlet excited state has been detected with the femtosecond frequency upconversion method in the subpicosecond time scale, showing a fast fluorescence decay.[6] In addition to the phosphorescent triplet state formation, an excited state pathway exists which leads some systems to the dissociation of the NO_2 group into nitrogen oxide NO$\cdot$ and an aryoxyl radical Ar–O$\cdot$.[7–9] In the absence of such photoreaction, the fast fluorescent decay can be explained based on the internal conversion (IC) and the intersystem crossing (ISC) transition between the electronic states.

The 1-nitronaphthalene molecular system has been studied together with other compounds by Morales-Cueto *et al.*,[6] being this the only compound that presents a simple exponential decay. Subsequently, an experimental study of this system[10] indicated that in all environments the S_1 lifetime is 100 fs or less, being this the organic compound which presents the fastest multiplicity change ever measured. Since no photoproducts have been detected,[2,4,11,12] the ultrafast multiplicity change has been assigned to an extreme manifestation of the El-Sayed rule,[13] allowing the fast ISC from the first singlet state to the triplet manifold.[10,11]

The experimental transient absorption spectroscopy of the 1-nitronaphthalene molecular system studied by Zugazagoitia *et al.*[14] and Reichardt *et al.*[15] seem to have proven the existence of a triplet state acting as an intermediary in the deactivation of the excited state, followed by an IC to a phosphorescent triplet state. However, there is no definitive consensus about the electronic states involved and the mechanism that makes the ultrafast multiplicity change so efficient in this molecular system.

An efficient intersystem crossing requires both small singlet-triplet energy gap allowing large vibrational overlap and large spin-orbit coupling (SOC) between the involved electronic states,[16–20] since SOC is mainly responsible for the change in the spin state. The search for adequate conditions for an efficient ISC in the 1-nitronaphthalene molecular system is directed here to study the first singlet excited state (S_1) minimum energy relaxation pathway for finding degeneracy

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regions with the triplet manifold. At the same time the SOC and the ISC rate between the singlet and triplet states will be evaluated.

The right description of the experimental transient absorption bands,[14,15] as well as the absorption and phosphorescence spectra[10,11,15] would be a strong support for the proposed nonradiative deactivation mechanism. For that reason, since in the experimental works several solvents have been used, including methanol and ethanol, it is necessary to consider the solvent effects in both the ground and excited states. Hence, the solvent effects were taken into account by using a sequential quantum mechanic-molecular mechanic (QM/MM) methodology.[21]

This paper is organized as follows. First, it will be studied if there exist adequate conditions for an efficient intersystem crossing, such as degeneracy regions and large SOC between the singlet and triplet manifolds, which allow a large ISC rate. For this purpose multiconfigurational methods will be used. Second, the experimental transient absorption spectra[14,15] will be theoretically rationalized based on the proposed deactivation mechanism, including the solvent effect for comparison with the experimental results. These electronic transitions calculations will be performed using configuration interaction (CI) methods.

This work joins to other recent theoretical results shedding some light on the photochemistry of the nitroaromatic compounds.

II. METHODOLOGY

A. Intersystem crossing

To study the ISC, the energies of the low-lying singlet and triplet states were determined at the multi-configurational second-order perturbation (CASPT2) (Ref. 22) level based on the CASSCF reference wavefunction. In the CASSCF calculations 12 electrons were correlated in 12 orbitals. This reference wavefunction is normally termed as CASSCF(12/12). The active space comprises the highest occupied π and oxygen lone-pair orbitals and the six lowest unoccupied π^* orbitals, which better describe the low-lying singlet and triplet states. It was used the atomic natural orbitals with large primitive (ANO-L) basis set[23,24] of split-valence double-zeta quality with polarization and diffuse functions on non-hydrogen atoms, C, O, N [$4s3p1d$]/H [$2s1p$]. The $1s$ core electrons of both the oxygen and carbon atoms were kept frozen in the second-order perturbation step. The CASSCF calculations used the state average procedure, in which one single set of molecular orbitals is used to compute the two lowest roots of the corresponding singlet and triplet electronic states (S_0, S_1 and T_1, T_2).

The minimum energy path (MEP) of the S_1 excited state after the Franck Condon transition was determined at the CASSCF level of calculation, selecting from the previous calculation the active orbitals that better characterize the S_1 excited state. In that way, the MEP was performed reducing the active space to four electrons in four orbitals because of the computational effort involved in that type of calculations. It used, as previously, the same ANO-L type basis set (C, O, N [$4s3p1d$]/H [$2s1p$]). In each point of the obtained MEP, CASPT2 calculations were performed using the CASSCF(12/12) reference wavefunction to better describe the low-lying singlet and triplet excited states (CASPT2//CASSCF approach) (Ref. 25).

