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Bromyl Fluoride. Vibrational Spectra, Force Field, and Thermodynamic Properties

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Infrared spectra are reported for $FBr^{18}O_2$ in the gas phase and for $FBr^{16}O_2$ in Ne, N_2, and Ar matrices at 3.6 K. Isotopic shifts were measured for ^{79}Br–^{81}Br and ^{16}O–^{18}O and were used for the computation of a valence force field. Thermodynamic properties were computed for $FBrO_2$ and $FClO_2$ in the range 0–2000 K.

Introduction

Bromyl fluoride was first synthesized by Schmeisser and Pammer[1,2] in 1955. Because of its low thermal stability and high reactivity, this compound had been only poorly characterized and was not further studied until 1975. In 1975, Gillespie and Spekkens published[3] the Raman spectra of solid and liquid $FBrO_2$ and proposed a monomeric pyramidal structure, similar to that[4] of $FClO_2$. Using Raman frequencies reported[3] for liquid $FBrO_2$, Baran calculated[5] a modified valence force field and mean amplitudes of vibration for $FBrO_2$, assuming all bond angles to be 108°. Very recently, Jacob succeeded[6] in obtaining good gas-phase infrared spectra for $FBrO_2$ in spite of the fact that gaseous $FBrO_2$ possesses a half-life of only 30 min at 15 °C. He also prepared a sample of $FBr^{18}O_2$ and reported preliminary infrared data for the gas and for the neat and the argon matrix isolated solid. Although the oxygen isotopic shifts were measured, no ^{79}Br–^{81}Br isotopic shifts were given.[24]

In this paper, we report higher resolution spectra and oxygen and bromine isotopic shifts for gaseous and for Ne, N_2, and Ar matrix isolated $FBrO_2$. In view of the interest[3,5] in the nature of bonding in $FBrO_2$, a new force field computation appeared warranted, particularly since the previously used[5] frequencies significantly differ from those of gaseous $FBrO_2$ and since the previously assumed[5] geometry of $FBrO_2$ was only a crude estimate. Furthermore, the availability of both oxygen and bromine isotopic shifts offered a unique opportunity to test the value of such additional data for the refinement of force fields for compounds, such as bromine oxyfluorides.

Experimental Section

The samples of $FBrO_2$ used for recording the gas-phase spectra were prepared, as previously described,[6] by low-temperature cocondensation of BrF_5 and H_2O. The infrared spectra of gaseous $FBrO_2$ were recorded at 15 °C on a Perkin-Elmer Model 325 spectrophotometer in the range 4000–290 cm^{-1} using a nickel cell with AgBr windows attached to an external mirror system (optical path length 110 cm).

The samples of $FBrO_2$ used for the matrix isolation study were obtained as a byproduct during a spectroscopic study[7] of BrF_3O. The spectrometer and handling have been previously described.[7]

Results and Discussion

Infrared Spectra of Gaseous $FBrO_2$. A survey infrared spectrum of gaseous $FBr^{18}O_2$ is shown in Figure 1. The corresponding spectrum of $FBr^{16}O_2$ has previously been re-

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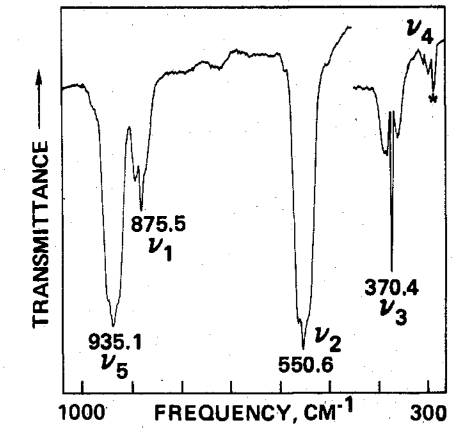


Figure 1. Survey infrared spectrum of gaseous $FBr^{18}O_2$ recorded at 15 °C in a nickel cell equipped with AgBr windows with an optical path length of 110 cm^{-1}. The band marked by an asterisk in due to HF.

