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ESR Spectra and Structure of the Perchloryl Fluoride Radical Anion ($FClO_3^-$): A 33 Valence Electron Radical with C_{3v} Symmetry

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Abstract: The isotropic and anisotropic ESR spectra of $FClO_3^-$ have been observed, the former in the SF_6 matrix and the latter in both the $FClO_3$ and $(CH_3)_4Si$ matrices. The isotropic hyperfine coupling constants derived from the anisotropic parameters agree with the values (^{35}a = 656 MHz, ^{37}a = 546 MHz, ^{19}a = 726 MHz) obtained from the isotropic spectrum. Moreover, the analysis of the anisotropic spectrum reveals that the chlorine and fluorine hyperfine tensors have cylindrical symmetry with their largest principal values lying along the same principal axis. This result rules out a trigonal-bipyramidal structure for this 33 valence electron radical but is entirely consistent with a C_{3v} structure in which the Cl–F bond represents the symmetry axis (z). Most of the spin density is concentrated in the antibonding σ_{Cl-F}^* orbital which is composed of the 3s and 3p$_z$ orbitals of chlorine ($\rho_{3s} = 0.14$, $\rho_{3p} = 0.40$) in combination with the 2p$_z$ orbital of fluorine ($\rho = 0.35$). These results are in qualitative agreement with CNDO/2 calculations which also show that the Cl–F bond is longer in the radical anion than in the parent molecule. As expected from a consideration of its electronic structure, $FClO_3^-$ dissociates to give the neutral ClO_3 radical which has been detected in the SF_6 matrix.

Recent ESR studies on 33 valence electron radicals possessing four ligands bound to a central atom have revealed a structural dichotomy for phosphoranyl radicals,[2] the most widely investigated family of radicals in this class. Thus, although a trigonal-bipyramidal arrangement appears to be the most widely adopted geometry as exemplified by PF_4,[3,4] $POCl_3^-$,[5] and POF_3^-,[6,7] a C_{3v} structure obtains in the case of Ph_3PCl.[8] It is therefore of interest to examine other radicals in this general class, and especially those in which the central atom is one of the other main-group elements in the second row of the periodic table. In this connection, a particularly interesting isoelectronic series of radical anions consists of SiF_4^-,[9] POF_3^-,[6,7] $SO_2F_2^-$,[10] $FClO_3^-$, and the hypothetical species ArO_4^-. While the first three members of this series have been investigated and found to possess trigonal-bipyramidal structures, we now present evidence based on a comprehensive ESR study that $FClO_3^-$ adopts a C_{3v} geometry.

Previous work on chlorine-centered radicals in the above class has been confined to ClO_4^{2-},[11-13] although other hypervalent species such as ClF_4[14,15] (35 valence electrons) and ClF_6[15,16] (49 valence electrons) are well established. The ESR results for ClO_4^{2-} have been interpreted[11-13] in terms of the expected distortion from tetrahedral symmetry which takes place on electron capture by ClO_4^-, one apparent manifestation being the presence of inequivalent sites for the ClO_4^{2-} centers in orthorhombic crystalline $KClO_4$ resulting from the loss of a C_3 symmetry element about any one of the chlorine–oxygen bonds.[11] It was also argued, however,[12] that the low values (<0.1) for the 3s and 3p spin densities on chlorine indicated a much smaller distortion from T_d symmetry for ClO_4^{2-} than that represented by the C_{2v} structure of PF_4.

Experimental Section

Perchloryl fluoride ($FClO_3$) was obtained from Ozark-Mahoning, sulfur hexafluoride from Matheson, and tetramethylsilane (Me_4Si) from Mallinckrodt. Samples of pure $FClO_3$ and of solid solutions containing up to 5 mol % $FClO_3$ in SF_6 and in Me_4Si matrices were prepared by standard vacuum techniques in Spectrosil or Suprasil quartz tubes. The samples were rapidly quenched to 77 K and irradiated at this temperature with γ rays from a ^{60}Co source (Gammacell 200, Atomic Energy of Canada Ltd.) for total doses in the range of 1.0–1.5 Mrad.

