where $\alpha$ is determined by the amount of admixture of the P state in the $^4$F state. In our discussion we will consider the admixture to be zero which forces $\alpha$ to be $^3/_2$. To obtain the energy levels of the $^4$F state when split by spin–orbit interaction, one uses a representation in which $l_z'$ and $S_z$ are diagonal. Solving the characteristic matrices in this representation one finds the splitting of the $^4T_{1g}$ to be $^{15}/_4\lambda$ for $m = \pm ^1/_2$; $^6/_4\lambda$ for $m = \pm ^1/_2, \pm ^3/_2$; and $-^9/_4\lambda$ for $m = \pm ^1/_2, \pm ^3/_2, \pm ^5/_2$. The lowest sublevel is $^{15}/_4\lambda$, since $\lambda$ is negative for the d$^7$ ion. This level will be split by a magnetic field into $|m = ^1/_2\rangle$ and $|m = -^1/_2\rangle$. The wave functions are given as

$$|^1/_2\rangle = \frac{1}{\sqrt{2}}|-1, ^3/_2\rangle - \frac{1}{\sqrt{3}}|0, ^1/_2\rangle + \frac{1}{\sqrt{6}}|1, -^1/_2\rangle \quad (6)$$

$$|^1/_2\rangle = \frac{1}{\sqrt{2}}|1, -^3/_2\rangle - \frac{1}{\sqrt{3}}|0, -^1/_2\rangle + \frac{1}{\sqrt{6}}|-1, ^1/_2\rangle \quad (7)$$

For a pure octahedral field the magnetic splitting is described by an isotropic $g = g_{||} = g_\perp$ and $h\nu = g\beta\vec{H}\cdot\vec{S}$ with

$$g = 2\langle ^1/_2|L_z + 2S_z|^1/_2\rangle \text{ or } g = 4.333 \quad (8)$$

Low[10] has pointed out that to second order the spin–orbit interaction can result in mixing some of the $^4T_{2g}$ into the $^4T_{1g}$ state with the additional contribution to $g$ of $-(^{15}/_2)(\lambda/10Dq)$. In addition, in our case we expect if the site has been distorted toward the octahedral symmetry, the sites in general will not be pure. Distortions on octahedral symmetry will produce a slight anisotropic effect which we do observe in our broad lines.

We must now consider the earlier optical measurements on $Co^{2+}$–$CdF_2$. The important results of these experiments are: (1) The electronic spectrum of $Co^{2+}$–$CdF_2$ does not appear to change in band shape or complexity with increasing $Co^{2+}$ concentration but does from the outset show a rather complex series of maxima. (2) The optical intensity-giving mechanism appears to be vibronic at low $Co^{2+}$ concentrations but is essentially static at high $Co^{2+}$ concentrations; *i.e.*, there are no $Co^{2+}$ sites which retain a perfect center of symmetry.

These results are, in the main, consistent with our esr results. It appears that there is but one $Co^{2+}$ site at very low $Co^{2+}$ concentrations[6] and that this site is a cubic eightfold coordinated one. As the concentration of $Co^{2+}$ is increased, the lattice begins to distort. One type of distortion involves the slight elongation of two CoF bonds and produces the pseudooctahedral resonance at $g = 4$. The second type of distortion most likely produces a site which has four nearest fluorides in a tetrahedral arrangement (this is the $g = 2$ site). By the time a concentration of 8 mol % $Co^{2+}$ has been reached all $Co^{2+}$ ions are in one of these two types of sites.

It is clear that the number of $Co^{2+}$ ions in pseudooctahedral sites increases from zero to a concentration approximately equal to that of the "tetrahedral" sites (the epr signal at $g = 4$ is of equal intensity to that at $g = 2$ for a $Co^{2+}$ concentration of 8%). It is also evident that the $g = 2$ sites are no longer cubic at 8% $Co^{2+}$ as there is no vibronic contribution to the intensity at this concentration.

On the other hand, the symmetry of both the "$g = 2$" and "$g = 4$" sites must be similar to one another and to the original eightfold cubic site as only minor changes appear in the optical spectrum as the concentration of $Co^{2+}$ is increased.