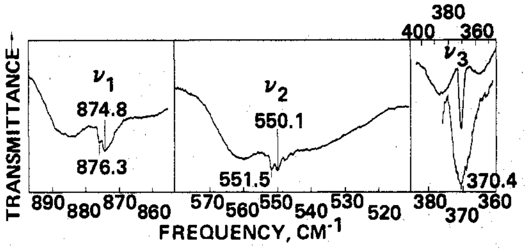


Figure 2. Band contours of ν_1, ν_2, and ν_3 of gaseous $FBr^{18}O_2$ recorded under higher resolution conditions with scale expansion. For ν_1 and ν_2 the frequencies of the ^{79}Br and ^{81}Br Q-branch centers are marked. For ν_3, only the unresolved Q branch is shown at the same scale as that used for ν_1 and ν_2. The complete band envelope is shown at a 2.5× compressed scale.

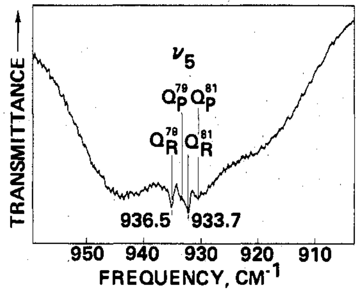


Figure 3. Band contour of ν_5 of gaseous $FBr^{18}O_2$ showing the double Q branches for both bromine isotopes.

ported.[6] Figures 2 and 3 show the band contours of each band recorded under higher resolution conditions and scale expansion.

The observed gas-phase frequencies of $FBrO_2$ are compared in Table I to those[3,6] previously reported for the liquid and the solid. As can be seen from Table I, the gas-phase frequencies significantly deviate from those of liquid and solid $FBrO_2$, indicating some degree of association in the condensed phases. The BrF stretching mode, ν_2 (A′), exhibits the most pronounced frequency change (−62 cm^{-1}) on going from the gas to the solid, whereas the mean frequency change of the two BrO_2 stretching modes, ν_1 (A′) and ν_5 (A″), is only −17 cm^{-1}. This indicates that association takes place mainly through the fluorine ligands. Preferential association through fluorine ligands has previously also been demonstrated[7] for BrF_3O.

Infrared Spectra of Matrix-Isolated $FBrO_2$. In order to obtain unambiguous bromine isotopic shifts (bromine contains two naturally occurring isotopes, ^{79}Br and ^{81}Br, of almost equal

Table I. Vibrational Spectra of $FBrO_2$

	obsd freq, cm^{-1}, and rel intens																
	Infrared												Raman[b]			anharmonic isotopic shifts, cm^{-1}	
					matrix isolated						solid[a] (−87 °C)						
	gas				Ne		N_2		Ar				solid −75 °C	liquid −10 °C	BrF_5 soln room temp		
assignment in point group C_s	$F^{79}Br^{16}O_2$	$F^{81}Br^{16}O_2$	$F^{79}Br^{18}O_2$	$F^{81}Br^{18}O_2$	$F^{79}Br^{16}O_2$	$F^{81}Br^{16}O_2$	$F^{79}Br^{16}O_2$	$F^{81}Br^{16}O_2$	$F^{79}Br^{16}O_2$	$F^{81}Br^{16}O_2$	$F^{79,81}Br^{16}O_2$	$F^{79,81}Br^{18}O_2$	$F^{79,81}Br^{16}O_2$	$F^{79,81}Br^{16}O_2$	$F^{79,81}Br^{16}O_2$	$\Delta_{^{16}O^{18}O}$	$\Delta_{^{79}Br^{81}Br}$
A′ ν_1	921.0	919.5	876.3	874.8	921.6	920.1	922.3	920.8	914.8	913.3	918 vs	867	908 (100)	908 (100) p	916 (100) p	44.7	1.5
ν_2	551.9	550.4	551.5	550.1	546.2	544.8	535.7	534.3	537.0	535.6	490 vs, br	486	524 sh 496 (25) 487 sh	506 (36) p		0.4	1.4
ν_3	385.8		370.4		386.8		391.2		384.0		387 ms	369	400 sh 386 (10)	394 (14) p		15.4	
ν_4	~310		~296								305 mw	290	305 (20) 294 sh	305 (21) p		~14	
A″ ν_5	978.9	976.2	936.5	933.7	976.2	973.6	971.2	968.6	967.2	965.6	947 vs, br	902	963 (5) 940 (20)	953 (14) dp	962 (8) dp	42.4	2.7
ν_6											276 mw 271	260	267 (15)	271 (16) dp			

[a] Data from ref 6. [b] Data from ref 3.

