REACTIONS IN AROMATIC CLUSTER CATIONS INVESTIGATED BY IR/UV DOUBLE RESONANCE SPECTROSCOPY

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Structures and reactions of isolated cations can be investigated in molecular beam experiments by applying different IR/UV double resonance techniques (IR/Photo Induced Rydberg Ionization, IR-photodissociation). In combination with ab initio calculations the structures are derived from the frequencies of the OH, NH, and CH stretching vibrations. The chosen mass, isomer, and state selective spectroscopical methods can be applied to cluster cations of aromatic molecules with water. In the case of the isolated 4-aminophenol$(H_2O)_1$ cation a rearrangement reaction of the water molecule is observed as a function of the excess energy within the ion. In contrast to the 4-aminophenol$(H_2O)_1$ cation no rearrangement reaction is observed in the 3-aminphenol$(H_2O)_1$ cation. The different behavior of the two clusters is explained on the basis of CASSCF and DFT calculations along different reaction pathways. Furthermore it is shown that the anharmonic OH and NH stretching frequencies of hydrogen-bonded OH and NH_2 groups can be predicted by CASSCF/CASPT2 calculations along the proton transfer coordinates.