

# STUDY OF THE *CIS-TRANS* PHOTOISOMERIZATION IN A MODEL POLYATOMIC MOLECULE

ESTUDIO DE LA FOTOISOMERIZACIÓN *CIS-TRANS* EN UNA MOÉCULA POLIATÓMICA MODELO

F. RODRÍGUEZ-HERNÁNDEZ, A. MARTÍNEZ MESA<sup>†</sup>, L. URANGA PIÑA

Facultad de Física, Universidad de La Habana, Cuba. aliezer@fisica.uh.cu

<sup>†</sup> corresponding author

**PACS:** Semiclassical theories in atomic physics, 31.15.xg; Isomerization reactions, 82.30.Qt; Ultrafast processes in femtochemistry, 82.53.-k

*Cis-to-trans* photoisomerization represents a paradigmatic example of a dynamical process driven by a conical intersection [1] and it plays an important role in several phenomena in physics, chemistry and biology. For example, it is a key step in both photosynthesis and vertebrates vision [2]. Likewise, it is at the heart of the design of novel nanoscale devices such as molecular switches, sensors and motors [3], owing to the distinct macroscopic chemical and physical properties that correspond to each isomer [4].

The intrinsic many-body character of these processes makes numerically converged calculations of the isomerization rates difficult to achieve. Photoisomerization yields are chiefly determined by the nuclear dynamics near conical intersections, thereby ruling out the possibility to carry out a quantum treatment of the molecular dynamics within the Born-Oppenheimer approximation. Fortunately, very often there is a clear separation between the chromophore, which actively responds to photoexcitation, and the rest of the system. This separation enables to apply, to the analysis of photoisomerization, the nowadays available theoretical and computational tools for the accurate study of the quantum dynamics of small molecular systems.

A possible route to undertake the computer simulation of *cis-trans* photoisomerization is the introduction of hybrid quantum-classical integration schemes. Since the quantum character of the isomerization process can not be completely neglected, its numerical investigation relies, at present, on the accuracy of the mixed quasi-classical approaches. As a consequence, new models are continuously developed and tested [5]. Simple models are specially valuable as they provide intuitive representations of reaction mechanisms and they constitute ideal test grounds for new computational approaches. The purpose of the present work is to carry out the study of non-adiabatic *cis-trans* photoisomerization of a prototype polyatomic molecule, within the framework of

quantum-classical molecular dynamics, for a two-state two-mode model previously introduced in the literature [6]. To this aim, the simultaneous resolution of the time-dependent Schrödinger equation, along the active modes of the chromophore, and the canonical equations of motion, for the classical subsystem, are tackled via the symplectic algorithm introduced in Ref. [7]. The availability of previous theoretical results, from quasi-classical and reduced density matrix integration schemes [8], provides an ideal benchmark to assess the performance of this integration scheme in this specific problem. Moreover, the results reported in Ref. [8] are complemented by the analysis of the dynamical state of the bath.

Following Refs. [6, 8-10], we assume that a two-state model involving two nuclear modes is capable to account for the essential aspects of the isomerization process. The model Hamiltonian  $\hat{H}_S$ , in the diabatic representation, in terms of the two lowest electronic states,  $|\psi_n\rangle$  and  $|\psi_m\rangle$ , is written as follows:

$$\hat{H}_S = \sum_{n,m=0,1} |\psi_n\rangle (\hat{T} \delta_{nm} + \hat{V}_{nm}) \langle \psi_m | \quad (1)$$

The dependence of the diabatic potential matrix  $\hat{H}_{SB}$  and the kinetic energy operator  $\hat{T}$ , on the dimensionless (mass-weighted) variables  $q$  and  $\varphi$ , has been described elsewhere [6]. The vibrational coordinate  $q$  effectively accounts for all the normal modes of oscillation in the chromophore, while the reaction coordinate  $\varphi$  parametrizes the twist of the molecular fragment corresponding to isomerization. It should be noticed that the interval  $-\frac{\pi}{2} \leq \varphi \leq \frac{\pi}{2}$  corresponds to the *cis* configuration while the range  $\frac{\pi}{2} \leq \varphi \leq \frac{3\pi}{2}$  corresponds to the *trans* geometry, the value  $\varphi = \frac{\pi}{2}$  corresponds with the geometry of the conical intersection. The remaining  $N$  degrees of freedom are represented by a bath of harmonic oscillators. The dynamics of the bath oscillators is modeled classically by the Hamiltonian  $\hat{H}_B$ , and this classical subsystem is coupled to the chromophore through the

coupling term  $\hat{H}_{SB}$ . The explicit expressions and the values of the parameters appearing in the different terms of the total Hamiltonian:

$$\hat{H} = \hat{H}_S + \hat{H}_B + \hat{H}_{SB} \quad (2)$$

were taken from the literature [8].

