Combined Picosecond Time-Resolved and NMR techniques used as a useful tool for investigation of excited state processes.

The case of excited state intramolecular charge separation and T-T energy transfer.

J. Dobkowski, M. Pietrzak, M. Kijak, M. Vengris, J. Waluk

1 Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland, e-mail: jdobkowski@ichf.edu.pl
2 Vilnius University, Sauliutekio 10, LT10223 Vilnius, Lithuania

Excited state reaction, such as proton/electron transfer can generate significant changes in the molecular geometry. The excited states characterized by significant or full transfer of electron from a donor to an acceptor group can be categorized applying the minimum/maximum overlap rule. This rule postulates that the overlap between the donor and acceptor molecular orbitals involved in the electron transfer should reach the maximum or minimum value [1]. The subject of this presentation deals with significant geometry transformation of the molecular skeleton, which leads to the donor and acceptor decoupling (Twisted Intramolecular Charge Transfer, TICT state [2]).

For monitoring temporal sequences of the elementary events femto/pico time-resolved techniques are commonly used. However, these techniques cannot determine the geometry transformation which occurs on the excited state energy degradation path. The NMR spectroscopy is commonly used to determine the ground state geometry of molecules. The UV-induced time-resolved NMR techniques enable observing the transient perturbation of the ground state population produced by the excited state relaxation processes. This provides a possibility to deduce the excited state geometry transformation [3].

The registration of the NMR spectra of an excited triplet state may seem to be a hopeless case; nevertheless, we gave it a try. Two factors are critical for a successful realization of such experiment: lifetimes of the triplet state and the efficiency of the intersystem crossing transition.

The $^3\pi\pi^*$ triplet states are short-lived, and therefore only molecules that have the lowest state of $^3\pi\pi^*$ type can be considered as the objects giving the chance for a successful realization of the NMR experiment. Let us concentrate our attention on the naphthalene molecule. The triplet state of naphthalene can be produced without intermediacy of its singlet by triplet-triplet energy transfer, either inter- or intramolecular. In the case of intermolecular energy transfer the concentration of the donor and acceptor should be high, even $10^{-7}$ M, which limits the penetration length of the exciting pulses inside the volume of the sample and generates serious experimental difficulties. That is the reason why the intramolecular mechanism of the generation of the naphthalene triplet state was selected. The objects of our studies were spirol[9,10-dihydro-9-oxoanthracene-10,2'-5,6'-benzindan] and spirol[9,10-dihydro-9-oxoanthracene-10,2'(3'H) phenalene] [4]. The results show that for T-T energy transfer mutual arrangement of the planes of the donor and acceptor groups plays the crucial role.

Keywords: NMR, TICT state

References