Contribution from Rocketdyne, A Division of Rockwell International, Canoga Park, California 91304,
and the Centre d'Etudes Nucléaires de Saclay, 91190 Gif-sur-Yvette, France

Bromine Trifluoride Oxide. Vibrational Spectrum, Force Constants, and Thermodynamic Properties

KARL O. CHRISTE,* E. C. CURTIS, and ROLAND BOUGON

Received September 9, 1977

The infrared spectra of gaseous, solid, and matrix-isolated BrF_3O and the Raman spectra of solid and liquid BrF_3O and of its HF and $FClO_3$ solutions are reported. Nine fundamental vibrations were observed, and some $^{79}Br-^{81}Br$ isotopic shifts were measured in Ne, Ar, and N_2 matrices. These data support a pseudo-trigonal-bipyramidal structure of symmetry C_s with two fluorine atoms at the apexes and one fluorine, one oxygen, and one localized free electron pair at the remaining corners. A modified valence force field was computed using the isotopic data. The results show that the equatorial Br–F bond (f_R = 3.51 mdyn/Å) is significantly stronger than the two axial Br–F bonds (f_r = 2.93 mdyn/Å) and that the bond order of the Br–O bond is close to 2 (f_D = 7.68 mdyn/Å). The vibrational and ^{19}F NMR spectra show that in the liquid and solid state BrF_3O is associated through the axial fluorine atoms. Thermodynamic properties were computed for BrF_3O in the range 0–2000 K.

Introduction

The synthesis of the novel bromine oxyfluoride BrF_3O has recently been reported[1] by Bougon and Bui Huy. On the basis of incomplete vibrational spectra, a structure of symmetry C_s was proposed[1] for BrF_3O. In this paper, the results of a detailed investigation and analysis of the vibrational and ^{19}F NMR spectra of this interesting compound are given which confirm the previously proposed structure.

Experimental Section

Bromine trifluoride oxide was prepared, as previously described,[1] from $KBrF_4O$ and O_2AsF_6 by a displacement reaction in BrF_5. The starting materials $KBrF_4O$ and O_2AsF_6 were obtained by literature methods.[2,3] The vacuum lines, spectrometers, instruments, and sampling techniques used at C.E.N have previously been described.[4,5]

At Rocketdyne, the BrF_3O was prepared in a passivated sapphire reactor which was connected through a small-volume Teflon FEP U-trap to a stainless steel Teflon FEP vacuum system. The crude BrF_3O was collected in this U-trap by fractional condensation at −20 °C and was further purified by briefly pumping off the more volatile components at 0°. The U-trap was incorporated into the matrix-isolation apparatus so that the diluent gas could be swept through the trap into the matrix-isolation inlet system. The length and diameter of the matrix inlet tube were kept at a minimum to avoid decomposition of the BrF_3O. The molar ratio of diluent to sample was controlled by the temperature and hereby the vapor pressure of BrF_3O in the U-trap. In order to avoid extensive decomposition of BrF_3O, rapid deposition rates were required. The matrix-isolation experiments were carried out at 3.6 K using CsI windows and an apparatus previously described.[6,7] A Perkin-Elmer Model 283 spectrometer was used which was calibrated by comparison with standard gas calibration points.[8,9] The reported frequencies and isotopic shifts are believed to be accurate to ±1 and ±0.1 cm^{-1}, respectively.

The recording of infrared spectra of gaseous BrF_3O was found difficult due to rapid attack of the AgCl or AgBr windows. Since the attack of the AgBr windows was very rapid, they were protected by a 1 mm thick polyethylene sheet. To ensure that the observed bands were indeed belonging to BrF_3O, the cell was periodically evacuated and refilled with fresh BrF_3O. One of the decomposition products found in the infrared cell was BrF_3.

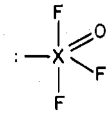
The concentrated solution of BrF_3O in HF was obtained by dissolving a sample of $CsBrF_4O$ in a thin-walled 6 mm o.d. Kel-F capillary in anhydrous HF. When the HF was added, the following displacement reaction occured in quantitative yield:[10]

$$CsBrF_4O + HF \rightarrow CsHF_2 + BrF_3O$$

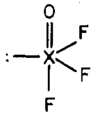
The Raman spectra of this solution were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line. A Claassen filter was used to eliminate plasma lines.[11] Polarization measurements were carried out by method VIII as described by Claassen et al.[11]

Results and Discussions

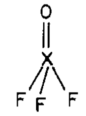
As previously discussed[12] in detail for ClF_3O, a monomeric halogen trifluoride oxide molecule theoretically could possess one of the following three structures:



I (C_s)



II (C_s)



III (C_{3v})

It has previously been shown[12] that ClF_3O has structure I, and the same arguments also hold for BrF_3O. Thus, the observed number of fundamental vibrations, the Br isotopic shifts, the infrared gas band contours, and relative band intensities and frequencies all rule out structures II and III. The following paragraphs can, therefore, be limited to a discussion of the experimental data in terms of structure I.