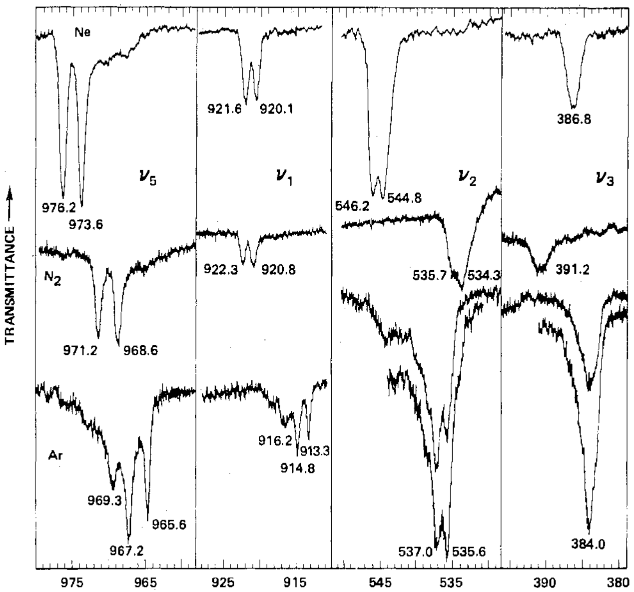


Figure 4. Infrared spectra of Ne, N_2, and Ar matrix isolated $FBr^{16}O_2$, recorded at 3.6 K with 20-fold scale expansion under higher resolution conditions using CsI windows and a mole ratio of ~1000:1.

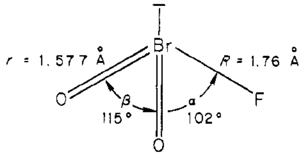
abundance) for $FBrO_2$, the infrared spectra of matrix-isolated $FBr^{16}O_2$ were recorded at 3.6 K. Since, for the related BrF_3O[7] and BrF_3[8] molecules, pronounced and unpredictable matrix effects and splittings were observed, the spectra of $FBrO_2$ were recorded in three different matrix materials, i.e., Ne, N_2, and Ar. The observed spectra, recorded under higher resolution conditions with 20-fold scale expansion, are shown in Figure 4. The observed frequencies are listed in Table I. By analogy with previous reports on matrix-isolated BrF_3[8,9] and BrF_3O,[7] the $FBrO_2$ spectra exhibited pronounced matrix frequency shifts. As for BrF_3[8] and BrF_3O,[7] a Ne matrix was found to give the best results and frequency values very close to those found for the gas phase (see Table I). Association effects were most pronounced in the Ar matrix.

Assignments and Determination of Isotopic Shifts. The assignments for $FBrO_2$ in point group C_s are straightforward and are well supported by Raman polarization data,[3] by ^{18}O isotopic shifts,[6] and by comparison with the spectra of the closely related $FClO_2$[10] and SeO_2F^{-3} species. They are listed in Table I and require no further comment.

For the determination of the ^{16}O–^{18}O isotopic shifts in $FBrO_2$, the gas-phase anharmonic infrared frequencies listed in Table I were used. However for compounds exhibiting such large isotopic shifts, anharmonicity corrections of these shifts are important for force field calculations. Unfortunately, no experimental data are available for $FBrO_2$ to permit reliable anharmonicity corrections. However for RuO_4, which possesses a central atom of a mass similar to that of Br and exhibits comparable ^{16}O–^{18}O isotopic shifts, anharmonicity corrections were estimated[11] to be about 1.4 and 0.5 cm^{-1} for the ^{16}O–^{18}O isotopic shifts of the ν_3 stretching and the ν_4 deformation modes, respectively. Assuming similar correction values for $FBrO_2$, the magnitude of the expected anharmonicity corrections obviously is significantly larger than the 0.1 cm^{-1} uncertainty in the values of the observed anharmonic frequencies. Therefore, we have treated the observed anharmonic oxygen isotopic shifts in the following normal-coordinate analysis as the lower limit and have used 1.6 and 1.0 cm^{-1} larger shifts as the upper limits for the stretching modes ν_1 and ν_5 and the deformation mode ν_3, respectively. As will be shown, the force field analysis supports this choice.