ESR measurements were made as described elsewhere,[17] using an X-band spectrometer equipped with an NMR gaussmeter. The ESR spectra of the γ-irradiated samples were monitored at various temperatures in the range between 77 and 113 K for the SF_6 solution, at 77 K for the pure $FClO_3$ solid, and at 88 K for the Me_4Si solution, the experimental methods being similar to those employed in a previous study.[18]

Results

ESR Studies in the SF_6 Matrix. The SF_6 matrix has proven to be very useful for studies of trapped inorganic radicals since their ESR spectra in the rotator phase above the solid–solid transition temperature at 94 K are frequently isotropic.[3,15,16,18] This property is again in evidence for the radicals present in a γ-irradiated solution of $FClO_3$, as illustrated in Figure 1. The upper spectrum recorded at 103 K consists of three distinct hyperfine patterns, two of which can be assigned in a straightforward manner to the ClO_3[19] and SF_5[20] radicals on the basis of their known parameters. For example, the ClO_3 parameters of g_{iso} = 2.0095 and ^{35}a = 346 MHz (^{37}a = 287 MHz) obtained in this work are almost identical with the values of g_{iso} = 2.011 and ^{35}a = 343 MHz reported for ClO_3 in $KClO_4$.[19] Also, it might be noted that the SF_5 radical[19] is invariably present at these temperatures after γ irradiation of solid SF_6.[3,15,16,18,21] Our interest, therefore, is largely centered on the remaining species showing hyperfine

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Table I. ESR Parameters and Spin Densities for the $FClO_3^-$ Radical Anion

radical	matrix	T/K	$g_\perp$	$g_\parallel$	g_{iso}	nucleus	$A_\perp$/ MHz	$A_\parallel$/ MHz	a_{iso}/ MHz	e^2Qq/ MHz	ρ_s[a]	ρ_p[a]
$FClO_3^-$	SF_6	103			2.0107	^{35}Cl			656		0.139	
						^{37}Cl			546		0.139	
						^{19}F			726		0.015	
$FClO_3^-$	$FClO_3$	77	2.0129	2.0019	2.0092	^{35}Cl	580	748	636[b]	83	0.135	0.402
						^{37}Cl	482	622	529[b]	65	0.135	0.402
						^{19}F	135	1737	669[b]		0.014	0.351
$FClO_3^-$	$Si(CH_3)_4$	88	2.0120	2.0018	2.0086	^{35}Cl	572	743	629[b]	83	0.134	0.402
						^{37}Cl	476	619	524[b]	65	0.134	0.402
						^{19}F	107	1718	644[b]		0.013	0.353

[a] Spin densities were derived with use of the magnetic properties listed by: Goodman, B. A.; Raynor, J. B. *Adv. Inorg. Chem. Radiochem.*, 1970, *13*, 135. These parameters were calculated from the wave functions given by: Froese, C. *J. Chem. Phys.*, 1966, *45*, 1417. [b] Derived from the anisotropic hyperfine parameters which are assumed to have the same sign. The assumption of opposite signs would lead to much poorer agreement with the values determined directly from the isotropic spectrum. The isotropic couplings for chlorine and fluorine also have the same sign (see ref 23), and since negative signs would involve an untenable spin distribution, the signs of the hyperfine couplings are therefore all taken to be positive.

interaction with one chlorine ($I = {}^3/_2$) and one fluorine ($I = {}^1/_2$). Before proceeding to consider the nature of this third radical, however, it is instructive to establish the spectral changes which take place on annealing the solid solution.

A comparison of the two spectra in Figure 1 shows that the ClO_3 radical grows in during annealing at the expense of the third radical. Since it is clear, therefore, that this radical showing hyperfine coupling to both chlorine and fluorine is a direct precursor of ClO_3, it seems reasonable to propose that the species is $FClO_3^-$ which is formed by electron capture and can dissociate to give ClO_3 and F^-. Independent evidence that the parent compound $FClO_3$ is a very effective electron scavenger comes from the observation that no trace of SF_6^- was detectable in the spectrum of the γ-irradiated $FClO_3/SF_6$ solution at 103 K, although SF_6^- can easily be observed at this temperature following γ irradiation of pure SF_6 at 77 K.[21] There is, therefore, a consistent pattern of strong chemical evidence in favor of assigning the third radical to $FClO_3^-$.

