

HALOGEN BONDS AND HYDROGEN BONDS IN THE GAS PHASE: SIMILARITY REVEALED THROUGH ROTATIONAL SPECTROSCOPY.

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Many hydrogen-bonded species $B \cdots HX$, where B is a simple Lewis base and X is halogen atom, were extensively investigated by rotational spectroscopy in the 1980/90's to yield various properties of the isolated complexes. Systematic variation of B, and then X, allowed generalisations concerned with the hydrogen bond to be identified. More recent examinations of several series of complexes $B \cdots XY$, where XY is either a homo- or hetero-dihalogen molecule, have revealed striking parallelisms between the properties of the $B \cdots XY$ and those of their hydrogen-bonded counterparts $B \cdots HX$, thereby suggesting that the generalisations made for the hydrogen-bonded series also apply to $B \cdots XY$. Accordingly, the weak intermolecular bond in $B \cdots XY$ has been called a halogen bond. Here, attention will focus mainly on angular geometry for selected pairs $B \cdots HCl$ and $B \cdots ClF$. It will be shown that $B \cdots HCl$ and $B \cdots ClF$ are essentially isomorphous for a given B, but with the hydrogen bond exhibiting a greater propensity to be non-linear. To test the effect that weakening the hydrogen bond has on its deviation from linearity, reference will be made to some complexes $B \cdots HCCH$ in which ethyne is the H-atom donor.