The spin-orbit coupling elements were calculated with the approximate one electron effective Hamiltonian[26] using the Restricted Active Space State Interaction (RASSI) program which computes CASSCF states interaction properties,[27] like oscillator strength and SOC. The one electron effective Hamiltonian approach is considered feasible because the spin-orbit coupling is dominated by single excitations.[28,29] The SOC strength between the involved electronic states (l, k) was evaluated as in Ref. 30

$$\mathrm{SOC}_{\mathrm{lk}} = \sqrt{\sum_{\mathrm{u}} \left|\langle T_{\mathrm{l,u}}\right| \hat{H}_{\mathrm{SO}}\left|S_{\mathrm{k}}\rangle\right|^2}\mathrm{u} = \mathrm{x, y, z}, \tag{1}$$

where u represents each spin component of the triplet state. The dynamic correlation effects were included in the calculation shifting the diagonal elements of the spin-orbit Hamiltonian to the energies obtained in the CASPT2 calculations. RASSI program is implemented in MOLCAS 7.6 program package,[31] which is used in this work for all multiconfigurational calculations.

The ISC rate between an initial state l and a final state k was approximately calculated using the golden-rule expression for radiationless transition[32,33]

$$k_{ISC}^{IF} = \frac{2\pi}{\hbar}\mathrm{SOC}_{\mathrm{lk}}^2 f, \tag{2}$$

where f is a factor related to the vibrational overlap of the initial and final states. In the high-temperature limit f is obtained as[34]

$$f = \frac{1}{\sqrt{4\pi\lambda RT}}\exp\left[-\frac{(\Delta E+\lambda)^2}{4\lambda RT}\right], \tag{3}$$

λ being the Marcus reorganization energy, which corresponds, in first approximation, to the energy variation when switching from the equilibrium geometry of the initial singlet excited state to the corresponding equilibrium geometry of the final triplet excited state. ΔE is the vertical energy difference between the initial and final states.

B. Electronic transitions calculations and solvent effect

The calculation of the absorption, transient absorption, and phosphorescence spectra of 1-nitronaphthalene in the respective solvent environment was performed using the size-extensive configuration interaction with single excitations and double included perturbatively, CIS(D) (Ref. 35) model. This method approximately introduces the double excitations by perturbation correction to the single excitations configuration interaction reference wavefunction. The correlated-consistent basis set aug-cc-pVDZ (Ref. 36) was used in these calculations. This level of theory was adopted for the spectra calculation because it requires less computational effort compared to CASPT2 and has offered good results for excitation energy calculations.[37,38] The equilibrium geometries of the triplet electronic states were optimized at CIS/aug-cc-pVDZ level of calculation. These are necessary for calculating excitation energies originating in the triple states. The optimized geometry of the ground electronic states, used for describing the ground state absorption transition, was determined at the MP2/aug-cc-pVDZ level of calculation. The GAUSSIAN 03 program package was used in these calculations.[39]

The solvent effect was taken into account using the sequential QM/MM methodology.[21] Monte Carlo (MC) simulations were made to generate solute-solvent configurations to be used in the QM calculations of the electronic transitions. The MC simulations were performed similar to previous applications in our laboratory[40,41] but here it was also applied in the solvation of the excited states. We used the Metropolis sampling technique[42] in the NPT ensemble implemented in the DICE program.[43] In the simulations using methanol we used one molecule of 1-nitronaphthalene and 500 molecules of methanol in a cubic box with periodic boundary conditions and image method,[42] at room conditions ($T = 25\,^{\circ}$C and $P = 1$ atm). In the case of ethanol the same conditions were used but taking one molecule of 1-nitronaphthalene and 350 molecules of ethanol.

The molecular interaction was described by Lennard-Jones plus Coulomb potentials, with three parameters for each atom i (ε_i,σ_i, andq_i), where the Lennard-Jones parameters are combined to generate the pair-potential parameters by $\varepsilon_{ij} = (\varepsilon_i\varepsilon_j)^{1/2}$ and $\sigma_{ij} = (\sigma_i\sigma_j)^{1/2}$. For 1-nitronaphthalene in the ground and triplet excited states these parameters were obtained from the suggestions of Jorgensen and Severance for aromatic rings[44] and R–NO_2 group.[45] For methanol and ethanol these parameters and atomic charges were taken from the works of Jorgensen[46] and Martin *et al.*,[47] respectively. The atomic charges q_i for 1-nitronaphthalene in the ground electronic state and the triplet states have been obtained taking into account the electronic polarization of each electronic state caused by the solvent. But, in each electronic transition studied is analyzed if the electronic polarization is relevant, taking into account the lifetime of the electronic state in which the transition originates.

