Contribution from Rocketdyne, a Division of North American Rockwell Corporation, Canoga Park, California 91304, and the Abteilung fur Anorganische Chemie, Universitat, Ulm, Germany

Vibrational Spectrum and Force Constants of the SF_5O^- Anion

KARL O. CHRISTE,* CARL J. SCHACK, DONALD PILIPOVICH, E. C. CURTIS, and WOLFGANG SAWODNY

Received August 30, 1972

The $CsF{\cdot}SF_4O$ adduct has been prepared and characterized by infrared and Raman spectroscopy. All eleven fundamental vibrations expected for a pseudooctahedral anion of symmetry C_{4v} have been observed and are assigned. A modified valence force field has been computed for SF_5O^- and suggests an SO bond order of approximately 1.5.

Introduction

The existence of a $CsF{\cdot}SF_4O$ adduct has been reported[1] in 1960 by Smith and Englehardt and in 1964 by Ruff and Lustig.[2] However, no details were given regarding its preparation or properties. In a subsequent paper Lustig and Ruff described[3] the synthesis of $Cs^+SF_5O^-$ from CsF and SF_4O in CH_3CN solution. The ionic formulation of this adduct was substantiated[3] by its ^{19}F nmr spectrum which showed a characteristic AB_4 pattern. The vibrational spectrum of this interesting compound is essentially unknown, since only four infrared absorptions were published.[3] In this paper we wish to report the complete vibrational spectrum of the SF_5O^- anion and the results from a force constant computation.

Experimental Section

Materials and Apparatus. Volatile materials used in this work were manipulated in a well-passivated (with ClF_3) stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke, Inc., 425 1F4Y). Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%). Sulfur oxide tetrafluoride was prepared by the method[2] of Ruff and Lustig from SF_2O and F_2 and was purified by fractional condensation. Cesium fluoride was fused in a platinum crucible and powdered in a drybox prior to use. The purity of the volatile starting materials was determined by measurements of their vapor pressures and infrared spectra. Solid products were handled in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in the range 4000–250 cm^{-1} with an accuracy of ±2 cm^{-1} for sharp bands. 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 with an accuracy of ±2 cm^{-1} using a Coherent Radiation Laboratories Model 52 Ar 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 melting point capillaries were used as sample containers. For the conical tubes the axial viewing–transverse excitation technique and for the capillaries the transverse viewing–transverse excitation techniques were used.

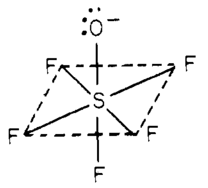
Preparation of $CsSF_5O$. A prepassivated (with ClF_3) 30-ml 316 stainless steel cylinder was loaded with dry, powdered CsF (9.93 mmol). Purified SF_4O (16.1 mmol) was added to the cylinder at −196°. After warming to ambient temperature overnight, the cylinder was heated at 90° for 5 days. Upon recooling to room temperature, all volatiles were removed *in vacuo* and trapped at −196°. The recovered SF_4O (7.32 mmol) indicated that 88.5% of the CsF had been converted to $CsSF_5O$. Confirmation of this was obtained by pyrolyzing a sample of the complex at approximately 250° for 10 min while pumping the evolved gas through a trap cooled to −196°. The evolved gas was identified as SF_4O and the amount found corresponded to an 82% conversion of CsF to $CsSF_5O$. A similar experiment exposing KF to SF_4O at temperatures up to 125° for several days did not result in any complexing.

Results and Discussion

Synthesis and Properties. In the absence of a solvent, heating was required to achieve a significant conversion of CsF to $CsSF_5O$. The conversion obtained in the present study is comparable to that of 76% previously achieved[3] by the use of CH_3CN as a solvent. The reversibility of the formation reaction was demonstrated by the pyrolysis experiment which resulted in SF_4O as the only volatile product. $CsSF_5O$ is a white, crystalline solid and does not show any detectable dissociation pressure at ambient temperature; attempts to synthesize the analogous potassium salt failed under similar reaction conditions. This is not surprising since the stability of salts of this type generally decreases with decreasing cation size.

