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W. Sudholt, A.L. Sobolewski, A. Staib, W. Domcke

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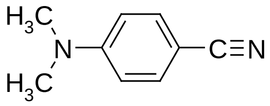
WIBKE SUDHOLT[a], ANDRZEJ L. SOBOLEWSKI[b], ARNULF STAIB[a], WOLFGANG DOMCKE[c]

[a]*Institute of Theoretical Chemistry, Heinrich-Heine-University, D-40225 Düsseldorf, Germany*
[b]*Institute of Physics, Polish Academy of Sciences, PL-02-668 Warsaw, Poland*
[c]*Institute of Physical and Theoretical Chemistry, Technical University of Munich, D-85747 Garching, Germany*



DMABN

4-(N,N-Dimethylamino)benzonitrile (DMABN) is the prototype of a group of organic donor-acceptor compounds that can undergo intramolecular charge transfer (ICT) in the excited singlet state. In polar solvents, it exhibits dual fluorescence: Apart from “normal” emission out of the locally-excited (LE) state, which is also present in the gas phase and in nonpolar solvents, in polar solvents a second, “anomalous”, strongly red-shifted band is observed in the spectrum, attributed to a charge-transfer (CT) state [1]. This phenomenon has been mostly explained by the twisted ICT (TICT) mechanism [2], which claims that the electron transfer is induced by a rotation of the amino group around its bond to the benzene moiety. According to the wagged ICT (WICT) model [3], another possible source of charge separation is the pyramidalization of the amino nitrogen. Recently, a new concept for understanding the dual fluorescence, called rehybridized ICT (RICT) [4], which involves bending and stretching of the nitrile group, was proposed.

In the poster, we will present single-point calculations of CASPT2 potential-energy profiles and CASSCF dipole moments at CIS optimized geometries of isolated DMABN along the TICT, WICT and RICT reaction paths in the lowest excited singlet states [5]. All results appear to be strongly dependent on the amount of electron correlation included. Already in the Franck-Condon region a moderately polar L_b and a strongly polar L_a state are found with the L_b state lying below the L_a state. Twisting is the sole reaction coordinate that leads to an intersection of the two states and appropriate dipole-moment changes. Wagging causes only minor changes of the potential-energy profiles and dipole moments. Along the rehybridization reaction path, another CT state is strongly stabilized, but does not become the global singlet excited-state minimum.

Solvent effects along the TICT reaction path were examined by combining the CASPT2 potential energies and CASSCF atomic charges with molecular dynamics (MD) simulations in the solvents cyclopentane and acetonitrile [6]. Adiabatic potential-energy profiles and vertical energy gaps were evaluated using equilibrium MD simulations. Solvent effects in cyclopentane turn out to be negligible. In acetonitrile, the L_a state is shifted below the L_b state and develops a potential-energy minimum at the fully-twisted geometry. Fluorescence at this geometry is strongly red-shifted, mainly due to the increase of the ground-state energy upon twisting. The calculated vertical excitation energies are in good agreement with experiment, whereas the Stoke’s shift in acetonitrile is underestimated by about 0.4 eV. The solvation dynamics in acetonitrile directly after absorption was investigated by nonequilibrium MD simulations. The solvent response is very rapid and consists of two parts, the major of which is completed within about 0.2 ps.

The present calculations support the TICT mechanism for the occurence of dual fluorescence in DMABN in polar solvents.

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