The electronic polarization is known to be important[40,48,49] and it was included by performing an iterative and sequential QM/MM procedure previously described,[40] which brings the solute molecule in the respective electronic state into electrostatic equilibrium with the solvent. To obtain an initial estimate of the atomic charges for the iterative procedure, a quantum mechanic calculation was performed for 1-nitronaphthalene using the polarizable continuum model (PCM) (Ref. 50) and the charges from electrostatic potentials using a grid based method (CHELPG).[51] After this, statistically uncorrelated configurations[52] of the liquid were selected from the MC simulation to calculate the average atomic charges and the solute dipole moment embedded in the electrostatic field of the solvent. These QM calculations of the charge and dipole moment use the average solvent electrostatic configuration (ASEC) (Ref. 53) model, where an average configuration is used. ASEC follows the idea of the average solvent electrostatic potential.[49,54] It is a simple configurational version of the average electrostatic potential. In the iteration, the calculated average atomic charges of the solute are then updated in the Coulomb part of the potential for another MC simulation. This process was repeated until the convergence in the average dipole moment was obtained. The solute dipole moments and charges were calculated at HF and CIS level of calculation for ground and excited states, respectively, by using the aug-cc-pVTZ basis set. After convergence, 100 statistically uncorrelated solute-solvent configurations[52] out of the 6.0×10^5 generated in each simulation were selected to be used in the QM calculations of the absorption and/or emission spectra of the corresponding electronic state.

The absorption and emission energies of the 1-nitronaphthalene molecular system in the solvent environment were determined using the ASEC model.[53] Explicit use of solvent molecules are not considered because of the very high computational effort involved.

III. RESULTS AND DISCUSSION

A. Proposed deactivation mechanics

At the ground state equilibrium geometry the absorption energy calculated at the CASPT2 level using the state average CASSCF(12/12) reference wavefunction indicates that there are two triplet excited states energetically below the S_1. The oscillator strengths show that the absorption from S_0 to S_1 is the main transition to the singlet excited states. The transition energy of 3.91 eV is in good agreement with other theoretical results shown in Subsection III B. The S_1 excited state, according to our calculations, is mainly described by the transition from HOMO-4 to LUMO+2. The HOMO-4 molecular orbital is formed by a π component in the naphthalene rings and a nonbonding component at the oxygen atoms with the nodal planes perpendicular to the NO_2 plane. The first triplet excited states T_1 has a $\pi\rightarrow\pi^*$ character mainly represented by the HOMO→LUMO+2 transition and the second triplet excited state is mainly represented by the HOMO-2→LUMO transition. The HOMO-2 molecular orbital is a nonbonding orbital localized in the oxygen atoms, but with the nodal plane coplanar with the NO_2 plane. In Fig. 1 the spatial configurations of these molecular orbitals are shown.

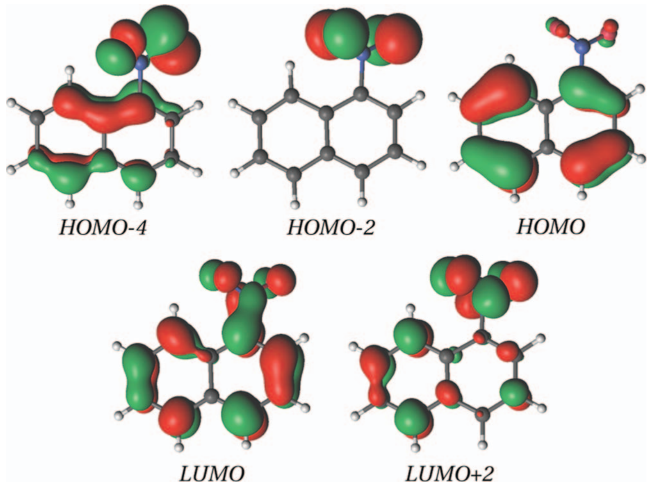

FIG. 1. Representation of the molecular orbitals involved in the electronic transitions from the ground to the first singlet and triplet electronic states.

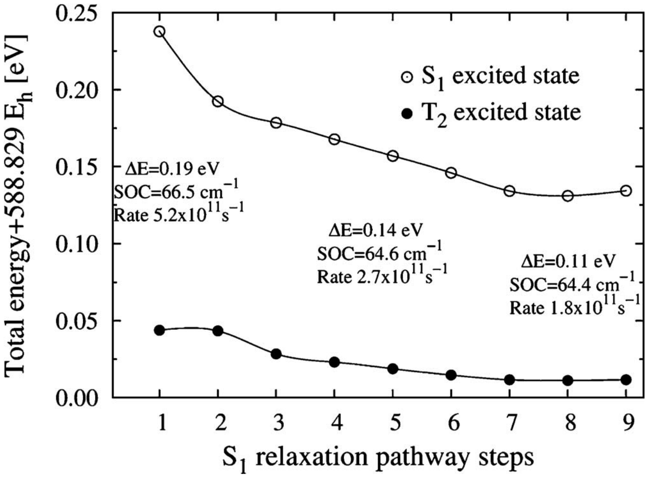

FIG. 2. Energetic profile of the S_1 and T_2 electronic states calculated in the S_1 relaxation MEP. Also shown are the SOC and ISC rate calculated in the first, fifth, and eighth steps of the MEP.

