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Contribution from Rocketdyne, a Division of
Rockwell International, Canoga Park, California 91304

The Hexafluorobromine(VII) Cation, BrF$_6^+$. Infrared Spectrum and Force Field

Karl O. Christe* and Richard D. Wilson

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The syntheses of BrF$_6^+$AsF$_6^-$ and BrF$_6^+$Sb$_2$F$_{11}^-$ from BrF$_5$ and the corresponding KrF$_2$·(Lewis acid) adducts have recently been reported by Gillespie and Schrobilgen.[1,2] These BrF$_6^+$ salts were characterized by ^{19}F nmr and Raman spectroscopy.[2] Since complete vibrational spectra and modified valence force fields are known for ClF$_6^+$ [3] and IF$_6^+$,[4-6] similar information on BrF$_6^+$ was desirable to obtain more quantitative data on the bonding in these unusual high oxidation state cations.

Experimental Section

Apparatus and Materials. The materials used in this work were manipulated in a well-passivated (with ClF$_3$ and BrF$_5$) 304 stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke, Inc., 4251 F4Y). Pressures were measured with a Heise Bourdon tube type gauge (0–1500 mm ± 0.1%). Because of the rapid hydrolytic interaction with moisture, all materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer. The spectra of solids at room temperature were obtained by pressing two small single-crystal platelets of either AgCl or AgBr to a disk in a Wilks minipellet press. The powdered sample was placed between the platelets before starting the pressing operation. The low-temperature spectra were recorded at −196° using a cell and transfer technique similar to one previously described.[7] The inner windows of the cell were AgCl; the outer ones, CsI disks. The instrument was calibrated by comparison with standard calibration points.[8]

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line and a Claassen filter[9] for the elimination of plasma lines. For low-temperature work a Miller Harney device[10] was used. Passivated quartz, Teflon FEP, or Kel-F capillaries were used as sample tubes in the transverse-viewing, transverse-excitation technique.

Debye–Scherrer powder patterns were taken using a GE Model XRD-6 diffractometer with copper Kα radiation and a nickel filter. Samples were sealed in quartz capillaries (~0.5-mm o.d.).

The purification of BrF$_5$ and AsF$_5$ and the preparation of BrF$_5$·2SbF$_5$ have previously been described.[11] Krypton difluoride was prepared from Kr (Matheson, 99.995%) and F$_2$ using glow discharge at −183°. Our method was similar to that[12] of Schreiner, *et al.*, except for the elimination of the gas circulation system. The KrF$_2$ was collected at the end of a run in a tared Teflon FEP U trap maintained at −78°. The only detectable impurity in the KrF$_2$ was a small amount of N$_2$O$_5$ which could be removed by treatment of the crude KrF$_2$ with BF$_3$ at −78 and −10°, which converted the N$_2$O$_5$ to nonvolatile NO$_2^+$BF$_4^-$.[13] Pure KrF$_2$ was obtained by pumping off the volatile material and trapping the KrF$_2$ at −78°.

Preparation of BrF$_6^+$ Salts. The BrF$_6^+$AsF$_6^-$ salt was prepared by the method of Gillespie and Schrobilgen[2] using a KrF$_2$:AsF$_5$ mole ratio of 2:1 and a large excess of BrF$_5$. Complete material balances were obtained for the experiments. The yields of BrF$_6^+$AsF$_6^-$ were found to range from 5.3 to 7.0 mol % based on KrF$_2$ and the correct amounts of Kr and F$_2$ were evolved.

