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The nature of the interaction of molecular fluorine and Lewis bases B from a comparison of the properties of $B\cdots F_2$ and $B\cdots HF$

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Comparison of angular geometries, radial geometries and intermolecular stretching force constants k_σ of the two series of complexes $B\cdots F_2$ and $B\cdots HF$, where B is H_2S, HCN, CH_3CN, H_2O, $(CH_2)_2O$ or NH_3, allows conclusions about the nature of the interaction in $B\cdots F_2$ and the shape of the F atom in F_2.

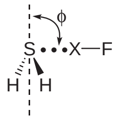
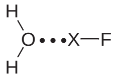
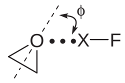
The reactivity of elemental fluorine is legendary. It results from the ease with which the F–F bond is broken, coupled with the great strength of the bonds E–F (E = H,C or N) that are formed. Hence, the reactions of F_2 with many simple compounds are highly exothermic. Once sufficient concentrations of F atoms have been produced, presumably initially at surfaces and then through the temperature rise as the reaction begins, self-acceleration sets in through chain processes. Explosions can then result. But what of the interactions of the difluorine molecule F_2 itself with other molecules B when the possibility of reactions proceeding through fluorine atoms is precluded?

We have recently demonstrated that, by using a simple device, the complexes $B\cdots F_2$ formed by simple Lewis bases B with F_2 may be isolated and characterised before any chemical reaction can occur.[1–6] The device is called a fast-mixing nozzle.[7] It consists of a pair of concentric, coterminal tubes of circular cross section that issue into the evacuated Fabry–Pérot cavity of a Fourier-transform microwave spectrometer.[8] The inner tube is a glass capillary of 0.3 mm internal diameter but the outer is constructed from Teflon. A dilute mixture of F_2 in argon is pulsed *via* a solenoid valve down the outer tube while the pure Lewis base B is flowed continuously into the vacuum chamber through the glass capillary. The coaxial gas flows undergo adiabatic expansion as they emerge from the tubes and so molecules of B and F_2 meet only when F_2 is moving away from surfaces at rate of *ca.* 5×10^4 cm s^{-1}, which is the terminal speed of the gas pulse for argon as carrier gas.[8] Complexes $B\cdots F_2$ so formed are rapidly cooled to their lowest rotational and vibrational energy states and achieve collisionless expansion in *ca.* 10 μs. Thereafter, the complexes are effectively frozen and no chemical reaction is possible. The $B\cdots F_2$ can then be characterised through their rotational spectrum in the relatively long period before the gas encounters a vessel wall, *etc.*

Analysis of the rotational spectrum of $B\cdots F_2$ leads to details of the radial and angular geometry and to the strength of the interaction, as discussed elsewhere for complexes $B\cdots HX$.[9] Sufficient $B\cdots F_2$ have now been characterised to allow general conclusions about the nature of the interaction of F_2 with simple Lewis bases B. Table 1 summarises the radial and angular geometries of the six complexes $B\cdots F_2$[1–6] and the six analogous hydrogen-bonded complexes $B\cdots HF$,[10–16] where B is H_2S, HCN, CH_3CN, H_2O, $(CH_2)_2O$ or NH_3. Also included in Table 1 are the intermolecular stretching force constants k_σ. These are available from the centrifugal distortion constants D_J or Δ_J for weakly bound complexes in the quadratic approximation with the assumption of rigid, unperturbed subunits B and F_2 by using expressions developed by Millen[17] and provides one measure of the strength of the B–F_2 interaction.

Several general points emerge from Table 1. First, the angular geometries of the pair $B\cdots F_2$/$B\cdots HF$ are isomorphous for a given B. The detailed similarity within the pair for $H_2O\cdots XF$ (X = F or H), for $H_2S\cdots XF$ and for $(CH_2)_2O\cdots XF$, in each of which the geometry is not dictated by the symmetry of B, is remarkable. Although both $H_2O\cdots F_2$ and $H_2O\cdots HF$ are

