Tetramethylammonium Difluorobromate(I), $(CH_3)_4N^+BrF_2^-$

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The thermolysis of $(CH_3)_4N^+Br(OCF_3)_2^-$ between −70 and −10 °C, evolving F_2CO during the decomposition, gave $(CH_3)_4N^+BrF_2^-$. The characterization of $(CH_3)_4N^+BrF_2^-$ was carried out by IR, Raman, and ^{19}F- and ^{13}C-NMR. For BrF_2^- two infrared absorption bands at 236 and 450 cm^{-1} and one band in the Raman spectrum at 460 cm^{-1} were observed in accord with a centrosymmetric structure. Ab initio calculations are presented for BrF_2^- the isoelectronic KrF_2, and other related compounds with $D_{\infty h}$ symmetry.

Introduction

Fluorohalogenates $[XF_2]^-$ (X = Cl, Br, I) are well-known from the literature. However, a controversy about their vibrational spectroscopy is still going on.[1−6]

The first triatomic fluorohalogenate, ClF_2^-, was prepared by Christe and Guertin in 1965.[1] It was based on the reaction of ClF with NOF and identified by infrared spectroscopy. Later the full characterization of ClF_2^- was achieved via Raman and IR spectra with cesium, rubidium, and potassium as cations.[2] The theoretically predicted linear structure with $D_{\infty h}$ symmetry was apparently not observed. The IR spectra showed an intense band attributed to ν_s(Cl−F), which is forbidden for a linear centrosymmetric structure. The difference between the theoretically predicted $D_{\infty h}$ symmetry and the experimental results was explained as a result of crystal field effects.

First attempts to prepare IF_2^- were described by Meinert and Klamm.[7] Unfortunately no spectroscopic data were reported. Further attempts to synthesize IF_2^- failed.[8,9] Only disproportion products such as I_2 and Cs_3IF_6 were obtained.[8]

The synthesis and full characterization of $(C_2H_5)_4N^+IF_2^-$ was recently performed by Naumann and Meurer, by the direct reaction of IF with $(C_2H_5)_4N^+F^-$.[3] Two IR- and one Raman-active frequencies were observed in the vibrational spectra. This is consistent with a linear structure of symmetry $D_{\infty h}$.

The first attempts to prepare BrF_2^- from CsF and BrF were described by Surles et al.[4] The Raman spectrum of the reaction product showed four frequencies instead of the one frequency expected for $D_{\infty h}$ symmetry. Surles et al. explained their data with symmetry reduction from $D_{\infty h}$ to C_{2v}. The synthesis of $Cs^+BrF_2^-$ by codepositing CsBr salt with an argon/fluorine mixture was described by Miller and Andrews.[6] In the IR spectrum of the deposit, two bands at 533 and 527 cm^{-1} were attributed to the BrF_2^- anion, while the IR-active deformation frequency was not observed.

Although many attempts to prepare BrF_2^- were made since 1965, the anion could never be isolated and its symmetry is still unclear because of conflicting spectroscopic data.

For the preparation of BrF_2^-, alkali-metal cations should not be used as counterions to avoid distortions of the anion which are well described in the literature.[2−4]

Recently we reported the preparation of the new bromate(I) salt $(CH_3)_4N^+(CF_3O)_2Br^-$.[10] The compound was synthesized by the reactions of $(CH_3)_4N^+Br^-$ or $(CH_3)_4N^+BrCl_2^-$ with an excess of CF_3OCl at −78 °C. It was assumed, that the salt might be a suitable precursor for $(CH_3)_4N^+BrF_2^-$.

Experimental Section

All synthetic work and sample handling were performed by employing standard Schlenk techniques and a standard glass vacuum line. The glass vacuum line and the reaction vessels were dried by vacuum and treated with CF_3OCl. Nonvolatile materials were handled under dry nitrogen. CF_3OCl was prepared, according to the literature method, from F_2CO with ClF and a CsF catalyst.[22,23] The infrared spectra were recorded on a Bruker IFS 113v FT-IR spectrometer in a cooled cell[24] equipped with CsBr plates.

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The Raman spectra were recorded on a T 64000 Jobin Yvon, using the 514.5 nm exciting line of an Ar^+ laser tube (Spectra Physics). Owing to their hygroscopic nature, the BrF_2^- salts were measured in the dry nitrogen atmosphere of a duran glass cell.[25]

The NMR spectra of $(CH_3)_4N^+BrF_2^-$ in CH_3CN solution were recorded at −38 °C on a Bruker AM 300 with $CFCl_3$ as external reference.