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# The Difluorochlorate(V) Anion, $ClO_2F_2^-$. Vibrational Spectrum and Force Constants

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The infrared and the Raman spectra of solid $CsF\cdot ClO_2F$ have been recorded. They are consistent with a $ClO_2F_2^-$ anion of symmetry $C_{2v}$. The structure can be derived from a trigonal bipyramid, where the two F atoms occupy the axial and the two O atoms and the lone electron pair occupy the equatorial positions. A modified valence force field has been computed for $ClO_2F_2^-$, indicating double-bond character for the ClO bonds and rather weak ClF bonds with high ionic contributions.

## Introduction

Huggins and Fox have recently reported[1] the existence of $CsClO_2F_2$. However, they did not succeed in obtaining any spectroscopic or structural data on this interesting compound. In this paper, we report the vibrational spectrum and the results of a force-field computation for $CsClO_2F_2$.

## Experimental Section

**Materials and Apparatus.**—The materials used in this work were manipulated in a well-passivated (with $ClF_3$) 304 stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke Inc., 425 IF4Y). Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ±0.1%). Chloryl fluoride (prepared in this laboratory from $KClO_3$ and $F_2$[2]) was purified by fractional condensation. Its purity was determined by measuring its vapor pressure and infrared spectrum. Cesium fluoride was fused in a platinum crucible and powdered in a drybox prior to use. Because of their hygroscopicity, materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on Perkin–Elmer Model 337 and 457 spectrophotometers in the range 4000–250 cm$^{-1}$.

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(1) D. K. Huggins and W. B. Fox, *Inorg. Nucl. Chem. Lett.*, **6**, 337 (1970).

(2) A. Engelbrecht, *Angew. Chem.*, **66**, 442 (1954).

TABLE I

VIBRATIONAL SPECTRUM OF $Cs^+ClO_2F_2^-$ AND ITS ASSIGNMENT COMPARED TO THOSE OF SIMILAR MOLECULES AND IONS

| Obsd freq, $cm^{-1}$, and intens | | | | | | | | | | Assignment for $XO_2F_2$ in point group $C_{2v}$ | Approx description of vibration |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $Cs^+ClO_2F_2^-$ | | $XeO_2F_2$[a] | | | | | | | | | |
| Ir | Raman | Ir | Raman | $ClO_2^-$[b] | $ClO_2$[b] | $ClO_2^+$[c] | $ClO_2F$[d] | $ClF_3$[e] | $ClF_2^-$[f] | | |
| 1225<br>1191 vs | 1221 (0.8)[g] | 905 s | 902 w | 844 | 1111 | 1296 | 1271 | | | $\nu_8(B_2)$ | $\nu_{as}(XO_2)$ |
| 1070 s | 1076 (10)<br>1064<br>1055 | 848 ms | 845 vs | 786 | 945 | 1044 | 1106 | | | $\nu_1(A_1)$ | $\nu_s(XO_2)$ |
| 855 vw | | | | | | | | | | $\nu_3 + \nu_6(B_1)$ ? | |
| 559 m | 559 (1.2) | 328 ms, sh | 333 ms | 402 | 445 | 521 | 547 | | | $\nu_2(A_1)$ | $\delta_s(XO_2)$ |
| 510 vs, br | | 585 vs | 578 w | | | | | 702 | 635 | $\nu_6(B_1)$ | $\nu_{as}(XF_2)$ |
| | 480 (1), br | | | | | | | | | $\nu_5(A_2)$ ? | $\tau$ |
| 330–370 m | 363 (10) | | 490 s | | | | | 529 | 475 | $\nu_3(A_1)$ | $\nu_s(XF_2)$ |
| | 337 (8) | 324 s<br>317 ms | 313 ms | | | | | | | $\nu_7(B_1)$, $\nu_9(B_2)$ | $\delta_{rock}$, $\delta_{wag}$ |
| | 198 (0.7) | | 198 w | | | | | 328 | | $\nu_4(A_1)$ | $\delta_s(XF_2)$ |

[a] H. H. Claassen, *et al.*, *J. Chem. Phys.*, **49,** 2531 (1968). [b] H. Siebert, "Anwendungen der Schwingungsspektroskopie in der anorganischen Chemie," Springer-Verlag, West Berlin, 1966. [c] K. O. Christe, *et al.*, *Inorg. Chem.*, **8,** 2489 (1968). [d] D. F. Smith, *et al.*, *Spectrochim. Acta*, **20,** 1763 (1964). [e] H. Selig, H. H. Claassen, and J. H. Holloway, *J. Chem. Phys.*, **52,** 3517 (1970). [f] K. O. Christe, *et al.*, *Inorg. Chem.*, **6,** 1159 (1967). [g] The relative intensities of the Raman bands have not been corrected for the variation of instrument sensitivity with frequency.