For the bromine isotopic shifts, anharmonicity corrections are much less of a problem due to the smallness (0–3 cm^{-1}) of these shifts. Therefore, possible anharmonicity corrections for these shifts should not exceed the measured uncertainties (±0.1 cm^{-1}) of these shifts. The best values for the isotopic shifts are listed in the last two columns of Table I. The agreement between the bromine isotopic shifts observed for gaseous $FBrO_2$ and those observed for the matrix-isolated species is generally good if one takes into consideration that the Q-branch band contours of ν_1 and ν_2 are distorted on the P-branch side by hot bands and that for ν_5 a double Q branch is observed for each bromine isotope.

Force Field Computations. A normal-coordinate analysis was carried out for $FBrO_2$ to obtain more reliable force constants for this interesting molecule and to examine the usefulness of isotopic shifts for such an analysis. The potential and kinetic energy matrices were computed by a machine method.[12] The geometry was assumed for this computation, based on the known geometries of $FBrO_3$,[13] $FClO_3$,[14] and $FClO_2$[4] and an extrapolation between BrO bond length and stretching frequency, similar to that[15] used for ClO bonds, using the data published for BrO_4^-[16,17] and $FBrO_3$.[13,18] This geometry appears more likely than that ($\alpha = \beta = 108°$, $r = 1.63$ Å) chosen[5] by Baran for his computation. The symmetry coordinates used for $FBrO_2$ were identical with those previously given[10] for $FClO_2$, except for the correction of the obvious typographical error in the factor of S_4. The bending coordinates were weighted by unit (1 Å) distance.



The force constants were adjusted by trial and error with the aid of a computer to give an exact (0.1 cm^{-1}) fit between all observed and computed frequencies. The observed ^{79}Br–^{81}Br and ^{16}O–^{18}O isotopic shifts were used as additional constraints. We will first discuss our choice of a force field for the A″ block since it contains only one stretching and one deformation mode.

The force constants of F_{55} and F_{66} were computed as a function of F_{56}. The resulting curves are shown in Figure 5. We have also computed the bromine and oxygen isotopic shifts over the same range of F_{56} and have plotted their values in Figure 5. The observed isotopic shifts, $\Delta_{Br_{\nu_5}}$ ± 0.1 cm^{-1} and $\Delta_{O_{\nu_5}}$ ± 1.6 cm^{-1} (see above discussion of anharmonicity corrections), were used to define the probable range of the force constants. The values thus obtained are given in Figure 5 and Table II. Figure 5 demonstrates the importance of the anharmonicity corrections for $\Delta_{O_{\nu_5}}$, i.e., a better overlap with the $\Delta_{Br_{\nu_5}}$ force field constraint, as previously demonstrated[19] by McDowell and Goldblatt for OsO_4. Furthermore, it shows that the preferred force field closely corresponds to F_{66} being a minimum, a condition previously shown[19,20] to be a good approximation to the general valence force field values for similar weakly coupled systems.

For the A′ block of $FBrO_2$ the problem of defining a preferred force field is more difficult since this block contains two stretching and two deformation modes. Numerical experiments showed that only three of the six off-diagonal symmetry force constants were essential for fitting the isotopic data. These three off-diagonal constants were F_{13}, F_{24}, and F_{34}, with F_{13} and F_{34} being more important then F_{24}. This result is in good agreement with the previous findings[10] for the related $FClO_2$ molecule and is not surprising in view of

Table II. Observed Frequencies for $F^{79}Br^{16}O_2$, Symmetry Force Constants,[a] Computed and Observed $^{16}O-^{18}O$ and $^{79}Br-^{81}Br$ Isotopic Shifts, and Potential Energy Distribution[b]