Infrared Spectrum of the Gas. Figure 1 shows the infrared spectrum of gaseous BrF_3O. Due to the low vapor pressure and low thermal stability of BrF_3O, only the five most intense infrared bands were observed in the gas phase. Figure 2 shows the band contours of four of these bands with scale expansion under higher resolution conditions. From the estimated (see below) geometry of BrF_3O, the three rotational constants were computed to be $A = 0.189$, $B = 0.119$, and $C = 0.086$ cm^{-1}. On the basis of these values, the infrared band contours of BrF_3O should be intermediate between those of sets 25 and 24 in the tables of Ueda and Shimanouchi.[13] The band at 601 cm^{-1} shows a P–R branch separation of about 17 cm^{-1} (see Figure 2), in excellent agreement with the 17 cm^{-1} estimate[13] for an A-type band. This confirms the assignment of this band to the antisymmetric axial F–Br–F stretching mode, ν_7 (A″). For this mode, the change of dipole moment occurs along the axis with the smallest moment of inertia. The second band for which a well-defined band contour was observed is the Br–O stretching mode, ν_1 (A′), at 995 cm^{-1}. This band does not exhibit well-defined P and R branches, as expected[13] for a blend of the B and C type.

Infrared Spectra of Matrix-Isolated BrF_3O. Due to the limited availability of gas-phase data and the tendency of BrF_3O to associate in the liquid and solid state (see below), it was important to obtain matrix-isolation spectra. Furthermore, these spectra were expected to yield information about the nature of the association of BrF_3O. Since for the closely related BrF_3[14] and $FBrO_2$[15] molecules pronounced and unpredictable matrix effects and splittings were observed, the spectra of BrF_3O were recorded in three different matrix materials, i.e., Ne, Ar, and N_2. A survey scan of BrF_3O in N_2 is shown in Figure 3, trace A. Spectra of BrF_3O in Ne, Ar, and N_2, recorded with scale expansion and under high resolution conditions, are given in Figures 4–7, together with the observed frequencies. As can be seen, the matrix data confirm the presence of the five bands observed in the gas-

0020-1669/78/1317-1533$01.00/0

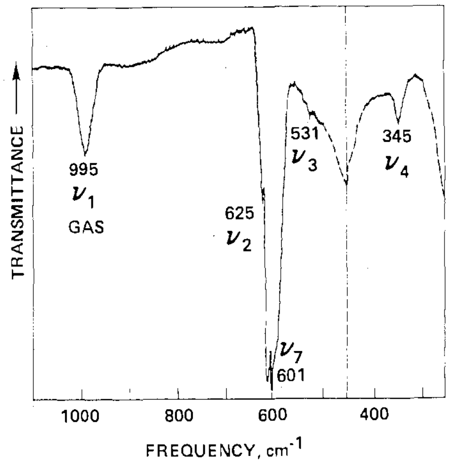


Figure 1. Infrared spectrum of gaseous BrF_3O at 5 mm pressure. The window material used above 450 cm^{-1} was AgCl and below 450 cm^{-1} was AgBr protected by a 1 mm thick polyethylene sheet. The broken lines indicate absorption due to the window material.

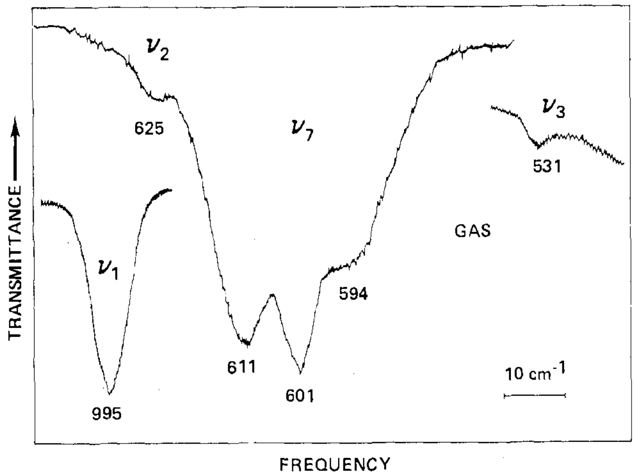


Figure 2. Infrared band contours recorded for gaseous BrF_3O with 10-fold scale expansion under higher resolution conditions.

phase spectra. Two additional fundamental vibrations were observed at about 400 and 250 cm^{-1}, in agreement with the Raman data (see below). By analogy with previous reports[14,16] on matrix-isolated BrF_3, the BrF_3O spectra exhibited pronounced matrix frequency shifts and splittings. As for BrF_3[14] and $FBrO_2$,[15] a Ne matrix was found to give for most bands the simplest spectrum and the frequency values closest to those observed for the gas phase.

