(11) C. F. Bender and H. F. Schaefer, *J. Am. Chem. Soc.*, **92**, 4984 (1970).
(12) G. M. Schwenzer, S. V. O'Neil, H. F. Schaefer, C. P. Baskin, and C. F. Bender, *J. Chem. Phys.*, **60**, 2787 (1974).
(13) S. V. O'Neil, H. F. Schaefer, and C. F. Bender, *J. Chem. Phys.*, **55**, 162 (1971).
(14) C. F. Bender and E. R. Davidson, *J. Phys. Chem.*, **70**, 2675 (1966).
(15) B. Rosen, "Spectroscopic Data Relative to Diatomic Molecules", Pergamon Press, Oxford, 1970.
(16) D. R. Stull and H. Prophet, JANAF Thermochemical Tables, 2nd ed, National Bureau of Standards, Washington, D.C., 1971.
(17) (a) C. F. Bender, H. F. Schaefer, D. R. Franceschetti, and L. C. Allen, *J. Am. Chem. Soc.*, **94**, 6888 (1972); (b) P. J. Hay, W. J. Hunt, and W. A. Goddard, *Chem. Phys. Lett.*, **13**, 30 (1972); (c) J. F. Harrison, *Acc. Chem. Res.*, **7**, 378 (1974); (d) V. Staemmler, *Theor. Chim. Acta*, **35**, 309 (1974); (e) for an experimentally based discussion of the singlet-triplet separation, see H. M. Frey and G. J. Kennedy, *J. Chem. Soc., Chem. Commun.*, 233 (1975).
(18) C. F. Bender, P. K. Pearson, S. V. O'Neil, and H. F. Schaefer, *J. Chem. Phys.*, **56**, 4626 (1972).
(19) S. V. O'Neil, P. K. Pearson, H. F. Schaefer, and C. F. Bender, *J. Chem. Phys.*, **58**, 1126 (1973).
(20) S. V. O'Neil, H. F. Schaefer, and C. F. Bender, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 104 (1974).
(21) C. W. Bauschlicher, H. F. Schaefer, and C. F. Bender, research in progress.
(22) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).
(23) H. F. Schaefer, *Chem. Br.*, **11**, 227 (1975).
(24) C. W. Bauschlicher, unpublished work.

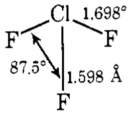
Molecular Structure of the ClF_2 and ClF_4 Radicals. A Theoretical Study[1]

Steven R. Ungemach and Henry F. Schaefer III*

Contribution from the Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720. *Received July 2, 1975*

Abstract: ClF_2 and ClF_4 are two interesting inorganic radicals whose quantitative molecular structures have not been determined experimentally. A priori electronic structure theory has been used in the present research to predict the structures of these radicals and their positive and negative ions. Self-consistent-field theory has been employed in conjunction with both minimum and double ζ basis sets. For ClF_2 more extended basis sets were used in addition. The ClF_2^+ ion has a bent (bond angle 97.4°) structure quite similar to that of the isoelectronic SF_2 molecule, while ClF_2^- is linear. ClF_2 is predicted C_{2v} with bond length 1.72 Å and bond angle near 148°. Both minimum and double ζ basis sets predict ClF_4^+ to be square pyramidal, in contrast with the known stucture of the isoelectronic SF_4 molecule. Finally, both ClF_4 and ClF_4^- are predicted to be planar. However, these structural predictions are qualitatively altered when chlorine 3d functions are added to the basis set. Electronic structures are discussed in terms of orbital energies and Mulliken populations.

For some time now the interhalogen compounds have been known to have a rich and interesting chemistry.[2,3] However, for the most part, this chemistry has been limited to molecules with closed-shell ground states, hence an even number of electrons. For example, consider the chlorine fluorides ClF_n, which are the subject of the present research. Of these, the even-electron molecules ClF, ClF_3, and ClF_5 are long-lived at room temperature and have at least reasonably well-defined physical properties.[3] Moreover, the structures of all three are known. ClF has a bond distance of 1.628 Å and a dipole moment of 0.88 A (Cl^+F^-).[4,5] ClF_3 has a dipole moment of 0.56 D[6] and is a planar T-shaped molecule[7]



(1)

Although less precisely determined, the shape of ClF_5 is thought to be a square pyramid,[8] with apical and basal Cl-F bond distances of 1.62 and 1.72 Å.

