these halosulfinate ions would provide a somewhat better basis for discussion, the available vibrational and electronic spectral data do indicate the trend in the S–X bond order to be S–F > S–Cl < S–Br < S–I. For a given cation, the difficulty of removal of SO_2 from the solid solvates also parallels this trend. Since the ionogenic character of halogen-containing solutes in liquid SO_2 is, undoubtedly, due to halosulfinate formation, this trend in stability suggests that iodides and bromides should be more ionized than chlorides. In support of this proposition, Lichtin[62] has indicated that triphenylbromomethane, unlike the corresponding chloride, is almost completely ionized in liquid SO_2. Studies investigating the validity of these suggestions with a variety of halogen-containing molecules are now under way.

Acknowledgments.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. The author also wishes to thank Professor G. E. Leroi of Michigan State University for the use of the laser Raman spectrometer.

[62] N. N. Lichtin in "Carbonium Ions," Vol. I, G. A. Olah and P. von R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1968, p 135.

CONTRIBUTION FROM ROCKETDYNE, A DIVISION OF NORTH AMERICAN ROCKWELL,
CANOGA PARK, CALIFORNIA 91304

Selenium Pentafluoride Chloride, SeF_5Cl. Vibrational Spectrum, Force Constants, and Thermodynamic Properties

BY K. O. CHRISTE,* C. J. SCHACK, AND E. C. CURTIS

Received May 26, 1971

The infrared spectrum of gaseous and the Raman spectrum of liquid SeF_5Cl are reported. The observed spectrum is consistent with symmetry C_{4v}. The structure of SeF_5Cl can be derived from an octahedron with one chlorine and five fluorine atoms occupying the six corners. A modified valence force field and thermodynamic properties in the range 0–2000°K were computed for SeF_5Cl.

Introduction

The existence of the novel selenium fluoride chloride, SeF_5Cl, has recently been discovered.[1] In this paper, we wish to report its vibrational spectrum, force constants, and thermodynamic properties.

Experimental Section

The preparation, purification, physical properties, and handling of SeF_5Cl are described elsewhere.[1] The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in the range of 4000–250 cm^{-1}. The instrument was calibrated by comparison with standard calibration points.[2] Stainless steel cells of 5- or 10-cm path length fitted with AgCl or AgBr windows were used as sample containers. The Raman spectrum of liquid SeF_5Cl was recorded 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 $\sim -25°$, and a dc ammeter. Polarization measurements were carried out using a Model 310 polarization rotator from Spectra-Physics. Clear Kel-F tubes (~2-mm i.d.) were used as sample containers in the transverse viewing–transverse excitation technique.

Results and Discussion

Vibrational Spectrum.—Figures 1 and 2 show the infrared spectrum of gaseous SeF_5Cl and the Raman spectrum of liquid SeF_5Cl, respectively. The observed frequencies are listed in Table I.

Since SeF_5Cl can be considered as a monosubstituted derivative of octahedral SeF_6, it should belong to point group C_{4v}. The 11 normal modes of SeF_5Cl of symmetry C_{4v} can be classified as $4\,a_1 + 2\,b_1 + b_2 + 4\,e$. Of these, all 11 modes will be Raman active, whereas only the a_1 and e modes will be infrared active. Of the Raman lines, the four a_1 modes should be polarized, the rest being depolarized. The assignment of the observed bands to individual modes (Table I) is based on the following arguments. There are four clearly polarized Raman lines at 721, 656, 443, and 385 cm^{-1}. As predicted by theory, these have counterparts in the infrared spectrum. Hence, these four bands must belong to species a_1. The two higher frequency lines are within the range expected for stretching modes of mainly covalent Se–F bonds. They are assigned, respectively, to the SeF and the symmetric SeF_4 stretching vibrations on the basis of their relative Raman intensities.[3] Similarly, the SeCl stretching mode should be of higher Raman intensity than the SeF_4 umbrella deformation.[3] Therefore, the 443-cm^{-1} band is assigned to the SeF_4 deformation. This assignment is further supported by the fact that in the infrared spectra of both $SeF_4(OF)_2$ and SeF_5OF[4] very strong infrared bands were observed at about 430 cm^{-1}.