The S_1 relaxation pathway after the absorption transition was studied, following the methodology previously discussed, with the aim of finding degeneracy regions between S_1 and the triplet states. The SOC elements between the S_1 excited state and the closest triplet electronic states were evaluated along the S_1 MEP. Large SOC values in the order of 65 cm^{-1} were found between S_1 and T_2. The values obtained with the other triplet exited states were vanishingly small. In Fig. 2 is shown the energetic profiles of both S_1 and T_2 excited states, calculated at CASPT2//CASSCF level in each point of the S_1 MEP. The SOC and the ISC rate between these electronic states are also shown. As can be seen, at every relaxation step the S_1 and T_2 excited states are getting closer and the SOC remains large. The calculated point of closest proximity between the S_1 and T_2 indicates an energetic difference between them of 0.11 eV. The obtained SOC elements (of about 65 cm^{-1}) are considerably large values, compared to the typical values of the order of 1–40 cm^{-1} for organic molecules.[55] The spin-orbit coupling between some singlet and triplet electronic states in nitroaromatic compounds is expected to be large.[13,56,57] An example is a recent theoretical study of three different nitroarenes,[58] where the spin-orbit couplings between the S_1 and T_2 electronic states for nitrobenzene, 2,4,6-trinitrotoluene and 2,4,6-trimitroaniline are equal to 53.0, 60.1, and 50.4 cm^{-1}, respectively. We attribute the large spin-orbit coupling in the 1-nitronaphthalene to the perpendicularity between the nodal planes of the HOMO-4 and HOMO-2 nonbonding orbitals in the NO_2 group, since by the El-Sayed rule, the spin flip has to be accompanied by a change in the spatial symmetry.

The ISC rate was approximately evaluated using Eq. (2), which depends on the energy separation between S_1 and T_2. These states are located close in energy along the MEP, as indicated in Fig. 2, which is an important element for obtaining significant vibrational overlap. The reorganization energy was calculated at the CASPT2 level, as –0.42 eV, i.e., after the T_2 electronic state is populated it reaches the equilibrium geometry located 0.42 eV below the S_1 minimum energy. The obtained values of the ISC rate, as shown in Fig. 2, are in the order of 1.8×10^{11} s^{-1} to 5.2×10^{11} s^{-1}, representing large values which can compete in a very efficient way with the S_1 fluorescence decay, even more when the obtained oscillator strengths from S_1 to S_0 in the S_1 equilibrium geometry are small (0.0023). Values of ISC rate are reported for organic compounds ranging from 10^6 s^{-1} to 10^{11} s^{-1}.[59] Although the ISC rate remains large along the MEP of the S_1 excited state, the maximum rate appears in the first steps of the MEP. According to Eq. (3), there is a maximum when $|\Delta E| \approx \lambda$.

The deactivation mechanism occurring through the intersystem crossing between the S_1 and T_2 electronic states was pointed out, in equivalent time scales, for the nitrobenzene in the experimental and theoretical work of Takezaki *et al.*[60] That, together with our results, seems to show that the ISC is a characteristic of the photophysics of nitroaromatic compounds. The aromatic rings may play a minor role in the nonradiative deactivation, because the geometrical changes in the S_1 MEP and in the excited states equilibrium geometries are mainly described by changes of the nitro group rather than in the aromatic rings (see Fig. 4).

A recent theoretical study,[58] also for the nitrobenzene and other nitroaromatic compounds, arrived to the same description of the deactivation mechanism, but some differences were obtained in comparison with our results for the 1-nitronahtalene. In that theoretical study, the S_1 electronic state is a dark $n \rightarrow \pi^*$ excited state, which they assume is populated by some mechanism from the bright S_4 electronic state. The S_1 minimum energy path leads to a conical intersection with the ground electronic state energetically available to the system. The main geometrical changes in the MEP are related to the nitro group, going from a planar configuration to an out of plane and pyramidal NO_2 group one. They conclude that the $S_1 \rightarrow T_2$ intersystem crossing dominates over the decay through the conical intersection due to weak coupling of the S_0 and S_1 states in the nonadiabatic region. In our results, the main transition from the ground electronic state is to the S_1 excited electronic state, characterized by a $\pi \rightarrow \pi^*$ transition. The S_1 MEP is mainly characterized by the pyramidalization of the nitro group, as shown in Fig. 4. Conical intersections were not found near the S_1 minimum of the 1-nitronaphthalene and the ISC is the only nonradiative deactivation proposed here for the S_1 electronic state.

These calculations pertain to the gas phase and some relative shifting in the states is expected when going into the solution phase, where the experimental measurements have been made. The S_1 lifetime has not yet been measured in gas phase, but remains less that 100 fs in various types of solvents.[10]

In Fig. 3 is shown schematically the energetic profile of the electronic states participating in the proposed nonradiative deactivation mechanism. The shadow area represents the main region where ISC may occur. This model should be capable of describing the transient absorption bands obtained experimentally by Zugazagoitia *et al.*[14] and Reichardt *et al.*[15] This is the focus of Subsection III B.