In contrast, relatively little is known about interhalogens with an odd number of electrons. In fact, in their recent review Downs and Adams[3] indicate, except for two or three reported observations, "interhalogen radicals are the subject more of speculation than of first-hand evidence". Of specific interest here are the ClF_2 and ClF_4 radicals. ClF_2 was first prepared by Mamantov and coworkers,[9] who have assigned the vibrational frequencies[10] $\nu_1 = 536$ cm^{-1} (symmetric stretch), $\nu_2 = 242$ cm^{-1} (bending), and $\nu_3 \sim 575$ cm^{-1} (asymmetric stretch). Based on their assignments Mamantov et al. determined the ClF_2 bond angle to be 136 ± 15° or 144 ± 15°, depending on whether they used computer-simulated or observed frequencies. In any case, their final result of 140 ± 19° implies a measurably bent triatomic molecule. This result is of particular interest since it contrasts with Nelson and Pimentel's conclusion,[11] also based on matrix isolation spectroscopy, that the related Cl_3 radical is linear. It should also be noted that ClF_2 has been hypothesized as an intermediate in a number of chemical reactions, and a value of the heat of formation, -19 ± 2 kcal/mol, has been determined.[12]

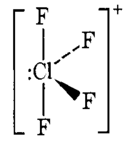
Our initial interest in ClF_2 and ClF_4 was due to the proposal of Krogh and Pimentel[13] that the $H_2 + ClF_3$ system might yield a chain-branching chemical laser. Their proposal[13] led to an interesting exchange between Suchard[14] and Pimentel,[15] and in turn to molecular beam[16] and flow system[17] studies of the $H + ClF_3 \rightarrow HF + ClF_2$ reaction. While the flow experiments give no evidence of product HF at mean collision energies of 1-2 kcal/mol, the beam experiments (carried out at ~10 kcal/mol collision energy) do yield HF as an observable product.

Quite recently, Morton and Preston have detected ClF_4 as a product in the fluorination of Cl_2 or HCl by hypofluorite photolysis.[18] Based on the observed ESR spectrum, Morton and Preston concluded that ClF_4 is a planar molecule belonging to the point group D_{4h} and having a $^2A_{1g}$ ground electronic state. Semiempirical theoretical studies of ClF_4 have been reported by Gregory.[19] Using several variants of the CNDO and INDO schemes, Gregory in each case predicts ClF_4 to be planar or slightly nonplanar with a very small (1-4 cm^{-1}) inversion barrier.

There have been a number of experimental studies of the positive and negative ions of ClF_2 and ClF_4. Both the ClF_2^+ and ClF_2^- ions have been observed experimentally by Christe and co-workers.[20,21] Based on the infrared and

Raman spectra of $ClF_2^+ AsF_6^-$, the ClF_2^+ bond angle was limited to a range of 90–120°. Following qualitative Walsh-type arguments[22] the ClF_2^+ bond angle is predicted to be very close to that of SF_2[23] (98.3°), and this does appear to be the case. The same arguments predict ClF_2^- to have a structure similar to ArF_2, which if made would presumably be linear and symmetric like KrF_2.[24] This qualitative prediction of a $D_{\infty h}$ structure for ClF_2^- is consistent with Christe and Guertin's observation[21] of only a single infrared stretching vibration.

Both the vibrational[25] and ^{19}F NMR[26] spectra of ClF_4^+ have been taken and both are consistent with a structure similar to that of the isoelectronic SF_4 molecule


(2)

For the purpose of determining force constants, Christe and Sawodny[25] have hypothesized the following ClF_4^+ structure: $r(Cl\text{–}F_{eq}) = 1.59$ Å, $r(Cl\text{–}F_{ax}) = 1.66$ Å, $\theta(F_{eq}\text{–}Cl\text{–}F_{eq}) = 97°$. The same research group[27] has studied the anion ClF_4^- and concluded that it has a square-planar structure.

The primary goal of the present theoretical research was to make a priori predictions of the structures of ClF_2^+, ClF_2, ClF_2^-, ClF_4^+, ClF_4, and ClF_4^-. Although structures for all six of these species have been proposed, none has been precisely determined. In addition, we are interested in the electronic structure per se, and for this reason report orbital energies and Mulliken populations.

Previous ab initio calculations on the closed-shell species ClF_2^+, ClF_2^-, ClF_4^+, and ClF_4^- have been reported by Guest, Hall, and Hillier.[28] They employed a minimum basis augmented by a set of d functions on the central Cl atoms. Such a basis has the disadvantage[29] of being unbalanced; that is Cl d functions are far less important (as we shall show for ClF_2) than additional s and p functions on Cl and F. Assuming fixed Cl–F distances of 1.66 Å, Guest et al. predicted the bond angles of the above four ions.

Details of the Calculations

All work reported here was carried out at the self-consistent-field (SCF) level of theory. For the most part, two basis sets were used. The first was a minimum basis set (MBS), i.e., 1s, 2s, $2p_x$, $2p_y$, $2p_z$, 3s, $3p_x$, $3p_y$, $3p_z$ Slater functions on chlorine and 1s, 2s, $2p_x$, $2p_y$, $2p_z$ functions on fluorine. Standard four-Gaussian least squares fits[30] to each Slater function were used. This simple basis set is usually adequate for geometry predictions, although there are some notable exceptions.[31,32] A more reliable basis set is the double ζ (DZ) basis, essentially twice as large as the MBS. We have used Dunning's contracted Gaussian DZ basis sets for Cl[33] and F[34] in the present work. In general, geometry predictions made at this level of theory are quite accurate.[32]

The computations were carried out on the Datacraft 6024/4 minicomputer using the Cal Tech–Ohio State–Berkeley version of POLYATOM[35] and the program GAUSSIAN 70.[36] Representative times for ClF_4^- were 35 min using the MBS and 92 min using the DZ basis set. The latter time does not include the 38 min required to generate the list of nonzero unique integrals; however, this step is required only once, with all additional calculations using the same list.