Vibrational Spectra. Figures 1 and 2 show the Raman and the infrared spectra, respectively, of $CsSF_5O$. The absorption between 300 and 250 cm^{-1} in the infrared spectrum is due to the AgBr window material. The observed frequencies are listed in Table I.

Analogy with isoelectronic SF_5Cl[4,5] and the typical AB_4 ^{19}F nmr pattern previously reported[3] for SF_5O^- suggests the following square-bipyramidal structure of symmetry C_{4v} for SF_5O^-



For this ion of symmetry C_{4v} 11 fundamentals are expected. These are classified as $4\ A_1 + 2\ B_1 + B_2 + 4\ E$. All 11 modes should be Raman active, whereas only the A_1 and E modes should be infrared active. The assignment of the observed bands to the individual modes is given in Table I and is supported by the following arguments. The very intense infrared band at 1154 cm^{-1} must be due to the SO stretching mode. As expected for an A_1 mode it was also observed in the Raman spectrum. Its high frequency rules out any alternate assignment. Comparison with the cor-

---

* Address correspondence to this author at Rocketdyne.

[1] W. C. Smith and V. A. Englehardt, *J. Amer. Chem. Soc.*, 82, 3838 (1960).

[2] J. K. Ruff and M. Lustig, *Inorg. Chem.*, 3, 1422 (1964).

[3] M. Lustig and J. K. Ruff, *Inorg. Chem.*, 6, 2115 (1967).

[4] L. H. Cross, H. L. Roberts, P. Goggin, and L. A. Woodward, *Trans. Faraday Soc.*, 56, 945 (1960).

[5] J. E. Griffiths, *Spectrochim. Acta, Part A*, 23, 2145 (1967).

Table I. Vibrational Spectrum of $CsSF_5O$ Compared to Those of SF_5Cl and IF_5O

Obsd freq, cm^{-1}, and intens						Assignment in point group C_{4v}		Approximate description of vibration
$CsSF_5O$		SF_5Cl[a]		IF_5O[b]				
Ir	R	Ir	R	Ir	R			
1154 vs	1153 (1)	402 s	403 (10) p	927 s	928 (4) p	A_1	ν_1	$\nu(XY)$
735 vs	722 (0.2)	855 vs	833 (0.2) p	680 s	680 (10) p		ν_2	$\nu(XF)$
697 m	697 (10)	707 s	704 (3.0) p	640 w	640 (9+) p		ν_3	$\nu_{sym}(XF_4)$
506 s	506 (1)	602 s	603 (0.2) p	360 s	c		ν_4	δ_{sym}(out-of-plane XF_4)
	541 (3.3)		625 (0.7) dp		640 (9+) p	B_1	ν_5	ν_{sym}(out-of-phase XF_4)
	472 (0.2)			(275)[d]			ν_6	δ_{asym}(out-of-plane XF_4)
	452 (0.9)		505 (0.2) dp		305 (1) dp	B_2	ν_7	δ_{sym}(in-plane XF_4)
785 vs, br	780 (0.1) br	909 vs	927 (0.2) dp	710 vs	700 (0+) sh	E	ν_8	$\nu_{asym}(XF_4)$
606 s	607 (2.2)	287 vw	271 (0.6) dp	369 s	374 (1) dp		ν_9	$\delta(YXF_4)$
530 sh	530 (2)	579 mw	584 (0.1) dp	342 s	340 (4) dp		ν_{10}	$\delta(FXF_4)$
325 mw		441 m	442 (0.8) dp	e	205 (0+)		ν_{11}	δ_{as}(in-plane XF_4)

[a] L. H. Cross, M. L. Roberts, P. Goggin, and L. A. Woodward, *Trans. Faraday Soc.*, **56**, 945 (1969); J. E. Griffiths, *Spectrochim. Acta, Part A*, **23**, 2145 (1967); K. O. Christe, C. J. Schack, and E. C. Curtis, *Inorg. Chem.*, **11**, 583 (1972). [b] D. F. Smith and G. M. Begun, *J. Chem. Phys.*, 43, 2001 (1971). [c] Band masked by ν_9 and ν_{10}. [d] Not observed; value estimated from combination band. [e] Below frequency range of spectrometer used.