assignment in point group C_s	approx description of mode	freq, cm^{-1}	symmetry force constants		isotopic shifts, cm^{-1} calcd Δ_O	calcd Δ_{Br}	obsd Δ_O	obsd Δ_{Br}	PED
A′ ν_1	$\nu_{sym}(BrO_2)$	921.0	$F_{11} = f_r + f_{rr}$	6.931 ± 0.095	45.23	1.56	44.7	1.5	96 F_{11}
ν_2	$\nu(BrF)$	551.9	$F_{22} = f_R$	2.750 ± 0.04	0.31	1.40	0.4	1.4	99 F_{22}
ν_3	$\delta_{sciss}(BrO_2)$	385.8	$F_{33} = f_\beta$	1.453 ± 0.08	15.65	1.12	15.4		76 F_{33}, 16 F_{34}
ν_4	$\delta_{sym}(FBrO_2)$	310	$F_{44} = f_\alpha + f_{\alpha\alpha}$	1.487 ± 0.08	11.74	0.52			103 F_{44}, 37 F_{33}, −41 F_{34}
			$F_{13} = f_{r\beta}$	−0.40 ± 0.19					
			$F_{24} = f_{R\alpha}$	0.095 ± 0.09					
			$F_{34} = f_{\alpha\beta}$	0.49 ± 0.07					
A″ ν_5	$\nu_{asym}(BrO_2)$	978.9	$F_{55} = f_r - f_{rr}$	7.037 ± 0.06	43.28	2.70	42.4	2.7	100 F_{55}
ν_6	$\delta_{asym}(FBrO_2)$	273	$F_{66} = f_\alpha - f_{\alpha\alpha}$	0.762 ± 0.004	7.21	0.33			100 F_{66}
			$F_{56} = f_{r\alpha} - f_{r\alpha'}$	0.14 ± 0.22					

[a] Stretching constants in mdyn/Å, deformation constants in mdyn Å/rad², and stretch-bend interaction constants in mdyn/rad. [b] Percent contributions. Contributions of less than 9% to the PED are not listed.

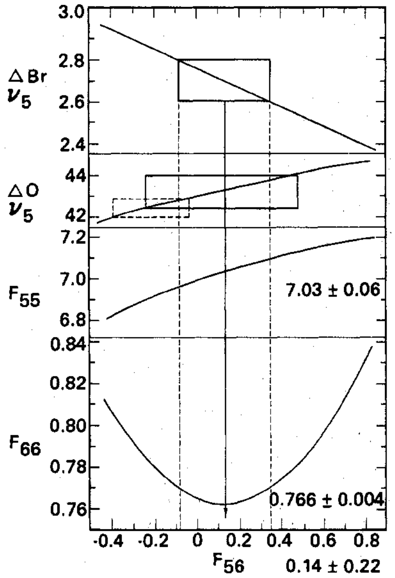


Figure 5. Force constant display of the A″ block of $FBrO_2$ using the observed bromine (2.7 ± 0.1 cm^{-1}) and oxygen (42.4 ± 1.6 cm^{-1}) isotopic shifts as constraints. F_{55}, F_{66}, and F_{56} have units of mdyn/Å, mdyn Å/rad², and mdyn/rad, respectively. The rectangle of Δ_{O,ν_5} marked by broken lines represents the observed anharmonic oxygen shift of ν_5 ± 0.4 cm^{-1}, whereas the solid rectangle assumes the observed anharmonic oxygen shift as the lower limit and a 1.6 cm^{-1} higher value, for anharmonicity corrected, as the upper limit. The broken and the solid vertical lines indicate the plausible force constant ranges and the preferred force field, respectively.

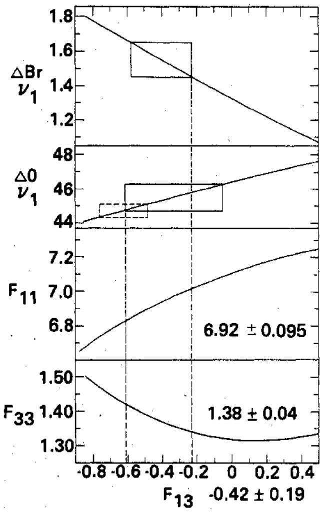


Figure 6. Force constant display of the A′ block. All off-diagonal constants were set to zero, except for F_{13}. Only those diagonal constants are shown which were significantly influenced by changes in the interaction constant F_{13}. For additional explanation see caption of Figure 5.