In Fig. 4 we show the spatial configurations of the optimized geometries, wherein the nitro group defining angle is indicated, the full geometry information of these structures can be found in the supplementary material.[62] Some structural data are available for the equilibrium geometry of the

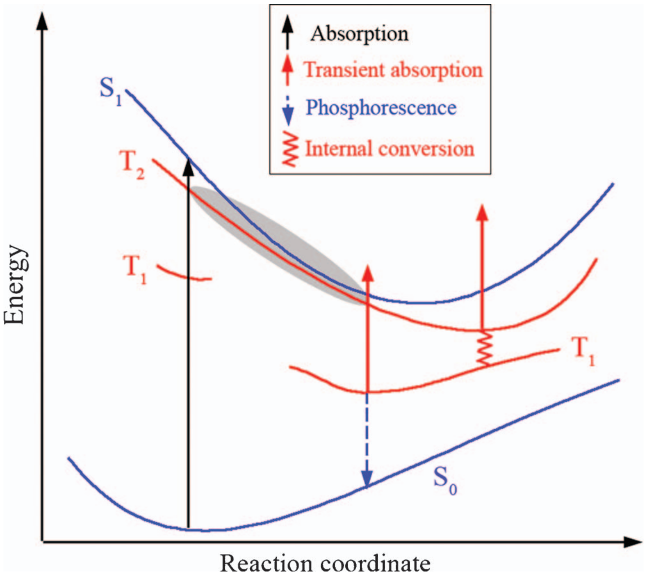

FIG. 3. Schematic energetic profile of the low-lying electronic states and the transitions discussed in this work. The shadow area is very favorable for ISC.

1-nitronaphthalene in the ground electronic state calculated using density functional theory, but some discrepancies are observed between them. In Ref. 61, a planar structure was obtained in gas phase using the B3LYP functional with various basis sets. Instead, a nonplanar configuration with the NO_2 group twisted about 28° in relation to the naphthalene plane was obtained by Zugazagoitia *et al.*[10] at PBE0/6-311G(d,p) level in gas phase and about 32° in methanol using the PCM model. In the same way, Reichardt *et al.*[15] obtained an out of plane NO_2 group twisted about 34° in cyclohexane and methanol, using the PCM model at B3LYP/6-311++G(d,p) level of theory. The equilibrium geometry calculated in the present study at MP2/aug-cc-pVDZ presents the NO_2 group twisted out of the plane of the naphthalene rings 43° and has almost no pyramidalization angle, as shown in Fig. 4 by the φ dihedral angle. This geometry is in reasonable agreement with the nonplanar previous results. Structural data are not available for the excited states equilibrium geometries for comparison with our results.

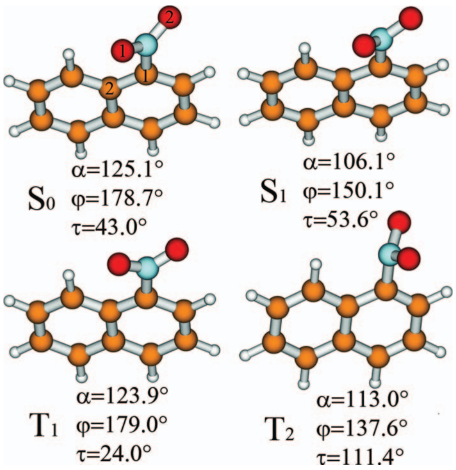

FIG. 4. Optimized structures for the corresponding electronic states. The NO_2 defining angles are: α = angle (O_1NO_2), φ = dihedral ($O_1O_2NC_1$), and τ = dihedral $O_1NC_1C_2$.

When the system moves toward the S_1 equilibrium geometry, after the absorption transition, the NO_2 group adopts a pyramidal geometry (see Fig. 4). Once the T_2 electronic state is populated it reaches its equilibrium geometry with the NO_2 group more twisted out of the plane of the naphthalene rings, forming a slightly pyramidal geometry. In the equilibrium geometry of the T_1 electronic state the NO_2 plane forms 23° with the naphthalene rings plane without forming pyramidal structure.

B. Transient absorption spectra including the solvent effect

The dynamics of the excited states of 1-nitronaphthalene was studied by Zugazagoitia *et al.*[14] and Reichardt *et al.*[15] by using transient absorption spectroscopy. In their work they detected that in the extent that the S_1 emission disappears an intermediate triplet state is populated. That intermediate state is detected by a transient absorption band with a maximum below 400 nm (between 350 and 400 nm) obtained about 200 fs after the ground state absorption transition. This is explained here by the efficient ISC between S_1 and T_2 discussed above. Subsequently, after about 2 and 45 ps, two absorption bands appear, one wide band in the visible region between 500 and 600 nm and the other in the UV region with maximum of about 400 nm. These absorption bands are assigned to the T_1 electronic state, which is populated by IC from the intermediate triplet electronic states. Some spectral evolution mostly due to vibrational cooling of the T_1 electronic state is considered to take place in the few picoseconds time scale.

