Hybrid QM/QM simulations of photochemical reactions in the molecular crystal *N*-salicylidene-2-chloroaniline.

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Streszczenie

In this paper, we report the application of the QM/QM hybrid simulation technique to the photoisomerisation reactions of anils (*i.e.*, Schiff bases of salicylaldehyde with aniline derivatives) in the solid state, on the example of the photochromic polymorph of *N*-salicylidene-2-chloroaniline. By propagating molecular dynamics on a potential energy surface constructed using a combination of time-dependent DFT and ground-state DFT calculations, two reaction pathways of the *cis*-enol isomer were observed, which occur with approximately equal probability. In the first pathway, the photoexcited molecule undergoes an intramolecular proton transfer reaction on average 25 fs after photoexcitation. It then persists in the *cis*-keto form for a few hundred femtoseconds before undergoing a pedal motion through which it reaches an S_1/S_0 conical intersection. This pathway, whose existence has previously been proposed in the literature to rationalize the feasibility of the photoisomerisation reaction in the confined environment of the crystal lattice, is predicted to lead to the formation of the *trans*-keto form. The second pathway is nonreactive and is analogous to a previously characterised radiationless de-excitation pathway of the isolated molecule. The *cis*-enol to *trans*-keto photoisomerisation is reversible. Following the photoexcitation of a *trans*-keto molecule, it persists in a largely unchanged geometry for a period of time ranging from a few hundred femtoseconds to over a picosecond, and subsequently undergoes a pedal motion in the same direction as the one involved in the *cis*-enol to *trans*-keto photoisomerisation, leading to the *cis*-keto isomer through another S_1/S_0 conical intersection.

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