The spectra of gases were obtained using 304 stainless steel cells of 5-cm path length fitted with AgCl windows. Screw-cap metal cells with AgCl or AgBr windows and Teflon FEP gaskets were used for obtaining the spectra of solids as dry powders at ambient temperature. The quality of the infrared spectra could be somewhat improved by pressing two small single-crystal platelets of either AgCl or AgBr to a disk in a pellet press. The powdered sample was placed between the platelets before starting the pressing operation.

The Raman spectra were recorded using a Coherent Radiation Laboratories Model 52 Ar ion laser as a source of 1.3 W of exciting light at 5145 Å. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to ∼−25°, and a dc ammeter. Pyrex-glass tubes (7-mm o.d.) with a hollow inside glass cone for variable sample thicknesses or Pyrex or clear Kel-F capillaries were used as sample containers. For the capillaries the transverse viewing–transverse excitation technique and for the conical tube the axial viewing–transverse excitation technique were used.

**Preparation of $CsClO_2F_2$.**—Dry CsF (7.64 mmol) was placed into a 10-ml prepassivated (with $ClF_3$) 316 stainless steel cylinder and $ClO_2F$ (22.50 mmol) was added at −196°. The cylinder was kept at −25° for 24 hr and subsequently placed on a mechanical shaker for 24 hr at 25°. Unreacted $ClO_2F$ (16.89 mmol) was removed *in vacuo* at 25°, indicating that 73.4% of the CsF had been converted to $CsClO_2F_2$.

## Results and Discussion

**Synthesis and Properties.**—The synthesis and properties of $CsClO_2F_2$ were in good agreement with those previously reported.[1] The hydrolysis of $CsClO_2F_2$ was studied by exposing a sample of $CsClO_2F_2$ between AgCl plates to atmospheric moisture and by monitoring the changes in its infrared spectrum. It was shown that the decrease of the relative intensity of the bands characteristic for $ClO_2F_2^-$ (see below) was accompanied by the appearance of the bands characteristic[3,4] for the $ClO_3^-$ and $HF_2^-$ anions. This indicates the hydrolysis reaction $ClO_2F_2^- + H_2O \rightarrow ClO_3^- + 2HF$.

**Vibrational Spectra.**—Figures 1 and 2 show the infrared and Raman spectra, respectively, of solid $CsClO_2F_2$. Weak absorptions owing to $ClO_3^-$ (960, 940, 620, and 480 $cm^{-1}$) and $HF_2^-$ (1420 and 1230 $cm^{-1}$) were almost always observed in the infrared spectrum. The appearance of the $ClO_3^-$ and $HF_2^-$ bands in the infrared spectrum is due to the pronounced hygroscopicity of $CsClO_2F_2$ and to the small sample size used for infrared spectroscopy. The observed frequencies are listed in Table I, together with their assignment.

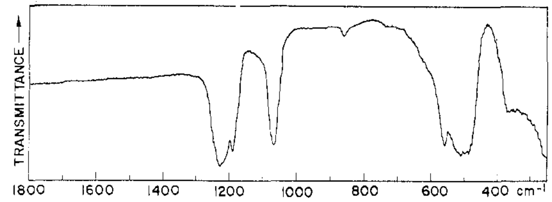

Figure 1.—Infrared spectrum of solid $Cs^+ClO_2F_2^-$ as dry powder in an AgBr disk.