These transient absorption bands have to be described in order to support the proposed deactivation model indicated in Fig. 3. The description of the electronic transitions now will use the simulations of the solvent effect for proper comparison with the experimental results. This is the aim of the present section, where the absorption, transient absorption, and phosphorescence spectra are studied also in solvent environment.

For the description of the solvent effect in the absorption transition, a simulation of the methanol solvent in electrostatic equilibrium with the ground electronic state of the 1-nitronaphthalene was made. Another simulation using methanol in electrostatic nonequilibrium with the second triplet excited state was made, with the aim of describing the transient absorption spectrum observed around the 200 fs, which corresponds to the absorption of the intermediate triplet state in the experiment.[15] Two more simulations using methanol and ethanol were also made in electrostatic equilibrium with the first triplet excited state T_1, with the aim of describing the transient absorption bands observed after about 45 ps (Refs. 14 and 15) and the phosphorescence spectrum of 1-nitronaphthalene.[11] The geometries used for describing the electronic transitions are the corresponding ones of the equilibrium configurations of the electronic state where the transition starts.

Before analyzing the solvent effect in the electronic transitions, it is convenient to discuss the electronic polarization of the solute in the corresponding electronic states. In

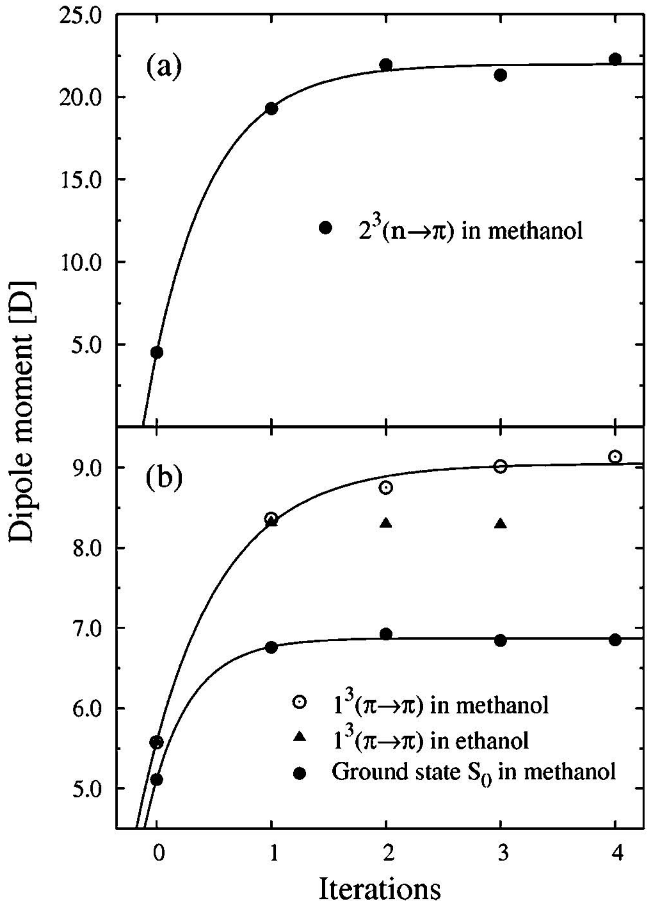

FIG. 5. Calculated changes in the average values of the dipole moments of the electronic states with respect to the number of iterations in the sequential QM/MM procedure of solute polarization.

TABLE I. Ground state absorption and phosphorescence spectra of the 1-nitronaphthalene in gas phase and in solvent. The FWHM are indicated in parentheses.

Absorption		Phosphorescence	
Gas	Methanol solvent	Gas	Ethanol solvent
4.11[a]	3.93[a]	2.70[a]	2.67[a]
4.12[b]	3.81 (3.26–4.67)[b]	…	2.38[b]
3.62[c]	3.81 (3.35–4.13)[c]	…	…
	3.80 (3.40–4.18)[d]	…	…

[a] *Ab initio* results obtained at CIS(D)/aug-cc-pVDZ level. The calculations in solvent were made in the solute-solvent configurations obtained from the simulations.

[b] Mikula *et al.*'s[11] results in gas phase was calculated at the semiempirical CNDO-CI level of theory. The results in solvent were obtained experimentally, using isopentane for the absorption.

[c] Zugazagoitia *et al.*'s[10] results in gas phase was calculated at the DFT/PBE0 level and the result in solvent was obtained experimentally.

