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## Joint ITC and DFT Study of the Affinity of Some Lewis Bases to HFIP in Solution

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HFIP, i.e. 1,1,1,3,3,3-hexafluoropropan-2-ol, was found to be an exceptional medium,[1] either as solvent or co-solvent, that allows many reactions to occur.[2-5] However, the exact role and mode of action of HFIP in various chemical transformations still remains elusive. Despite many reports dealing with water/HFIP complexes, little has been published on other molecular complexes of HFIP as well as on thermochemistry of the formation of such complexes.[6]

Within this study the affinity of a series of eight different Lewis bases (3 sulfoxides, 3 Nsp<sup>2</sup> pyridine derivatives, 1 aromatic amine, 1 cyclic aliphatic ether) to HFIP (as Lewis acid) is investigated experimentally by Isothermal Titration Calorimetry (ITC) and theoretically using static DFT-D calculations.

Measured ITC association enthalpy values  $\Delta H_{aITC}$  spanned -9.3 kcal/mol - -14 kcal/mol. Computations including a PCM implicit solvation model produced similar exothermicity of association of all studied systems -  $\Delta H_a$  values ranging -8.5 - -12.7 kcal/mol. In general, most of interaction energy is due to the hydrogen bonding and not due to formation of significantly strong halogen bonds. An additional set of calculations combining implicit and explicit solvation by chlorobenzene of the reactants, pointed out the relatively low interference of the solvent with the HFIP-base complexation, which main effect is to slightly enhance the Gibbs energy of the HFIP-Lewis base association. It is speculated that the interactions of bulk HFIP with Lewis bases therefore may significantly intervene in catalytic processes not only via the dynamic microstructuration of the medium but also more explicitly by affecting bonds' polarization at the Lewis bases.

### References

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