The matrix spectra exhibit, in addition to site and bromine isotopic splittings (see below), bands due to associated BrF_3O. Most of these are marked by a P in Figures 4–7. Their assignment to associated BrF_3O was confirmed by variation of the matrix ratio, controlled-diffusion experiments, and the recording of the spectrum of neat solid BrF_3O at 3.6 K (see trace B of Figure 3). Their interpretation will be discussed later.

Reliable determination of the bromine isotopic shifts (bromine has two natural isotopes, ^{79}Br and ^{81}Br, of about equal abundance) was important for the assignments and force field computations. Whereas matrix splittings depend on the matrix material, the isotopic splittings should be matrix independent and be observable in all three matrix materials.

In a Ne matrix, monomeric BrF_3O appears to occupy only one matrix site, as evidenced by the observation of a single isotopic doublet for ν_1, ν_2, and ν_7 (see Figures 4–7). The splittings observed for ν_3, ν_8, and ν_5 in Ne are too large for bromine isotopes and also were not observed for the Ar and N_2 matrices which contained much less associated BrF_3O. Consequently, one of the two bands in each of these pairs is attributed to associated BrF_3O.

In Ar or N_2 matrices, monomeric BrF_3O occupies at least two different matrix sites. When the site symmetry splittings are of the same magnitude as the bromine isotopic splittings, the two central lines will coincide and the bands can have the appearance of a triplet with a more intense central component. Typical examples for such apparent triplets are the bands at about 580 cm^{-1} in Ar and at about 998 and 618 cm^{-1} in N_2. The observed and computed ^{79}Br–^{81}Br isotopic shifts will be given and discussed in the force field section. The doublet at 985.6 and 982.9 cm^{-1}, observed for the N_2 matrix (see Figure 4, lower trace), exhibits a splitting (2.7 cm^{-1}) too large for

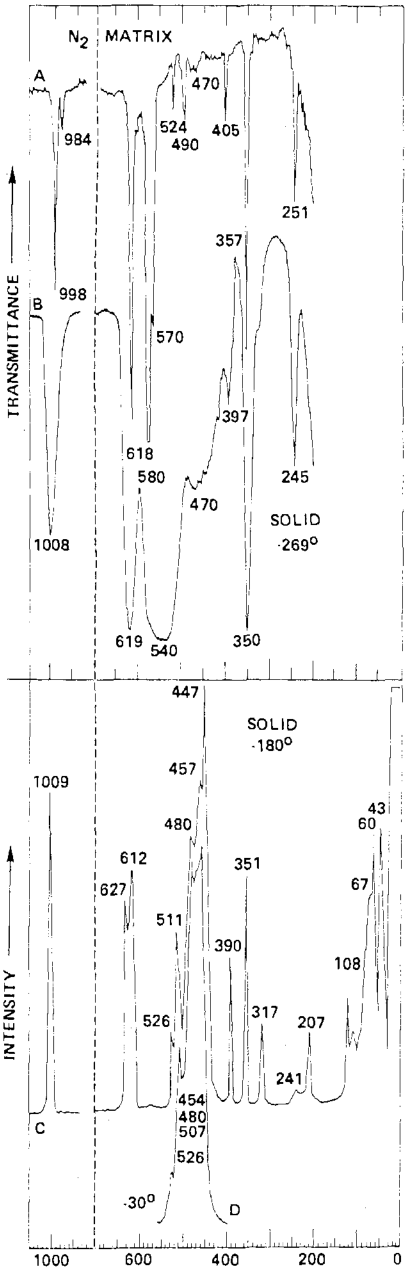


Figure 3. Vibrational spectra of solid BrF_3O: trace A, infrared spectrum of BrF_3O in a N_2 matrix (MR ~ 1000:1), recorded at 3.6 K using CsI windows; trace B, infrared spectrum of neat BrF_3O, recorded at 3.6 K using CsI windows; traces C and D, Raman spectra of neat BrF_3O, recorded at −180 and −30 °C, respectively. The parts of the −30 °C spectrum, not shown in this figure, closely resembled those of trace C.