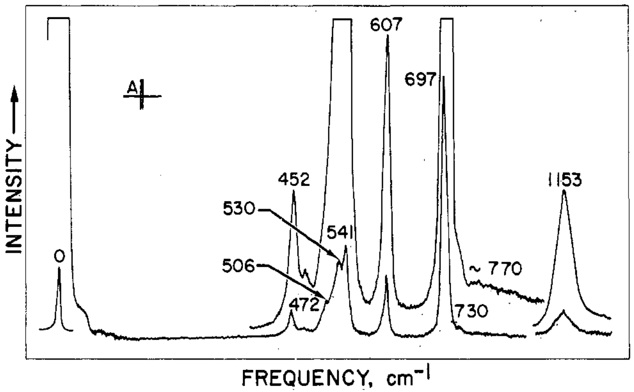


Figure 1. Raman spectrum of solid $Cs^+SF_5O^-$. A indicates spectral slit width.

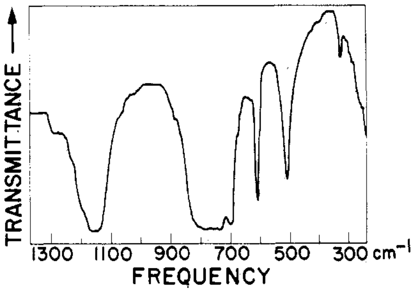


Figure 2. Infrared spectrum of solid $Cs^+SF_5O^-$ as an AgBr disk.

responding mode in SF_3O^+ (1538 cm^{-1})[6] and SF_4O (1380 cm^{-1})[7] shows the expected frequency decrease with an increasing formal negative charge. The SF_5O^- anion should have four additional stretching modes. Three of these belong to the approximately square-planar SF_4 part and one involves the unique fluorine ligand. Of these, the totally symmetric SF_4 stretching mode of species A_1 should result in the most intense Raman line and is consequently assigned to the Raman band at 697 cm^{-1}. As expected for species A_1, this Raman band has an infrared counterpart. The antisymmetric SF_4 and the SF stretching modes in SF_5Cl are both of very high intensity in the infrared and of very low intensity in the Raman spectrum[4,5] and occur at frequencies higher than that of $\nu_{sym}(SF_4)$ (A_1). Consequently, for SF_5O^- these two modes are assigned to the two weak Raman lines at 780 and 722 cm^{-1}, respectively. Of these two, the 780-cm^{-1} line is attributed to $\nu_{as}(SF_4)$ owing to its width, lower Raman intensity, and larger frequency separation from $\nu_{sym}(SF_4)$ (A_1). Both Raman bands show as expected a very intense infrared counterpart. Owing to the broadness of $\nu_{as}(SF_4)$, these two bands are poorly resolved in the infrared spectrum. The broadness of ν_{as} was also observed for several other approximately square-planar XF_4 groups, such as BrF_4^-,[8] ClF_4^-,[9] or those in SF_5^- and SeF_5^-,[10] and hence appears to be quite general. The remaining, yet unassigned, stretching mode, ν_{sym}(out-of-phase SF_4) (B_1), should be of medium Raman intensity, should ideally have no infrared counterpart, and should occur in the range 500–600 cm^{-1}. Since both the 506- and 607-cm^{-1} Raman lines show very intense infrared counterparts, only the 530- or the 541-cm^{-1} line might belong to $\nu_{sym}(SF_4)$ (B_1). Based upon its higher Raman intensity and frequency, we prefer to assign 541 cm^{-1} to $\nu_{sym}(SF_4)$ (B_1).

There are six frequencies left for assignment to the six deformational modes. Of these, the O–SF_4 wagging mode (E) should have the highest frequency since it involves a motion of the oxygen atom which has partial double-bond character (see below). Furthermore, this mode should result in a relatively intense band in both the infrared and Raman spectra. Consequently, this mode is ascribed to 607 cm^{-1}. By comparison with SF_5Cl,[4,5] SF_5^-,[10] and SeF_5Cl[11] one would expect δ_{asym}(in-plane SF_4) (E) to have the lowest frequency of the SF_5 group deformational modes and to be infrared active. Consequently, this mode is assigned to the 325-cm^{-1} infrared band. Of the remaining two yet unassigned infrared-active deformational modes, the δ_{sym}(out-of-plane SF_4) or umbrella mode (A_1) should result in a very intense infrared band of relatively high frequency.[4,5,10,11] Consequently, this mode is assigned to 506 cm^{-1}, leaving 530 cm^{-1} for assignment to the F–SF_4 wagging mode (E). The two remaining, yet unassigned in-

---

(6) M. Brownstein, P. A. W. Dean, and R. J. Gillespie, *Chem. Commun.*, 9 (1970).