Preparation of $(CH_3)_4N^+BrF_2^-$. A dry 35 mL cap glass vessel containing 1 g (3.08 mmol) of tetramethylammonium bis(trifluoromethoxy)bromate(I) $(CH_3)_4N^+(CF_3O)_2Br^-$ [10] was slowly warmed from −78 to −10 °C. Carbonyl difluoride, which is formed during the thermolysis, was removed continously. The completion of the reaction was checked by weighing the reaction product. $(CH_3)_4N^+BrF_2^-$ is a colorless solid which is extremely sensitive toward hydrolysis and can be stored without decomposition at −70 °C for several weeks. At room temperature in a disproportionation reaction the solid decomposes into Br^- and BrF_4^-, whereas the solution decomposes at −35 °C.

Ab Initio Calculations. Ab initio calculations for BrF_2^- were performed with the Gaussian 94 program[27] at the Hartree−Fock level using standard 3-21G*, 6-31*, 6-31+G*, and 6-311G** basis sets. Including electron correlation, the anion was also calculated at the MP2 level of theory and with a 6-31+G* basis set. Harmonic vibrational frequencies were computed for the minimum-energy structures and scaled by empirical factors to maximize their fit with the experimentally observed frequencies. The calculated frequencies for all basis sets are corrected throughout by 10% on the Hartree−Fock level[28,29] and by 5% when electron correlation is taken into account.[30]

For a consistent comparison with the isoelectronic KrF_2 and other related compounds, only calculations on a small 3-21G* basis set could be performed. However, it is well-known that a 3-21G* basis set is already quite successful in accounting for hypervalent structures. The mean absolute deviations of calculated from experimental bond lengths between heavy atoms are only 1.5 pm for this basis set which is the same as for the larger 6-31G* basis. The same is true for calculated frequencies where the scatter in the 3-21G* data is much less than that resulting from the 3-21G basis.[31]

Results and Discussion

Formation and Stability. The thermolysis of $(CH_3)_4N^+(CF_3O)_2Br^-$ in the temperature range −70 to −10 °C (eq 1)

$$(CH_3)_4N^+(CF_3O)_2Br^- \xrightarrow{-70\text{ to }-10\ °C} (CH_3)_4N^+BrF_2^- + 2F_2CO \quad (1)$$

yields tetramethylammonium difluorobromate(I), $(CH_3)_4N^+BrF_2^-$. $(CH_3)_4N^+BrF_2^-$ can be stored at −70 °C for several weeks without decomposition. The salt disproportionates at room temperature to $(CH_3)_4N^+BrF_4^-$ and Br_2.

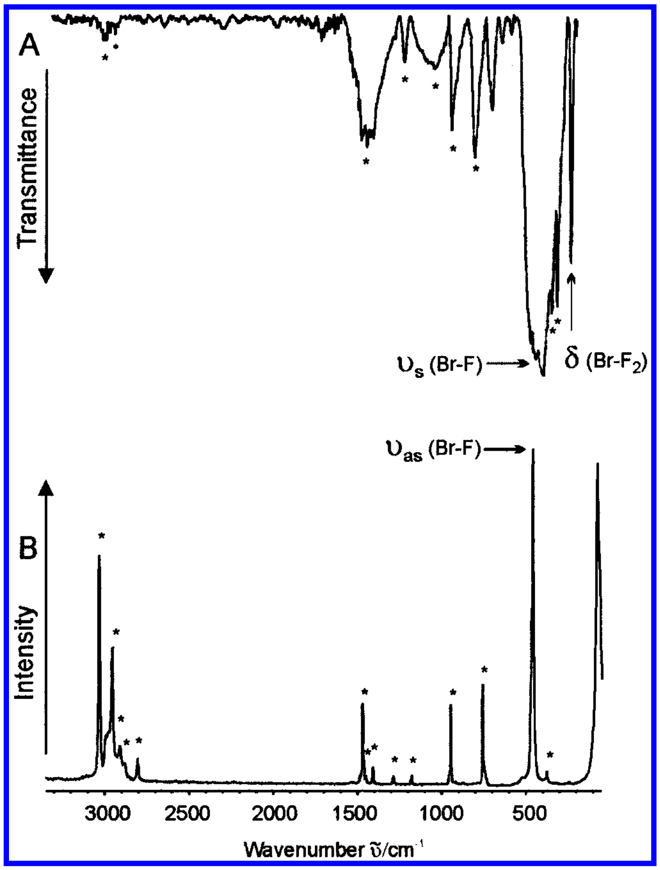

Figure 1. Vibrational spectra of $(CH_3)_4N^+BrF_2^-$: Trace A, spectrum of the solid on CsBr plates at −70 °C; trace B, Raman spectrum of the solid at −78 °C (cation bands marked with an asterisk).

