Intersystem crossing driven by vibronic spin–orbit coupling: a case study on psoralen†

Jörg Tatchen, Natalie Gilka and Christel M. Marian*

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For 7H-furo[3,2-g][1]benzopyran-7-one (psoralen), intersystem crossing (ISC) rate constants have been computed. Employing the Fermi golden rule, the harmonic approximation, and a pure-spin Born–Oppenheimer basis, both direct and vibronic spin–orbit (SO) coupling has been taken into account. Necessary data on electronic excitation energies and potential energy hypersurfaces originate from correlated all-electron calculations applying (time-dependent) density functional theory and the density functional theory/multireference configuration interaction approach. SO coupling has been treated by means of the one-center mean-field approximation. Vibronic SO couplings have been evaluated via numerical differentiation of SO matrix elements. Accounting only for direct SO coupling, rate constants of the order of \( k_{\text{ISC}} \approx 10^{10} \text{ s}^{-1} \) result for \( S_2(n \rightarrow \pi^*) \simarrow T_1(\pi \rightarrow \pi^*) \) ISC, whereas the rates of the channels \( S_1(\pi \rightarrow \pi^*) \simarrow T_{1,2,3}(\pi \rightarrow \pi^*) \) do not exceed \( k_{\text{ISC}} \approx 10^7 \text{ s}^{-1} \). Including vibronic SO coupling, rate constants of \( k_{\text{ISC}} \approx 3 \times 10^8 \text{ s}^{-1} \) are obtained for the \( S_1(\pi \rightarrow \pi^*) \simarrow T_1(\pi \rightarrow \pi^*) \) ISC. The radiationless transition from the \( S_1(\pi \rightarrow \pi^*) \) state to the nearly degenerate \( T_3(\pi \rightarrow \pi^*) \) state has been estimated to be slightly less efficient (\( k_{\text{ISC}} \approx 10^7 \text{ s}^{-1} \)). Based on our computed rates of ISC and excited state solvent shifts, we conclude that the experimentally observed appreciable triplet quantum yields of psoralen in polar protic media are primarily due to \( S_1(\pi \rightarrow \pi^*) \simarrow T(\pi \rightarrow \pi^*) \) channels. For heteroaromatic systems, \( (\pi \rightarrow \pi^*)/(\pi \rightarrow \pi^*) \) ISC driven by vibronic SO coupling is expected to be a common triplet state population mechanism.

1. Introduction

In organic molecular photochemistry, singlet–triplet intersystem crossing (ISC) is a very important determining factor of molecular photoactivity: Typically, the chromophore exhibits a closed-shell singlet electronic ground state \( S_0 \). By absorption of electromagnetic radiation in the UV/Vis range, a singlet excited state (\( S_n \)) is populated. Photoexcitations of the type \( S_0 \rightarrow S_n \) with \( n \geq 2 \) will usually be followed by rapid internal conversion (IC) \( S_n \simarrow S_1 \). The most important intramolecular mechanisms for the subsequent depopulation of the \( S_1 \) state are comprised by fluorescence (F), IC \( S_1 \simarrow S_0 \), or singlet–triplet ISC \( S_1 \simarrow T_n \). The relative rates of these processes depend on the particular system and the experimental conditions. In close analogy to \( S_n \) with \( n \geq 2 \), almost every triplet state \( T_n \) with \( n \geq 2 \) will be transient, i.e., it will be immediately depopulated by a radiationless transition of the type \( T_n \simarrow T_{n' < n} \). Due to this fast radiationless dephasing, in general both the \( T_n \) and the \( S_0 \) states with \( n \geq 2 \) will neither undergo photochemical reactions nor will they luminesce to a noteworthy extent (Kasha’s rule). The intrinsic lifetime of the \( T_1 \) state typically exceeds that of \( S_1 \) by orders of magnitude. Thus, when photoreactivity is discussed, both the \( S_1 \) and \( T_1 \) excited states have to be taken into account. For many systems, the \( S_1 \) and \( T_1 \) states were actually found to react quite differently, i.e., they may be regarded as distinct chemical species. Then, the efficiency of the various possible singlet–triplet ISC processes \( S \simarrow T \) (especially \( S_1 \simarrow T_n \) and \( S_1 \simarrow T_1 \)) will be of utmost importance to trigger the photochemistry towards a specific (desired) product distribution.

As a vivid example of this general scenario (parent) psoralen (Fig. 1) may be considered as will be outlined now. Throughout, the term psoralens serves as a short-hand notation for parent psoralen and its derivatives. These compounds are utilized as drugs for the photo- (chemo-) therapy of various skin disorders.\(^1\)–\(^4\) In psoralen plus UV-A (PUVA) therapy, which is very effective against psoriasis and vitiligo, the psoralen application is accompanied by subsequent exposure of the affected skin areas to radiation from the UV-A interval (320–400 nm). However, undesired side effects such as erythema, in the long run premature skin aging, and in the extreme case even skin cancer may occur.\(^4\)–\(^5\)

\[\text{Fig. 1 Structure of 7H-furo[3,2-g][1]benzopyran-7-one (psoralen).} \]

\[\text{Left: Numbering frequently used in the older literature. Right: Numbering according to IUPAC conventions.}\]