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Matrix isolation infrared spectroscopy and structures of weak (O-H... π) and strongly bound (O-H...O) binary hydrogen bonded complexes

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Matrix isolation infrared spectroscopic studies of two binary O-H... π hydrogen bonded complexes of formic acid (FA) and phenol (Ph) with benzene (Bz), and a series of binary O-H...O hydrogen bonded fluoro-phenol-water complexes will be reported. In the first category, complexation results in red shifts of O-H stretching fundamentals (ν_{OH}) of Ph and FA by ~ 78 and ~ 120 cm^{-1} , respectively, and the latter is the largest shift known so far for a binary complex of an O-H donor with π -orbitals of Bz as acceptor. We propose to use these observed red-shifts as benchmarks to test the accuracy of electronic structure methods in predicting geometries of the two complexes. We have noted that popularly used electronic structure theory methods with larger sized basis sets do not always predict structures that are consistent with the observed ν_{OH} shifts. This holds especially for the complex of Bz with FA, which will be discussed in detail. In the case of binary fluoro-phenol-water complexes, we have observed systematic ν_{OH} red-shifts of the fluoro-phenol-donors, which increase by $\sim 90\%$ from phenol to pentafluorophenol. Surprisingly, the magnitudes of the spectral shifts of the binary complexes display excellent linear correlation with the aqueous phase pK_a values of the fluorophenols. Furthermore, the shifts display poor correlation with the total binding energies of the complexes, as signatures of deviation from the well-known Badger-Bauer rules. On the other hand, it has been shown that the spectral shifts relate nicely with the local quantum-chemical charge transfer (CT) interactions at the site of hydrogen bonding. We infer that this local interaction is the primary determining factor for spectral red-shifts of the donor in such binary complexes, and the same also holds for O-H... π hydrogen bonded dimers.

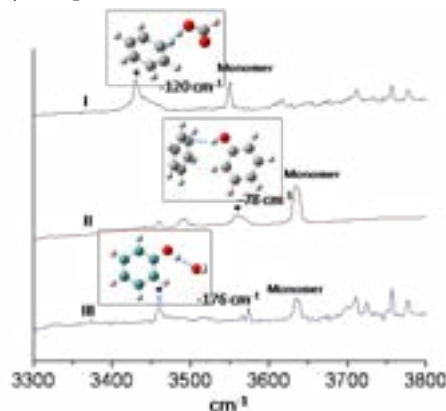


Figure 1: Matrix isolation IR spectra depicting ν_{OH} red-shifts of the donor in the binary complexes of (I) Formic acid-benzene (II) Phenol-benzene and (III) Phenol-water. The asterisks denote the bands corresponding to the binary hydrogen bonded complexes.

Biography

Pujarini Banerjee has expertise in the technique of matrix isolation spectroscopy, and her research interests include the infrared spectroscopic probing of binary hydrogen bonded complexes. She completed her Doctoral degree from University of Calcutta, and is currently working as a Post-doctoral Researcher under the supervision of Prof. Tapas Chakraborty in the Department of Physical Chemistry, Indian Association for the Cultivation of Science, Kolkata, India.

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