On the basis of the single-configuration SCF results obtained here both ClF_2 and ClF_4 are predicted to be unbound relative to their separated atom limits. For example, with the largest basis set employed, ClF_2 is predicted to lie 1.91 eV above Cl + F + F. Although this may appear a discouraging result, it is in fact characteristic of the Hartree–Fock approximation to fail to predict binding in systems (such as the interhalogens) where the dissociation energies are small. An accurate prediction of the dissociation energies of ClF_2 and ClF_4 would require the use of configuration interaction (CI) or some other technique to describe electron correlation, the instantaneous repulsions between pairs of electrons. Although such CI methods have been applied[38] to molecules as large as KrF_2 and XeF_2, they are beyond the scope of the present research.

Triatomic Structures

In analogy[37] with OF_2 and SF_2, the expected ground state electron configuration for ClF_2^+ is

$$1a_1^2\,2a_1^2\,1b_2^2\,3a_1^2\,4a_1^2\,2b_2^2\,1b_1^2\,5a_1^2\,3b_2^2\,6a_1^2\,2b_1^2\,7a_1^2\,4b_2^2\,1a_2^2\,5b_2^2\,8a_1^2\,3b_1^2 \tag{3}$$

Similarly, in analogy with ArF_2, the linear ClF_2^- ion should have as its lowest electron configuration

$$1\sigma_g^2\,2\sigma_g^2\,1\sigma_u^2\,3\sigma_g^2\,2\sigma_u^2\,1\pi_u^4\,4\sigma_g^2\,5\sigma_g^2\,3\sigma_u^2\,4\sigma_u^2\,2\pi_u^4\,1\pi_g^4\,3\pi_u^4\,6\sigma_g^2 \tag{4}$$

To allow a direct comparison with the ClF_2^+ orbital occupancy, this $D_{\infty h}$ result may be resolved into point group C_{2v}:

$$1a_1^2\,2a_1^2\,1b_2^2\,3a_1^2\,2b_2^2\,4a_1^2\,1b_1^2\,5a_1^2\,6a_1^2\,3b_2^2\,4b_2^2\,7a_1^2\,2b_1^2\,1a_2^2\,5b_2^2\,8a_1^2\,3b_1^2\,9a_1^2 \tag{5}$$

Hence, the logical ground state electron configuration for neutral ClF_2, assuming a bent structure, is

$$\ldots 5a_1^2\,3b_2^2\,6a_1^2\,2b_1^2\,7a_1^2\,4b_2^2\,1a_2^2\,5b_2^2\,8a_1^2\,3b_1^2\,9a_1 \quad {}^2A_1 \tag{6}$$

Assuming a linear structure, this orbital occupancy becomes

$$\ldots 5\sigma_g^2\,3\sigma_u^2\,4\sigma_u^2\,2\pi_u^4\,1\pi_g^4\,3\pi_u^4\,6\sigma_g \quad {}^2\Sigma_g^+ \tag{7}$$

Since there are no AB_2 molecules with 21 valence electrons whose geometry has been precisely determined, one cannot readily use Walsh's rules to predict whether ClF_2 is bent or linear. Recall that 20 valence-electron molecules are generally bent (~100° bond angle), while 22 valence-electron molecules are linear.

Although electron configurations 6 and 7 are the logical first choice for the ground state of ClF_2, the $3b_1$ and $9a_1$ (or, for the linear configuration, $3\pi_u$ and $6\sigma_g$) orbitals might be nearly degenerate.[38] In this case the configurations

$$\ldots 5a_1^2\,3b_2^2\,6a_1^2\,2b_1^2\,7a_1^2\,4b_2^2\,1a_2^2\,5b_2^2\,8a_1^2\,3b_1\,9a_1^2 \quad {}^2B_1 \tag{8}$$

and

$$\ldots 5\sigma_g^2\,3\sigma_u^2\,4\sigma_u^2\,2\pi_u^4\,1\pi_g^4\,3\pi_u^3\,6\sigma_g^2 \quad {}^2\Pi_u \tag{9}$$

should be given theoretical consideration as well as (6) and (7).

Table I summarizes our geometry predictions for ClF_2^+, ClF_2, and ClF_2^-. For the ions, the minimum and double ζ basis sets yield qualitatively similar results. Consistent with Walsh's rules, ClF_2^+ is found to have a structure similar to that of SF_2.[23] In fact the double ζ ClF_2^+ bond angle differs by only (97.4 − 98.3°) = 0.9° from that of SF_2. The Cl–F bond distance in ClF_2^+ is predicted to be 1.70 Å, 0.07 Å