(7) P. L. Goggin, H. L. Roberts, and L. A. Woodward, *Trans. Faraday Soc.*, 57, 1877 (1961).

(8) K. O. Christe and C. J. Schack, *Inorg. Chem.*, 9, 1852 (1970).

(9) K. O. Christe and W. Sawodny, *Z. Anorg. Allg. Chem.*, 374, 306 (1970).

(10) K. O. Christe, E. C. Curtis, C. J. Schack, and D. Pilipovich, *Inorg. Chem.*, 11, 1679 (1972).

(11) K. O. Christe, C. J. Schack, and E. C. Curtis, *Inorg. Chem.*, 11, 583 (1972).

Table II. Symmetry Force Constants of SF_5O^- [a]

A_1	ν_1	1154	$F_{11} = f_D$	6.46
	ν_2	733	$F_{22} = f_R$	3.75
	ν_3	697	$F_{33} = f_r + 2f_{rr} + f_{rr}'$	5.43
	ν_4	506	$F_{44} = {}^1/_2(f_\beta + 2f_{\beta\beta} + f_{\beta\beta}' + f_\gamma + 2f_{\gamma\gamma} + f_{\gamma\gamma}' - 2f_{\beta\gamma} - 4_{\beta\gamma}' - 2f_{\beta\gamma}'')$	2.52
			$F_{12} = f_{RD}$	0.66
B_1	ν_5	541	$F_{55} = f_r - 2f_{rr} + f_{rr}'$	3.28
	ν_6	472	$F_{66} = {}^1/_2(f_\beta - 2f_{\beta\beta} + f_{\beta\beta}' + f_\gamma - 2f_{\gamma\gamma} + f_{\gamma\gamma}' - 2f_{\beta\gamma} + 4f_{\beta\gamma}' - 2f_{\beta\gamma}'')$	3.19
B_2	ν_7	452	$F_{77} = f_\alpha - 2f_{\alpha\alpha} + f_{\alpha\alpha}'$	1.46
E	ν_8	785	$F_{88} = f_r - f_{rr}'$	2.84
	ν_9	607	$F_{99} = f_\gamma - f_{\gamma\gamma}'$	2.22
	ν_{10}	530	$F_{1010} = f_\alpha - f_{\alpha\alpha}'$	2.62
	ν_{11}	325	$F_{1111} = f_\beta - f_{\beta\beta}'$	1.21
			$F_{89} = f_{r\gamma} - f_{r\gamma}''$	0.40
			$F_{810} = \sqrt{2}(f_{r\alpha} - f_{r\alpha}')$	0.50
			$F_{811} = f_{r\beta} - f_{r\beta}''$	0.28

[a] Stretching constants in mdyn/Å, deformation constants in mdyn/Å radian^2, and stretch–bend interaction constants in mdyn/Å radian.

frared-inactive modes of species B_1 and B_2, respectively, belong to the Raman lines at 472 and 452 cm^{-1}. Since, for numerous structurally related species, δ_{asym}(out-of-plane SF_4) (B_1) either has not been observed or was of very low intensity,[8,9,12] this mode is assigned to the very weak Raman line at 472 cm^{-1}. Hence, the last yet unassigned Raman line at 452 cm^{-1} should represent δ_{sym}(in-plane SF_4) (B_2).

Comparison of the SF_5O^- assignment with that made for SF_5Cl[4,5] (it should be noted that the assignment given in ref 7 for ν_{11} (E) is likely to be incorrect[11]) shows satisfactory agreement (see Table I). The slight discrepancy in the relative Raman intensities observed for ν_{10} (E) between the two species might be ascribed to increased coupling between ν_9 and ν_{10} in SF_5O^- due to O being more similar in mass to F than Cl. This might result in a symmetric and antisymmetric rather than in a characteristic F-SF_4 and OSF_4 wagging motion. This assumption appears to be supported by the spectrum[13] of isoelectronic IF_5O (see Table I) for which the Raman intensity of ν_{10} is higher than that of ν_9.