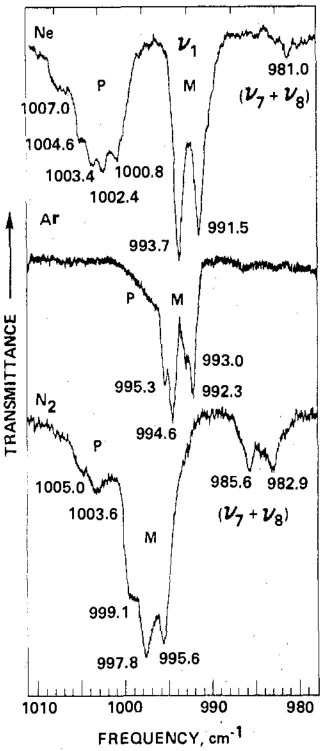


Figure 4. Infrared spectra of matrix-isolated BrF_3O (ν_1 region), recorded at 3.6 K with 20-fold scale expansion under higher resolution conditions. The upper, middle, and lower traces were recorded for Ne, Ar, and N_2 matrices, respectively. (MR ~ 1000:1). Bands due to monomeric and to associated BrF_3O are marked by M and P, respectively.

either ν_1 (2.25 cm^{-1}) or an N_2 site splitting but has about the right frequency separation (2.9 cm^{-1}) for the bromine isotopes in the combination band ($\nu_7 + \nu_8$) and, therefore, is assigned in this manner.

Raman Spectra. Raman spectra of BrF_3O were recorded for the solid at −180 and −30 °C (Figure 3, traces C and D), for the liquid at 20 °C, and for HF solutions at high and low concentrations (Figure 8, traces A, B, and C). The spectra of the solid, liquid, and HF solutions agree well with each other, except for the symmetric axial F–Br–F stretching mode, ν_3 (A′), which, due to association effects (see below), shows varying degrees of splitting and frequency shifts to lower frequencies. The infrared spectra (see above) had shown seven of the nine fundamental vibrations, expected[12] for BrF_3O of symmetry C_s. The remaining two fundamental vibrations are readily identified from the Raman spectra and have frequencies of about 200 and 330 cm^{-1}. Polarization measurements were carried out for the concentrated HF solution (traces B, Figure 8) and show the number of polarized and depolarized bands expected for model I (6 A′ + 3 A″).

Assignments. Assignment of the nine fundamental vibrations observed for BrF_3O is straightforward. By analogy with ClF_3O,[12] model I of symmetry C_s should possess 6 A′ and 3 A″ modes, all being infrared and Raman active. In the Raman spectrum, only the A′ modes should be polarized. The experimental observations are in agreement with these predictions.

Of the six fundamental vibrations in species A′, three should be stretching modes involving the Br=O, the equatorial Br–F, and the axial F–Br–F bonds, respectively. The Br=O stretching mode should have a significantly higher frequency than the Br–F modes and, therefore, is assigned to the band at about 1000 cm^{-1}. The equatorial Br–F stretching mode should have a higher frequency and infrared intensity and a significantly larger ^{79}Br–^{81}Br isotopic splitting than the

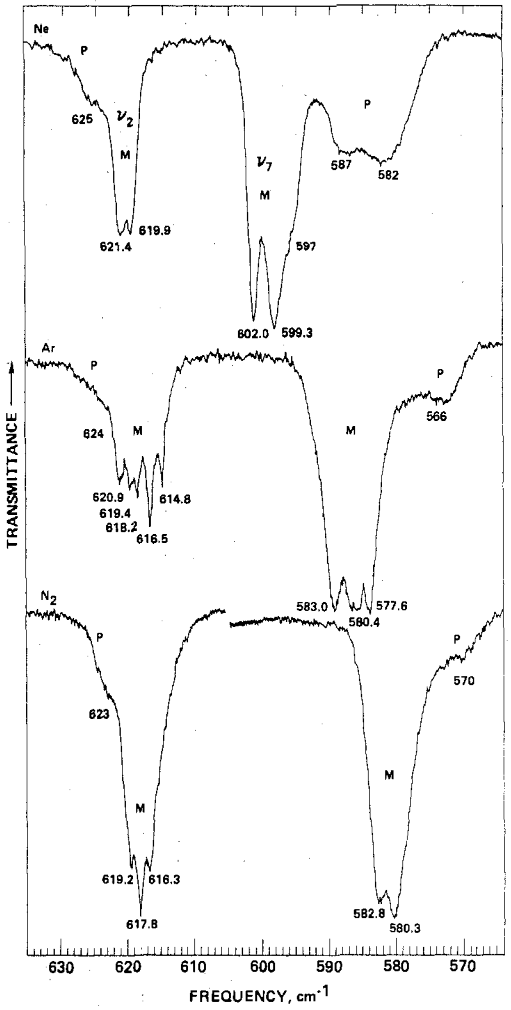


Figure 5. Infrared spectra of matrix-isolated BrF_3O (ν_4 and ν_5 region). The ν_2 band in N_2 matrix was recorded for a thicker sample.