Table I. Molecular Structure Predictions for ClF_2^+, ClF_2, and ClF_2^-

Species	Basis set	Electronic state	Total energy	r(Cl–F), Å	Bond angle, deg
ClF_2^+	MBS	$^1A_1$	−654.0763	1.72	98.2
	DZ	$^1A_1$	−657.7177	1.70	97.4
ClF_2	MBS	$^2A_1$ ($^2\Sigma_g^+$)	−654.3749	1.83	Linear
		$^2B_1$ ($^2\Pi_u$)	−654.2353	1.79	Linear
	DZ	$^2A_1$	−658.1439	1.83	145.2
		$^2B_1$ ($^2\Pi_u$)	−658.1104	1.82	Linear
	Extended	$^2A_1$	−658.1455	1.83	145.2
	Polarized Cl	$^2A_1$	−658.1868	1.72	148.8
ClF_2^-	MBS	$^1A_1$($^1\Sigma_g^+$)	−654.2418	1.87	Linear
	DZ	$^1A_1$ ($^1\Sigma_g^+$)	−658.3305	1.93	Linear

longer than that in diatomic ClF, but essentially identical with the two equivalent bond lengths in the T-shaped ClF_3 molecule. As anticipated, ClF_2^- is predicted to be a linear symmetric ion. The Cl–F bond distance is quite long (1.93 Å) relative to the known bond distances of ClF, ClF_3, and ClF_5.

Minimum basis set SCF methods predict the ClF_2 radical to be linear, while the double ζ results suggest a bent molecule with bond angle 145.2°. The double ζ barrier to linearity is substantial, 7.7 kcal/mol. This clear conflict is particularly distressing due to the absence of a solid experimental determination of the structure of any triatomic molecule with 21 valence electrons. Although we would of course favor the double ζ result in vacuo, it was decided that further calculations were necessary for an unambiguous determination of the structure.

The entry in Table I labeled "Extended" basis set refers to a calculation in which a more flexible contraction of the 2p functions was employed. Thus while the double ζ basis may be labeled Cl(12s 9p/6s 4p), F(9s 5p/4s 2p), the extended basis is Cl(12s 9p/6s 5p), F(9s 5p/4s 3p). For the fluorine atom the Gaussian p functions are contracted 41 in the double ζ set, and 311 in the extended basis. The effect of this more flexible basis is to allow for a more correct description of the distortion of the Cl 3p and F 2p orbitals within the molecular framework. However, as Table I shows, this extended basis set provides an identical geometry prediction and an energy lowering of only 0.0016 hartree. This is, of course, quite a compliment to the contraction schemes of Dunning for the Cl and F atoms.

Also shown in Table I is an entry labeled "Polarized Cl". This refers to the addition of a set of d-like functions (d_{xx}, d_{yy}, d_{zz}, d_{xy}, d_{xz}, and d_{yz}), with orbital exponent $\alpha = 0.6$, to the Cl atom. In this regard we note that in triatomic species such as ClF_2, polarization functions on the central atom (Cl here) are far more important than those on the terminal atoms (F here).[39] Further, d functions on fluorine are usually relatively unimportant in any case. Thus it seems likely that a basis including one set of d functions on chlorine will recover most of the energy lowering due to polarization functions in ClF_2. As Table I shows, the lowering relative to double ζ is substantial, 0.0429 hartree. However, there is only a 3.6° increase in the predicted bond angle, thus strongly reinforcing the double ζ and extended basis predictions that ClF_2 is significantly bent. This conclusion is consistent with Mamantov's experimental estimate[10] of 140 ± 19° for the ClF_2 bond angle. A final point of particular interest is the fact that the polarized Cl basis yields a bond distance fully 0.11 Å shorter than the double ζ results. This general trend is well known[40] but the magnitude is quite large here. The polarized Cl value of 1.72 Å is much closer to the observed bond distances of ClF, ClF_3, and ClF_5, and is probably more realistic than the double ζ prediction.

Table II. Molecular Structure Predictions for ClF_4^+, ClF_4, and ClF_4^-

Species	Basis set	Electronic state	Total energy	r(Cl–F), Å	Apex angle, deg
ClF_4^+	MBS	$^1A_1$	−851.1882	1.78	148.4
	DZ	$^1A_1$	−856.2678	1.76	143.5
ClF_4	MBS	$^2A_1$ ($^2A_{1g}$)	−851.4372	1.82	Planar
		$^2B_1$ ($^2B_{1g}$)	−851.3418	1.92	Planar
	DZ	$^2A_1$ ($^2A_{1g}$)	−856,7535	1.83	Planar
		$^2B_1$ ($^2B_{1g}$)	−856,6734	1.92	Planar
ClF_4^-	MBS	$^1A_1$ ($^1A_{1g}$)	−851.3222	1.88	Planar
	DZ	$^1A_1$ ($^1A_{1g}$)	−856.9899	1.88	Planar

In attempting to understand the shape of the ClF_2 radical, there are at least three factors which bear consideration. It is the subtle interplay of these factors[22] which determines the structure of ClF_2.

(a) During the symmetrical bending of linear ClF_2 an increase in electronic stability is achieved by the delocalization of the $3\pi_u$ lone pairs (LP) of electrons. These LP's are primarily localized in the space of the chlorine $3p_x$ and $3p_y$ AO's in linear ClF_2. In C_{2v} ClF_2 the $3\pi_u$ MO becomes the $8a_1$ and $3b_1$ orbitals. Associated with the delocalization is a decrease in the energies of the latter orbitals.

