

Charge Transfer and Excitation Energy of TICT Molecules upon Solvation

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INTRODUCTION

Twisted Intramolecular Charge Transfer (TICT) effects are commonplace in molecules bearing an electron donor and acceptor pair connected by a single bond.¹ Their fluorescence spectra have two bands: a localized excited state and intermolecular charge transfer (CT). Upon torsion these bands may shift in energy. Moreover, absorption/emission spectra of TICT molecules depend on solvent polarity and relaxation. TICT molecules have been used as benchmark for several quantum chemistry methods and solvent descriptions.² The most studied TICT molecule, the 4-N,N-dimethylaminobenzonitrile (DMABN), was studied in this work. A DMABN derivative with an increased donor chain that shows a large dependence of solvent polarity,³ *trans*-ethyl *p*-(dimethylamino) cinnamate (EDAC), was also investigated. Absorption spectrum of both molecules were investigated using a continuum model. Excitation energies, dipole moments and charge transfer values as function of the dihedral angle were computed.

METHODS

The ground state geometry was optimized using MP2. For the excited states the ab initio wave function algebraic diagrammatic construction method to second order, ADC(2), was used in combination with the SV(P) Gaussian basis set. Solvent effects were included using the conductor-like screening continuum solvation model COSMO in two versions: in the excited states are optimized. The first three excited states were investigated. ADC(2) method known to describe accurately CT effects and does not have the inherent problems that DFT in describing such effects. Three different solvents with distinct polarities were considered, namely, benzene, DMSO and water.

RESULTS AND DISCUSSION

For planar DMABN, the computed S₁ and S₂ gas phase transition energies are respectively 4.51 eV and 4.77 eV in good agreement with

experiment (4.25 eV and 4.65 eV¹). After vertical excitation, the molecule twists. In gas phase and upon solvation in benzene, the S₁ and S₂ excited states intersect at an angle of about 30°. For the polar solvents water and DMSO, this intersection disappears. This effect is reversed in EDAC molecule. The use of COSMO model that optimizes the excited state mainly affects the twisted structures.

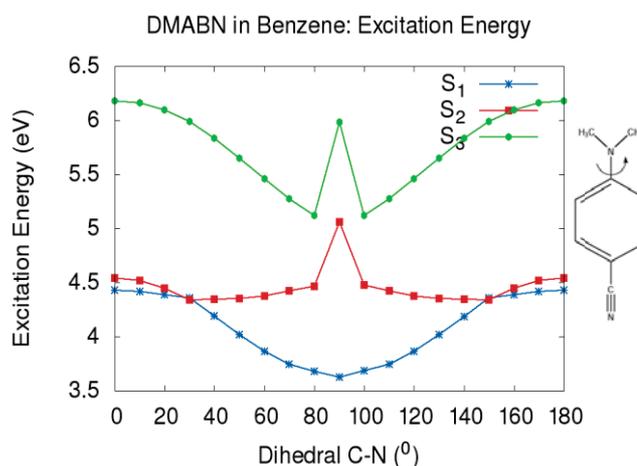


Figure 1. Torsion potential curves of DMABN first three excited states solvated in benzene.

CONCLUSIONS

Gas-phase vertical transitions are well described by the ab initio ADC(2) method. The change of intersection position depends on the solvent polarity as expected. Emission calculations of both molecules are underway and will be presented at SBQT.

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