The dynamical state of the system evolves according to the coupled set of equations:

$$\begin{aligned} i \frac{\partial \Psi(q, \varphi, t)}{\partial t} &= [\hat{H}_S + \hat{H}_{SB}(\vec{x}(t))] \Psi(q, \varphi, t) \\ \dot{\vec{x}} &= \frac{\partial H_B}{\partial \vec{p}} \\ \dot{\vec{p}} &= -\frac{\partial H_B}{\partial \vec{x}} - \frac{\partial}{\partial \vec{x}} \langle \Psi | \hat{H}_{SB} | \Psi \rangle \end{aligned} \quad (3)$$

The vectors  $\vec{x}$  and  $\vec{p}$  span the full phase space of the harmonic bath. Hereafter, we shall use the atomic units ( $\hbar=1$ ). The symplectic PICKABACK scheme [1] allows to update the states of the quantum and classical subsystems, explicitly taking into account the interaction between them. As in previous studies [7], the discretized thermal bath is built by 200 harmonic oscillators, with homogeneously distributed frequencies in the range  $0 < \omega_\alpha < 0.3$  eV. An ensemble of up to  $N_{\text{copies}}=5000$  copies for each oscillator were used in the calculation of the observables. The initial conditions of the copies sample the quantum distribution, in position and momentum spaces, corresponding to the ground state of each oscillator.

For the quantum subsystem, we need to solve the coupled time-dependent Schrödinger Eq. (3). In the diabatic representation, the wavefunction reads:

$$\Psi(q, \varphi, t) = \sum_{n=0,1} \phi_n(q, \varphi, t) |\psi_n\rangle \quad (4)$$

Since the laser excitation pulse is assumed to be instantaneous, the initial wavepacket promoted to the excited electronic state is the exact copy of the ground state wavefunction corresponding to the (separable) potential  $V_{00}(q, \varphi)$ . For the vibrational ground state, the dependence of the initial wavefunction  $\phi_0(q, \varphi, t=0)$  on the vibrational coordinate  $q$  is known analytically. The dependence of the two-dimensional wavefunction  $\phi_0(q, \varphi, t=0)$  on the isomerization angle  $\varphi$  is obtained using a Numerov's finite-difference scheme [12]. The initial wavepacket is evolved in time by introducing a finite-difference representation of the Hamiltonian in a two-dimensional grid. The split-operator technique was used to represent the evolution operator. Both quantum and classical equations of motion were integrated using a time-step of  $dt=0.1$  a.u. A total of  $2.5 \times 10^6$  updates of the molecular state  $(\vec{x}, \vec{p}) \Psi(q, \varphi, t)$  were carried out, equivalent to a time interval of about 6 ps after photoexcitation.

In Figure 1, the time evolution of the total energy

corresponding to the bath modes is represented (only the first 3 ps after the initial excitation are shown). The overall behaviour confirms the absorption of the excess energy by the classical subsystem. As it is shown in the figure, there is an initial increase of the bath energy by approximately 0.03 eV taking place during the first 20 fs upon photoexcitation, followed by a slower energy uptake over a period of about 580 fs. The sudden increase of bath's energy by 0.017 eV, happening at 600 fs, is followed by a further rise lasting about 200-300 fs. After 1 ps, the bath have absorbed about 0.4 meV per mode on average. Since the drop in the average energy of the chromophore is governed by the system-bath coupling  $\hat{H}_{SB}$ , which is chosen to be position-dependent, its course before and after  $t=600$  fs suggests that a marked restructuring of the molecule occurs at this time. From 1 ps onwards, it ceases the net energy drift from the chromophore to the bath. It is replaced by a plateau-like behaviour, where only relatively small fluctuations 5% occur around the asymptotic energy of the bath modes.

