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Hydrogen Bonding in Polyfluoride Ions

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Synopsis. Hydrogen bonding in the polyfluoride ions ($H_nF_{n+1}^-$, n=1 to 4) has been discussed in the light of atomic charges, bond ionicities, valencies and bond indices calculated from CNDO/2 wave functions. The hydrogen-bond energy in these ions is found to bear a qualitative relation with the bond index of the hydrogen bond.

The polyfluoride ions, in $H_nF_{n+1}^-$, wther n=1 to 4 have been experimentally characterized[1] as strong hydrogen-bonded systems. They are formed by the interaction of F^- with HF molecules. The experimentally determined structures of the polyfluorides show that the HF molecules are all hydrogen bonded to the central fluoride ion. Clark et al.[2] carried out ab initio SCF calculations and determined the electronic structure and hydrogen-bond energy of these systems. They found that HF_2^- possesses a symmetric linear structure, $H_2F_3^-$ a C_{2v} structure, $H_3F_4^-$ a D_{3h} structure and $H_4F_5^-$ a tetrahedral structure. All these ions contain adjacent strong hydrogen bonds and the average hydrogen-bond energy decreases with increasing n. We have in the present note discussed the hydrogen bonding in the polyfluoride ions in the light of atomic charges, bond ionicities, valencies and bond indices. All these quantities were obtained using CNDO/2 wave function.[3]

Method of Calculation. The experimental geometry being not available for all the species, calculations were performed at their ab initio SCF geometry.[2] Valencies (V_A) and bond indices (B_{AB}) where calculated using the following expressions: [4]

$$V_A = 2P_{AA} - \sum_{\lambda}^{A}\sum_{\sigma}^{A}(P_{\lambda\sigma})^2,$$

$$B_{AB} = \sum_{\lambda}^{A}\sum_{\sigma}^{B}(P_{\lambda\sigma})^2,$$

where, P_{AA} is the charge density on atom A and $P_{\lambda\sigma}$ is an element of the density matrix defined over the atomic orbitals. The percentage of ionic character or the ionicity of the bond A-B was calculated from the relation,

$$\%\ \text{Ionic character} = \frac{n_A - n_B}{n_A + n_B} \times 100,$$

where, n_A and n_B are the populations of atom A and B respectively. In order to calculate the atomic populations associated with a given bond, energy localized molecular orbitals (LMO) were obtained for each molecule using the criterion of Edmiston and Ruedenberg.[5]

Results and Discussion

All the LMO's were obtained with a high degree of localization. The nature of the LMO's indicates that the electronic structure of the polyfluoride ions can be described in a classical manner with an adequate numbers of HF bonds and lone pairs on the fluorine atoms. The hydrogen atom was found to be fractionally bonded in all the molecules.

Table 1. Bond Ionicities of the HF Bonds in Polyfluorides

Molecule	Bond	Population		% Ionic character
	X Y	X	Y	
HF	F-H	1.23	0.77	23.00
HF_2^-	F-H	1.63	0.35	63.78
$H_2F_3^-$	F-H	1.46	0.53	46.73
	F···H	1.82	0.14	85.71
$H_3F_4^-$	F-H	1.38	0.62	38.24
	F···H	1.90	0.08	91.92
$H_4F_5^-$	F-H	1.35	0.65	35.06
	F···H	1.93	0.06	93.46

Table 2. Atomic Charges, Valencies, and Bond Indices of Polyfluorides

Molecule	Atom	Atomic charge	Valency	Bond	Bond index
HF	F	−0.23	0.95	F-H	0.95
	H	+0.23	0.95		
HF_2^-	F	−0.65	0.58	F-H	0.46
	H	+0.30	0.92		
$H_2F_3^-$	F^t	−0.48	0.77	F^t-H	0.68
	H	+0.31	0.90	F^c···H	0.22
	F^c	−0.66	0.61		
$H_3F_4^-$	F^t	−0.40	0.84	F^t-H	0.78
	H	+0.30	0.91	F^c···H	0.13
	F^c	−0.70	0.56		
$H_4F_5^-$	F^t	−0.36	0.87	F^t-H	0.82
	H	0.29	0.91	F^c···H	0.09
	F^c	−0.72	0.55		

The percentage of ionic character of the HF bonds is given in Table 1. Of the four hydrogen-bonded species the HF_2^- ion is unique in the sense that it contains two equivalent bonds each of which can be described either by a normal H–F bond as in the HF molecule or by a dotted bond H···F as it is used to describe a hydrogen bond. The other species contain both types of bonds. The HF bond in HF_2^- is found to be more ionic compared to that in the isolated HF molecule, which indicates that the hydrogen-bond formation is accompanied by the weakening of the HF bond. In the other species the ionic character of the F–H bonds decreases and that of the F···H bonds increases as n increases. This implies that the strength of the hydrogen bond in polyfluorides should decrease with increasing n. Ab initio calculations of Clark et al.[2] support this prediction.

Atomic charges, valencies and bond indices of the polyfluoride ions are given in Table 2. The atomic charge of the central fluorine increases as we go from HF_2^- to $H_4F_5^-$, which indicates that the magnitude of charge transferred from F^- (central fluorine) to HF molecules decreases with increasing n. Since charge transfer plays a very important role in the formation of the hydrogen bond, one may conclude that the strength of the hydrogen bond progressively decreases with the increasing number of HF molecules interacting with F^- ion to form polyfluorides.

Compared to that in the isolated HF molecule, the hydrogen valency decreases slightly upon hydrogen-bond formation. In HF_2^-, the status of the two H–F bonds and consequently that of the two fluorine atoms are identical. The valency of the terminal F atom increases and that of the central fluorine atom decreases with the increasing size of the polyfluoride ion.

The bond index of the F···H bonds gradually decreases and that of the F–H bond increases with increasing n. Since the bond index represents half the number of electrons engaged in covalent bonding, the above trend in bond index indicates that the strength of the hydrogen bond decreases gradually as we pass from HF_2^- to $H_4F_5^-$. Thus we find that the hydrogen-bond energy in the polyfluorides bears a qualitative relation with the bond index of the F···H bond. This can be understood from the fact that the diatomic contribution to the total CNDO/2 energy contains the term $-B_{AB}\gamma_{AB}/2$ which represents the exchange repulsion contribution to the binding energy. In order to verify whether the qualitative relation between bond index and hydrogen-bond energy holds good for other systems, we calculated the hydrogen-bond indices of the dimers and mixed dimers of NH_3, H_2O, and HF. The results are as follows: $(NH_3)_2$ (0.0026), $(H_2O)_2$ (0.0073), NH_3–H_2O (0.0106), $(HF)_2$ (0.0142), H_2O–HF (0.0199), and NH_3–HF (0.0302), where the figures in the parentheses indicate bond index. The experimental hydrogen-bond energy[6] in the above dimers follows the same order. It may be noted that the hydrogen-bond indices in these dimers are considerably less than those in the polyfluorides. It is consistent with the fact that the above dimers are weak hydrogen-bonded systems, while the polyfluorides are very strong hydrogen-bonded systems.

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