Of the remaining six depolarized Raman bands, the 745-, 424-, and 336-cm^{-1} lines have counterparts in the infrared region and, consequently, belong to species e. The very intense infrared band at 745 cm^{-1} obviously represents the antisymmetric SeF_4 stretching vibration. For $SeF_4(OF)_2$ and SeF_5OF, this mode was observed[4] at 743 and 750 cm^{-1}, respectively. By analogy with the known spectrum[3,5] of the SF_5Cl molecule, one might

---

[1] C. J. Schack, R. D. Wilson, and J. F. Hon, *Inorg. Chem.*, **11**, 208 (1972).

[2] E. K. Plyler, A. Danti, L. R. Blaine, and E. D. Tidwell, *J. Res. Nat. Bur. Stand.*, **64**, 841 (1960).

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

[4] J. E. Smith and G. H. Cady, *Inorg. Chem.*, **9**, 1293 (1970).

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

TABLE I

VIBRATIONAL SPECTRUM OF SeF_5Cl

Obsd freq, cm^{-1}		Assignment for point group C_{4v}
Infrared, gas	Raman, liquid	
1449 vw		$2\nu_1 = 1442$ (A_1)
1380 w		$\nu_5 + \nu_8 = 1381$ (E)
865 vw		$\nu_3 + \nu_9 = 861$ (E)
821 w		$\nu_3 + \nu_4 = 824$ (A_1)
745 vvs	745 (0.3) dp	ν_8(e)
729 ms, sh	721 (1.8) p	ν_1(a_1)
654 w	656 (10) p	ν_2(a_1)
...	636 (0.6) dp	ν_5(b_1)
587 vw		$\nu_7 + \nu_{11} = 593$ (E)
529 w		
468 w, sh		
440 vs	443 (2.2) p	ν_3(a_1)
421 s	424 (0.4) dp	ν_9(e)
384 mw	385 (8.5) p	ν_4(a_1) Cl^{35}
...	380 dp	ν_7(b_2) + ν_4(a_1) Cl^{37}
334 m	336 (1.2) dp	ν_{10}(e)
	213 (1.4) dp	ν_{11}(e)

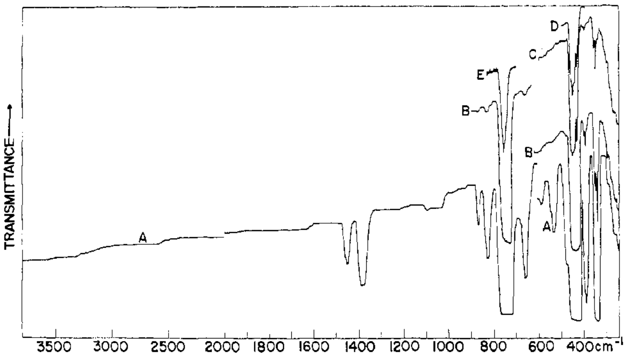

Figure 1.—Infrared spectrum of gaseous SeF_5Cl at 434 (A), 40 (B), 10 (C), 2 (D), and 1.5 mm (E) pressure in a 10-cm cell; window material AgBr.

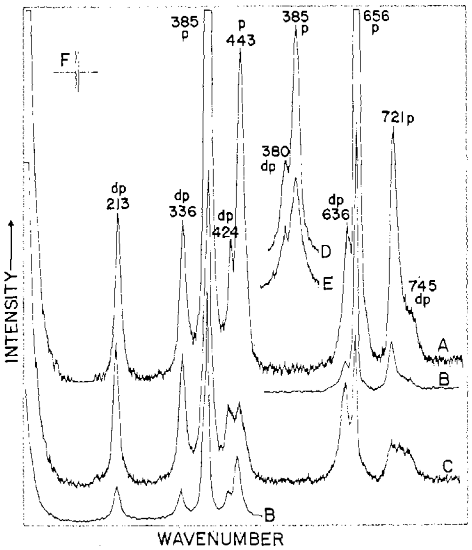

Figure 2.—Raman spectrum of liquid SeF_5Cl: traces A, B, and D, incident polarization perpendicular; traces C and E, incident polarization parallel. Traces A and B were recorded at different recorder voltages; traces D and E, under higher resolution. Experimental conditions were identical for A and C and for D and E, except for change of direction of polarization. F indicates spectral slit width.

