Abstract:

Noncovalent interactions such as hydrogen bonding dictate the physical properties of molecular systems from nanoscale self-assembled architectures to biological building blocks. They are prevalent in nature and contribute to important processes such as molecular recognition and self-assembly. Nitrogen containing heterocyclic molecules mimic the interactions found in nature and involving commercial chemical products. Within hydrogen bonded networks the delocalization of charge and the introduction of excess charge dramatically affect the chemical activity of nitrogen containing heterocycles. The accurate description of noncovalent interactions involving such species is accomplished by the analysis of experimental Raman vibrational spectra using results from electronic structure calculations on discrete hydrogen-bonded molecular complexes. In the case of pyrimidine, partial charge transfer from nitrogen to extended hydrogen bonded networks results in blue shifting of normal modes. The accommodation of an excess electron is described by the comparison of gas phase spectra of cluster anions to results from electronic structure calculations on discrete hydrogen-bonded molecular cluster anions. Although pyrimidine molecular anions are shown theoretically and experimentally to be unstable, the addition of just one hydrogen bonded water molecule stabilizes the negative ion.