Numerous structural models can be written for $ClO_2F_2^-$. However, their number can be restricted since the chlorine central atom possesses a free electron pair which should be sterically active. Consequently, this chlorine atom should be pentacoordinated, thus resulting in a pseudo-trigonal-bipyramidal structure for $ClO_2F_2^-$. For this structural type, five different arrangements of the ligands are possible. Comparison with the known structures of related molecules, such as substituted phosphorus pentafluorides,[5-10] $XeO_2F_2$,[11] or $IO_2F_2^-$,[12] shows that the two axial positions are always occupied by the two most electronegative ligands.[13] Theoretical explanations for this behavior have previously been given.[13-16] Therefore, the most plausible structure for $ClO_2F_2^-$ is

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(3) J. L. Hollenberg and D. A. Dows, *Spectrochim. Acta*, **16,** 1155 (1960).

(4) J. A. Salthouse and T. C. Waddington, *J. Chem. Phys.*, **48,** 5274 (1968).

(5) I. R. Beattie, K. M. S. Livingston, and D. J. Reynolds, *ibid.*, **51,** 4269 (1969).

(6) R. R. Holmes, *ibid.*, **46,** 3730 (1967), and references cited therein.

(7) J. A. Salthouse and T. C. Waddington, *Spectrochim. Acta, Part A*, **23,** 1069 (1967).

(8) J. E. Griffiths, *J. Chem. Phys.*, **49,** 1307 (1968).

(9) J. Goubeau, R. Baumgärtner, and H. Weiss, *Z. Anorg. Allg. Chem.*, **348,** 286 (1966).

(10) A. J. Downs and R. Schmutzler, *Spectrochim. Acta, Part A*, **23,** 681 (1967).

(11) H. H. Claassen, E. L. Gasner, H. Kim, and J. L. Huston, *J. Chem. Phys.*, **49,** 253 (1968).

(12) L. Helmholz and M. T. Rogers, *J. Amer. Chem. Soc.*, **62,** 1537 (1940).

(13) R. F. Hudson, *Angew. Chem., Int. Ed. Engl.*, **6,** 749 (1967).

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(15) P. C. Van Der Vorm and R. S. Drago, *J. Amer. Chem. Soc.*, **88,** 3255 (1966).

(16) L. S. Bartell, *Inorg. Chem.*, **5,** 1635 (1966).

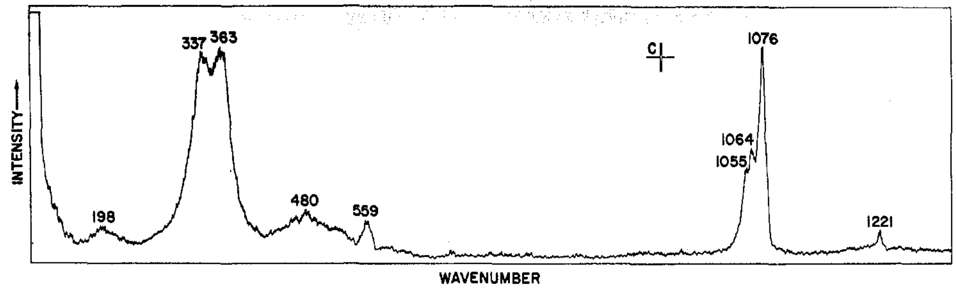
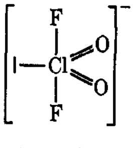


Figure 2.—Raman spectrum of solid $Cs^+ClO_2F_2^-$; sample container, glass capillary; C indicates spectral slit width.



This type of structure has also been suggested[11] for $XeO_2F_2$ which is isoelectronic with $ClO_2F_2^-$.

The correctness of the proposed model can be tested by inspection of the observed vibrational spectrum. Spectroscopically, this model should contain the elements of the $ClO_2^+$ cation and the $ClF_2^-$ anion, both of which have recently been characterized.[17-20] The $ClO_2^+$ cation is preferred over the $ClO_2$ radical and $ClO_2^-$ anion because $ClO_2^+$ and $ClO_2F_2^-$ contain a chlorine of the same oxidation state (+V). Furthermore, in $ClO_2F_2^-$, the electron-withdrawing effect of the two highly electronegative fluorine ligands is expected partially to compensate for the bond weakening influence of the formal negative charge. On the other hand, one should expect the two ClF bonds to be rather weak for the following reasons. Generally, in chlorine fluorides, replacement of two fluorine atoms by one doubly bonded oxygen atom significantly weakens the remaining ClF bond.[21] Furthermore, the formal negative charge in anions always decreases the ClF bond strength by increasing the ionic contribution to these bonds. This can be easily understood since the formal negative charge will not be concentrated at the central atom but will be distributed mainly over the highly electronegative fluorine ligands. Since $ClO_2F_2^-$ contains two doubly bonded oxygen atoms and a formal negative charge, the ClF bonds in $ClO_2F_2^-$ should be at least as weak as or weaker than in $ClF_2^-$. A closer inspection of Table I immediately reveals that the above predictions are indeed correct. The three fundamentals involving only a motion of the $ClO_2$ part of the ion exhibit frequencies very close to those of $ClO_2^+$ [17] and $ClO_2F$.[22] The bands assignable to the three corresponding $ClF_2$ motions show frequencies somewhat lower than those[20] observed for $ClF_2^-$.