Table 1. Raman and Infrared Frequencies[a] of $(CH_3)_4N^+BrF_2^-$

Raman	IR	assgnt
470 (sh)		2δ(F−Br−F)
460 (100)		ν_s(Br−F)
	450 (vs, br)	ν_{as}(Br−F)
	236 (m)	δ(F−Br−F)
79 (96)		lattice
66 (70)		lattice
	3048 (w)	$\nu(CH_3)$
3036 (69)	3035 (w)	$\nu(CH_3)$
2958 (43)	2964 (w)	$\nu(CH_3)$
2913 (14)		$\nu(CH_3)$
2829 (11)		$2\delta_s(CH_3)$
1474 (27)	1483 (sh)	$\delta_{as}(CH_3)$
1449 (8)	1455 (vs)	$\delta_{as}(CH_3)$
1412 (8)	1424 (m)	$\delta_s(CH_3)$
	1399 (vw)	$\rho(CH_3)$
1290 (5)	1288 (w)	$\rho(CH_3)$
1178 (6)	1181 (w)	$\rho(CH_3)$
	1033 (m)	$\rho(CH_3)$
950 (26)	953 (vs)	$\nu_{as}(C_4-N)$
759 (32)	750 (w)	$\nu_s(C_4-N)$
	709 (m)	
	470 (sh)	$\delta_{as}(C_4-N)$
	455 (m)	$\delta_s(C_4-N)$
377 (2)		$\delta(C_4-N)$

[a] Frequencies in cm^{-1}.

Vibrational Spectra. The Raman and infrared spectra of $(CH_3)_4N^+BrF_2^-$ are shown in Figure 1. The observed frequencies are listed in Table 1 along with their assigments. Figure 2 shows expanded sections of the Raman spectrum of $(CH_3)_4N^+BrF_2^-$ (A) as well as of the decomposition spectrum of BrF_2^- (B). Figure 3 depicts a correlation diagramm of the experimental and calculated frequencies.

The assignment for the normal modes of the tetramethylammonium cation is obtained from comparison with tetramethylammonium tetrafluorohalogenates(III) $(CH_3)_4N^+ClF_4^-$

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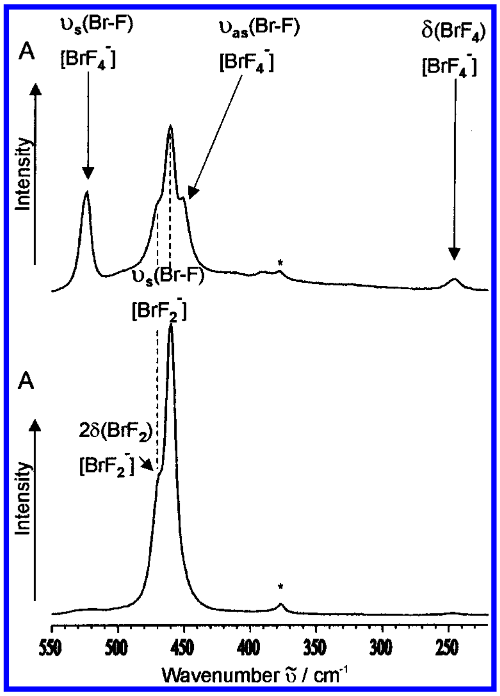

Figure 2. Trace A: Scale expansion of the Raman spectrum of $(CH_3)_4N^+BrF_2^-$ and assignment of the resonances. Trace B: Partial decomposition of $(CH_3)_4N^+BrF_2^-$. Beside ν_s(Br−F) and the first overtone δ(F−Br−F) of BrF_2^-, disproportionation product BrF_4^- is seen (cation bands marked with an asterisk).

