

MATRIX ISOLATION IR SPECTROSCOPY AND QUANTUM CHEMISTRY STUDY OF 1:1 H-HYDROGEN BONDED COMPLEXES OF BENZENE WITH A SERIES OF FLUOROPHENOLS

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O-H stretching infrared fundamentals (ν_{OH}) of phenol and a series of fluorophenol monomers and their 1:1 complexes with benzene have been measured under a matrix isolation condition (8K). For the phenol-benzene complex the measured shift of ν_{OH} is 78 cm^{-1} and for 3, 4, 5-trifluorophenol it is 98 cm^{-1} . Although the cold matrix isolation environment is very different from an aqueous medium, the measured spectral shifts display an interesting linear correlation with the aqueous phase acid dissociation constants (pK_a) of the phenols. The spectral shifts predicted by quantum chemistry calculations at several levels of theory are consistent with the observed values. Correlations of the shifts are also found with respect to energetic, geometric and several other electronic structure parameters of the complexes. Partitioning of binding energies of the complexes into components following the Morokuma-Kitaura scheme shows that dispersion is the predominant component of attractive interaction, and electrostatics, polarization and charge-transfer terms also have contributions to overall binding stability. NBO analysis reveals that hyperconjugative charge-transfers from the filled π -orbitals of the hydrogen bond acceptor (benzene) to the anti-bonding $\sigma^*(\text{O-H})$ orbital of the donors (phenols) display correlations which are fully consistent with the observed variations of spectral shifts. The analysis also shows that the O-H bond dipole moments of all the phenolic species are nearly the same, implying that local electrostatics has only a little effect at the site of hydrogen bonding.