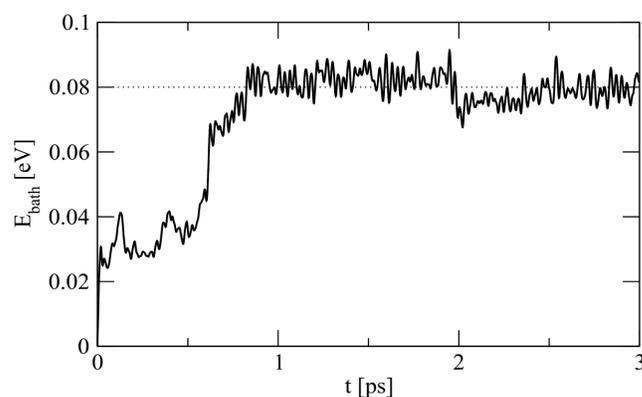


Figure 1. Time evolution of the total energy corresponding to the bath modes.

In Figure 2 it is shown the time-evolving population corresponding to the *cis* geometry (the population of the *trans* isomer mirrors this curve), during the first 3 ps after photoexcitation. The initial value  $P_{\text{cis}}(t=0)=1$  follows from the initial conditions for the wavepacket, centred around the potential energy minimum of the *cis* configuration.

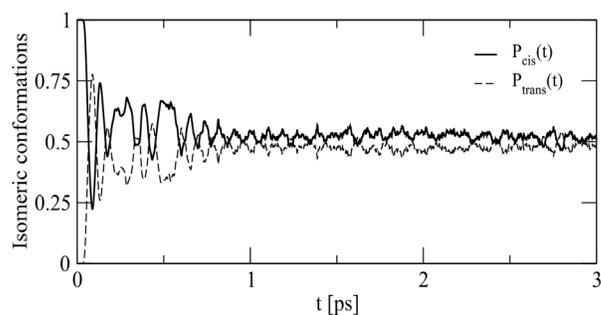


Figure 2. Time-evolving population corresponding to the *cis* and *trans* geometry.

Upon photoexcitation, the geometrical rearrangement of the molecule takes place in two stages. During the first 90 fs, a fast decrease of the probability  $P_{\text{cis}}$

occurs. After attaining its minimal value, it begins a gradual recovery of the *cis* population. This increase occurs in a much larger time scale: the *cis* and *trans* populations reach their asymptotic limits in about 1 ps. This early phase is characterized by strong recurrences, which get continuously damped until the equilibrium is reached.

A more microscopical understanding of the time evolution of the molecular rearrangement is provided by the probability distribution  $\rho(\varphi, t)$  along the reaction coordinate  $\varphi$ . This probability density is shown in Figure 3 for selected points in time in the interval  $0 \leq t \leq 110$  fs. It can be noticed how, during the first 30 fs, the wavefunction describing the displacement in the diabatic state  $n=1$  gets progressively broader, under the influence of the  $V_{11}$  potential energy surface, while it keeps its nearly Gaussian shape. At  $t=30$  fs, the right front of the wavepacket reaches the position of the conical intersection, giving rise to transitions between the electronic states, as it can be seen in the right panel. This moment also marks the beginning of the transfer of population to the *trans* geometry. From 30 fs onwards, there is an increasingly larger fraction of the wavepacket lying in the neighbourhood of the point of degeneracy, thereby strengthening the rate at which electronic transitions take place. After 110 fs, as it is shown in the right panel of Figure 3, as a consequence of these transitions, the diabatic state  $V_{00}$  has been repopulated up to a significant extent ( $P_0^{\text{diab}} = P_1^{\text{diab}} = 0.5$ ). The simultaneous population of the two diabatic states is reflected by the further splitting of the nuclear wavepacket into two parts which move away from the conical intersection in opposite directions. Albeit exhibiting a comparatively large probability of being around the conical intersection, the electronic transitions tend to balance beyond 600 fs. Hence, after that moment, the possibility of a net population transfer between the electronic states to occur is largely reduced and the displacement along the isomerization coordinate slows down, leading to the stabilization of the *cis* and *trans* populations presented above. Interestingly, at short times, the diabatic populations shown in Figure 3 agree qualitatively with the previous simulations carried out for the same model, based on Redfield theory [8]. In particular, within the subpicosecond time scale, the quantum-classical methodology employed in this work performs better than the classical mapping formalism introduced in Ref. [8], despite the extent of quantum corrections brought into that model.

