INTRAMOLECULAR CHARGE TRANSFER DYNAMICS OF 4-(DIMETHYLAMINO)BENZONITRILE: ULTRAFAST BRANCHING FOLLOWED BY A TWO-FOLD DECAY MECHANISM

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4-(Dimethylamino)benzonitrile (DMABN) is a paradigm molecule system that exhibits dual fluorescence and intramolecular charge transfer (ICT) in polar solvents. Although numbers of different experimental and theoretical methods have been carried out to date for elucidating the basic mechanism of its energy relaxation, there are still some crucial problems that remain unanswered.

The time-resolved transient absorption and time-resolved fluorescence upconversion will be presented, as combined with *ab initio* CASPT2//CASSCF calculations, which indicate that a more complex mechanism may be suggested in the ICT reaction in a polar environment. A scheme of ultrafast branching relaxation followed by two-fold decay is proposed in which, whereas the fully twisted ICT (TICT) state is responsible for the transient absorption, a distinct partially twisted ICT (pTICT) structure is for the fluorescent ICT state, both displaying clearly different decay rates.