

Gas-Phase Vibrational Spectroscopy of Fluoride – Hexafluoroisopropanol Complexes: Solvation-Suppressed Proton Transfer and Isotopic Effects

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The selectivity and yield of fluorination reactions depend on a solvent's ability to moderate the fluorinating reagents' properties, typically by hydrogen bonding. Recently reported fluorination strategies are particularly efficient when 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) is the reaction solvent.¹ HFIP, an increasingly popular organic solvent, is known for its exceptional hydrogen-bond (HB) donor ability² and HB network formation. However, understanding HFIP's solvation properties and the formed HB network is far from trivial. Valuable insights can be gained by studying isolated, microsolvated ions in the gas phase, which can be treated by sophisticated computational models.

In these studies, we examine the effects of HFIP aggregation on the HB formed in the complexes $F^-(HFIP)_{1-3}$ and $F^-(H_2O/HDO/D_2O)$. To characterize the first, the complexes are compared to $Cl^-(HFIP)_{1,2}$. For $F^-(HFIP)$, a strong ionic hydrogen bond with an equally-shared proton motif is observed, which results from a nearly symmetric, single-well potential. The second and third HFIP molecule also directly bind to the fluoride anion, leading to a weakening of the symmetry-equivalent ionic HBs. More detailed information on the nature of the hydrogen bond interaction in these systems is obtained from an energy decomposition analysis.³

The strong hydrogen bond interaction between HFIP and the fluoride anion also influences how HOD binds to F^- in mixed-solvent complexes. Fluoride is known to be the only halide anion to bind to the proton rather than to the deuteron in $[X^-, HDO]$ complexes. However, in the $F^-(HFIP)(HOD)$ complex, the $(HFIP \cdots F^- \cdots DOH)$ motif is identified.

[1] N. Shida *et al.*, *J. Org. Chem.* **86**, 16128 (2021).

[2] M. Barp *et al.*, *Chem. Sci.* **16**, 5174 (2025).

[3] M. Barp *et al.*, *J. Phys. Chem. Lett.*, accepted.

Keywords

Strong Hydrogen Bond, Gas Phase, Infrared Photodissociation Spectroscopy, Isotopic Effects

This abstract is submitted for....

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