(b) In linear ClF_2 the $6\sigma_g$ MO is a singly occupied nonbonding orbital. As ClF_2 assumes a C_{2v} structure the $6\sigma_g$ MO becomes the $9a_1$ orbital. The latter MO possesses a significant amount of chlorine $3p_z$ character (z axis is taken as the axis of rotation). Consequently, electron density is placed in the shrinking region of space between the two already negatively charged fluorine atoms. This situation contributes to the overall electronic instability of C_{2v} ClF_2. In fact, fully occupying the $9a_1$ MO forces a species such as ClF_2^- to assume a more stable linear geometry.

(c) Finally, it should be noted that bending ClF_2 (for fixed Cl–F separation) monotonically increases the nuclear repulsion energy. This adds to the electronic instability of bent ClF_2.

Evidently, the delocalization of the $3\pi_u$ LP's is sufficiently stabilizing so as to compensate for the instability brought about the last two processes mentioned above. Hence, C_{2v} ClF_2 is more favorable energetically.

The expected first excited state of ClF_2, qualitatively described by electron configuration 8 or 9, has also been studied. Both minimum and double ζ basis sets predict this state to be linear and hence of $^2\Pi_u$ symmetry. This result is in accord with Walsh's rules, since the doubly occupied $9a_1$ orbital is characteristic of linear systems with 22 valence electrons. Further, the predicted bond distance for this excited electronic state is comparable to that of the $^2A_1$ ground state. One important feature for which the minimum and double ζ calculations differ markedly is the excitation energy $\Delta E(^2A_1 \rightarrow {}^2\Pi_u)$. For the minimum basis we find ΔE = 0.1396 hartree = 3.08 eV, whereas the double ζ separation is only 0.0335 hartree = 0.91 eV. The double ζ result is certainly the more trustworthy and we conclude that the first excited state of ClF_2 is quite low lying.

Five-Atom Structures

If we assume an analogy between ClF_4^+ and the isoelectronic SF_4 molecule, then the ClF_4^+ electron configuration should be[41]

$$1a_1^2\,2a_1^2\,1b_2^2\,3a_1^2\,1b_1^2\,4a_1^2\,5a_1^2\,2b_2^2\,2b_1^2\,6a_1^2\\ 3b_2^2\,3b_1^2\,7a_1^2\,8a_1^2\,9a_1^2\,4b_2^2\,4b_1^2\,1a_2^2\,5b_2^2\\ 10a_1^2\,11a_1^2\,2a_2^2\,12a_1^2\,6b_2^2\,13a_1^2,\,14a_1^2 \quad (10)$$

Table III. Orbital Energies for Chlorine Fluorides[a]

ClF_2^+		ClF_2		ClF_2^-		ClF_4^+		ClF_4		ClF_4^-	
$1a_1$	−105.417	$1a_1$	−105.029	$1\sigma_g$	−104.732	$1a_1$	−105.551	$1a_{1g}$	−105.209	$1a_{1g}$	−104.972
$2a_1$	−26.732	$2a_1$	−26.361	$2\sigma_g$	−25.994	$1b_1$	−26.700	$1b_{1g}$	−26.390	$1b_{1g}$	−26.083
$1b_2$	−26.732	$1b_2$	−26.361	$1\sigma_u$	−25.994	$1e$	−26.700	$1e_u$	−26.390	$1e_u$	−26.083
$3a_1$	−11.130	$3a_1$	−10.746	$3\sigma_g$	−10.450	$2a_1$	−26.700	$2a_{1g}$	−26.390	$2a_{1g}$	−26.083
$2b_2$	−8.596	$2b_2$	−8.214	$2\sigma_u$	−7.916	$3a_1$	−11.252	$3a_{1g}$	−10.916	$3a_{1g}$	−10.677
$4a_1$	−8.594	$4a_1$	−8.210	$1\pi_u$	−7.912	$2e$	−8.718	$2e_u$	−8.381	$2e_u$	−8.139
$1b_1$	−8.590	$1b_1$	−8.208			$4a_1$	−8.714	$1a_{2u}$	−8.376	$1a_{2u}$	−8.135
$5a_1$	−1.997	$5a_1$	−1.604	$4\sigma_g$	−1.256	$5a_1$	−2.005	$4a_{1g}$	−1.674	$4a_{1g}$	−1.381
$3b_2$	−1.951	$3b_2$	−1.593	$3\sigma_u$	−1.249	$3e$	−1.934	$3e_u$	−1.629	$3e_u$	−1.340
$6a_1$	−1.501	$6a_1$	−1.166	$5\sigma_g$	−0.884	$2b_1$	−1.900	$2b_{1g}$	−1.608	$2b_{1g}$	−1.322
$2b_1$	−1.084	$2b_1$	−0.718	$4\sigma_u$	−0.416	$6a_1$	−1.547	$5a_{1g}$	−1.258	$5a_{1g}$	−1.018
$7a_1$	−1.078	$7a_1$	−0.709	$2\pi_u$	−0.383	$4e$	−1.114	$4e_u$	−0.810	$4e_u$	−0.549
$4b_2$	−1.065	$5b_2$	−0.725[b]			$7a_1$	−1.104	$2a_{2u}$	−0.799	$2a_{2u}$	−0.530
$1a_2$	−1.041	$1a_2$	−0.693	$1\pi_g$	−0.349	$1b_2$	−1.057	$1b_{2g}$	−0.748	$1b_{2g}$	−0.455
$5b_2$	−0.991	$5b_2$	−0.668			$5e$	−1.021	$1e_g$	−0.723	$1e_g$	−0.434
$8a_1$	−0.958	$8a_1$	−0.590	$3\pi_u$	−0.268	$3b_1$	−1.001	$1b_{2u}$	−0.714	$1b_{2u}$	−0.426
$3b_1$	−0.878	$3b_1$	−0.553			$6e$	−0.978	$5e_u$	−0.697	$5e_u$	−0.415
		$9a_1$		$6\sigma_g$	−0.250	$1a_2$	−0.976	$1a_{2g}$	−0.690	$1a_{2g}$	−0.400
						$8a_1$	−0.927	$3a_{2u}$	−0.618	$3a_{2u}$	−0.363
						$4b_1$	−0.818	$3b_{1g}$	−0.575	$3b_{1g}$	−0.350
								$6a_{1g}$	−0.552	$6a_{1g}$	−0.274