[d] Experimental results of Reichardt *et al.*[15]

Fig. 5 are shown the changes of the average dipole moments obtained in the iterative and sequential QM/MM procedure of the electronic polarization. As can be seen in Fig. 5(a), the T_2 triplet state shows a very large electronic polarization when interacting with the methanol solvent. The dipole moment increases dramatically from the gas phase value of 4.50 D to 21.86 D in the solvent. This electronic state, according to our calculations, is the intermediate between S_1 and the triplet manifold in the nonradiative decay. In the ground electronic state of 1-nitronaphthalene, the dipole moment increases by about 36% compared with the gas phase, reaching 6.85 D in methanol. The first triplet state T_1 is also polarized increasing the dipole moment by about 64% in methanol and 49% in ethanol (Fig. 5(b)).

We now consider the electronic transitions starting our discussion with absorption transition to the S_1 electronic state and the phosphorescence spectrum. These two processes are shown in Fig. 3 by the up (black) and down (blue) arrows, respectively. In Table I are shown previous theoretical and experimental results of the absorption spectrum that will be compared with our results. The previous theoretical and experimental results of the phosphorescence decay are also shown. The theoretical absorption transition obtained here at the CIS(D)/aug-cc-pVDZ level indicates a medium intensity transition with an oscillator strength of 0.13, in agreement with other previous results in gas phase of 0.10 and 0.18.[10,11] The transition energy of 4.11 eV from gas phase is in good agreement with the 4.12 eV of Mikula *et al.*[11] using the semiempirical method, complete neglect of differential overlap with configuration interaction (CNDO-CI), and the result using time-dependent density functional theory (TD-DFT) with the functional of Perdew, Burke and Ernzerhof (PBE0) of Zugazagoitia *et al.*[10] obtained 3.62 eV.

The results obtained from the MC simulations considering the methanol solvent effects in the absorption transition show a red shift of 0.18 eV, changing to 3.93 eV, in good agreement with the experimental results[10,11] of a band maximum at 3.81 eV with a full width at half maximum (FWHM) of 0.78 eV (see Table I). The phosphorescence spectrum corresponding to the T_1 triplet state presents a small red shift of 0.03 eV, changing from 2.70 eV in gas phase to 2.67 eV in ethanol, in reasonably good agreement with the experimental result with maximum at 2.38 eV.[11]

The transient absorption spectrum, observed around the 200 fs after the absorption transition to S_1, was obtained experimentally by Reichardt *et al.*[15] and it was associated with the absorption of the host triplet state. Thus, the theoretical description of this experimental spectrum is very important in understanding the photophysics of 1-nitronaphthalene, since the receptor triplet state is the intermediate between the S_1 state and the triplet manifold in the nonradiative decay. In the present interpretation of the deactivation mechanism this spectrum corresponds to the absorption transitions of the T_2 excited state. In that way, using the equilibrium geometry of the T_2 electronic state (Fig. 4), two absorption transitions $T_2\to T_6$ and $T_2\to T_7$ were obtained in gas phase, with energies of 3.39 and 3.64 eV, respectively, computed at CIS(D)/aug-cc-pVDZ level. These transitions could be associated with the experimental band[15] obtained in methanol solution with maximum at 3.35 eV, as can be seen in Table II. As previously discussed, the electronic polarization of the 1-nitronaphthalene in the T_2 electronic state is very large, considerably increasing the dipole moment in methanol (Fig. 5(a)). However, taking into account that the experimental results of Zugazagoitia *et al.*[14] and Reichardt *et al.*[15] indicate that the internal conversion between the intermediate

TABLE II. Transient absorption spectra of the 1-nitronaphthalene in gas phase and in solvent. In parenthesis are indicated the FWHM.

Transient abs. ∼200 fs		Transient abs. 2–45 ps			
		1st band		2nd band	
Gas $T_2 \rightarrow T_6/T_2 \rightarrow T_7$	Methanol solvent $T_2 \rightarrow T_6/T_2 \rightarrow T_7$	Gas	Methanol/ethanol solvent	Gas	Methanol/ethanol solvent
3.39/3.64[a]	3.37/3.45[a]	2.40[a]	2.25/2.29[a]	3.33[a]	3.23/3.25[a]
…	…	…	2.11 (1.91–2.34)[b]	…	…
…	3.35 (3.20–3.54)[c]	…	2.11 (1.91–2.36)[c]	…	3.01 (2.83–3.31)[c]

[a] *Ab initio* results obtained at the CIS(D)/aug-cc-pVDZ level. The calculations in solvent were made in the solute-solvent configurations obtained from the Monte Carlo simulations.