The analysis of the hyperfine pattern now assigned to $FClO_3^-$ is unambiguous by virtue of the presence of two sets of components originating from the ^{35}Cl and ^{37}Cl isotopes with relative intensities of 3:1 and a chlorine hyperfine coupling ratio of 1.20. It is evident, however, that the spectrum of $F^{35}ClO_3^-$ is characterized by pronounced higher-order effects[22] attributable to the near equivalence of the ^{35}Cl (^{35}a ca. 647 MHz) and ^{19}F (^{19}a ca. 732 MHz) coupling constants with identical signs, and this topic will be discussed in detail elsewhere.[23] By using the above estimates of the hyperfine couplings as initial values, the ESR parameters were derived by fitting the calculated field positions of the transitions to the measured line positions. These calculations were performed with use of a matrix diagonalization computer program[17] which provided an exact solution for the determinant of the energy matrix constructed from the spin Hamiltonian for an isotropic system (1), the use of the first three terms resulting in nonzero diagonal

$$\mathcal{H} = g_{iso}\beta H_z S_z - \sum_{i=Cl,F} g_{iN}\beta_N H_z I_{iz} + \sum_{i=Cl,F} a_i I_{iz} S_z + \text{either} \sum_{i=Cl,F} a_i (I_{ix}S_x + I_{iy}S_y) \text{ or } \tfrac{1}{2} \sum_{i=Cl,F} a_i (I_{i+}S_- + S_+I_{i-}) \quad (1)$$

matrix elements and of the last term in nonzero off-diagonal matrix elements. As shown by the correspondence of the line positions to the calculated stick diagrams in Figure 1, excellent agreement was obtained for the best-fit ESR parameters listed in Table I.

Although the spectrum of $FClO_3^-$ in Figure 1 can be regarded as isotropic, there are significant line width variations as exemplified by a comparison of the signal heights for the first two components of the $F^{35}ClO_3^-$ spectrum at low field. As the temperature of the sample was raised from 103 to 122 K, the ratio

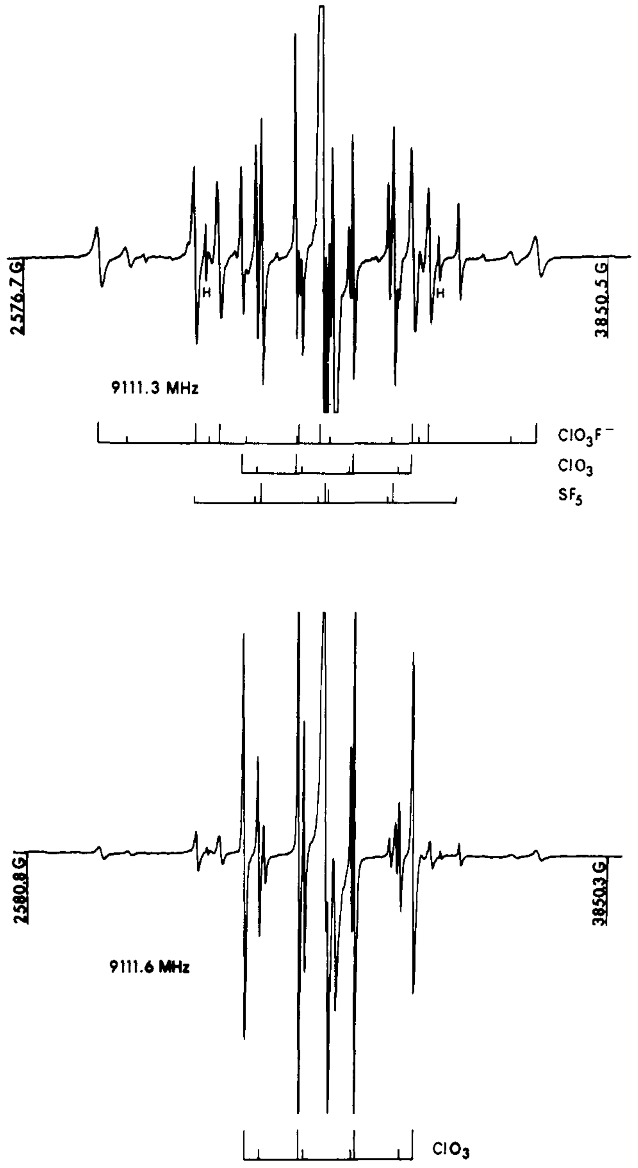

Figure 1. First-derivative ESR spectra of a γ-irradiated solid solution of 5 mol % $FClO_3$ in SF_6 recorded with the same spectrometer settings at 103 K before (upper spectrum) and after (lower spectrum) annealing the sample for 20 min at 113 K. The stick diagrams for the $FClO_3^-$ radical anions ($F^{35}ClO_3^-$ and $F^{37}ClO_3^-$) show the calculated line positions according to the isotropic parameters given in Table I. Stick diagrams for ClO_3 and SF_5 are also shown in the figure.