expect the F–SeF_4 wagging to have the highest and the $ClSeF_4$ wagging mode to have the lowest frequency of the three remaining e modes, with the antisymmetric in-plane SeF_4 deformation being intermediate. Consequently, the bands at 424 and 336 cm^{-1} are assigned to the F–Se–F_4 wagging and the antisymmetric in plane SeF_4 deformation modes, respectively. Since the infrared spectrum was not recorded below 250 cm^{-1}, it is not known if the 213-cm^{-1} Raman band has indeed a counterpart in the infrared spectrum. However, the assignment of the 213-cm^{-1} Raman line to the fourth e mode, the Cl–SeF_4 wagging mode, appears very plausible for the following reasons. The SeCl stretching mode, ν_4, occurs at a frequency (385 cm^{-1}) considerably lower than those of the three SeF_4 stretching modes. Hence, the Cl–SeF_4 deformation frequency should be lower than 300 cm^{-1} and must be assigned to 213 and not to 380 cm^{-1}, the only remaining alternative.

TABLE II

FUNDAMENTAL FREQUENCIES OF SeF_5Cl AND SF_5Cl[a]

		SF_5Cl	SeF_5Cl
a_1	ν_1 $\nu(XF')$	855	729
	ν_2 $\nu_{sym}(XF_4)$	707	654
	ν_3 $\delta_{sym}(XF_4)$ out of plane	602	440
	ν_4 $\nu(XCl)$	402	384
b_1	ν_5 $\nu_{sym}(XF_4)$ out of phase	625	636
	ν_6 $\delta_{as}(XF_4)$ out of plane	...	...
b_2	ν_7 $\delta_{sym}(XF_4)$ in plane	505	380
e	ν_8 $\nu_{as}(XF_4)$	909	745
	ν_9 $\delta(FXF_4)$	579	421
	ν_{10} $\delta_{as}(XF_4)$ in plane	441	334
	ν_{11} $\delta(ClXF_4)$	287	213

[a] Frequency values taken from ref 3.

For the assignment of the remaining three (2 b_1 and b_2) modes, we are left with only two Raman lines. The unobserved Raman line is assumed to be the antisymmetric out-of-plane SeF_4 deformation mode, ν_6. The fact that this mode has not been observed is not surprising. For the structurally similar halogen pentafluorides (ClF_5, BrF_5, and IF_5) and for SF_5^- and TeF_5^-,[6] all belonging to point group C_{4v}, this mode was not observed. Of the two available Raman lines (636 and 380 cm^{-1}), the higher frequency value obviously belongs to the symmetric out-of-phase SeF_4 stretching mode, leaving the 380-cm^{-1} band to be assigned to the SeF_4 scissoring mode.

In the infrared spectrum of the gas, several bands of very low relative intensity were observed which cannot be attributed to fundamental vibrations. Most of them can satisfactorily be assigned to overtones and combination bands (see Table I).

The above given assignments rest mainly on the Raman lines, the polarization measurements, relative intensities, and the presence or absence of counterparts in the infrared spectrum. It appears interesting to examine to what extent the infrared band contours agree with theoretical predictions. It should be kept in mind, however, that band contours are sometimes subject to unpredictable changes and, hence, do not always agree with the predictions. Ideally, the a_1 modes should show PQR structure as expected for parallel bands of a symmetric-top molecule with I_A and I_B being similar to I_C. Indeed, ν_3 and ν_4 show the expected band shape. The band shape of ν_1 is not clear-cut; however, its band shape may have been influenced by Coriolis interaction with ν_8(e), which occurs at almost the same frequency. The band contour of ν_2 does not show a sharp PQR structure. This was also the case for ν_2 of SF_5Cl.[3,5]

---

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

The band contour of ν_9(e) agrees with that expected for a perpendicular band, but that of ν_{10} closely resembles that of the parallel bands. It is interesting to note that ν_{10}(e) of SF_5Cl[3] and the corresponding ν_9(e) mode of ClF_5[7] also showed a PQR structure different from those of the remaining perpendicular bands in species e. The fact that the band contour of the lowest perpendicular band resembles those of the parallel bands has been observed for a number of symmetric-top molecules and can be attributed to first-order Coriolis perturbations.[8] In summary, the band contours of SeF_5Cl agree well with those[3] observed for SF_5Cl, even though differing somewhat from those predicted on the basis of the rigid-rotor, harmonic-oscillator approximation.