[a] The results were obtained from double ζ basis calculations at the predicted equilibrium geometries of the respective species. [b] Note that this orbital is energetically out of order relative to ClF_2^+.

ClF_4^- on the other hand is expected to be square planar,[27] and, if analogy with XeF_4 is appropriate, should have electron configuration[42]

$$1a_{1g}^2\ 1e_u^4\ 2a_{1g}^2\ 1b_{1g}^2\ 3a_{1g}^2\ 2e_u^4\ 1a_{2u}^2\ 4a_{1g}^2\ 2b_{1g}^2\ 3e_u^4\ 5a_{1g}^2\ 4e_u^4\ 2a_{2u}^2\ 1b_{2g}^2\ 1e_g^4\ 1b_{2u}^2\ 5e_u^4\ 1a_{2g}^2\ 3b_{1g}^2\ 3a_{2u}^2\ 6a_{1g}^2 \quad (11)$$

Should ClF_4- be a square pyramid, its electron configuration would become, after resolution[43] of the D_{4h} result,

$$1a_1^2\ 1e^4\ 2a_1^2\ 1b_1^2\ 3a_1^2\ 2e^4\ 4a_1^2\ 5a_1^2\ 2b_1^2\ 3e^4\ 6a_1^2 \times 4e^4\ 7a_1^2\ 1b_2^2\ 5e^4\ 3b_1^2\ 6e^4\ 1a_2^2\ 4b_1^2\ 8a_1^2\ 9a_1^2 \quad (12)$$

According to the ClF_4^- calculations of Guest,[28] the totally symmetric $6a_{1g}$ orbital is significantly higher (~0.1 hartree) than the other occupied valence orbitals. Hence the ground electronic state of the ClF_4 radical should be of $^2A_{1g}$ symmetry (if square planar) or $^2A_1$ symmetry (if a square pyramid). The symmetry of the first excited state of ClF_4 will be related to the nature of the second highest occupied orbital. Gregory[19] has suggested from CNDO calculations that the . . . $3a_{2u}$ $6a_{1g}^2$ configuration corresponds to the first excited state for the square-planar case.

Table II summarizes our geometry predictions for ClF_4^+, ClF_4, and ClF_4^-. The present minimum basis result for ClF_4^+ agrees with that of Guest et al.[28] in predicting a square-pyramidal structure. Further, our more reliable double ζ treatment of ClF_4^+ also predicts a C_{4v} structure, with a similar apex angle. Thus there would appear to be a deviation from Walsh's rules,[22] which requires ClF_4^+ to have a structure analogous to SF_4. To further pursue this anomaly, Radom and Schaefer[44] have made a comparable study of SF_4 itself. They find the minimum basis to predict a square-pyramidal SF_4, but the double ζ set to yield a C_{2v} structure in good qualitative agreement with experiment. Thus our first conclusion is that minimum basis sets can give qualitatively erroneous predictions of the shapes of AB_4 molecules. Second, it appears likely that the equilibrium structures of the isoelectronic molecules SF_4 and ClF_4^+ are very different. However, a near Hartree-Fock study (including d functions on Cl and F atoms) may be necessary to solidify our second conclusion. Should the addition of chlorine 3d functions have a qualitative effect on the geometry of ClF_4^+, this could be perhaps the first unequivocal demonstration of the importance of d orbitals in systems containing second-row atoms.[45]