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(23) The higher-order effects which are particularly important in defining the exact spectral positions of line 6 $\{M_1^{Cl} = -{}^3/_2, M_1^F = +{}^1/_2\}$ and line 7 $\{M_1^{Cl} = -{}^1/_2, M_1^F = -{}^1/_2\}$ in the isotropic spectrum of $F^{35}ClO_3^-$ (Figure 1) can only be explained if the chlorine and fluorine couplings have the same sign. A detailed discussion of the theory and calculations pertaining to this and other examples of higher-order effects is given elsewhere. Hasegawa, A.; Hayashi, M.; Kerr, C. M. L.; Williams, F. *J. Magn. Reson.* submitted for publication.

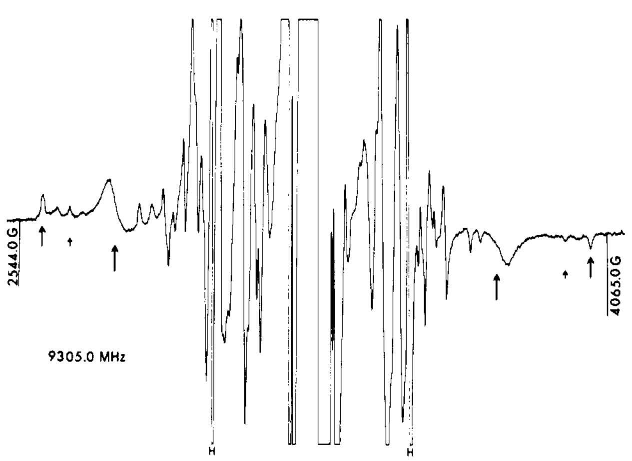

Figure 2. First-derivative ESR spectrum of a γ-irradiated solid solution of 5 mol % $FClO_3$ in SF_6 recorded at 77 K immediately after irradiation.

of these line heights approached unity in an asymptotic manner, indicating that the tumbling motion of ClO_3F^- in the SF_6 matrix at 103 K is not rapid enough to average out the anisotropy. These observations led us to examine the spectrum at 77 K (Figure 2). In the wings of this spectrum the two outermost pairs of features possessing a 3:1 intensity ratio and marked by the lighter arrows consist of ^{35}Cl and ^{37}Cl parallel components associated with a powder pattern. In addition, a pair of broad asymmetric lines marked by heavier arrows can be seen just to the inside of the parallel features, the positions of these broad lines corresponding closely to the outermost lines of $F^{35}ClO_3^-$ in the isotropic spectrum (Figure 1). This identity was verified by observing the narrowing of these lines between 77 and 103 K. In contrast, the outermost parallel features disappeared completely over this temperature range. In each case the changes were reversible and the relative intensity of the two different ^{35}Cl spectral components was unchanged by annealing. Accordingly, there appear to be two different sites for the $FClO_3^-$ radical anion in the SF_6 matrix at 77 K, one being characteristic of the stationary radical resulting in a powder pattern while the other allows slow tumbling to produce a broadened isotropic spectrum. Unfortunately, further analysis of the $FClO_3^-$ powder pattern was prevented by the absence of resolvable perpendicular features which are presumably obscured by overlapping components from the anisotropic spectra of SF_5[21] and ClO_3 in the SF_6 matrix at 77 K. We have resorted, therefore, to studies of the powder spectrum in pure solid perchloryl fluoride and in Me_4Si.

The Anisotropic ESR Spectrum of $FClO_3^-$. Figure 3 shows the spectrum of γ-irradiated pure $FClO_3$ at 77 K, and it is immediately apparent that the wing features closely resemble the outermost parallel features of the spectrum in Figure 2 which we have tentatively attributed to stationary $FClO_3^-$ radicals in the SF_6 matrix. Much more detail is revealed in Figure 3, however, regarding the $FClO_3^-$ powder pattern, four parallel and four perpendicular components being present in the regions outside the hydrogen-atom doublet.