Table III. Internal Force Constants[a] of $FBrO_2$ Compared to Those Previously Reported

	this work	ref 5	b
f_r	6.984 ± 0.08	6.76	6.78
f_R	2.750 ± 0.04	2.25	2.24
f_{rr}	−0.05 ± 0.08	0	0.14
f_α	1.125 ± 0.04	1.090	1.066
f_β	1.453 ± 0.08	1.664	1.485
$f_{\alpha\alpha}$	0.363 ± 0.04	0.344	0.288
$f_{\alpha\beta}$	0.49 ± 0.07	0.01	
$f_{R\alpha}$	0.095 ± 0.09	0.034	
$f_{r\alpha}$	−0.07 ± 0.11	0	
$f_{r\alpha'}$	+0.07 ± 0.11	0	

[a] Units are identical with those of Table II. [b] R. Bougon, P. Joubert, and G. Tantot, *J. Chem. Phys.*, **66**, 1562 (1977).

the fact that G_{13}, G_{24}, and G_{34} are the major off-diagonal **G** matrix terms in the A′ block. It was also shown that the variation of F_{13}, F_{24}, and F_{34} strongly influenced only the corresponding diagonal terms. This relative independence of the interaction constants permitted us to examine each of them separately. The results of these computations were again summarized in graphical form and are presented in Figures 6–8. In this manner, the values of F_{13}, F_{24}, and F_{34}, required to duplicate all of the observed isotopic data, were determined. These three interaction constants were then combined in a single force field, and a satisfactory fit of the isotopic data could be achieved with only minor adjustments. The resulting force field is given in Table II. The computed oxygen shifts were intentionally kept slightly larger than those observed to leave some room for any future anharmonicity corrections.

Figures 6 and 7, dealing with the stretch–bend interaction constants F_{13} and F_{24}, respectively, are analogous to Figure 5, which has been discussed above in detail for the A″ block, and therefore do not require any further comment. Figure 8 shows the dependence of the two diagonal bending constants F_{33} and F_{44} on the bend–bend interaction constant F_{34}. In order to be able to fit the observed oxygen shift of ν_3, either a rather large positive or a small negative value is required for F_{34}. Of these two possibilities, the former is preferred, since it results in more plausible force constants. For F_{34} = 0.2, the potential energy distribution (PED) is essentially 100% characteristic (F_{44} = minimum), whereas, for the extreme values of F_{34}, ν_3 and ν_4 become about even mixtures of F_{33} and

Table IV. Stretching Force Constants (mdyn/Å) of $FBrO_2$ Compared to Those of Other Bromine Compounds

	BrO_3^- [a]	BrO_4^- [b]	$BrF_2O_2^-$ [k]	BrF_4O^- [c]	BrF_4^- [d]	$FBrO_2$	$FBrO_3$ [e]	BrF_3O [f]	BrF	BrF_3 [g]	BrF_5 [h]	BrF_2^+ [i]	BrF_6^+ [j]
f_r(BrO)	5.28	6.05	6.32	6.70		6.98	6.92	7.68					
f_R(BrF)			1.63	2.14	2.23			2.93		3.10	3.24		
						2.75							
f_R'(BrF)							3.22	3.51	4.07	4.07	4.02	4.60	4.90

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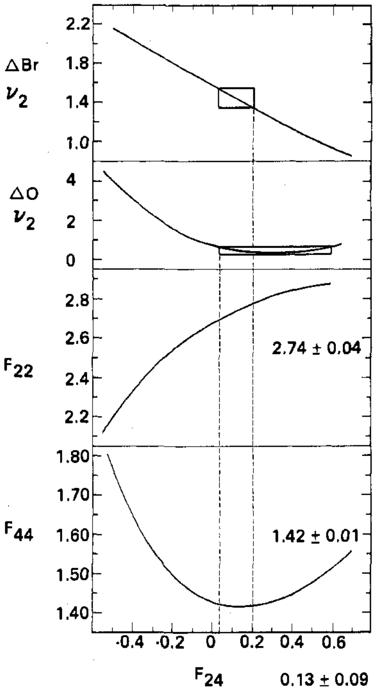

Figure 7. Force constant display of the A′ block showing the dependence of F_{22} and F_{44} on F_{24}. For additional explanation see captions of Figures 5 and 6.