Comparison between the vibrational spectra of SF_5Cl[3,5] and SeF_5Cl shows good agreement. However, the SeF_5Cl data and results from force constant calculations[9] indicate that for SF_5Cl, the original assignment of the S–Cl wagging mode, ν_{11}(e), to the 287-cm^{-1} band by Cross, *et al.*,[5] should be retained. The revision of this assignment by Griffiths[3] was based on the fact that he observed an infrared counterpart for the 396-cm^{-1} Raman band. The latter, however, might equally well be interpreted as the ^{37}Cl isotope band of the S–Cl stretching mode, ν_4, at 402 cm^{-1}, the splitting and relative intensity being in good agreement with predictions. Furthermore, the infrared spectrum of SF_5Cl showed[3] a broad band at about 280 cm^{-1} which might represent the counterpart to the Raman band at 271 cm^{-1}. Hence, the original assignment[5] for ν_{11} does not violate the selection rules and results in a more reasonable frequency value. The high relative intensity of the 396-cm^{-1} band in the Raman spectrum of SF_5Cl and its infrared activity also argue against its proposed assignment[5] to ν_6 since for all the remaining related molecules, it either has not been observed or has been of very low intensity. Consequently, we propose that for SF_5Cl, ν_6 either has not been observed or is hidden underneath the intense ν_4 band. In summary, the vibrational spectrum of SeF_5Cl is consistent with symmetry C_{4v}. Ten out of eleven fundamentals were observed and assigned in agreement with the selection rules for 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,[9] assuming the following geometry and coordinate definitions: $R_{SeF'} = 1.68$ Å, $D_{SeCl} = 2.14$ Å, $r_{SeF} = 1.68$ Å, $\alpha = \angle FSeF = 90°$, $\beta = \angle F'SeF = 90°$, and $\delta = \angle ClSeF = 90°$, where F′ refers to the axial (unique) fluorine ligand. The deformation coordinates were weighted by unit (1 Å) distance. The bond lengths were estimated using the Schomaker–Stevenson rule.[10]

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 38 constants and there are only ten observed frequencies. However, numerical experiments showed 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 $f_R = 4.42$, $f_D = 2.75$, $f_r = 4.31$, $f_{rr} = 0.07$, and $f_{rr'} = 0.35$ mdyn/Å; $f_\alpha = 1.26$, $f_\beta = 1.92$, $f_\delta = 1.16$, $f_{\beta\beta'} = 0.30$, and $f_{\delta\delta'} = 0.18$ mdyn/Å radian^2; and $f_{D\delta} = 0.28$ mdyn/Å radian. The two interactions $f_{\beta\beta'}$ and $f_{\delta\delta'}$ were determined from only one symmetry force constant value making the assumption $f_{\beta\beta'}/f_{\delta\delta'} = f_\beta/f_\delta$.

The values of the stretching force constants f_R and f_r of SeF_5Cl are not significantly different indicating similar bonding for both the axial and the equatorial fluorine ligands. Furthermore, their magnitude (4.3–4.4 mdyn/Å) approximates those obtained for other mainly covalent, hexavalent selenium compounds such as SeF_6 (5.01 mdyn/Å),[11] SeO_2F_2 (4.44 mdyn/A),[12] or SeO_3F^- (4.23 mdyn/Å)[12] with bond orders[12-14] close to 1. The slight decrease of the stretching force constant values from SeF_6[11] toward SeF_5Cl parallels that found for the analogous pair SF_6[15] and SF_5Cl[12] (see Table III).

TABLE III

STRETCHING FORCE CONSTANTS (IN MDYN/Å) OF SeF_6 AND SeF_5Cl COMPARED TO THOSE OF SF_6 AND SF_5Cl

	SF_6[a]	SF_5Cl[b]	SeF_6[c]	SeF_5Cl
R		4.83		4.42
	5.26		5.01	
f_r		4.52		4.31

[d] Reference 15. [b] Reference 12. [c] Reference 11.