For the synthesis of the SbF$_5$ salt, weighed amounts of BrF$_4^+$Sb$_2$F$_{11}^-$ were dissolved in BrF$_5$, and KrF$_2$ was added at −196°. The mixture was kept at 25° until no further gas evolution was observed. Volatile materials were removed at room temperature. The Raman spectrum of the solid residue was identical with that previously reported.[2] Since in a separate experiment we had demonstrated that BrF$_4^+$Sb$_2$F$_{11}^-$ can be removed under a dynamic vacuum at 50°, this residue was warmed to 50° for 1 week under a dynamic vacuum. Starting originally with 1.02 mmol of BrF$_4^+$Sb$_2$F$_{11}^-$ and 7.63 mmol of KrF$_2$, 23.2 mg of a white solid residue was obtained which according to its infrared and Raman spectra was mainly BrF$_6^+$SbF$_6^-$·xSbF$_5$ with x being less than 1.

Results and Discussion

Synthesis and Properties. The synthesis data are in excellent agreement with the reports[2] of Gillespie and Schrobilgen. The following observations deserve some comment. In the previous study[2] no material balances were obtained. In our study the yield of BrF$_6^+$AsF$_6^-$ was found to be about 6 mol % based on the assumption that 1 mol of KrF$_2$ could produce 1 mol of BrF$_6^+$ salt. In addition, it was established that BrF$_6^+$SbF$_6^-$·xSbF$_5$ can be separated from BrF$_4^+$Sb$_2$F$_{11}^-$ by vacuum sublimation. However, the resulting product was not of sufficient quantity and purity to allow further characterization and to determine whether the anion was mainly SbF$_6^-$ or Sb$_2$F$_{11}^-$. When samples of BrF$_6^+$ salts were placed in passivated quartz capillaries and flame sealed, Raman spectroscopy showed that at ambient temperature the BrF$_6^+$ salts attacked the quartz with formation of the corresponding O$_2^+$ salts. Similarly, the BrF$_6^+$ salts interacted at ambient temperature with AgCl. The attack of AgCl by BrF$_6^+$AsF$_6^-$ was much faster than that by the corresponding SbF$_5$ salt and preempted the recording of BrF$_6^+$AsF$_6^-$ infrared spectra at room temperature. In Teflon FEP containers the BrF$_6^+$ salts were stored at room temperature for prolonged periods without noticeable decomposition.

X-Ray Powder Data. The observed and calculated X-ray powder diffraction data for BrF$_6^+$AsF$_6^-$ are listed in Table I. The pattern was corrected for lines[14] due to NO$_2^+$AsF$_6^-$ resulting from the interaction[13] between AsF$_5$ and some N$_2$O$_5$ which was present as an impurity in the KrF$_2$ starting material. The powder pattern of BrF$_6^+$AsF$_6^-$ very closely resembles that[4,15] of IF$_6^+$AsF$_6^-$ indicating that the two compounds are isomorphous. By analogy with IF$_6^+$AsF$_6^-$, it was indexed in the face-centered cubic system with $a = 9.394$ Å. As expected, the unit cell of BrF$_6^+$AsF$_6^-$ is slightly smaller than that of

Table I. X-Ray Powder Data for $BrF_6^+AsF_6^-$

d, Å					
Obsd	Calcd	Intens	h	k	l
4.69	4.69	vs	2	0	0
3.32	3.32	s	2	2	0
2.712	2.712	ms	2	2	2
2.509	2.511	w	3	2	1
2.102	2.100	m	4	2	0
2.002	2.003	w	3	3	2
1.916	1.918	ms	4	2	2
1.661	1.661	m	4	4	0
1.565	1.566	ms	4 6	4 0	2 0
1.486	1.486	mw	6	2	0
1.417	1.416	mw	6	2	2
1.356	1.356	w	4	4	4
1.302	1.303	m	6	4	0
1.278	1.279	vw	7 6 5	2 3 5	1 3 2
1.256	1.255	m	6	4	2
1.193	1.193	w	7 6	3 5	2 1
1.174	1.174	w	8	0	0
1.140	1.141	mw	8 6	2 4	0 4
1.107	1.107	mw	8 6	2 6	2 0
1.077	1.078	w	6	6	2
1.051	1.050	w	8	4	0
1.025	1.025	w	8	4	2
0.940	0.939	w	8 10	6 0	0 0
0.922	0.921	w	10	2	0

$IF_6^+AsF_6^-$ (9.49 Å).[4,15] This relatively small change in the unit cell dimensions is not surprising because the small radii of the +VII halogen ions allow them to occupy interstices in the fluoride packing. Assuming four molecules per unit cell and neglecting contributions to the volume from the highly charged central atoms, a plausible average volume[16,17] of 17.27 $Å^3$ per F and a calculated density of 3.068 g/cm^3 are obtained.