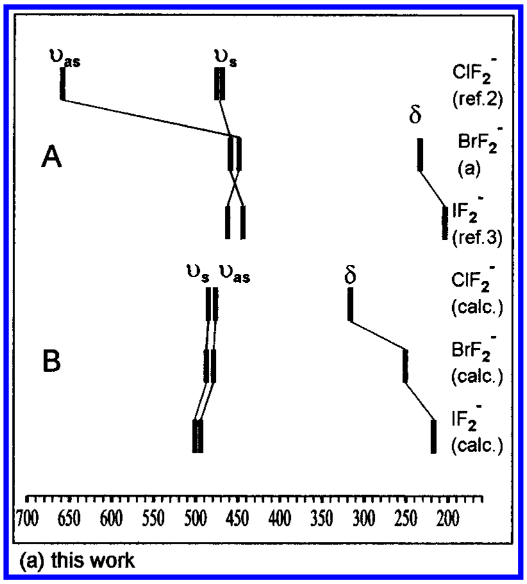

Figure 3. Correlation diagram of the experimental frequencies of BrF_2^-, KrF_2, and other related compounds with $D_{\infty h}$ symmetry (A) compared with the frequencies calculated with a HF-3-21G* basis set (B).

and $(CH_3)_4N^+BrF_4^-$,[11] as well as $(CH_3)_4N^+I(NO_3)_2^-$, $(CH_3)_4N^+I(NO_3)_4^-$, and $(CH_3)_4N^+Br(NO_3)_2^-$.[12]

For a linear, centrosymmetric triatomic ion such as XY_2^- three normal modes of vibration, classified as $(\Sigma_g^+ + \Pi_u + \Sigma_u^+)$, are expected, where ν_2 (Π_u) and ν_3 (Σ_u^+) are only infrared active and ν_1 (Σ_g^+) is only Raman active.

The recorded Raman spectrum of $(CH_3)_4N^+BrF_2^-$ shows an intense line at 460 cm^{-1} which is assigned as the symmetric Br−F stretch. A comparison of ν_s(Br−F) with ν_s(Kr−F) for the isoelectronic Krypton difluoride[13] at 462 cm^{-1} yields good agreement.

A shoulder on the high-frequency side of the symmetric BrF_2^- stretching mode is attributed to the first overtone of the deformation mode whose intensity is enhanced by Fermi resonance (Figure 2A). Under the assumption of Fermi resonance,[14] the unperturbated frequencies of ν_1 and $2\nu_2$ are expected at 463 and 467 cm^{-1}, respectively.[15] In contrast Claassen et al. observed no Fermi resonance for the isoelectronic krypton difluoride and explained their findings by the large difference of about 16 cm^{-1} between ν_1 and $2\nu_2$.[13] The intense lines at 77 and 66 cm^{-1} in the Raman spectrum are attributed to lattice vibrations.

In the infrared spectrum of $(CH_3)_4N^+BrF_2^-$ the antisymmetric Br−F stretching mode appears at 450 cm^{-1} and the bending mode was observed at 236 cm^{-1}. The bending frequency of 236 cm^{-1} is in good agreement with that of 232.6 cm^{-1} observed for the isoelectronic krypton difluoride, whereas the antisymmetric stretching mode exhibits a significant shift toward smaller wavenumbers.[13]

This effect is well-known for pentatomic fluorohalogenates. A comparison of IF_4^- [16] with the isoelectronic XeF_4[17] shows that the antisymmetric stretching mode of the anion is 138 cm^{-1} lower than that of the isoelectronic, neutral compound. The antisymmetric stretching mode also has a lower frequency than the symmetric stretching mode.

The vibrational spectroscopic data of BrF_2^- clearly suggest a linear anion with $D_{\infty h}$ symmetry. The large tetramethylammonim cations are preventing interanionic contacts and distortion of the linear structure. This observation is in agreement with the results of Naumann and Meurer, who obtained a linear IF_2^- anion with tetraethylammonium as counterion.[3]

Ab Initio Calculations. Ab initio calculations are of great help for the assignment of the BrF_2^- resonances in the experimental infrared and Raman spectra. In Table 2 and Figure 3, BrF_2^- is compared to isoelectronic KrF_2 and other related species with $D_{\infty h}$ symmetry. Unfortunately structures with atoms larger than Br could be calculated only with a small 3-21G* basis set. However, this basis set is known to yield quite reasonable geometries and frequencies for hypervalent structures. For consistency, all species were calculated with this basis set. For all species only positive force constants were obtained (see Table 3). This result is in contradiction to calculated force constants for BrF_2^- [5] and KrF_2[13] using the FG-matrix method, which due to the underdetermined nature of the problem could not yield well-determined interaction constants.

