

REACTIVE PATHWAYS IN THE CHLOROBENZENE-AMMONIA DIMER CATION RADICAL: NEW INSIGHTS FROM EXPERIMENT AND THEORY

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Previously, we have studied non-covalent interactions in mono-halogenated benzene clusters using mass selected resonant 2-photon ionization methods. We have extended our studies by investigating the interaction between these mono-halobenzenes with a prototypical N atom donor (NH_3). Thus, we have obtained electronic spectra of $\text{PhX} \cdots (\text{NH}_3)_n$ ($X=\text{F}$, Cl , Br and $n=1,2, \dots$) complexes in the region of the PhX monomer S_0 - S_1 ($\pi\pi^*$) transition. Here we are mainly focusing on $\text{PhCl} \cdots \text{NH}_3$ dimer. We found that upon ionization of the dimer, three reactive pathways of the $[\text{PhCl} \cdots \text{NH}_3]^{+\cdot}$ have been evidenced. The primary pathway is the Cl atom elimination, previously evidenced. The second and third pathways, HCl elimination and H atom elimination are identified for the first time in the R2PI studies of the dimer. Electronic spectra obtained for the three pathways shows that they originate from a common precursor. The reactive pathways in this system were extensively characterized computationally. We used DFT and post-Hartree Fock electronic structure calculations, Frank-Condon analysis to support our experimental findings. The results were consistent with previous direct ab initio molecular dynamics calculations, we found two nearly iso-energetic Wheland intermediates which lie significantly lower in energy than the initially formed dimer cation radical $[\text{PhCl} \cdots \text{NH}_3]^{+\cdot}$.