Table 1 Comparison of properties of complexes $B\cdots F_2$ and $B\cdots HF$

	Angular geometry		$r(Z\cdots F)$/Å			k_σ/N m^{-1}	
B	Type	Details (ϕ/°)	$B\cdots F_2$	$B\cdots HF$	$\sigma(Z)+\sigma(F)$[a]/Å	$B\cdots F_2$	$B\cdots HF$
H_2S		X = F $\phi = 113(5)$[b] X = H $\phi = 91$[c]	3.20(1)[b]	3.249[c]	3.20	2.36(4)[b]	12(2)[d]
HCN	$HCN\cdots X–F$	$C_{\infty v}$(X = F and H)[e,f]	2.803(3)[e]	2.805(1)[f]	2.85	2.61(1)[e]	18.26(5)[f]
CH_3CN	$CH_3CN\cdots X–F$	C_{3v}(X = F and H)[g,h]	2.748(3)[g]	2.751(1)[h]	2.85	1.49(1)[g]	19.83(5)[h]
H_2O		Effectively planar, C_{2v}(X = F and H)[i,j]	2.719(4)[i]	2.684(16)[k]	2.75	3.63(7)[i]	25(2)[l]
$(CH_2)_2O$		X = F $\phi = 76(4)$[m] X = H $\phi = 72.0(2)$[n]	2.63(6)[m]	2.629(5)[n]	2.75	—[o]	—[o]
NH_3	$H_3N\cdots XF$	C_{3v}(X = F and H)[p,q]	2.708(7)[p]	2.71[q]	2.85	4.70(3)[p]	32.8[q]

[a] Sum of van der Waals radii from ref. 26; σ(N) = 1.50 Å, σ(O) = 1.40 Å, σ(S) = 1.85 Å σ(F) = 1.35 Å. [b] Ref. 5. [c] Ref. 10. [d] Ref. 11. [e] Ref. 3. [f] Ref. 12. [g] Ref. 2. [h] Ref. 13. [i] Ref. 4. [j] Ref. 14 and 18; [k] Refitted to rotational constants of $H_2{}^{16}O\cdots HF$, $H_2{}^{18}O\cdots HF$, $D_2{}^{16}O\cdots DF$ from ref. 14. [l] Calculated from Δ_J of ref. 15 by method of ref. 17. [m] Ref. 6. [n] Ref. 16. [o] Expressions in ref. 17 are not appropriate to calculation of k_σ from Δ_J for molecules of this geometry. [p] Ref. 1. [q] Calculated from B_0 or D_J values communicated to the author by B. J. Howard and P. R. R. Langridge-Smith (unpublished).

recorded as effectively planar, $H_2O\cdots HF$ has been shown[18] to have a small potential energy barrier (126 cm^{-1}) to the planar C_{2v} conformation that separates the two equivalent equilibrium geometries of C_s symmetry having a pyramidal configuration at O. The top of the barrier lies only slightly above the zero-point energy level and the vibrational wavefunctions have C_{2v} symmetry. In view of the much weaker bond in $H_2O\cdots F_2$, it is likely that the barrier in this species is even lower. This interpretation is reinforced by the fact that a low-lying vibrational satellite attributed to internal rotation of the H_2S subunit is observed in $H_2S\cdots F_2$ but not in $H_2S\cdots HF$, which is rigidly pyramidal.

Secondly, we note from Table 1 that the k_σ for the $B\cdots F_2$ are smaller than those of the $B\cdots HF$ by a factor of 6 to 8. Indeed, the $B\cdots F_2$ are so weak that their k_σ values are closer to those of $B\cdots Ar$ complexes. For example, k_σ = 3.6(4) N m^{-1} and 2.18 N m^{-1} for oxirane$\cdots F_2$[6] and oxirane$\cdots$Ar,[19] respectively.

Thirdly, the distance $r(Z\cdots F)$ from the acceptor atom Z in B to the nearest F atom is almost identical within a given pair $B\cdots F_2$/$B\cdots HF$.