[b] Experimental results of Zugazagoitia *et al.*[14]

[c] Experimental results of Reichardt *et al.*[15]

and the T_1 triplet state occurs in a time scale of 1 to 16 ps and 2 to 4 ps, respectively, it can be inferred that the 1-nitronaphthalene in the T_2 electronic state does not have enough time to reach the solute-solvent electrostatic equilibrium shown in Fig. 5(a). Based on this, the absorption transitions $T_2 \rightarrow T_6$ and $T_2 \rightarrow T_7$ in methanol should be calculated with solute-solvent configurations in the previous electrostatic equilibrium with the ground electronic state. At the same time, the fast response of the solvent has to be equilibrated to the new electronic distribution of the 1-nitronaphthalene in the T_2 electronic state. This physical behavior was approximately described here by performing one Monte Carlo simulation with the 1-nitronaphthalene in the T_2 electronic state, but starting the simulation from solute-solvent configurations previously equilibrated with the ground electronic state. The dipole moment calculated in solvent after the Monte Carlo simulation was 5.23 D, indicating, in accord with Fig. 5(a), that the system in the T_2 electronic state is far from the solute-solvent electrostatic equilibrium. Using the solute-solvent configurations, obtained from that simulation, the spectral shifts of the $T_2 \rightarrow T_6$ and $T_2 \rightarrow T_7$ transitions, previously obtained in gas phase, were calculated. The average $T_2 \rightarrow T_6$ and $T_2 \rightarrow T_7$ absorption energies in methanol were 3.37 and 3.45 eV, respectively. These values are in excellent agreement with the experimental result of 3.35 eV obtained by Reichardt *et al.*,[15] with a FWHM of 0.34 eV (see Table II).

As previously commented, when the absorption transition observed around 200 fs disappears the T_1 electronic state begins to be populated by IC from the intermediate triplet state and is detected by two absorption bands observed after about 45 ps of the ground state absorption transition. In Table II are shown these two experimental transient absorption bands. In the work of Zugazagoitia *et al.*[14] only one band was fully traced due to the spectral region of those measurements, while Reichardt *et al.*[15] obtained two transient absorption bands. In both works, the first wide band appears with maximum at about 2.11 eV and FWHM of approximately 0.44 eV. The second band has the maximum at ca. 3.01 eV with the FWHM of about 0.48 eV. These absorption bands were obtained in the present work using the optimized geometry of the T_1 triplet electronic state (see Fig. 4) and considering the solvent effect with the solvent in electrostatic equilibrium with this triplet electronic state. Table II shows the T_1 absorption energies calculated at the CIS(D)/aug-cc-pVDZ level in gas phase and in solution. The first absorption band is described by the electronic transition $T_1 \rightarrow T_3$ with energy of 2.40 eV in gas phase which shifts to 2.25 and 2.29 eV in methanol and ethanol solvents, respectively. These results are in good agreement with the experimental works, being very close to the maximum of 2.11 eV, with the experimental FWHM of about 0.44 eV. The second transient absorption band is described by the transition $T_1 \rightarrow T_5$ changing from 3.33 eV in gas phase to 3.23 and 3.25 eV in methanol and ethanol solvents, respectively. Although these values are a little more separated from the maximum of the band, they still remain within the experimental FWHM.

Some important conclusions can be drawn from this section. The transient absorption spectrum experimentally observed around the 200 fs (Ref. 15) is described here by the electronic transitions $T_2 \rightarrow T_6$ and $T_2 \rightarrow T_7$ which are close to each other. This indicates T_2 to be the intermediate triplet electronic state between S_1 and the triplet manifold, as previously indicated by the efficient ISC between S_1 and T_2. The two transient absorption bands observed between 2 and 45 ps[14,15] are described by the transitions $T_1 \rightarrow T_3$ and $T_1 \rightarrow T_5$, supporting the idea that the intermediate triplet state decays by internal conversion to T_1, which presents a theoretical phosphorescent spectrum in agreement with the experimental results.

IV. CONCLUSIONS

The ultrafast multiplicity change of the 1-nitronaphthalene molecular system, after the absorption transition, has been basically explained by an efficient ISC between the singlet and triplet manifolds involving specific receptor triplet states, which may dominate over the fluorescence decay. The large ISC rate obtained is a consequence of the large SOC and the vibrational coupling approximately evaluated. This result together with other theoretical and experimental works seems to show a common characteristic of the nitroaromatic compounds, where the photophysics is mainly determined by the ISC between the singlet and triplet manifolds.

Using the proposed deactivation model, the transient absorption spectra experimentally observed[14,15] have been theoretically described here, considering the solvent effects in the ground and excited states for proper comparison with the experimental results. The present description of the experimental spectra reaffirms the role of the T_1 and T_2 electronic states in the photophysics of 1-nitronaphthalene.

The present theoretical calculations indicate that the non-radiative decay of the 1-nitronaphthalene is described in the following way: after the absorption transition to the S_1 singlet state, the system passes quickly, in the time scale of 100 fs or less, to the T_2 triplet state through the efficient ISC between these electronic states. In the next few tens of picoseconds an internal conversion occurs between T_2 and T_1, staying in the latter state which finally decays to the ground state on much longer time scales, as indicated by the T_1 phosphorescence spectrum.

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