INFLUENCE OF SOLVATION ON 1-AMINONAPHTHALENE PHOTOPHYSICS: ULTRAFAST RELAXATION IN THE ISOLATED MOLECULE, MOLECULAR CLUSTER AND SOLUTION

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The electronic spectroscopy and photophysics of naphthalene (NPH) and its mono-substituted derivatives is highly influenced by the nonadiabatic coupling between its two lowest electronic excited states, S_1 (L_b) and S_2 (L_a) and with the ground state. Trying to understand better the nature of these couplings and the influence of solvation on it, the relaxation dynamics of 1-aminonaphthalene (AMN) isolated in a supersonic expansion and forming molecular clusters of the form AMN(H₂O)n=1-3, was tracked following excitation to the S_1 and S_2 excited states in the range (30000-37500 cm⁻¹), at the ultrafast time scale. The experiments were carried out in a time of flight mass spectrometer, using a well known pump-probe ionization scheme (1+n') that involves the probe of the molecule by single or multiphoton ionization. While in the case of NPH the $L_a(S_2)$ state relaxes to the lower $L_b(S_1)$ at ultrafast rate (τ =30 fs) through a conical intersection placed nearby the L_a surface minimum, for AMN, no dynamical signature of the surface crossing is found. However, two additional relaxation channels, internal conversion to the ground state and intersystem crossing, have been observed for the L_a state. The solvation by water molecules induces dramatic changes in the relaxation of the AMN molecule. The inclusion of a single water molecule deactivates the IC channel to the ground state, while for the clusters containing two or three water molecules, ultrafast IC between the L_a to L_b and excited states is observable in the transients. The photophysical behavior observed in the molecular clusters, will be also compared with experiments in solution, where the relaxation dynamics is resolved by fluorescence up-conversion. The role of individual solvent-solute interactions will be discussed.