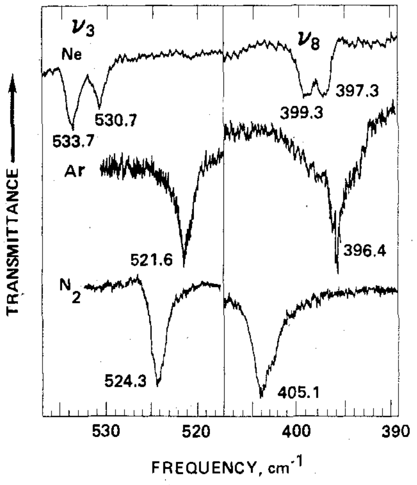
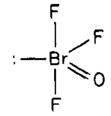
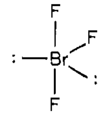
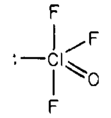
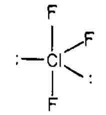


Figure 6. Infrared spectra of matrix-isolated BrF_3O (ν_7 and ν_8 region).

symmetric axial F–Br–F stretch. Consequently, these two modes are assigned to the bands at 625 and 531 cm^{-1}, respectively.

For the assignment of the three A′ deformation modes, three polarized Raman bands at about 350, 240, and 200 cm^{-1} are available. The three deformation modes can be approximately described as an equatorial F–Br–O scissoring motion and as two axial F–Br–F bending motions. Since only one of these three involves the doubly bonded oxygen ligand, it should have the highest frequency and is assigned to the 350-cm^{-1} fun-

Table I. Vibrational Spectra[a] of BrF_3O Compared to Those of BrF_3,[b] ClF_3O,[c] and ClF_3[b]

Obsd freq, cm^{-1} (rel intens[d])										
								Assign for XF_3O in point group C_s		Approx description of mode
IR	R[g]	IR	R	IR	R	IR	R			
995 s	1008 s, p			1224 s	1222 (1.5) p			A′	ν_1	$\nu(X{=}O)$
625 s	619 vs, p	675 s	675 s, p	692 s	694 (2.6) p	751 s	752 s, p		ν_2	$\nu(XF_{eq})$
531 mw	502 vs, p	552 w	552 vs, p	481 m	482 (10) p	530 m	529 vs, p		ν_3	ν_{sym} $(F_{ax}XF_{ax})$
345 ms	350 m, p			491 ms	489 (1)				ν_4	δ_{sciss} (OXF_{eq})
240 m[e]	235 w	242		318 m	319 (0.1)	328			ν_5	δ_{sciss} $(F_{ax}XF_{ax})$ out of FXF plane
	198 mw, p	242	233 w, p	230 mw	224 (0.4) p	328	329 w, p		ν_6	δ_{sciss} $(F_{ax}XF_{ax})$ in FXF plane
601 vs		614 vs	612 vvw	676 vs		702 vs		A″	ν_7	ν_{as} $(F_{ax}XF_{ax})$
397 mw[f]	394 mw, dp	350 vw		501 m	500 (1)	442 w	431 w, dp		ν_8	δ_{wag} (OXF_{eq})
	330 sh, dp			412 w	414 (0.2) dp				ν_9	$\tau(OXF_{eq})$

[a] All frequencies are gas-phase values except as noted. [b] Data from ref 17. [c] Data from ref 12. [d] Uncorrected Raman intensities. [e] Ne matrix value. [f] Neat solid. [g] Concentrated HF solution.

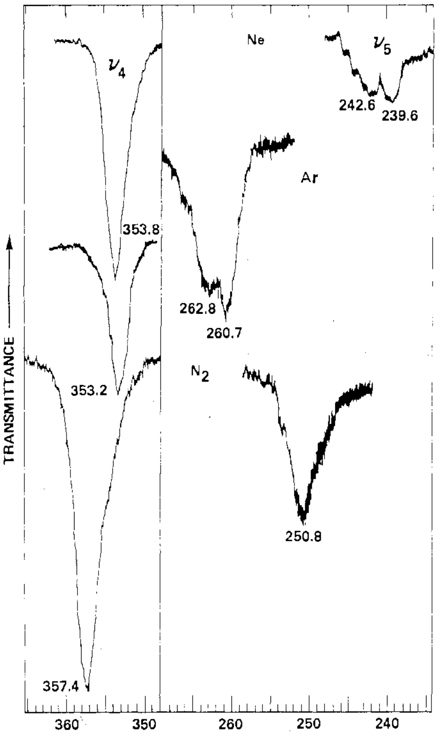


Figure 7. Infrared spectra of matrix-isolated BrF_3O (ν_4 and ν_5 region). The ν_4 and ν_5 bands in N_2 and the ν_5 band in Ar were recorded for a thicker sample.