In summary, the structural modification of a generic molecular system was investigated, employing a model hamiltonian which describes the chromophore as a quantum system with only two degrees of freedom, while the rest of the generalized molecular coordinates are treated as a set of classical harmonic oscillators. Only the ground and the first excited electronic states are considered to take part in the process. The main features of the mechanism of photoisomerization are explained in terms of the probability density along the isomerization coordinate, i.e., the splitting of

the wavepacket and the electronic transitions induced by non-adiabatic couplings in the vicinity of the degeneracy seam. For this model, the *cis*-to-*trans* reaction yield is found to be about 0.5, while the isomerization process does not occur in a single step. The early time evolutions of the populations of the *cis* and *trans* isomers (and also those of the diabatic electronic states) exhibit rather large recurrences, which reflects the coherent dynamics of the nuclear wavepacket. From the comparison with previous reports on the non-adiabatic dynamics of similar systems, and owing to the universal features of the model employed, it can be concluded that the present quantum-classical simulation strategy is capable to describe the process of *cis*-to-*trans* photoisomerization in a satisfactory manner. The methodology can be readily applied to polyatomic molecular systems interacting with realistic bath models, where the coherent character of the nuclear dynamics or the large number of degrees of freedom involved prevent, respectively, the use of purely classical approaches or more rigorous schemes, like the MCTDH package.

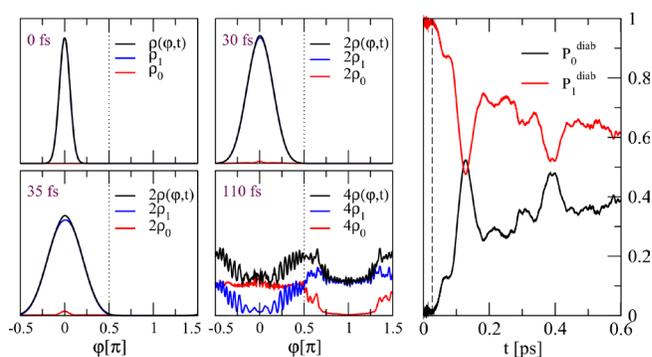


Figure 3. Probability distribution  $\rho(\varphi, t)$  along the coordinate  $\varphi$  for some representative instants of time. In the right panel it is shown the time evolution of the diabatic electronic states population.

- [1] F. Bernardi, M. Olivucci, M. A. Robb, *Chem. Soc. Rev.* 25, 321 (1996).
- [2] G. Wald, *Science* 162, 230 (1968).
- [3] A. B. Cubitt, R. Heim, S. R. Adams, A. E. Boyd, L. A. Gross, R. Y. Tsien, *Trends Biochem. Sci.* 20, 448 (1995).
- [4] C. Zhang, M. H. Du, H. P. Cheng, X. G. Zhang, A. E. Roitberg, J. L. Krause, *Phys. Rev. Lett.* 92, 158301 (2004).
- [5] U. Müller, G. Stock, *J. Chem. Phys.* 107, 6230 (1997).
- [6] L. Seidner, W. Domcke, *Chem. Phys.* 186, 27 (1994).
- [7] P. Nettesheim, F.A. Bornemann, B. Schmidt, C. Schütte, *Chem. Phys. Lett.* 256, 581 (1996).
- [8] I. Uspenskiy, B. Strodel, G. Stock, *Chem. Phys.* 329, 109 (2006).
- [9] S. Hahn, G. Stock, *J. Phys. Chem. B* 104, 1146 (2000).
- [10] B. Balzer, G. Stock, *Chem. Phys.* 310, 35 (2005).
- [11] X. Chen, V. S. Batista, *J. Photochem. Photobiol. A: Chem.* 190, 274 (2007).
- [12] G. Delgado-Barrio, A. M. Cortina, A. Varadt, P. Mareca, P. Villarreal, S. Miret-Artes, *J. Comput. Chem.* 7, 208 (1986).