SUB-PICOSECOND INTERSYSTEM CROSSING AND VIBRATIONAL COOLING IN THE TRIPLET MANIFOLD OF 1-NITRONAPHTHALENE

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The electronic energy relaxation of 1-nitronaphthalene (1NN) was studied in different solvents using broadband transient absorption spectroscopy with femtosecond time resolution. UV excitation of 1NN populates an unrelaxed $S_1(\pi\pi^*)$ state, which decays by conformational relaxation (primarily twisting of the NO_2 group) with a time constant of 100 fs. The twisting of the NO_2 group and formation of a structurally relaxed singlet state opens up a doorway for ultrafast intersystem crossing (ISC) to a high-energy receiver triplet state $T_n(n\pi^*)$, which then undergoes internal conversion to form a vibrationally excited $T_1(\pi\pi^*)$ state. Quantum chemical calculations that include solvent effects support the experimental observations. Our results show that an essentially barrierless path connects the initial S_1 state to the receiver T_n state, which enables the observation of vibrational energy transfer and its dependence on the surrounding solvent. According to this kinetic model, which was first proposed by Crespo-Hernández et al. for 1-nitropyrene[1], the $S_1(\pi\pi)$ electronic energy decays rapidly and irreversibly to dark triplet states, explaining why small nitro-polycyclic aromatic compounds are typically considered to be nonfluorescent.

Reference

[1] C. E. Crespo-Hernández, G. Burdzinski, R. Arce, *J. Phys. Chem. A.*, **2008**, 112,6313