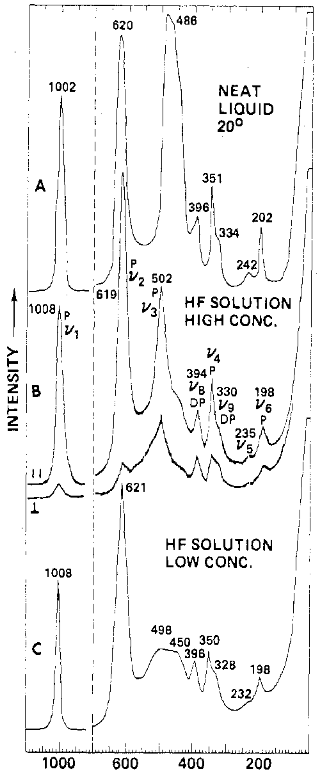


Figure 8. Raman spectra of liquid BrF_3O: trace A, neat liquid; traces B, concentrated HF solution with the incident polarization parallel and perpendicular; P and DP indicate polarized and depolarized bands, respectively; trace C, dilute HF solution.

damental. The two remaining fundamentals belong to the two axial F–Br–F bending modes. Since they are highly mixed (see below), their identity will be discussed in the force constant section.

There are three fundamental vibrations in species A″ with frequencies of about 600, 390, and 330 cm^{-1} available for assignment to the antisymmetric axial F–Br–F stretch and the equatorial F–Br–O wagging and torsion motions. On the basis of its high frequency, large ^{79}Br–^{81}Br isotopic splitting, and high infrared and low Raman intensity, the 600-cm^{-1} fundamental must be assigned to the antisymmetric axial F–Br–F stretching mode. Assignments for the two remaining deformation modes are made on the basis of their relative infrared intensities. The torsional mode should be of much lower intensity than the wagging mode and is, therefore, assigned to the 330-cm^{-1} fundamental. This leaves the 390-cm^{-1} fundamental for assignment to the wagging mode. The bands observed below 130 cm^{-1} in the Raman spectrum of solid BrF_3O have frequencies too low for internal modes and also were not observed for either the liquid or HF solutions. Consequently, they are assigned to lattice vibrations.

The above assignments are summarized in Table I and compared to those previously reported for ClF_3O[12] and BrF_3.[14,16,17] As can be seen, the agreement is excellent, thus lending additional support to our assignments. The decrease in the frequencies of the Hal–F stretching vibrations on oxygen addition is caused by the following effect. These halogen fluorides are more electronegative than oxygen. Consequently,

Table II. Observed Frequencies, Symmetry Force Constants,[a] Computed and Observed ^{79}Br–^{81}Br Isotopic Shifts, and Potential Energy Distribution[b] for BrF_3O

		Freq, cm^{-1}	Symmetry force constants		Isotopic shifts, cm^{-1}		PED
					$\Delta\nu_{comp}$	$\Delta\nu_{obsd}$	
A′	ν_1	995	$F_{11} = f_D$	7.68	2.28	2.25	$99 F_{11}$
	ν_2	625	$F_{22} = f_R$	3.51	1.54	1.5	$97 F_{22}$
	ν_3	531	$F_{33} = f_r + f_{rr}$	3.16	0		$100 F_{33}$
	ν_4	345	$F_{44} = f_\alpha$	1.21	1.01		$93 F_{44}$
	ν_5	236	$F_{55} = f_\beta + f_{\beta\beta'}$	1.70	0.54		$91 F_{55} - 63 F_{56} + 70 F_{66}$
	ν_6	201	$F_{66} = f_\gamma + f_{\gamma\gamma'}$	1.62	0.30		$45 F_{66} + 25 F_{56} + 24 F_{55}$
			$F_{56} = f_{\beta\gamma'} + f_{\beta\gamma''}$	0.65			
A″	ν_7	601	$F_{77} = f_r - f_{rr}$	2.70	2.68	2.7	$98 F_{77}$
	ν_8	394	$F_{88} = f_\beta - f_{\beta\beta'}$	1.23	0.23		$98 F_{88}$
	ν_9	330	$F_{99} = f_\gamma - f_{\gamma\gamma'}$	1.15	0.21		$96 F_{99}$
			$F_{78} = f_{r\beta} - f_{r\beta'}$	0.2			

[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.

Table III. Stretching Force Constants (mdyn/Å) of BrF_3O Compared to Those of Similar Molecules

	BrO_3^- [a]	BrO_4^- [b]	BrF_4O^- [c]	$FBrO_2$ [d]	BrF_3O	BrF_3 [e]	BrF_5 [f]	ClF_3O [g]	ClO_4^- [b]	ClF_3 [h]
f_D(XO)	5.28	6.05	6.70	6.98	7.68			9.37	8.24	
f_R(XF′)					3.51	4.07	4.02	3.16		4.19
f_r(XF)			2.14	2.75	2.93	3.10	3.24	2.34		2.70
f_{rr}			0.21		0.23	0.31	0.15	0.26		0.36

[a] H. Siebert, "Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie", Springer-Verlag, West Berlin, 1966. [b] Reference 22. [c] Reference 10. [d] K. O. Christe, E. C. Curtis, and E. Jacob, unpublished results. [e] Reference 16. [f] K. O. Christe, E. C. Curtis, C. J. Schack, and D. Pilipovich, *Inorg. Chem.*, **11**, 1679 (1972). [g] Reference 12. [h] Reference 14.