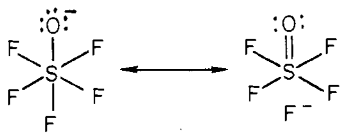
Of the four infrared bands previously reported[3] for $CsSF_5O$ only the two weaker ones agree with our observations. Furthermore, the previously suggested[3] assignment of the SO stretching mode to a broad band centered at 718 cm^{-1} is obviously incorrect.

In summary, all 11 fundamentals of SF_5O^- have been observed and an assignment is offered. The observed vibrational spectrum definitely supports the proposed structural model of symmetry C_{4v}.

Force Constants. A normal-coordinate analysis was carried out to aid the spectral assignment. The kinetic and potential energy metrics were computed by a machine method,[14] assuming the following geometry and coordinate definitions: $R_{SF}' = r_{SF} = 1.60$ Å, $D_{SO} = 1.47$ Å, α (FSF) = β (F′SF) = γ (OSF) = 90°, where F′ refers to the axial (unique) fluorine ligand. The symmetry coordinates used were identical with those reported[13] for IF_5O. The bond lengths were estimated by comparison with similar molecules using the correlation[15] noted by Gillespie and Robinson between stretching frequencies and bond lengths. The deformation coordinates were weighted by unit (1 Å) distance.

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. Unique force constants could not be computed since the general valence field has 36 constants and there are only 11 observed frequencies. It was found, that for the A_1 block the values of F_{11} and F_{22} were strongly influenced by the value of the interaction constant F_{12}. Since in isoelectronic SF_5Cl[16] and in IF_5O[13] the equatorial and axial fluorine atoms do not significantly differ in their stretching force constants and since in SF_5O^- the equatorial SF stretching force constant f_r is about 3.6 mdyn/Å, we prefer for SF_5O^- a force field with $F_{22} = F_R \approx f_r$. Surprisingly, the interaction constant $F_{13} = 2f_{rD}$ had little influence on the frequencies of ν_1 and ν_3. Hence, its value might be comparable to that of F_{12} although it is not required for obtaining a fit between the computed and observed frequencies. The computed symmetry force constants are listed in Table II. The interaction constants not listed were assumed to be zero.

The following values were obtained for the more important internal force constants: $f_D = 6.46, f_R = 3.75, f_r = 3.60, f_{RD} = 0.66, f_{rr} = 0.54$, and $f_{rr}' = 0.75$ mdyn/Å. Significantly larger values of about 4.6 and 7.7 mdyn/Å are possible for f_R and f_D, respectively, by assuming a much smaller value for f_{RD}. However, the resulting large difference between f_R and f_r renders such a force field less likely. In spite of these uncertainties in the force constants, certain conclusions can be reached. The value of the SO stretching force constant f_D (6.5 mdyn/Å) is much lower than those of 10-12 mdyn/Å generally found for S=O double bonds.[15,16] Its value is comparable to that found for the SO_4^{2-} anion (7.44 mdyn/Å[16]) indicating for SF_5O^- a SO bond order of about 1.5. Furthermore, the values of the SF stretching force constants, f_R and f_r, are somewhat lower than those generally found for covalent SF bonds (4.5-6 mdyn/Å[16]) indicating significant ionic contributions to the SF bonds in SF_5O^-. These results are best interpreted in terms of the resonance structures



etc.

These structures together with orbital-following effects could also account for the unusually strong coupling between the SO and SF stretching modes suggested by the force constant computation.

Registry No. CsF·SF_4O, 37862-11-6.

Acknowledgment. We are indebted to the Office of Naval Research, Power Branch, for financial support.

---

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

(13) D. F. Smith and G. M. Begun, *J. Chem. Phys.*, 43, 2001 (1965).

(14) E. C. Curtis, *Spectrochim. Acta, Part A*, 27, 1989 (1971).

(15) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, 41, 2074 (1963).

(16) W. Sawodny, Habilitationsschrift, University of Stuttgart, Stuttgart, Germany, 1969.