Weaker lines were observed having mixed, even and odd Miller indices. These are not expected for a simple NaCl structure but can readily be explained[4,15] by scattering from the fluorine atoms grouped around the Br and As atoms with these central atoms occupying the positions of Na and Cl in the NaCl lattice. By analogy with $IF_6^+AsF_6^-$,[15] the space group of $BrF_6^+AsF_6^-$ is *Pa*3.

Vibrational Spectra. The infrared spectra of $BrF_6^+AsF_6^-$ and of $BrF_6^+SbF_6^-{\cdot}xSbF_5$ after the removal of $BrF_4^+Sb_2F_{11}^-$ are shown in Figure 1. The Raman spectra of $BrF_6^+AsF_6^-$ and of the SbF_5 adduct before the removal of $BrF_4^+Sb_2F_{11}^-$ were identical with those previously reported.[2] The Raman spectrum of the SbF_5 adduct after the removal of $BrF_4^+Sb_2F_{11}^-$ had its most intense band at 660 cm^{-1} (ν_1 of SbF_6^-) with two pronounced shoulders on its high-frequency side. In addition to weak bands attributable to $Sb_2F_{11}^-$ stretching modes and to the SbF deformational modes in the 300–220 cm^{-1} frequency range, the BrF_6^+ deformation $\nu_5(F_{2g})$ was observed at 406 cm^{-1}.

In addition to the three previously reported[2] Raman-active modes, octahedral BrF_6^+ is expected to exhibit two infrared-active fundamentals. These are the antisymmetric stretch, $\nu_3(F_{1u})$, and the antisymmetric deformation, $\nu_4(F_{1u})$. By comparison with the known frequencies of the closely related ClF_6^+, IF_6^+, SF_6, SeF_6, and TeF_6 species, ν_3 and ν_4 of BrF_6^+ are expected to occur between 760 and 800 and between 400 and 450 cm^{-1}, respectively. Inspection of Figure 1 reveals that in both the AsF_5 and the SbF_5 adduct bands were observed at 775 and 430 cm^{-1}. Furthermore, these bands disappeared when the $BrF_6^+AsF_6^-$ ir sample was allowed to

Table II. Symmetry and Internal Force Constants (mdyn/Å) of BrF_6^+ Compared to Those of Related Octahedral Species[a]