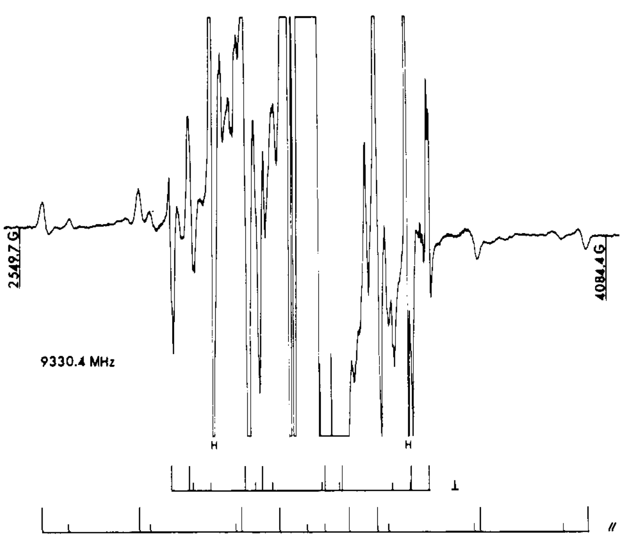

Figure 3. First-derivative ESR spectrum of γ-irradiated solid perchloryl fluoride ($FClO_3$) recorded at 77 K. The stick diagrams show the calculated line positions of the perpendicular and parallel components of the $FClO_3^-$ radical anions according to the anisotropic parameters listed for the $FClO_3$ matrix in Table I.

By concentrating first on the parallel set of components, the presence of both ^{35}Cl and ^{37}Cl lines with their characteristic 3:1 intensity ratio enables us to deduce from the total spectral widths and the $^{35}Cl/^{37}Cl$ gyromagnetic ratio that there must be a large doublet splitting associated with the spectrum, a first-order analysis suggesting ca. 620 G (1737 MHz) for this ^{19}F coupling together with values of ca. 270 and 225 G (757 and 630 MHz) for the ^{35}Cl and ^{37}Cl couplings, respectively. The analysis of the perpendicular spectrum is not quite so straightforward since the ^{37}Cl components are masked and only the four outer ^{35}Cl components can be clearly identified. However, the ambiguity can be removed by consideration of the second-order effects[24] implied by the unequal spacings between the $\{M_I^{Cl}, M_I^F = \pm^3/_2, \pm^1/_2\}$ and $\{M_I^{Cl}, M_I^F = \pm^1/_2, \pm^1/_2\}$ components at low field (positive signs) and high field (negative signs) in the *parallel* spectrum. These second-order effects establish that the larger coupling of ca. 200 G in the perpendicular spectrum must belong to ^{35}Cl ($I = ^3/_2$) rather than the ^{19}F ($I = ^1/_2$) nucleus. This interpretation of the splitting pattern also fits in with the observation that the phases of the two adjacent perpendicular components present just outside each line of the hydrogen-atom doublet are reversed with respect to each other, as expected for a ^{19}F doublet splitting. The total spread of the perpendicular spectrum can therefore be explained satisfactorily in terms of an ca. 200 G (564 MHz) interaction with chlorine (^{35}Cl) and a coupling of ca. 48 G (135 MHz) to fluorine.

By using the above estimated parameters as the initial values, the anisotropic ESR parameters were determined with the aid of a matrix diagonalization program by employing the following spin Hamiltonian,

$$\mathcal{H} = g_{\parallel}\beta H_Z S_Z + g_{\perp}\beta(H_X S_X + H_Y S_Y) - \sum_{i=\mathrm{Cl,F}} g_{iN}\beta_N(H_X I_{iX} + H_Y I_{iY} + H_Z I_{iZ}) + \sum_{i=\mathrm{Cl,F}} \{A_{\parallel i} S_Z I_{iZ} + A_{\perp i}(S_X I_{iX} + S_Y I_{iY})\} + \frac{e^2 Q q_{\mathrm{ClZ}}}{4I_{\mathrm{Cl}}(2I_{\mathrm{Cl}} - 1)}\{3I^2_{\mathrm{ClZ}} - I_{\mathrm{Cl}}(I_{\mathrm{Cl}} + 1)\}$$

where the terms have their usual meaning and the **g**, hyperfine, and nuclear electric quadrupole tensors have cylindrical symmetry with coincident principal axes.[25] The final parameters are listed in Table I, these values providing an excellent fit as may be judged by the close correspondence between the experimental spectrum and the calculated line diagrams in Figure 3. The only observable feature of the $FClO_3^-$ spectrum which is not accounted for is the small splitting on the perpendicular components, and this is probably attributable to a slight deviation of the **g** tensor from axial symmetry.