It can be explained by the substitution of one fluorine atom in XF_6 by a less electronegative ligand, such as Cl. This causes an increased polarity ($S^{\delta+}$–$F^{\delta-}$) of the remaining SF bonds. Since stretching force constants reflect only the contributions from covalent bonding,[12,14] their value should correspondingly decrease. The interaction constants are in accord with our experience with similar molecules.[6] The value given for $f_{D\delta}$ was determined from $\sqrt{2}(f_{D\delta} - f_{D\beta}) \approx 0.4$, which was required to fit ν_3 and ν_4. This is not too surprising considering the mixing of the two modes (see Table IV).

TABLE IV

POTENTIAL ENERGY DISTRIBUTION FOR SeF_5Cl[a]

a_1	ν_1	729	$0.88f_R$
	ν_2	654	$0.90f_r$
	ν_3	440	$0.41f_D + 0.36f_\beta + 0.21f_\delta + 0.11f_R$
	ν_4	384	$0.58f_D + 0.15f_\beta + 0.15f_\delta$
b_1	ν_5	636	$0.95f_r$
	ν_6	(336)	$0.54f_\beta + 0.33f_\delta$
b_2	ν_7	380	$1.10f_\alpha - 0.10f_{\alpha\alpha'}$
e	ν_8	745	$1.00f_r$
	ν_9	421	$1.04f_\beta - 0.16f_{\beta\beta'}$
	ν_{10}	334	$0.79f_\alpha$
	ν_{11}	213	$1.02f_\delta - 0.16f_{\delta\delta'}$

[a] Contributions of less than 0.10 are not listed.

No evidence was found for the similar terms $f_{R\beta}$, $f_{r\beta}$, and $f_{r\delta}$ being nonzero, although this cannot be ruled out and might be expected from our experience with similar molecules[6] or from orbital following arguments.

---

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

(8) R. E. Moynihan, Ph.D. Dissertation, Purdue University, 1954; University Microfilms, Ann Arbor, Mich., Publication 9881.

(9) E. C. Curtis, Rocketdyne Report R-6768, Oct 1966.

(10) L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 229.

(11) S. Abramowitz and I. W. Levin, *Inorg. Chem.*, **6**, 538 (1967).

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

(13) H. Siebert, *Z. Anorg. Allg. Chem.*, **273**, 170 (1953).

(14) J. Goubeau, *Angew. Chem.*, **78**, 565 (1966).

(15) A. Ruoff, *J. Mol. Struct.*, **4**, 332 (1969).

TABLE V

COMPUTED THERMODYNAMIC PROPERTIES OF SeF_5Cl[a]

T, °K	$C_p°$	$H° - H°_0$	$-(F° - H°_0)/T$	$S°$
0	0	0	0	0
100	12.035	0.895	51.149	60.103
200	21.720	2.604	58.534	71.554
298.15	27.800	5.062	64.494	81.472
300	27.885	5.113	64.600	81.644
400	31.338	8.091	69.959	90.186
500	33.331	11.333	74.746	97.412
600	34.548	14.732	79.053	103.605
700	35.336	18.228	82.954	108.994
800	35.870	21.790	86.512	113.750
900	36.248	25.397	89.778	117.998
1000	36.524	29.037	92.795	121.832
1100	36.731	32.700	95.596	125.323
1200	36.891	36.381	98.208	128.526
1300	37.016	40.077	100.656	131.484
1400	37.116	43.784	102.957	134.231
1500	37.197	47.499	105.128	136.795
1600	37.264	51.223	107.183	139.198
1700	37.320	54.952	109.134	141.458
1800	37.367	58.686	110.989	143.593
1900	37.406	62.425	112.759	145.614
2000	37.440	66.167	114.450	147.534

[a] Units for $C_p°$, $S°$, and $F°$ are calories, moles, and degrees Kelvin; for $H°$ units are kilocalories and moles.

Coriolis coupling coefficients were computed for SeF_5Cl in the belief that the e-block band contours could support the assignment. The computed values using the above given force constants were $\zeta_8 = 0.5$, $\zeta_9 = 0.5$, $\zeta_{10} = -0.4$, and $\zeta_{11} = 0.7$. However, the values of the moments of inertia are such that these values for ζ do not result in very distinctive band shapes.[8] The band shapes are further complicated by the natural chlorine and selenium isotopes and by hot bands. Although the observed band shapes are not inconsistent with those predicted, the contours could not be used to verify the computed ζ's.

