

Stepwise Solvation of the Intramolecular-Charge-Transfer Molecule *p*-(Dimethylamino)benzonitrile

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This paper presents a systematic study of gas-phase *p*-(*N,N*-dimethylamino)benzonitrile (DMABN) both in a supersonic jet expansion and in a thermalized vapor. From the jet studies, the excited- and ground-state vibrational spectra of the isolated molecule are resolved, and the spectroscopy of the stoichiometric complex with water, methanol, ammonia, and acetonitrile in the beam is reported. It is concluded that 1:1 complexes are not sufficient for the local perturbation to cause charge separation. At higher temperatures in the jet, we observe emission that we attribute to DMABN self-complexes. Under high pressure and temperature vapor conditions (>30 mTorr, 60 °C), red-shifted fluorescence from DMABN is observed. This is attributed to the charge-transfer state of DMABN in self-complexes.

Introduction

Many recent investigations have focused on the role of the solvent in the charge-transfer process for molecules in solution.¹⁻²⁰ Both intramolecular⁸⁻¹⁴ and intermolecular¹⁵⁻¹⁷ charge separations have been studied. The solute-solvent interactions can be passive, as observed in the cage effect where the primary role of the solvent is to trap the solute particles within a volume enabling them to collide and react with each other.¹⁸⁻²⁰ The solute can also be actively coupled to the medium, as in the case of charge-transfer reactions where the energies of initial, intermediate, and final states, the reaction pathways leading to different products, and the kinetics of the transitions can be dramatically affected by the solvent. Static^{1,3,10} and dynamic^{4,6,14} polarity effects, as well as local solute-solvent interactions²¹ such as hydrogen bonding are important in these latter processes.

An example of a molecule that interacts strongly with polar solvents is *p*-(dimethylamino)benzonitrile (DMABN). In polar solvents, an excited DMABN molecule undergoes a rotation of the dimethylamino group about the amino-phenyl bond to achieve a perpendicular geometry with respect to the plane of the benzene ring.²² This motion results in charge separation, as evidenced by the measured increase in the excited-state dipole moment from 6 to 16 D.²³ In polar solvents, the twisted, charge-separated form is stabilized, and a dual fluorescence appears. It consists of a UV component plus a new red-shifted emission that does not appear in nonpolar solvents. Rapid equilibration between the twisted and planar forms in polar media yields the dual fluorescence. This twisted internal-charge-transfer model (TICT), was first proposed by Grabowski and co-workers.²² Picosecond spectroscopic studies^{11,24} have confirmed that (i) the planar state is the precursor of the twisted state and (ii) equilibrium between the two states is established during the excited-state lifetime. Further, the dominant solvent effect on the dynamics of the charge separation in this case has recently been attributed to static polarity effects.¹⁰ The proposal of a barrier whose height changes with the polarity of the medium gives a simple explanation for the appearance of dual fluorescence in polar solvents and a single UV fluorescence in alkanes: a certain polarity is required before the TICT barrier is low enough to allow the forward TICT process to proceed within the lifetime of the initially excited state.

The recent work by Robinson et al.²⁵ and others²⁶ attempts to deduce the number of water molecules that must be present in order to induce effects such as the one described above for DMABN. The idea is that a critical number of solvent molecules

exists for a given charge-transfer or proton-transfer process. It is conceivable in the case of DMABN that a 1:1 DMABN/solvent complex could provide sufficient stabilization by charge-transfer or dipolar interactions to permit the photoisomerization of DMABN to its twisted charge-transfer state.²⁷⁻³⁰

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