The anisotropic spectrum of $FClO_3^-$ was also generated by γ irradiation of a solution of $FClO_3$ in the Me_4Si matrix, as shown in Figure 4. Recent work has demonstrated that this matrix is particularly suitable for the generation and ESR identification of negative ions by electron capture,[17,26-28] the anisotropic ESR spectra of radicals having C_{3v} symmetry (symmetric tops) being particularly well defined in many instances.[17,26,28] In keeping with

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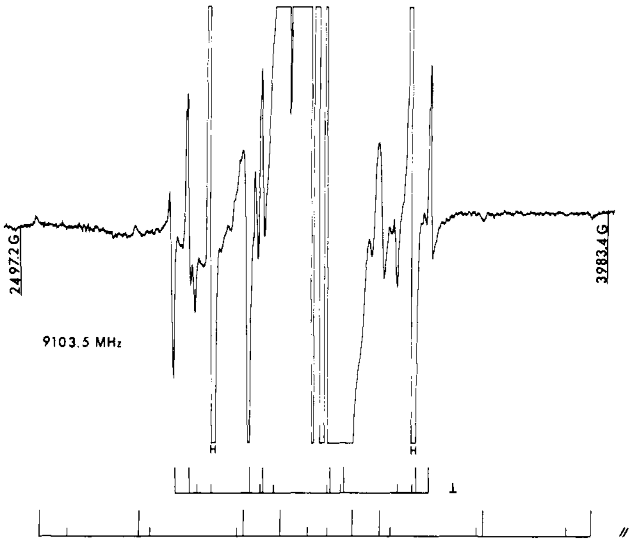

Figure 4. First-derivative ESR spectrum of a γ-irradiated solid solution of 5 mol % $FClO_3$ in tetramethylsilane recorded at 88 K. The stick diagrams show the calculated positions of the perpendicular and parallel components of the $FClO_3^-$ radical anions according to the parameters listed for the Me_4Si matrix in Table I.

this experience, the spectrum of $FClO_3^-$ in Me_4Si (Figure 4) is of much greater clarity than that obtained by γ irradiation of the pure compound (Figure 3), especially as regards the perpendicular components inside the hydrogen-atom lines. Indeed, except for the intense central lines originating from the matrix radical CH_2SiMe_3, the spectrum in Figure 4 is largely attributable to the $FClO_3^-$ radical anion. It is also noteworthy that in comparison with Figure 3, the perpendicular features are strongly enhanced suggesting the partial alignment of the $FClO_3^-$ radicals in the Me_4Si matrix. Finally, the spectrum in Figure 4 shows no suggestion of an additional splitting on the perpendicular features similar to that observed in Figure 3. If, as we have suggested, this splitting is caused by a lack of axial symmetry in the **g** tensor, then its absence in Figure 4 can be understood if the $FClO_3^-$ radical in Me_4Si is undergoing rapid rotation on the ESR time scale about the Cl–F axis. This type of motion would be expected to confer axial symmetry on the **g** and hyperfine tensors, and would be analogous to the rotation which renders the three fluorines equivalent in the ESR spectrum of the CF_3X^- (X = Cl, Br, I) radical anions.[17,26] The best-fit ESR parameters for $FClO_3^-$ in Me_4Si were obtained as described before and are compared in Table I with the results derived from the anisotropic spectrum in the $FClO_3$ matrix.

The data collected in Table I show that the ESR parameters of $FClO_3^-$ are not strongly perturbed by the matrix, save perhaps for the ^{19}F coupling (vide infra). It is particularly reassuring that the isotropic parameters obtained directly from the spectrum of the tumbling radical in the SF_6 matrix are in reasonable accord with the values deduced from the anisotropic spectra in the $FClO_3$ and Me_4Si matrices, assuming that the hyperfine tensor components have the same sign. The *neq* interaction of 83 MHz deduced for ^{35}Cl in $FClO_3^-$ is almost a factor of ten smaller than the ^{35}Cl hyperfine tensor components so that the characteristic effect of the *neq* in bringing about unequal spacings in the chlorine quartet is relatively minor. Consequently, the accuracy of the estimated value may be limited but the result is comparable to the values of 76 and 105 MHz obtained for $^{35}ClCO$ and $^{35}ClOO$, respectively.[29] From the structural point of view, the most significant result is that the largest principal values of the ^{35}Cl and ^{19}F hyperfine tensors (the parallel components) are directed along the same axis. It should be emphasized that the results are quite unambiguous on this point, and the importance of this finding will be brought out in the Discussion. Also included in Table I and discussed later are the spin densities calculated from the hyperfine parameters.