		PF_6^-	AsF_6^-	SbF_6^-	SF_6			SeF_6			TeF_6			ClF_6^+			BrF_6^+	IF_6^+
		F_{44} = min	F_{44} = min	F_{44} = min	GVFF[b]		F_{44} = min	GVFF[c]		F_{44} = min	GVFF[d]		F_{44} = min	$f_{rr'} = 0$		F_{44} = min	F_{44} = min	F_{44} = min
A_{1g}	$F_{11} = f_r + 4f_{rr} + f_{rr'}$	6.23	5.21	4.77		6.70[e]			5.59[e]			5.44[e]			5.16		4.88	5.61
E_g	$F_{22} = f_r - 2f_{rr} + f_{rr'}$	3.52	3.61	3.52		4.61[e]			4.86[e]			5.03[e]			4.44		5.02	6.00
F_{1u}	$F_{33} = f_r - f_{rr'}$	4.36	3.82	3.86	5.26		5.80	4.88		4.85	4.98		4.95	4.68		5.28	4.82	5.23
	$F_{34} = 2(f_{r\alpha} - f_{f\alpha}'')$	0.91	0.33	0.14	0.89		1.10	0.44		0.42	0.24		0.19	0.73		0.96	0.41	0.21
	$F_{44} = f_\alpha + 2f_{\alpha\alpha} - 2f_{\alpha\alpha}'' - f_{\alpha\alpha}'''$	0.83	0.55	0.30	1.04		1.02	0.64		0.65	0.40		0.41	0.96		0.93	0.63	0.45
F_{2g}	$F_{55} = f_\alpha - 2f_{\alpha\alpha}' + f_{\alpha\alpha}'''$	0.63	0.38	0.21		0.77[e]			0.46[e]			0.28[e]			0.74		0.46	0.32
	f_r	4.39	3.98	3.90	5.28		5.55	4.99		4.98	5.07		5.06	4.68		4.98	4.90	5.42
	f_{rr}	0.45	0.27	0.21		0.35			0.12			0.07			0.12		−0.03	−0.07
	$f_{rr'}$	0.03	0.16	0.04	0.02		−0.25	0.11		0.13	0.09		0.11	0		−0.30	0.08	0.19

[a] Frequencies (cm^{-1}) of ν_1-ν_5 used for force field computations: PF_6^-, 746, 561, 817, 557, 475; AsF_6^-, 682, 568, 696, 385, 369; SbF_6^-, 653, 561, 667, 280, 273; SF_6, 773.5, 641.7, 947.9, 614.5, 525; SeF_6, 706.9, 658.7, 778.5, 436, 405; TeF_6, 697.1, 670.3, 751, 326.5, 314; ClF_6^+, 679, 630, 890, 582, 513; BrF_6^+, 660, 670, 775, 430, 405; IF_6^+, 708, 732, 790, 343, 340. [b] Reference 19. [c] Reference 21. [d] Reference 20. [e] Using Raman frequencies from H. H. Claassen, G. L. Goodman, J. L. Holloway, and H. Selig, *J. Chem. Phys.*, 53, 341 (1970).

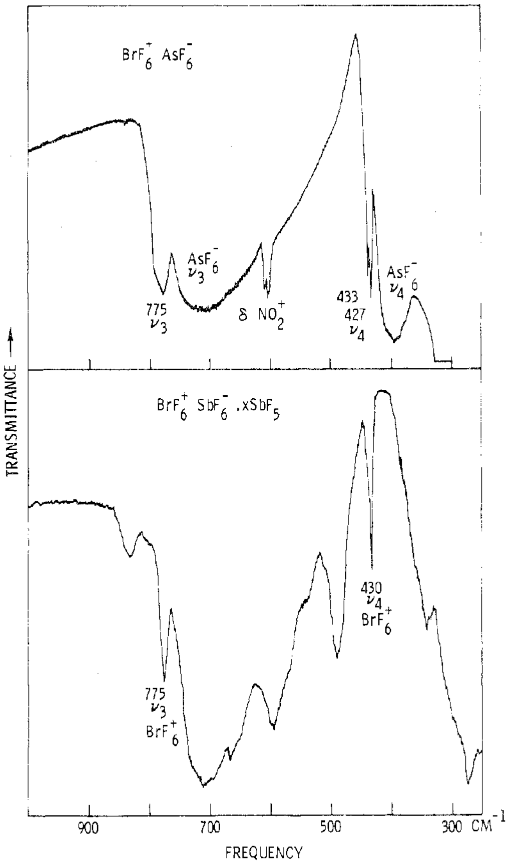

Figure 1. Infrared spectra of $BrF_6{}^+AsF_6{}^-$ recorded as a dry powder between AgCl plates at −196° and of $BrF_6{}^+SbF_6{}^-\cdot xSbF_5$ recorded as a AgBr disk at 25°. The increase in background at the low-frequency end of the spectra is due to absorption by the windows.

warm to ambient temperature or when the ir sample of the SbF_5 adduct was kept at ambient temperature for several hours. The remaining bands in the infrared spectra changed only little, thus supporting the assignment of the 775- and 430-cm^{-1} bands to ν_3 and ν_4, respectively, of the powerful oxidizing species $BrF_6{}^+$. The ready interaction between $BrF_6{}^+$ and the silver halide window material can also account for the weakening of the intensity of the $BrF_6{}^+$ infrared bands in the room-temperature spectrum of the SbF_5 adduct.