Table IV. Mulliken Population Analyses for the Chlorine Fluorides

		ClF_2^+	ClF_2	ClF_2^-	ClF_4^+	ClF_4	ClF_4^-
Cl	s	5.92	5.96	6.01	5.85	5.92	6.03
	p	9.88	10.38	10.60	9.65	9.80	9.63
	Total	15.80	16.34	16.61	15.50	15.72	15.66
F	s	4.01	3.99	3.98	4.01	3.99	3.98
	p	5.09	5.34	5.71	5.12	5.33	5.60
	Total	9.10	9.33	9.69	9.13	9.32	9.58
			Singly Occupied Orbital				
Cl	s		0.05			0.11	
	p		0.31			0.00	
	Total		0.36			0.11	
F	s		0.00			0.00	
	p		0.32			0.22	
	Total		0.32 (2 equiv)			0.22 (4 equiv)	

The ground and first excited state of ClF_4 and the ground state of ClF_4^- are predicted to be planar by both sets of calculations. As for the triatomic species, relatively long Cl-F bond distances are predicted and these would presumably be shortened by ~0.1 Å were d functions added to the Cl basis set. It is noteworthy that the excited state ClF_4 bond distance is 0.09 Å longer than that predicted for the ground state. The $^2A_{1g}$-$^2B_{1g}$ separation is 2.60 eV in the MBS treatment and 2.18 eV when the larger DZ basis is employed. In either case the first excited state of ClF_4 is seen to be quite low lying.

Electronic Structure Considerations

Our discussion here is based on Tables III and IV, which give orbital energies and Mulliken populations for the six molecular species of interest. Except for the ClF_2 $4b_2$ orbital, the ordering via Koopmans Theorem of the occupied levels is identical for the radical and the ClF_2^+ ion. The same ordering is followed by the ClF_2^- ion although the negative charge necessarily raises all the orbital energies. The closeness of the highest fully occupied ($3b_1$ and $3\pi_u$) and half-occupied ($9a_1$ and $6\sigma_g$) orbitals supports our prediction that the first excited electronic state of ClF_2 is low lying.

For the ClF_4 radical, the two highest occupied orbitals ($3b_{1g}$ and $6a_{1g}$) are very close together. It is also interesting to note that the level orderings for ClF_4 and ClF_4^- are identical and hence the notion of filling orbitals by the aufbau prinzip is justifiable.

The most obvious conclusion drawn from Table IV is that Cl is considerably less electronegative than F. In fact, for none of the six species does the Cl Mulliken population reach the atomic value of 17. A particularly interesting result (possibly an artifact of the Mulliken analysis) is that in going from ClF_4 to ClF_4^- the Cl population actually decreases from 15.72 to 15.66. Changes in the Cl and F s populations are in general small compared to those for the p orbitals.

The half-filled orbitals of the ClF_2 and ClF_4 radicals are of particular interest here. For ClF_2, the $9a_1$ orbital is seen to be a roughly equal combination of Cl 3p and F 2p atomic functions. For ClF_4, the results of Table IV may be compared with the conclusions of Morton and Preston[18] from their EPR spectrum. They note that there is considerable Cl 3s contribution to the orbital of the unpaired electron, and estimate the amount to be between 17% (assuming sp^3d^2 hydridization) and 50% (assuming sp hybridization). Comparison of their observed ^{35}Cl hyperfine interaction with that based on the unpaired electron occupying a purely atomic Cl 3s orbital suggests the lower value (17%) to be quite realistic within this model. The present Mulliken analysis suggests that 11% of the $6a_{1g}$ population should be labeled Cl 3s. In light of the inherent imprecision of both experimental and theoretical determinations of the amount of "Cl 3s character", we consider the agreement to be satisfactory.

Acknowledgment. This research was supported by the National Science Foundation (GP-41509X and GP-39317). We thank Professor Neil Bartlett, Professor David Craig, Dr. Leo Radom, and Mr. Ole Krogh for helpful discussions. Considerable progress on this manuscript was made while H.F.S. was a Visiting Fellow at the Australian National University, Canberra.