All nine fundamentals expected for $XO_2F_2$ of symmetry $C_{2v}$ (these are classified as $4\ A_1 + A_2 + 2\ B_1 + 2\ B_2$) were observed if a coincidence of $\nu_7(B_1)$ and $\nu_9(B_2)$ at 337 $cm^{-1}$ is assumed. This double coincidence might account for the surprisingly high relative intensity of the 337-$cm^{-1}$ Raman band and has also been observed[11] for isoelectronic $XeO_2F_2$. The assignment of the observed bands to the individual modes is straightforward and was made by comparison with the known spectra of the related molecules listed in Table I. Comparison between the corresponding XF modes in $XeO_2F_2$[11] and $ClO_2F_2^-$ shows that the deformational modes have similar frequencies but that the XeF stretching frequencies are considerably higher than the ClF ones. This is not surprising since Cl and Xe do not belong to the same period of the periodic system. Generally, by going to the next higher period, the electronegativity of the central atom decreases and its size increases, thus resulting in an increase of the XF stretching and a decrease of the XF deformation force constants, respectively. This effect causes the stretching and deformation frequencies to move further apart with increasing mass number and has been observed for several series of related molecules and ions, such as $ClF_5$, $BrF_5$, $IF_5$;[23] $SF_5^-$, $SeF_5^-$, $TeF_5^-$;[24] $ClF_2^+$, $BrF_2^+$;[25] or $ClF_4^-$, $BrF_4^-$.[26] The assignment of the weak and broad Raman band at 480 $cm^{-1}$ to $\nu_5(A_2)$ should be considered tentative. This band may contain some contribution from $\nu_6(B_1)$; however, its band center at 480 $cm^{-1}$ differs by 30 $cm^{-1}$ from the band center observed for $\nu_6$ in the infrared spectrum (510 $cm^{-1}$) and, hence, should belong to a different mode. In addition to the bands assigned to fundamental vibrations, a weak band was observed at 855 $cm^{-1}$ in the infrared spectrum of $ClO_2F_2^-$. This band cannot be due to a fundamental vibration and, hence, is assigned to the combination band, $\nu_3 + \nu_6(B_1)$. The splitting of $\nu_1(A_1)$ into three components in the Raman spectrum and of $\nu_8(B_2)$ into two components in the infrared spectrum is too large to be due to the two different chlorine isotopes. One would expect the isotope splittings in $ClO_2F_2^-$ to be similar to those found for $ClO_2^+$ [17] and $ClO_2F$.[22] Since the $ClO_2F_2^-$ spectra were recorded for crystalline samples, other effects, such as site symmetry splittings, are possible.

In summary, the observed number of bands, their frequencies, and relative intensities in both the infrared and Raman spectra are consistent with the predicted pseudo-trigonal-bipyramidal structure of symmetry $C_{2v}$. The agreement between the spectrum of $ClO_2F_2^-$ and those of related molecules is excellent.

**Force Constants.**—A normal-coordinate analysis was carried out to aid in the spectral assignment. The

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(17) K. O. Christe, C. J. Schack, D. Pilipovich, and W. Sawodny, *Inorg. Chem.*, **8**, 2489 (1969).

(18) H. A. Carter, W. M. Johnson, and F. Aubke, *Can. J. Chem.*, **47**, 4619 (1969).

(19) A. I. Karelin, K. Nikitina, Yu. Ya. Khavitonov, and V. Ya. Rosolovskii, *Russ. J. Inorg. Chem.*, **15**, 941 (1970).

