

Ultrafast Intersystem Crossing in SO₂ and Nucleobases

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Abstract: Mixed quantum-classical dynamics simulations show that intersystem crossing between singlet and triplet states in SO₂ and in nucleobases takes place on an ultrafast time decay (few 100 fs), directly competing with internal conversion.

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1. Introduction

Transitions involving a change in the spin are formally forbidden in a non-relativistic frame and are only mediated by spin-orbit couplings. The so-called intersystem crossing (ISC) process can convert eg. a singlet state radiationless into a triplet state, or a triplet state into a singlet one. Because spin-orbit couplings are typically small for organic molecules, ISC is assumed to be one of the slowest forms of relaxation in photochemistry and photophysics, taking place on the order of picoseconds to microseconds.

Using mixed quantum-classical molecular dynamics in the form of surface-hopping, according to Tully's fewest switches criterion [1] within the recently developed SHARC code [2] (Surface Hopping including ARbitrary Couplings) it is possible to simultaneously describe ISC and internal conversion (IC) processes. These processes are mediated by spin-orbit couplings and non-adiabatic couplings, respectively, and both types of couplings are considered in SHARC. In this presentation, two general topics will be covered: The excited-state dynamics of SO₂ and the photophysics of DNA/RNA nucleobases. Both cases show that despite the lack heavy atoms, ultrafast ISC takes place directly competing with IC.

2. Methodology

We distinguish between two bases for the electronic states. The first, is the basis of the eigenfunctions of the molecular Coulomb Hamiltonian (MCH), which is the basis employed in most electronic structure codes. In this representation, coupling between states of the same multiplicity are described by non-adiabatic couplings, while states of different multiplicity are coupled by off-diagonal elements in the Hamiltonian matrix. In the second basis, the Hamiltonian is diagonalized, and its eigenfunctions are spin-mixed states coupled only by non-adiabatic couplings. The transformation between the basis is expressed in terms of a unitary matrix \mathbf{U} :

$$\mathbf{H}^{\text{diag}} = \mathbf{U}^\dagger \mathbf{H}^{\text{MCH}} \mathbf{U} \quad \text{and} \quad \mathbf{c}^{\text{diag}} = \mathbf{U}^\dagger \mathbf{c}^{\text{MCH}}.$$

The latter basis is the one employed for surface hopping in the SHARC methodology [2, 3], since it presents a number of advantages. First, it includes the effect of the spin-orbit coupling on the shape of the potential energy surfaces, which is known as Zeeman effect. Second, in this basis all couplings are localized at regions of the potential energy surfaces where the states are close in energy. This implies that trajectories only hop in these localized regions—in the spirit of the fewest-switches approach [1]. Third, it correctly accounts for rotational invariance between the multiplet components and thus allows to easily include all of these components.

3. Results

In the following the photophysics of two different molecular systems will be discussed: The SO₂ and DNA/RNA nucleobases.

In SO₂ a complicated vibrational structure, arising from IC between the ¹A₂ and ¹B₁ singlet states, has been observed in the first allowed band of the absorption spectrum. Another band of very weak intensity exists, which was proposed to arise from ISC [4]. Modern quantum chemistry indicates the presence of three triplet states (³A₂, ³B₁, ³B₂), but neither

experiments nor static ab initio calculations could elucidate the relative importance of these triplet states in ISC. The results of SHARC simulations [5] on SO_2 based on MRCI wavefunctions (see Figure 1) show clearly that the 3B_2 state is strongly participating in the excited-state dynamics. Already after 700 fs, more than 40% of the population has crossed to the 3B_2 state.

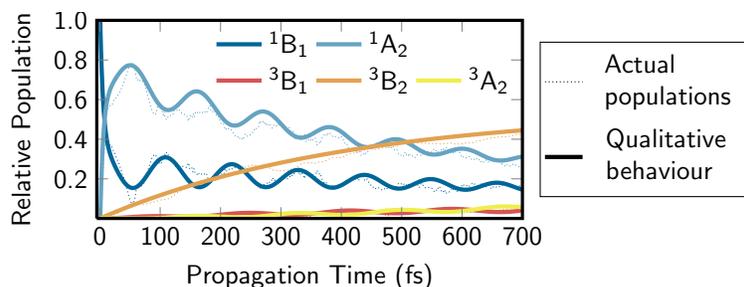


Fig. 1. Time evolution of the excited-state populations in SO_2 .

Knowledge of the excited-state dynamics of DNA nucleobases is important in order to understand DNA photodamage. Cytosine is a special case, first because it shows several stable tautomers in the gas phase, and second because theoretical investigations proposed the participation of triplet states in the ultrafast dynamics [6]. Our recent SHARC simulations [3] revealed that the dynamics of the keto and enol tautomers are significantly different (see Figure 2). The keto form exhibits a very fast ground-state relaxation and also shows ISC to the lowest triplet states. The enol tautomer on the other hand shows a slower relaxation and almost no ISC. Analogous SHARC simulations on thymine and uracil reveal that ISC also takes place on an ultrafast time scale.

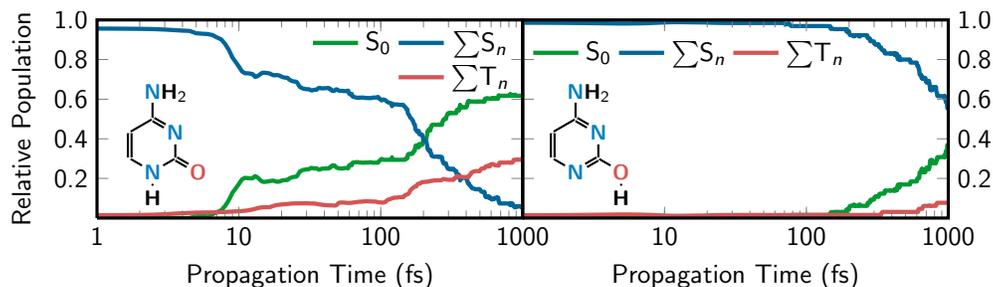


Fig. 2. Populations of the electronic states in cytosine tautomers (left: keto, right: enol).

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