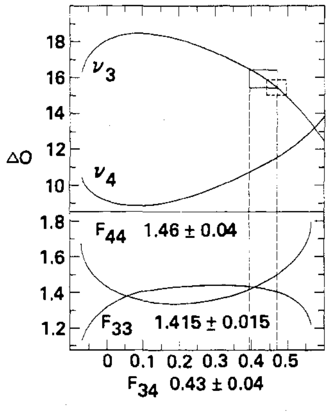

Figure 8. Force constant display of the A′ block showing the dependence of F_{33} and F_{44} on F_{34}.

F_{44}. The moderate amount of mixing obtained for ν_3 and ν_4 in our preferred force field (see Table II) is not surprising in view of their similar frequencies and motions involved. The remainder of the PED (see Table II) is highly characteristic and supports the approximate description of the modes given in Table II.

A comparison of the internal force constants of $FBrO_2$ with those previously reported is given in Table III. As can be seen, our force field significantly differs, particularly for f_R and $f_{\alpha\beta}$.

Table V. Thermodynamic Properties for $F^{79}Br^{16}O_2$

T, K	C_p°, cal/(mol deg)	$(H^\circ_T - H^\circ_0)$, kcal/mol	$-(F^\circ_T - H^\circ_0)/T$, cal/(mol deg)	S°_T, eu
0	0	0	0	0
100	9.493	0.831	48.749	57.059
200	12.831	1.957	54.945	64.732
298.15	15.033	3.332	59.119	70.295
300	15.066	3.360	59.188	70.388
400	16.527	4.945	62.576	74.938
500	17.467	6.648	65.438	78.734
600	18.082	8.427	67.931	81.977
700	18.498	10.258	70.144	84.797
800	18.789	12.123	72.134	87.288
900	18.998	14.013	73.944	89.513
1000	19.154	15.921	75.603	91.523
1100	19.272	17.842	77.134	93.355
1200	19.363	19.774	78.557	95.036
1300	19.436	21.714	79.885	96.589
1400	19.494	23.661	81.130	98.031
1500	19.541	25.613	82.303	99.378
1600	19.580	27.569	83.410	100.640
1700	19.613	29.529	84.458	101.828
1800	19.640	31.491	85.455	102.950
1900	19.664	33.456	86.404	104.013
2000	19.684	35.424	87.310	105.022

Our results show that the BrF bond in $FBrO_2$ is significantly stronger than previously assumed.[3,5]

Comparison with Similar Compounds and Bonding in $FBrO_2$. A comparison of the $FBrO_2$ stretching force constants with those of other bromine oxides, fluorides, and oxyfluorides is given in Table IV. The BrF stretching force constants are separated into two groups. The low f_R force constants observed for $BrF_2O_2^-$, BrF_4O^-, BrF_4^-, and some of the bonds in BrF_3 and BrF_5 can be attributed to significant contributions from semiionic, three-center, four-electron bonding while it is assumed that the bonds belonging to the f_R' group are largely covalent. The spread within each group is caused by secondary effects, such as formal charge (anion, neutral molecule, or cation), degree of fluorine substitution, and oxidation state of the central atom. These effects have previously been discussed[21,22] at length for the corresponding chlorine compounds and appear to be also applicable to the bromine compounds of Table IV, although for the latter they are somewhat less pronounced. This is caused by the fact that the larger bromine central atoms are more polarizable than chlorine, thereby causing the two types of bonds to become less distinct.

As far as $FBrO_2$ is concerned, it can be seen from Table IV that its stretching force constants do not fit too well the general trends of Table IV, and it is therefore placed between these two groups. A similar anomaly has previously been noted for $FClO_2$ and was explained by a weak highly polar $(p-\pi^*)\sigma$ bond.[22] The same explanation, i.e., bonding between a 2p electron of F and an antibonding π^* orbital of the BrO_2 radical, can be invoked for $FBrO_2$.