(20) K. O. Christe, W. Sawodny, and J. P. Guertin, *Inorg. Chem.*, **6**, 1159 (1967).

(21) K. O. Christe, unpublished results.

(22) D. F. Smith, G. M. Begun, and W. H. Fletcher, *Spectrochim. Acta*, **20**, 1763 (1964).

(23) G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, **42**, 2236 (1965).

(24) K. O. Christe, C. J. Schack, E. C. Curtis, and D. Pilipovich, *Inorg. Chem.*, in press.

(25) K. O. Christe and C. J. Schack, *ibid.*, **9**, 2296 (1970).

(26) K. O. Christe and C. J. Schack, *ibid.*, **9**, 1852 (1970).

kinetic and potential energy metrics were computed by a machine method,[27] assuming the following geometry: $r_{\mathrm{ClF}} = 1.79$ Å, $R_{\mathrm{ClO}} = 1.43$ Å, $\alpha = \angle \mathrm{OClO} = 120°$, $\beta = \angle \mathrm{OClF} = 90°$, and $\angle \mathrm{FClF} = 180°$. The ClF distance was taken as somewhat larger than those[28] of the two longer bonds in $\mathrm{ClF_3}$ due to the uncommonly low stretching frequencies in $\mathrm{ClO_2F_2^-}$. The ClO distance was estimated from the bond length–frequency correlation of Robinson.[29] The bond angles were assumed to be those of an ideal trigonal bipyramid, although they might be slightly reduced due to repulsion by the lone pair in accord with the Gillespie–Nyholm theory.[30]

The force constants were calculated by trial and error with the aid of a time-sharing computer to get exact agreement between the observed and computed frequencies using the simplest possible modified valence force field, *i.e.*, keeping the number of nonzero off-diagonal interaction terms at a minimum. Owing to the underdetermined nature of the problem (17 force constants from 9 vibrational frequencies), unique force constants could not be computed. However, numerical experiments established that some of the principal force constants are quite independent of the chosen interaction constants and, hence, should approach those of a general valence force field. The computed values are $f_R = 8.3$, $f_{RR} = 0.1$, $f_r = 1.6$, and $f_{rr} = -0.1$ mdyn/Å; $f_\alpha = 1.95$, $f_\beta = 1.2$, $f_{\beta\beta}' = 0.57$, and $f_{\beta\beta} = 0.1$ mdyn/Å radian$^2$; and $f_{r\beta} - f_{r\beta}' = 0.3$ mdyn/Å radian. The deformation coordinates were weighted by unit (1 Å) distance.

The force constants of greatest interest are the stretching force constants since they are a direct measure for the strength of the various bonds. Comparison with the values obtained for a number of related molecules and ions (see Table II) indicates for $\mathrm{ClO_2F_2^-}$ double-bond character for the two chlorine– oxygen bonds and unusually weak ClF bonds. The value of the Cl═O stretching force constant, $f_R$, is slightly lower than those in $\mathrm{ClO_2^+}$ [17] and $\mathrm{ClO_2F}$.[22] This slight decrease might be explained by factors such as the influence of the formal negative charge, change in hybridization due to the altered coordination number of the central atom, and different physical states (solid *vs.* gas). Hence, no attempt will be made to evaluate the relative contributions from each effect.

TABLE II

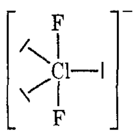
STRETCHING FORCE CONSTANTS (MDYN/Å) OF $\mathrm{ClO_2F_2^-}$ COMPARED TO THOSE OF RELATED MOLECULES AND IONS

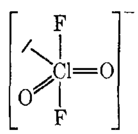
| | $\mathrm{ClO_2F_2^-}$ | $\mathrm{ClO_2^+}$ [a] | $\mathrm{ClO_2}$ [b] | $\mathrm{ClO_2^-}$ [c] | $\mathrm{ClO_2F}$ [d] | $\mathrm{ClF_2^-}$ [e] | $\mathrm{ClF_4^-}$ [f] | ClF [g] | $\mathrm{ClF_2^+}$ [h] |
|---|---|---|---|---|---|---|---|---|---|
| $f_R$ | 8.3 | 8.96 | 7.02 | 4.26 | 9.07 | | | | |
| $f_{RR}$ | 0.1 | −0.45 | −0.17 | 0.11 | −0.12 | | | | |
| $f_r$ | 1.6 | | | | 2.53 | 2.35 | 2.11 | 4.36 | 4.74 |
| $f_{rr}$ | −0.1 | | | | | 0.17 | 0.23 | | 0.14 |

