

Relaxation of Optically Excited States of p-Nitroaniline

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INTRODUCTION

The photophysics of para-nitroaniline (PNA) has been extensively studied by experimental techniques¹. The most intense absorption band of PNA was composed by a HOMO-LUMO charge-transfer transition. Two strong bands were observed in gas-phase, the first 4.24 eV and the second absorption band at 5.66 eV². The intramolecular charge-transfer makes this transition very susceptible to the solvent polarity. In water, the maximum was located at 3.25 eV, a shift of about 1.0 eV. Another characteristic feature is the absence of fluorescence; instead, a very fast nonradiative process is proposed, on which the lowest-lying triplet state is populated, via an intersystem crossing, and phosphorescence emission³ is observed. In this work, we examine the photoinduced processes of PNA in the gas phase and in water by theoretical calculations.

METHODS

Ground and excited states (singlets and triplets) potential energy surfaces were computed as function of the -NO₂ torsional coordinate. The DFT method, with the B3LYP functional, and 6-31G(d,p) basis sets were employed to calculate the ground state geometries. The non-equilibrium vertical excitation energies in gas phase and water were computed at the TD-B3LYP/NE-IRFPCM/6-31++G(d,p) level of theory.

RESULTS AND DISCUSSION

Figure 1 displays the potential energy surfaces computed as function of the torsional angle in water solvent. It suggests that the vertical excitation leads to the first excited state H-L (S1), which evolves barrierless to an ISC with the T2 state, in a region characterized by a nuclear configuration with the -NO₂ at 90°. From that, the T1 state is populated via a crossing between the

T2 and T1 state, giving rise to the observed phosphorescence.

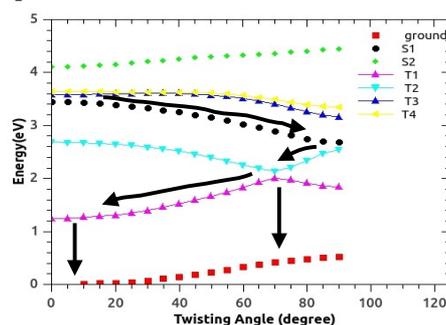


Figure 1. Potential energy surfaces for the ground and excited states: singlets (S1, S2) and triplets (T1, T2, T3 and T4) in water.

CONCLUSIONS

The photophysical events of PNA in water have been investigated by using the DFT/PCM method. The contributions of the hydrogen bonding on the electronic structures of PNA have also been studied. The solvation stabilizes the charge-transfer excited state, which becomes the S1 state. With these results, we propose a photophysical mechanism to explain the phosphorescence observed experimentally.

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