Predictions of Structures and Stabilities for Cl_2F_2, Cl_3F, and Cl_4

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Extensive *ab initio* calculations have predicted structures and energies for the T-shaped molecules Cl_2F_2, Cl_3F, and Cl_4; each is thermodynamically stable to atomisation, but not to dissociation into the appropriate mixture of ClF and Cl_2.

Although ClF_3 has been well known for many years, there are only fragmentary reports of any derivatives. Photolysis of a mixture of Cl_2 and F_2 in an inert matrix produces new i.r. bands, one of which has been assigned to Cl_2F_2.[1,2] Interaction of Cl_2 and IrF_6 leads to an unstable volatile substance, of stoicheiometry Cl_3F.[3] To help characterise these systems, I have performed an extensive series of *ab initio* calculations, and report stable local minima in the potential energy surfaces of Cl_2F_2 (2 isomers), Cl_3F (2 isomers), and Cl_4.

Geometries were optimised by gradient techniques, using the programs Gaussian 80[4] and Gaussian 82,[5] and a medium-sized 'double-zeta plus polarisation' basis A; (10,6,1)/[6,3,1]

Table 1. Calculated energies for F_2, ClF, Cl_2, ClF_3, Cl_2F_2, Cl_3F, and Cl_4.

			Atomisation[b]			Dissociation[b,c]		
	SCF[a]	ΔMP2[a]	SCF	MP2	Expt.[d]	SCF	MP2	Expt.[d]
F_2	−198.7326	−0.3198	−164	143	155			
ClF	−558.8470	−0.2811	24	243	253			
Cl_2	−918.9047	−0.2697	63	197	239			
ClF_3	−757.5854	−0.6382	−124	500	523	15	113	113
Cl_2F_2 (A)[e]	−1117.6269	−0.6154	−128	416		−176	−71	
(B)	−1117.6073	−0.6187	−180	373		−228	−114	
Cl_3F (A)[e]	−1477.6516	−0.5977	−176	300		−263	−140	
(B)	−1477.6379	−0.5959	−212	260		−299	−180	
Cl_4	−1837.6871	−0.5724	−196	193		−321	−200	

[a] In a.u.; 1 a.u. ~2.6256×10^3 kJ mol^{-1}. [b] In kJ mol^{-1}. [c] To appropriate mixture of F_2, ClF, Cl_2. [d] From refs. 7, 15, corrected for zero-point vibrational effects. [e] Isomers A and B identified in Figure 1.

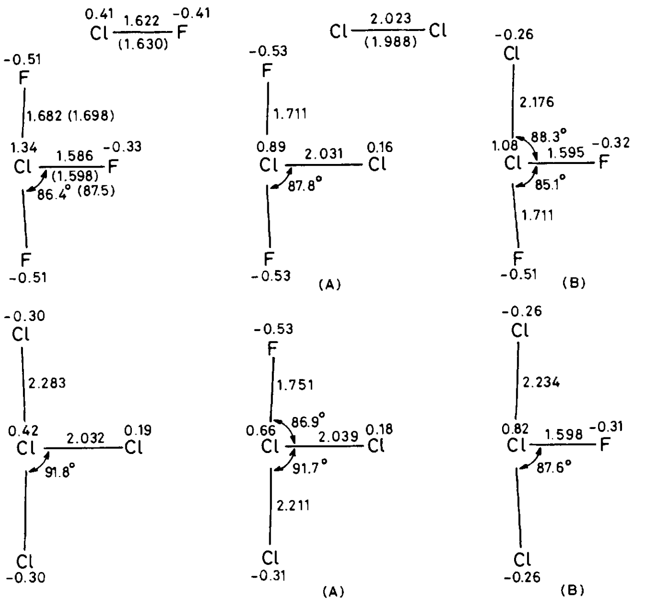

Figure 1. Scaled drawings of calculated structures for ClF, Cl_2, ClF_3, Cl_2F_2, FCl_3, and Cl_4. Bond lengths in Å, angles in degrees, converged to 0.001 Å or 0.1°. Experimental structural information in parentheses, where available. Net atomic charges, in units of e, shown by atoms.

on Cl, (8,4,1)/[4,2,1] on F.[6] To demonstrate the level of reliability in structural predictions achievable with this basis for interhalogens, I also report calculated geometries for ClF, Cl_2, and ClF_3 in Figure 1. All five structural parameters are within 1.7% of their experimental value,[7,8] with an average discrepancy of only 1.0%.