Thermodynamic Properties. The thermodynamic properties of $F^{79}Br^{16}O_2$ were computed with the molecular geometry

Table VI. Thermodynamic Properties of $F^{35}Cl^{16}O_2$

T, K	$C_p°$, cal/(mol deg)	$(H°_T - H°_0)$, kcal/mol	$-(F°_T - H°_0)/T$, cal/(mol deg)	$S°_T$, eu
0	0	0	0	0
100	8.507	0.805	46.851	54.898
200	11.267	1.790	52.666	61.618
298.15	13.509	3.012	56.456	66.559
300	13.545	3.037	56.519	66.643
400	15.167	4.478	59.581	70.775
500	16.318	6.055	62.180	74.291
600	17.134	7.730	64.459	77.342
700	17.718	9.474	66.495	80.030
800	18.143	11.268	68.339	82.425
900	18.459	13.099	70.026	84.581
1000	18.699	14.958	71.581	86.539
1100	18.884	16.837	73.023	88.330
1200	19.030	18.733	74.368	89.979
1300	19.147	20.642	75.629	91.507
1400	19.241	22.562	76.814	92.930
1500	19.318	24.490	77.934	94.260
1600	19.382	26.425	78.993	95.509
1700	19.436	28.366	80.000	96.686
1800	19.481	30.312	80.958	97.798
1900	19.520	32.262	81.872	98.852
2000	19.554	34.216	82.747	99.854

given above and the vibrational frequencies of Table II, assuming an ideal gas at 1 atm pressure and using the harmonic-oscillator, rigid-rotor approximation.[23] These properties are given for the range 0–2000 K in Table V. Since no thermodynamic data had previously been reported for $FClO_2$, we have also computed these properties for $F^{35}Cl^{16}O_2$ (see Table VI) using the previously published frequencies[10] and geometry.[4]

Conclusion

A force field has been computed for $FBrO_2$ using gas-phase frequency values and bromine and oxygen isotopic shifts. It was shown that the most important force constants, f_{BrO} and f_{BrF}, can be determined with an accuracy of about 0.08 and 0.04 mdyn/Å, respectively. The importance of anharmonicity corrections for the oxygen shifts was demonstrated. In the absence of such anharmonicity corrections, the bromine isotopic shifts are more useful for defining the force field because of the smaller anharmonicity corrections required. The BrF bond in $FBrO_2$ (2.75 mdyn/Å) is considerably stronger than previously assumed (2.25 mdyn/Å)[5] but is still somewhat weaker than predicted by comparison with related bromine compounds. This weakening effect might be explained by assuming a polar σ bond between a 2p electron of F and an antibonding π^* orbital of the BrO_2 radical.

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Registry No. $F^{79}Br^{16}O_2$, 67452-70-4; $F^{35}Cl^{16}O_2$, 35880-03-6; $FBrO_2$, 22585-64-4; $FBr^{18}O_2$, 64544-65-6; ^{18}O, 14797-71-8; ^{79}Br, 14336-94-8; ^{81}Br, 14380-59-7.

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Chemistry and Structure of $N_2F_3^+$ Salts

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The novel $N_2F_3^+$ salt $N_2F_3SbF_6$ was prepared from N_2F_4 and SbF_5 in anhydrous HF solution. A metathetical reaction between $N_2F_3SbF_6$ and Cs_2SnF_6 in HF produced N_2F_4 and the novel salt $N_2F_3SnF_5$. It was shown that N_2F_4 and BF_3 do not form a stable adduct at temperatures as low as −78 °C. The vibrational and ^{19}F NMR spectra of the $N_2F_3^+$ cation were reexamined. All the experimental data are consistent with a planar structure of symmetry C_s for $N_2F_3^+$. The previously reported vibrational assignments, made on the basis of a nonplanar structure of symmetry C_1, are revised for six fundamental frequencies.

Introduction

The first report on the formation of a stable adduct between N_2F_4 and a Lewis acid was published[1] in 1965 by Ruff. He showed[1,2] that SbF_5, when treated with an excess of N_2F_4 in AsF_3 solution, produced, depending on the pressure of N_2F_4, either the 1:2 adduct $N_2F_4 \cdot 2SbF_5$ or the 1:3 adduct $N_2F_4 \cdot 3SbF_5$. On the basis of the observed ^{19}F NMR spectrum and an incomplete infrared spectrum, he assigned to $N_2F_4 \cdot 2SbF_5$ the ionic structure $N_2F_3^+Sb_2F_{11}^-$ with hindered rotation around the N–N bond in $N_2F_3^+$. In 1967, Young and Moy published[3]

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