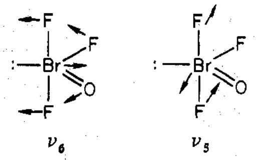
an added oxygen ligand releases electron density to the rest of the molecule. This increases the $F^{\delta-}$–$Hal^{\delta+}$ polarity of these bonds and thereby weakens them.

Force Constants. A normal-coordinate analysis was carried out for BrF_3O to support the above assignments. The potential and kinetic energy metrics were computed by a machine method.[18] The geometry assumed for this computation was D(Br–O) = 1.56 Å, R(Br–F′) = 1.72 Å, r(Br–F) = 1.81 Å, α(O–Br–F′) = 120°, β(O–Br–F) = γ (F′–Br–F) = 90°, based on the observed[19] geometry for BrF_3 and an extrapolation between Br–O bond length and stretching frequency, similar to that[20] used for Cl–O bonds, using the data published for BrO_4^- [21,22] and $FBrO_3$.[23,24] In the absence of structural data for BrF_3O, we assumed an idealized geometry with 90 and 120° bond angles. However, on the basis of the known increase in mutual repulsion within the series F < O < free electron pair, the true geometry of BrF_3O is expected to show a F′–Br–O bond angle of less than 120° and a slightly bent axial F–Br–F group. The latter prediction is also supported by the observation of the symmetric axial BrF_2 stretching mode as a weak band in the infrared spectrum of gaseous BrF_3O. The symmetry coordinates used for BrF_3O were identical with those previously given[12] for ClF_3O, except for interchanging S_3 and 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 fit between the observed and computed frequencies. The observed ^{79}Br–^{81}Br isotopic shifts were used as additional constraints, and the most simple force field was chosen which exactly duplicated these shifts. The computed force constants are listed in Table II. Uncertainty estimates are difficult to make. However, numerical experiments indicate that the uncertainties in the valence force constants should not exceed 0.1 mdyn/Å.

As can be seen from Table II, the observed frequencies and isotopic shifts can be accurately duplicated by a force field which, except for F_{56} and F_{78}, is diagonal. In the A″ block, a small value was required for F_{78} in order to be able to fit the isotopic shift observed for ν_7. The introduction of a nonzero value for F_{78} also resulted in the PED becoming significantly more characteristic. In the A′ block, a relatively large value was required for F_{56} in order to be able to fit ν_5 and ν_6. However, the remaining fundamentals were little influenced by the value of F_{56}.

The potential energy distribution (see Table II) shows that all fundamentals are highly characteristic, except for ν_5 and ν_6 which correspond to approximately equal mixtures of F_{55} and F_{66}. More information on the nature of ν_5 and ν_6 can be obtained from the eigenvector matrix **L**. Its important elements for ν_5 and ν_6 are as follows: ν_5, $-0.006S_4$, $0.133S_5$, $-0.119S_6$; ν_6, $-0.034S_4$, $0.057S_5$, $0.081S_6$. By analogy with ClF_3O[12], ν_6 and ν_5 correspond to a symmetric and an antisymmetric combination, respectively, of the symmetry coordinates S_6 and S_5. As shown by the stick diagram



ν_6 can be visualized as a symmetric bending motion of the two axial fluorine atoms in a plane containing the linear F–Br–F group and the free valence electron pair of bromine. The ν_5 fundamental can be considered as the corresponding bending motion perpendicular to this plane. As shown by the stick diagram, ν_6 also contains a significant contribution from the equatorial scissoring coordinate S_4.

The force constants of greatest interest are the stretching force constants since they are a direct measure for the strength and covalent character of the various bonds. A comparison of the stretching force constants of BrF_3O with those of similar molecules and ions is given in Table III. As can be seen, the value of the Br–O stretching force constant is in good agreement with our expectations for a BrO double bond. The general trend of the Br–O stretching force constants listed in Table III is similar to that observed for chlorine oxyfluorides.[25] The force constant increases with increasing fluorine substitution, oxidation state, and formal charge of the central atom. Consequently, it is not surprising that BrF_3O exhibits the highest f_D value of the listed compounds. The only presently known bromine oxyfluoride expected to have a higher

Table IV. ^{19}F NMR Spectra[a] of Neat BrF_3O and of BrF_3O in $FClO_3$ Solution

	Temp, °C				
	+10	−10	−20	−30	−40
Neat liquid	−165.2				
2.3 M soln	−165.2	−163.2	−161.4	−160.8	−160.2
2.5 × 10^{-2} M soln		−169.7	−169.5	−168.9	−167.2

[a] Chemical shifts in ppm. $CFCl_3$ was used as an external standard.

