EXPLORING THE DETAILS OF INTERMOLECULAR INTERACTIONS VIA A SYSTEMATIC CHARACTERIZATION OF THE STRUCTURES OF THE BIMOLECULAR HETERODIMERS FORMED BETWEEN PROTIC ACIDS AND HALOETHYLENES

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In the early 2000's, the work of Cole and Legon,[a,b] combined with that done earlier by Kisiel, Fowler, and Legon,[c] demonstrated that comparisons among the complexes of HF, HCl, and HCCH each with vinyl fluoride could provide information concerning the strength of intermolecular interactions. Specifically, that the length of the hydrogen bond and its deviation from linearity as a result of a secondary interaction with the nucleophilic portion of the protic acid could be correlated with the hydrogen bond strength. Building on this foundation, we undertook a systematic characterization of the molecular structures of complexes formed between these three acids and the remaining polar fluoroethylenes, seeking to unravel the nature of their intermolecular interactions. What started out as a simple confirmation of chemical intuition regarding relative interaction strengths developed into a fuller appreciation of the competition between electrostatic and steric forces in determining the lowest energy configuration for the heterodimer.

Additional surprises were in store for us as we expanded the study to chlorofluoroethylenes. Although the first few examples again served to confirm earlier conclusions, subsequent complexes provided unexpected results that signaled an increasing importance of the dispersion interaction in determining the geometry of the complex as well as the fundamental differences in the electron distributions surrounding the halogens in a C–F versus C–Cl bond.

Our work with these species has not only allowed us to investigate fundamental questions regarding intermolecular interactions, but obtaining and analyzing the spectra of these complexes along with those of the various haloethylene monomers and their complexes with the argon atom have provided an introduction to molecular spectroscopy and structure determination for many undergraduate students.

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[a] G.C. Cole and A.C. Legon, *Chem. Phys. Lett.* 369, 31-40 (2003).

[b] G.C. Cole and A.C. Legon, *Chem. Phys. Lett.* 400, 414-424 (2004).

[c] Z. Kisiel, P.W. Fowler, and A.C. Legon, *J. Chem. Phys.* 93, 3054-3062 (1990).