Theoretical Calculations. CNDO/2 calculations were carried out for the $FClO_3^-$ radical anion starting with the geometry of the parent molecule[30] and varying the Cl–F bond length. The minimum in the total energy was achieved for an interhalogen bond length of 192 pm which is 3 pm larger than in the parent molecule,[30] the other parameters for the optimized C_{3v} geometry being r_{Cl-O} = 140.4 pm and $\angle OClO$ = 116.6°. From the calculations, the spin density distribution for $FClO_3^-$ is predicted to be largely concentrated in the p orbitals of chlorine and fluorine directed along the Cl–F bond, the pertinent values being ρ_{3p} = 0.170 for chlorine and ρ_{2p} = 0.747 for fluorine. The corresponding spin densities in the s orbitals were found to be ρ_{3s} = 0.021 for chlorine and ρ_{2s} = 0.005 for fluorine. While a comparison of these calculated values with the experimental results in Table I does not yield good quantitative agreement, it is gratifying to find an important element of consistency, namely, that in each case the spin densities are largely confined to the orbitals of chlorine and fluorine which contribute to an a_1 (σ_{Cl-F}*) antibonding orbital directed along the Cl–F bond.

Discussion

The crucial experimental result bearing on the question of C_{3v} vs. C_s (trigonal-bipyramidal) symmetry for $FClO_3^-$ is the finding that the chlorine and fluorine hyperfine tensors have their largest principal values along the same axis (Table I). In a trigonal-bipyramidal structure, the p orbital possessing spin density on the central atom lies in a direction which is perpendicular (or nearly so) to the p orbital of the apical ligand which also contains appreciable spin density.[4,5] The expected result in this case is that the central atom hyperfine coupling will be a maximum when the ligand coupling is a minimum, and vice versa. This is clearly not the case for $FClO_3^-$. On the other hand, the p orbitals of the central atom and the unique axial ligand which usually contain most of the spin density are parallel in C_{3v} symmetry, as demonstrated conclusively for Ph_3PCl[8] and $^{13}CF_3Cl^-$.[31] This situation clearly also holds for $FClO_3^-$, the experimental results and the theoretical calculations showing that the unpaired electron occupies an a_1 (σ_{F-Cl}*) orbital mainly composed of the 3s and $3p_z$ orbitals of chlorine which are antibonding with the $2p_\sigma$ orbital of fluorine.

The observed dissociation path of $FClO_3^-$ to ClO_3 is predictable from the C_{3v} structure just discussed, given the very large spin densities which reside in the antibonding orbital between chlorine and fluorine. The general lability of this σ_{Cl-F}* bond may also explain the variation which is observed in the ^{19}F hyperfine couplings for $FClO_3^-$ in the three different matrices (Table I). While we are reluctant in general to ascribe small differences in ESR parameters to "matrix effects", the variation present in our ^{19}F results does appear to be outside reasonable error limits and could be symptomatic of a very weak bond being perturbed by the matrix and change of temperature. If this explanation is correct, however, it is not immediately obvious why the chlorine couplings show a much smaller effect than for fluorine.

In conclusion, it is interesting to compare the spin distribution in $FClO_3^-$ with that in the V_k center FCl^-.[32] As might be expected, the spin densities in the chlorine $3p_\sigma$ orbital (0.56) and the fluorine $2p_\sigma$ orbital (0.70) of FCl^- are higher than the respective values of 0.40 and 0.35 for the corresponding orbitals of $FClO_3^-$. Another significant difference is the much higher spin density in the chlorine 3s orbital for $FClO_3^-$, the value being 0.14 as compared to 0.03 for FCl^-. Of course, this difference simply reflects the greater sp hybridization of the chlorine central atom orbitals in a penta-atomic as opposed to a diatomic molecule.

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