Predicted geometries of Cl_2F_2, Cl_3F, and Cl_4 are displayed in Figure 1. Each was identified as a true local minimum, by the eigenvalue criterion of the analytically calculated second-derivative matrix. (However, the analogous species F_4 was shown not to have a similar local minimum.) All structures are planar, and can be described as trigonal-bipyramids, with two equatorial lone pairs. Isomerism is possible for Cl_2F_2 and Cl_3F; isomers A have axial fluorines only, and isomers B have an equatorial fluorine. Consistent structural trends are apparent in this series of chlorine fluorides, as in phosphoranes which are valence-shell isoelectronic.[9] As the number of fluorine atoms decreases, bonds lengthen at an increasing rate, with axial bonds more severely affected. Angles involving bonds to fluorine are smaller than to chlorine, consistent with valence shell electron pair repulsion (VSEPR) principles,[10] though the prediction of angles greater than 90° in Cl_3F (isomer A) and Cl_4 is a little surprising.

Final SCF calculations were performed using a fairly large basis B; (11,7,2)/[6,4,2] on Cl, (9,5,1)/[5,3,1] on F.[6] Since the Hartree–Fock method gives a poor account of the energies of interhalogens,[11—13] the influence of electron correlation was estimated using second-order Møller–Plesset perturbation theory,[14] at the SCF geometries, and basis B, but with only a single roughly optimised polarisation function on Cl, and a double-zeta s,p contraction for F. Core orbitals and their virtual counterparts were frozen. Although this procedure is less than exact, more rigorous treatments were not feasible for the largest systems studied, and I thought it important to use a uniform level of theory throughout. In Table 1, I report absolute and relative energies for the various species, and compare with experimental data where possible.[7,15] Binding energies calculated at the MP2 level are of useful accuracy in all cases where experimental results are available. Although this accuracy may be partly fortuitous,[12,13] one expects errors such as superposition to be comparable in a series of closely related molecules, so one may reasonably suppose that comparable accuracy will be achieved throughout.

Fluorine preferentially occupies axial sites in Cl_2F_2 and Cl_3F, as is generally found in trigonal-bipyramidal molecules.[9,16] Each of Cl_2F_2, Cl_3F, and Cl_4 is found to be stable towards atomisation, but the results show that all three compounds are likely to be thermodynamically *unstable* with respect to the appropriate mixture of ClF and Cl_2; the least unstable species, isomer A of Cl_2F_2, is predicted to lie 71 kJ mol^{-1} higher than 2ClF. It is most unlikely that the errors in the calculated dissociation energies are as large as 70 kJ mol^{-1}. However, kinetic stability for any or all of these species is not excluded, because I have not investigated whether the energy wells are deep enough to support at least one vibrational level.

The electronic structure of ClF_3 has been discussed in detail,[12,17] and the derivatives Cl_2F_2, Cl_3F, and Cl_4 are qualitatively similar. Although the central chlorine atom may appear in a similar environment in each compound, stability towards atomisation decreases steadily as the number of fluorine substituents decreases. This trend may be understood by considering the net atomic charges,[18] displayed in Figure 1. Since terminal F atoms bear a greater negative charge than terminal Cl, the central chlorine becomes progressively less positive in the series $ClF_3 \rightarrow Cl_4$. Simultaneously, its d orbital population decreases from 0.39 e in ClF_3, through 0.36 e in

Cl_2F_2, 0.31 e in Cl_3F, to only 0.23 e in Cl_4.The quantitative importance of d orbitals in ClF_3 has already been established.[12,17] We now see that decreasing thermodynamic stability in the series $ClF_3 \rightarrow Cl_4$ is associated with, and perhaps caused by, decreasing d orbital involvement of the central chlorine, as are the trends in bond lengths already mentioned.

Experimental characterisation of Cl_2F_2[1,2] and Cl_3F[3] rests on i.r. absorptions at 636[1,2] and 625 cm^{-1},[3] which presumably are Cl–F stretching modes. Unfortunately there is no direct relationship between bond lengths and stretching frequencies in polyatomic molecules. It is therefore premature to enquire how these observed frequencies compare with properties predicted for Cl_2F_2 and Cl_3F.

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