The potential energy distribution was computed using the above force constants and is shown in Table IV. The assignment listed in Table I is supported by these values. The mixing of ν_3 and ν_4 is large, so that, strictly, one is not a stretching and one a deformational mode, but rather a symmetric and antisymmetric combination of the two motions.

Thermodynamic Properties.—The thermodynamic properties were computed for this molecule using the rigid-rotor, harmonic-oscillator[16] approximation. The results are given in Table V. The frequencies used were those of Table II, assuming a computed value of 336 cm^{-1} for ν_6. The moments of inertia used were $I_x = I_y = 312$ and $I_z = 214$ amu Å^2 computed from the geometry assumed above, with a symmetry factor of 4.

Acknowledgment.—We are indebted to Dr. D. Pilipovich for continuous encouragement and to Dr. J. Cape for the use of the Raman spectrometer. This work was supported by the Office of Naval Research, Power Branch.

---

(16) J. E. Mayer and M. G. Mayer, "Statistical Mechanics," Wiley, New York, N. Y., 1940.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
McMASTER UNIVERSITY, HAMILTON, ONTARIO, CANADA

The Formation of Br_2^+, Br_3^+, $BrOSO_2F$, and $Br(OSO_2F)_3$ by the Oxidation of Bromine with Peroxydisulfuryl Difluoride in Solution in Fluorosulfuric Acid and the Superacid System SbF_5–$3SO_3$–HSO_3F

BY R. J. GILLESPIE* AND M. J. MORTON

Received July 15, 1971

The oxidation of bromine with peroxydisulfuryl difluoride, $S_2O_6F_2$, in solution in fluorosulfuric acid and in the superacid system SbF_5–$3SO_3$–HSO_3F has been studied by electrical conductivity and magnetic susceptibility measurements and by Raman spectroscopy. It is shown that in fluorosulfuric acid solution Br_3^+, $BrOSO_2F$, and $Br(OSO_2F)_3$ are stable species although $BrOSO_2F$ is disproportionated to some extent into Br_3^+ and $Br(OSO_2F)_3$. In the superacid system SbF_5–$3SO_3$–HSO_3F the Br_2^+ cation can also be obtained, but it is not very stable and is in equilibrium with the disproportionation products Br_3^+ and $BrOSO_2F$. The Raman spectra of the bromine cations Br_2^+ and Br_3^+ and the bromine fluorosulfates $BrOSO_2F$ and $Br(OSO_2F)_3$ have been obtained and the resonance Raman spectrum of the Br_2^+ cation is described.

The I_2^+ and I_3^+ cations of iodine are well established[1,2] but at the time the present investigation was commenced there was no evidence for the existence of the corresponding bromine cations Br_2^+ and Br_3^+. Although the I_3^+ cation is stabilized by the very weak basicity of sulfuric acid, the I_2^+ cation is almost completely disproportionated in this solvent and it needs the still weaker basicity of fluorosulfuric acid to enable it to exist in sufficient concentration for identification by its intense blue color (λ_{max} 640 nm). Nevertheless, the very small concentration of I_2^+ in 100% sulfuric acid can be detected by its strong-resonance Raman spectrum.[3] It is to be expected that the corresponding bromine cations would be stronger Lewis acids than the iodine cations and that they would only be stable in still less basic media than can be used to stabilize the iodine cations. Thus although Br_3^+ might be obtained in solution in fluorosulfuric acid it was anticipated that it would probably need the acidity of the superacid system SbF_5–$3SO_3$–HSO_3F[4] to stabilize the Br_2^+ cation.

---

(1) R. J. Gillespie and J. B. Milne, *Inorg. Chem.*, **5**, 1577 (1966).

(2) R. A. Garrett, R. J. Gillespie, and J. B. Senior, *ibid.*, **4**, 563 (1965).

(3) R. J. Gillespie and M. J. Morton, *J. Mol. Spectrosc.*, **30**, 178 (1969).

(4) R. C. Thompson, J. Barr, R. J. Gillespie, J. B. Milne, and R. A. Rothenbury, *Inorg. Chem.*, **4**, 1641 (1965).