In $BrF_6{}^+AsF_6{}^-$, the 430-cm^{-1} band shows a splitting of 6 cm^{-1}. Since the two components are of similar intensity, splitting due to the $^{79}Br^{81}Br$ isotopes must be considered. The following arguments augur against the splitting being caused by the bromine isotopes and favor its attribution to crystal field or site symmetry effects. (i) The SbF_5 adduct does not show a comparable splitting. (ii) The observed splitting of 6 cm^{-1} is much larger than that (~2 cm^{-1}) predicted for the Br isotopes. (iii) The $NO_2{}^+$ deformation in the same spectrum shows a comparable splitting. (iv) The site symmetry of $BrF_6{}^+$ in space group *Pa*3 is only C_{3i}.

Force Constants. Since both the infrared- and the Raman-active fundamentals are now known, it was interesting to compute a force field for $BrF_6{}^+$. This allows a more quantitative comparison of the relative bond strength of $BrF_6{}^+$ with those of related species.

Except for the F_{1u} block, all the symmetry force constants of $BrF_6{}^+$ are unique. The F_{1u} block is undetermined since only two frequency values are available for the determination of three force constants. Consequently, the usefulness of mathematical constraints, such as minimizing or maximizing the value of one of the symmetry force constants,[18] was tested for the isoelectronic series SF_6, SeF_6, and TeF_6, for which general valence force fields have been reported.[19-21] As can be seen from Table II, the condition F_{44} = minimum very closely duplicates the GVFF values for the two heavier molecules SeF_6 and TeF_6. Therefore, it is also expected to be a very good approximation for the force field of $BrF_6{}^+$. The values so obtained for $BrF_6{}^+$ are listed in Table II and correlate well with the remaining species of Table II. The modified valence force fields, listed for the lightest isoelectronic series, *i.e.*, $PF_6{}^-$, SF_6, and $ClF_6{}^+$, are less reliable since the lighter central atoms cause stronger coupling of the stretching and bending modes.

The force constant of greatest interest is the stretching force constant f_r. For $BrF_6{}^+$ its value of 4.9 mdyn/Å is the highest found to date for any BrF bond.[23-25] This is not surprising since the covalency and therefore also the force constant of such a bond tend to increase with increasing oxidation state of the central atom and a formal positive charge.[22] Since the Br–F bonds in $BrF_6{}^+$ are stronger than those in other bromine fluorides, the reactivity of these salts must be due to the high oxidizing power of $BrF_6{}^+$.

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Registry No. $BrF_6{}^+AsF_6{}^-$, 51063-29-7; $BrF_6{}^+SbF_6{}^-$, 53432-26-1; $PF_6{}^-$, 16919-18-9; $AsF_6{}^-$, 16973-45-8; $SbF_6{}^-$, 17111-95-4; SF_6, 2551-62-4; SeF_6, 7783-79-1; TeF_6, 7783-80-4; $ClF_6{}^+$, 38217-33-3; $IF_6{}^+$, 21303-14-0; $BrF_6{}^+$, 51063-27-5.

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Contribution from the Department of Chemistry,
University of Houston, Houston, Texas 77004

Carbon-13 Nuclear Magnetic Resonance Studies of Borane Adducts of Trimethylamine

R. A. Geanangel

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A recent study of ether–boron trihalide adducts by ^{13}C nmr (cmr) has shown[1] that the chemical shifts of the α-carbon