[a] Reference 17. [b] M. G. Krishna Pillai and R. F. Curl, Jr., *J. Chem. Phys.*, **37,** 2921 (1962). [c] H. Siebert, "Anwendungen der Schwingungsspektroskopie in der anorganischen Chemie," Springer-Verlag, West Berlin, 1966. [d] Reference 22. [e] Reference 20. [f] K. O. Christe and W. Sawodny, *Z. Anorg. Allg. Chem.*, **374,** 306 (1970). [g] A. H. Nielsen and E. A. Jones, *J. Chem. Phys.*, **19,** 1117 (1951). [h] Reference 25.

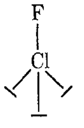
Whereas the ClO bonds in $\mathrm{ClO_2F_2^-}$ exhibit double-bond character, the value of the ClF stretching force constant, $f_r$, of 1.6 mdyn/Å is unusually low. In addition to the reasons discussed above, *i.e.*, oxygen substitution and formal negative charge, weak ClF bonds might be expected since $\mathrm{ClO_2F_2^-}$ has a pseudo-trigonal-bipyramidal structure. As pointed out previously,[31] this type of structure appears to be energetically unfavorable as also indicated by the low thermal stability of the $\mathrm{CsF \cdot ClO_2F}$ adduct.

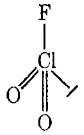
Comparison of the stretching force constant of $\mathrm{ClF_2O_2^-}$ with that[20] of $\mathrm{ClF_2^-}$ is particularly interesting owing to their close structural relationship. Both anions can be derived from a pseudo trigonal bipyramid. In $\mathrm{ClO_2F_2^-}$, two of the three free electron pairs on the Cl in $\mathrm{ClF_2^-}$ have been replaced by two doubly bonded oxygen atoms without significantly changing the geometry of the rest of the ion, *i.e.*





Hence, a pronounced decrease of the ClF stretching force constant from $\mathrm{ClF_2^-}$ (2.35 mdyn/Å)[20] to $\mathrm{ClF_2O_2^-}$ (1.6 mdyn/Å) should truly reflect the influence of the doubly bonded oxygen ligands. Comparison of the related pair





shows that the decrease of $f_r$ (see Table II) from ClF to $\mathrm{ClO_2F}$ is even larger than for the pair $\mathrm{ClF_2^-}$, $\mathrm{ClO_2F_2^-}$. The same trend has been found for a number of other molecules[21] and, hence, appears to be quite general.

The small negative value of the ClF stretch–stretch interaction constant, $f_{rr}$, is comparable to that found[32] for $\mathrm{KrF_2}$ for which an explanation was given by Coulson.[33] The values found for the OClF and OClO deformation constants are as expected. The large values found for the interaction constant $f_{\beta\beta}'$ and the stretch–bend interaction term, $f_{r\beta}$, are in accord with those obtained for the halogen pentafluoride molecules.[23]

From the above discussion of the stretching force constants, it became obvious that the Cl═O bonds are predominantly covalent, whereas the ClF bonds contain strong contributions from ionic bonds. This finding confirms the previous predictions[34] postulating the following bond model for a trigonal-bipyramidal type moiety with a free electron pair on the central atom. The two most electronegative ligands, *i.e.*, fluorine atoms, occupy the axial positions and the two oxygen atoms and the free electron pair the three equatorial positions of the trigonal bipyramid. The equatorial bonds should have mainly sp$^2$ character (ignoring the double-bond contributions), whereas the axial bonds involve

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mainly a delocalized p-electron pair of the chlorine central atom for the formation of a semiionic three-center four-electron p–$\sigma$ bond pair.[20,35–38] For an ideal semiionic three-center four-electron bond, one should therefore expect $f_r$ to have a value about half that of a covalent ClF bond. The low value of 1.6 mdyn/Å obtained for $\mathrm{ClO_2F_2^-}$ obviously fulfills these requirements (covalent ClF bonds show stretching force constants ranging from about 3.5 to 4.7 mdyn/Å) and supports the above bond model.