References and Notes

(1) Work performed under the auspices of the U.S. Energy Research and Development Administration.
(2) (a) L. Stein, "Halogen Chemistry", Vol. 1, V. Gutmann, Ed., Academic Press, London, 1967; (b) A. I. Popov, *ibid.*
(3) A. J. Downs and C. J. Adams, "Comprehensive Inorganic Chemistry", Vol. 2, A. F. Trotman-Dickenson, Ed., Pergamon Press, Oxford, 1973.
(4) D. A. Gilbert, A. Roberts, and P. A. Griswold, *Phys. Rev.*, **76**, 1723 (1949).
(5) S. Green, *J. Chem. Phys.*, **58**, 3117 (1973).
(6) D. W. Magnuson, *J. Chem. Phys.*, **24**, 344 (1956).
(7) D. F. Smith, *J. Chem. Phys.*, **21**, 609 (1953).
(8) G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, **42**, 2236 (1965).
(9) G. Mamantov, D. G. Vickroy, E. J. Vasini, T. Maekawa, and M. C. Moulton, *Inorg. Nucl. Chem. Lett.*, **6**, 701 (1970).
(10) G. Mamantov, E. J. Vasini, M. C. Moulton, D. G. Vickroy, and T. Maekawa, *J. Chem. Phys.*, **54**, 3419 (1971).
(11) L. Y. Nelson and G. C. Pimentel, *Inorg. Chem.*, **7**, 1695 (1968). Note, however, the very recent work of B. S. Ault and L. Andrews, *J. Am. Chem. Soc.*, **97**, 3824 (1975). They convincingly conclude that the species identified by Nelson and Pimentel is more likely to be Cl_3^-.
(12) J. A. Blauer, H. G. McMath, and F. C. Jaye, *J. Phys. Chem.*, **73**, 2683 (1969).
(13) O. D. Krogh and G. C. Pimentel, *J. Chem. Phys.*, **56**, 969 (1972).
(14) S. N. Suchard, *J. Chem. Phys.*, **58**, 1269 (1973).
(15) G. C. Pimentel, *J. Chem. Phys.*, **58**, 1270 (1973).
(16) J. B. Cross, *J. Chem. Phys.*, **59**, 966 (1973).
(17) S. W. Rabideau, *J. Chem. Phys.*, **59**, 1533 (1973).
(18) J. R. Morton and K. F. Preston, *J. Chem. Phys.*, **58**, 3112 (1973).
(19) A. R. Gregory, *J. Chem. Phys.*, **60**, 3713 (1974).
(20) K. O. Christe and W. Sawodny, *Inorg. Chem.*, **6**, 313, 1159 (1967).
(21) K. O. Christe and J. P. Guertin, *Inorg. Chem.*, **4**, 905 (1965).
(22) A. D. Walsh, *J. Chem. Soc.*, 2260 (1953), and the following five papers in the same journal.
(23) D. R. Johnson and F. X. Powell, *Science*, **164**, 950 (1969).
(24) W. Harshbarger, R. K. Bohn, and S. H. Bauer, *J. Am. Chem. Soc.*, **89**, 6466 (1967).
(25) K. O. Christe and D. Pilipovich, *Inorg. Chem.*, **8**, 391 (1969); K. O. Christe and W. Sawodny, *Inorg. Chem.*, **12**, 2879 (1973).
(26) K. O. Christe, J. F. Hon, and D. Pilipovich, *Inorg. Chem.*, **12**, 84 (1973).
(27) K. O. Christe and J. P. Guertin, *Inorg. Chem.*, **5**, 473 (1966); K. O. Christe and W. Sawodny, *Z. Anorg. Allg. Chem.*, **357**, 125 (1968); **374**, 306 (1970).
(28) M. F. Guest, M. B. Hall, and I. H. Hillier, *J. Chem. Soc., Faraday Trans. 2*, **69**, 1829 (1973).
(29) S. Rothenberg, R. H. Young, and H. F. Schaefer, *J. Am. Chem. Soc.*, **92**, 3243 (1970).
(30) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
(31) J. A. Pople, "Computational Methods for Large Molecules and Localized States in Solids," F. Herman, A. D. McLean, and R. K. Nesbet, Ed., Plenum Press, New York, N.Y., 1973, pp 11-22.
(32) H. F. Schaefer, "Critical Evaluation of Chemical and Physical Structural Information," D. R. Lide and M. A. Paul, Ed., National Academy of Sciences, Washington, D.C., 1974, pp. 591-602.
(33) T. H. Dunning, *Chem. Phys. Lett.*, **7**, 423 (1970).
(34) T. H. Dunning, *J. Chem. Phys.*, **53**, 2823 (1970).
(35) D. B. Neumann, H. Basch, R. L. Kornegay, L. C. Snyder, J. W. Moskowitz, C. Hornback, and S. P. Liebmann, Program No. 199, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.
(36) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.
(37) S. Rothenberg and H. F. Schaefer, *J. Am. Chem. Soc.*, **95**, 2095 (1973).
(38) P. S. Bagus, B. Liu, and H. F. Schaefer, *J. Am. Chem. Soc.*, **94**, 6635 (1972).
(39) S. Rothenberg and H. F. Schaefer, *Mol. Phys.*, **21**, 317 (1971).
(40) H. F. Schaefer, "The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results", Addison-Welsey, Reading, Mass. 1972.
(41) V. B. Koutecky and J. I. Musher, *Theor. Chim. Acta*, **33**, 227 (1974).
(42) H. Basch, J. W. Moskowitz, C. Hollister, and D. Hankins, *J. Chem. Phys.*, **55**, 1922 (1971).
(43) G. Herzberg, "Electronic Spectra of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1966.
(44) L. Radom and H. F. Schaefer, *Aust. J. Chem.*, in press.
(45) Note Added in Proof. In more extensive calculations including d functions, we have found that the present double ζ structure prediction *are* qualitatively altered. ClF_4^+ does take on an SF_4-like structure with $r_{ax} = 1.63$ Å, $r_{eq} = 1.57$ Å, $\theta_{ax} = 169.6°$, and $\theta_{eq} = 109.7°$. Similarly ClF_4 becomes a square pyramid with $r(Cl–F) = 1.69$ Å and $\theta_{ax} = \theta_{eq} = 163°$.