ULTRAFAST SINGLET-TRIPLET POPULATION DYNAMICS IN NITRO-AROMATIC COMPOUNDS

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The electronic energy relaxation of 2-nitronaphthalene (2NN), 1-nitronaphthalene (1NN) and 2-methyl-1-nitronaphthalene (2M1NN) were studied in various solvents using broadband transient absorption spectroscopy with femtosecond time resolution. As was previously shown for 1NN[a], excitation of the nitronaphthalene compounds at 340 nm populates the $S_1(\pi\pi^*)$ state, which is proposed to bifurcate into two almost barrierless nonradiative decay channels. The first channel connects the S_1 state with a receiver T_n state that has strong $n\pi^*$ character. Intersystem crossing is followed by internal conversion to the lowest triplet state, which is populated with excess vibrational energy. The ensuing vibrational cooling dynamics in the triplet manifold depends on both the solvent and the nitronaphthalene compound studied. The second minor channel involves conformational relaxation of the S_1 state to populate a dissociative singlet state that has significant charge-transfer character and negligible oscillator strength. It is proposed that the relative yield of the two initial nonradiative decay channels depends on the nitronaphthalene compound studied and correlates with their steady-state photochemistry. Quantum chemical calculations including solvent effects substantiate the assignment of the experimental observations.

[a] C. Reichardt, R. A. Vogt, C. E. Crespo-Hernández, *J. Chem. Phys.* **2009** 131: 224518