

THE EFFECT OF PROTIC ACID IDENTITY ON THE STRUCTURES OF COMPLEXES WITH VINYL CHLORIDE:
FOURIER TRANSFORM MICROWAVE SPECTROSCOPY AND MOLECULAR STRUCTURE OF THE VINYL
CHLORIDE-HYDROGEN CHLORIDE COMPLEX

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In all previous examples of complexes formed between protic acids and haloethylenes, we have observed similar modes of binding regardless of the specific identity of the acid, HF, HCl, or HCCH. Although details of the structures, such as hydrogen bond length and amount of deviation from linearity, do reflect the strength of the interaction and show clear correlations with the gas-phase acidity, the complexes of a given haloethylene with any of the acids have identical structural motifs. Vinyl chloride, on the other hand, has been observed to adopt different modes of binding in its interactions with HF and HCCH. The HF complex, reported two years ago, has a geometry with HF interacting across the double bond of vinyl chloride and forming a secondary interaction with the hydrogen *cis* to the chlorine atom, but in the complex with acetylene, reported last year, HCCH locates at one end of the vinyl chloride with the secondary interaction occurring with the geminal hydrogen atom. This variety continues and is expanded in the vinyl chloride-HCl complex. *Ab initio* theory predicts a complex that has the HCl molecule interacting across the double bond, but located out of the vinyl chloride plane. The microwave spectrum of the most abundant isotopologue of this complex is consistent with theoretical predictions and additionally shows the presence of large amplitude motion connecting two equivalent structures.