As can be seen from Figure 3, the δ(F−X−F) (X = Cl, Br, I) frequencies are in acceptable agreement with the available experimental data. The trend of increasing frequencies on going from IF_2^- to ClF_2^- allows the prediction of the δ(F−Cl−F) in ClF_2^-, which could not be observed by Christe et al. because the spectra were recorded only for wavenumbers larger than 400 cm^{-1}. The calculated symmetric and antisymmetric stretching modes are in agreement with the experimental spectra of BrF_2^- and IF_2^-. In particular the calculations indicate that both frequencies lie close together within 30 cm^{-1} and ν_{as}(Br−F) may be smaller than ν_s(Br−F). Naumann and Meurer[3] found the opposite behavior for IF_2^-, with ν_{as}(I−F) being observed at higher frequency than ν_s(I−F). On the basis of our own observations for BrF_2^- and other fluorohalogenates, we should point out that the accurate determination of the experimental frequencies of the antisymmetric stretching mode is difficult because of the large bandwidths in the IR spectra. This may cause uncertainties of about 20 cm^{-1} in the experimental values of ν_3.

The consistency of the calculated results definitely allows us to rule out the experimental assigment for ν_{as}(F−Cl−F)[2] at 661 cm^{-1}. Our calculations indicate that the intense IR band

Table 2. Experimental and Calculated Raman and Infrared Frequencies[a] and Calculated Bond Distances[b] and Energies[h] of $(CH_3)_4N^+BrF_2^-$, Compared to Those of Isoelectrronic KrF_2 and Other Related Compounds with $D_{\infty h}$ Symmetry

$Rb^+ClF_2^-$ [c]		$Me_4N^+BrF_2^-$		$Et_4N^+IF_2^-$ [d]		KrF_2 [e]		XeF_2 [f]		
IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	assgnt
661		450		462		588		557		ν_{as}/ν_3 (Σ_u^+)
			470[i]							$2\delta/2\nu_2$
470	476		460[i]		445		462		496	ν_s/ν_1 (Σ_g^+)
		236		206		232		213		δ/ν_2 (Π_u)
			79/66		111				108	lattice

ClF_2^- [g]		BrF_2^- [g]		IF_2^- [g]		KrF_2 [g]		XeF_2 [g]		
IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	assgnt
479		480		494		649		635		ν_{as}/ν_3 (Σ_u^+)
	487		489		501		558		583	ν_s/ν_1 (Σ_g^+)
317		250		219		267		236		δ/ν_2 (Π_u)

Calculated Bond Distances[b]

ClF_2^- [g]	BrF_2^- [g]	IF_2^- [g]	KrF_2 [g]	XeF_2 [g]
182.1	190.9	202.4	182.6	194.8

Calculated Energies[h] and Signs Reversed

ClF_2^- [g]	BrF_2^- [g]	IF_2^- [g]	KrF_2 [g]	XeF_2 [g]
655.11591	2758.03025	7085.72668	2936.97222	7398.44800

[a] Frequencies in cm^{-1}. [b] Bond distances in pm. [c] Data from ref 2. [d] Data from ref 3. [e] Data from ref 13. [f] Data from ref 26. [g] Ab initio calculations with a 3-21G* basis set. [h] Energies in Hartrees. [i] Fermi resonance.

Table 3. Calculated Frequencies[a] for BrF_2^- at the RHF and MP2 Levels Using Different Standard Basis Sets

HF-3-21G		HF-3-21G*		HF-6-31+G*		HF-6-311G**		MP2-6-31+G*		
IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	assgnt
391		480		368		393		434		ν_{as}/ν_3 (Σ_u^+)
	446		489		454		453		441	ν_s/ν_1 (Σ_g^+)
239		250		231		231		215		δ/ν_2 (Π_u)

[a] Frequencies in cm^{-1}.

at 470 cm^{-1} observed by Christe et al. must be the antisymmetric stretching mode and not the symmetric one. This assignment is in good agreement with $D_{\infty h}$ symmetry for ClF_2^- and follows the rule of mutual exclusion.

NMR Spectra. The resonance signal at 54.5 ppm in the ^{13}C-NMR spectrum can be assigned to the quaternary ammonium cation. Literature data for similar quaternary ammonium salts[18−20] are between 54.3 and 54.6 ppm. No signals in the range between 119 and 125 ppm for CF_3 groups remained. Obviously the reaction, as described in eq 1, was complete. Two resonances were observed in the ^{19}F-NMR spectrum due to some disproportination of BrF_2^- into Br^- and BrF_4^-. The signal at −35.9 ppm is assigned to BrF_4^-, in good agreement with literature values of about −37 ppm.[21] The second signal with a chemical shift of about −41.6 ppm belongs to the BrF_2^- anion.

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