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# Microwave Spectrum, Structure, Dipole Moment, and Quadrupole Coupling Constants of Chlorodifluorophosphine[1]

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The microwave spectra of $\mathrm{PF_2{}^{35}Cl}$ and $\mathrm{PF_2{}^{37}Cl}$ have been analyzed. The structural parameters are: $d(\mathrm{PF}) = 1.571 \pm 0.003$ Å, $d(\mathrm{PCl}) = 2.030 \pm 0.006$ Å, $\angle\mathrm{FPF} = 97.3 \pm 0.2°$, and $\angle\mathrm{FPCl} = 99.2 \pm 0.2°$. The dipole moment was determined to be $0.89 \pm 0.01$ D and the quadrupole coupling constants in $\mathrm{PF_2{}^{35}Cl}$ are $\chi_{aa} = -39.3 \pm 0.3$, $\chi_{bb} = 20.7 \pm 0.3$, and $\chi_{cc} = 18.6 \pm 0.3$ MHz. For $\mathrm{PF_2{}^{37}Cl}$, $\chi_{aa} = -31.1 \pm 0.3$, $\chi_{bb} = 16.6 \pm 0.5$, and $\chi_{cc} = 14.5 \pm 0.5$ MHz.

## Introduction

Chlorodifluorophosphine, $\mathrm{PF_2Cl}$, and dichlorofluorophosphine, $\mathrm{PFCl_2}$, were first prepared more than 30 years ago by the reaction of phosphorus trichloride with antimony trifluoride.[2] At that time the structure of $\mathrm{PFCl_2}$ was determined by electron diffraction[3] and compared to previously determined structures[4] of $\mathrm{PF_3}$ and $\mathrm{PCl_3}$. Since that time the structures of $\mathrm{PF_3}$ and $\mathrm{PCl_3}$ have been determined by microwave spectroscopy[5] and also redetermined by electron diffraction.[6,7]

Recently, a more convenient preparation of $\mathrm{PF_2Cl}$ was reported.[8] Since this compound was the only member of the series $\mathrm{PF}_n\mathrm{Cl}_{3-n}$ whose structure had not been determined, we decided to undertake a study of the microwave spectrum. Further inducement for such a study was provided by the expectation that a determination of the quadrupole coupling constants would yield information about the bonding in this series of phosphorus compounds, a subject of recent discussion.[9]

### Experimental Section

The sample was prepared by reaction of HCl with $\mathrm{(CH_3)_2NPF_2}$ by the method recently described.[8] The sample was purified by trap-to-trap distillation.

The spectra were obtained with a 100-kHz Stark-modulated spectrometer employing backward wave oscillators as microwave sources. The sample was contained in a 1.2-m X-band cell cooled by means of Dry Ice. The frequencies of the transitions were measured to an estimated precision of ±0.05 MHz.

## Microwave Spectrum

All of the measured rotational transitions appeared as multiplets due to the presence of the quadrupolar chlorine nuclei ($I = {}^3/_2$ for both $^{35}$Cl and $^{37}$Cl). The spectra of $\mathrm{PF_2{}^{35}Cl}$ and $\mathrm{PF_2{}^{37}Cl}$ were observed in natural abundance. Assignment of the rotational transitions was based on Stark effects, frequency fit, predicted quadrupole hyperfine splittings, and isotopic shifts. Only *c*-type transitions were observed.

Quadrupole coupling constants in the inertial axis systems were determined for both species by analysis of the hyperfine splittings of transitions with completely resolved multiplets. Hypothetical unperturbed center frequencies were computed for each multiplet and the rotational constants were determined from the hypothetical unsplit frequencies of the $1_{01}$–$2_{11}$, $1_{11}$–$2_{21}$, and $1_{10}$–$2_{20}$ transitions. The frequencies of the hyperfine components are compared with calculated frequencies in Table I. The rotational constants, principal moments of inertia, and principal second moments ($P_{aa} = (I_b + I_c - I_a)/2$, etc.) are given in Table II, and the quadrupole coupling constants appear in Table III.

Calculations based on an assumed structure led to the prediction that the *ac* inertial plane would be the

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