What explanation can be offered for these observations? The behaviour of the $B\cdots HF$ complexes was interpreted[20,21] on the basis of a simple electrostatic interaction of B and HF, *i.e.* between unperturbed electric charge distributions. The angular geometries of $B\cdots HF$ were first rationalised[20] on the basis of the simple rule which states that in the equilibrium geometry the axis of the HF molecule coincides with the axis of a non-bonding electron pair on the acceptor atom Z in forming a hydrogen bond with B. This rule was subsequently given a quantitative basis by a simple electrostatic model.[22] The variations of the k_σ in $B\cdots HF$ complexes has also been interpreted in terms of an electrostatic interaction.[23]

The results in Table 1 suggest a similar approach for $B\cdots F_2$. In that case, the fact that the leading term in the Taylor series expansion of the electric charge distribution of F_2, namely its electric quadrupole moment Q = 2.76 × 10^{-40} C m^2, is very small[24] while HF has an electric dipole moment[25] μ = 1.8265 D (6.0925 × 10^{-30} C m) ensures that the interaction $B\cdots{}^{\delta+}F^{\delta-}_{\delta-}F^{\delta+}$ will be much weaker than in $B\cdots{}^{\delta+}H{-}F^{\delta-}$. This is borne out by the k_σ values of Table 1. Moreover, the nearly spherical F_2 electric charge distribution explains why the magnitudes of k_σ for $B\cdots F_2$ are like those of $B\cdots Ar$. Presumably, the London dispersion interaction is more significant for $B\cdots F_2$ than for $B\cdots HF$, for which the preponderant contribution is electrostatic. In some ways F_2 behaves like its united atom Ar in complexes with B.

Evidently, the electrostatic part of the energy of interaction in $B\cdots F_2$ is still definitive of the angular geometry and hence the latter is of the same form for a given pair $B\cdots F_2$/$B\cdots HF$. Nevertheless, the weaker electrostatic term in the $B\cdots F_2$ is consistent with a lower barrier to internal rotation of the H_2S subunit in $H_2S\cdots F_2$ than in $H_2S\cdots HF$.

Given that the $B\cdots F_2$ interaction is weak, it seems likely that the distance $r(Z\cdots F)$ will be determined by the sum of the van der Waals radii $\sigma(Z)$ and $\sigma(F)$ of the atoms Z and F. Values of $\sigma(Z) + \sigma(F)$ generated from Pauling's radii[26] are given in Table 1. If a range of 0.05 Å is assigned to the Pauling radii, the $r(Z\cdots F)$ for both $B\cdots F_2$ and $B\cdots HF$ are identical with the sum $\sigma(Z) + \sigma(F)$, since the mean difference $\Delta r = \{\sigma(Z) + \sigma(F)\} - r(Z\cdots F)$ is only 0.07(6) for the $B\cdots F_2$ and 0.09(4) for the $B\cdots HF$. It was suggested earlier[22] that the distance $r(Z\cdots F)$ in hydrogen-bonded complexes can be taken as the sum of the van der Waals radii of Z and F, in view of the lack of a repulsive electron shell for the nearly bare proton $^{\delta+}H$ in HF. This is illustrated graphically in Fig. 1, in which the netted spheres of appropriate van der Waals radius drawn on the O and F atoms in the scale diagrams of $H_2O\cdots F_2$ and $H_2O\cdots HF$ just touch in each case.

The fact that Δr is effectively zero for $B\cdots F_2$ suggests that F_2 may not be 'snub-nosed' in the sense that Cl_2 is, *i.e.* that the van der Waals radius along the axis is not shorter than the value perpendicular to it. For several $B\cdots Cl_2$, the mean value of Δr is found to be *ca.* 0.5 Å. *Ab initio* calculations of the type[27] used to establish the anisotropy of the van der Waals radius of Cl_2 would settle this.

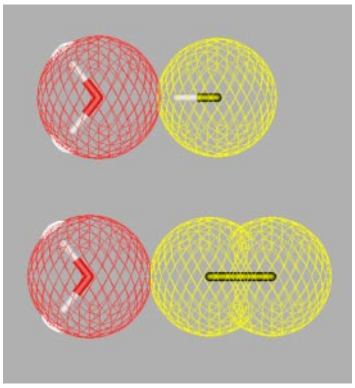


Fig. 1 Stick models of $H_2O\cdots HF$ (upper) and $H_2O\cdots F_2$ (lower) drawn to scale, with the experimental intermolecular separations $r(Z\cdots F)$ given in Table 1. The nets are spheres having the appropriate van der Waals radii (red for oxygen, yellow for fluorine, white for hydrogen). The sphere for the H of HF is not drawn, for the reason discussed in the text. For convenience, both molecules are depicted as planar. Note that the van der Waals spheres of oxygen and the inner fluorine atom just touch in each case.

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