Table V. Thermodynamic Properties for BrF_3O

T, K	$C_p°$, kcal mol^{-1} deg^{-1}	$H° - H_0°$, kcal mol^{-1}	$-(F° - H_0°)/T$, kcal mol^{-1} deg^{-1}	$S°$, cal mol^{-1} deg^{-1}
0	0	0	0	0
100	10.871	0.872	30.788	59.512
200	16.448	2.255	37.595	68.868
298.15	19.830	4.050	62.543	76.127
300	19.878	4.087	62.627	76.250
400	21.852	6.182	66.809	82.264
500	23.032	8.431	70.416	87.278
600	23.775	10.774	73.591	91.548
700	24.265	13.178	76.427	95.252
800	24.603	15.622	78.988	98.516
900	24.845	18.095	81.322	101.428
1000	25.023	20.589	83.466	104.055
1100	25.157	23.098	85.448	106.447
1200	25.261	25.619	87.291	108.641
1300	25.343	28.150	89.012	110.666
1400	25.409	30.688	90.627	112.547
1500	25.462	33.231	92.147	114.301
1600	25.506	35.780	93.584	115.946
1700	25.543	38.332	94.945	117.494
1800	25.574	40.888	96.239	118.955
1900	25.600	43.447	97.471	120.338
2000	25.623	46.008	98.648	121.652

f_D value is the BrF_2O^+ cation which has a Br–O stretching frequency of about 1050 cm^{-1}.[26-28]

The Br–F stretching force constants of BrF_3O are similar to those of BrF_3, although somewhat lower due to the electron density releasing effect of the oxygen substituent (see above). The difference between the equatorial and the axial Br–F stretching force constant of BrF_3O is significantly larger than their estimated uncertainties (see above). This indicates that the equatorial Br–F bond is significantly stronger than the two axial ones. The same effect has previously been observed for ClF_3O and was explained[12] by significant contributions from semiionic three-center four-electron pσ bonds[29-31] to the axial bonds.

NMR Data. ^{19}F NMR spectra were recorded for the neat liquid at +10 °C and for $FClO_3$ solutions of two different concentrations in the temperature range +10 to −40 °C (see Table IV). By analogy with ClF_3O,[25,32,33] only a single line signal was observed. However, it has been shown[34] by relaxation time measurements that ClF_3O contains two different kinds of fluorines with a chemical shift separation of 50 ppm. The observation of a single line signal was attributed to rapid exchange.[34] Consequently, the observation of a single line signal for BrF_3O might be explained in a similar manner and should not be used as an argument against the above proposed model of symmetry C_s.

The signal observed for BrF_3O was shifted to higher field with both decreasing temperature and increasing concentration. Both trends indicate that the resonance for associated BrF_3O (see below) occurs upfield from that of monomeric BrF_3O.

Association in the Liquid and Solid Phase. The physical properties of BrF_3O, i.e., its relatively high melting and boiling point and low vapor pressure, indicate association in the liquid and solid phase. This was experimentally confirmed by vibrational and NMR spectroscopy. By analogy with the findings for the similar pseudo-trigonal-bipyramidal molecules BrF_3, SF_4, ClF_3,[14,35] and ClF_3O,[12] it can be shown that condensed BrF_3O is associated through fluorine bridges. The bromine atom achieves pseudohexacoordination by accepting an axial fluorine atom of another BrF_3O molecule as a fourth equatorial ligand.

As expected[12] for this type of association, the axial F–Br–F stretching frequencies are shifted to significantly lower frequencies, whereas the Br–O and the equatorial Br–F stretch are only little affected. Thus, the Raman spectra of the neat liquid and of HF solutions of BrF_3O (see Figure 8) show that the band due to the symmetric axial F–Br–F stretching mode has decreased in frequency by 30–80 cm^{-1} and has become very broad. The Raman spectrum of a 2 × 10^{-2} M solution of BrF_3O in $FClO_3$ at −10 °C has also been recorded. However, in this relatively unpolar solvent, the monomer concentration is high, as evidenced by ν_{sym}(F–Br–F) having a frequency of 527 cm^{-1}. For the Br–O and the equatorial Br–F stretching mode, frequencies of 996 and 619 cm^{-1}, respectively, were observed which are also close to those of the corresponding gas-phase values.

For neat solid BrF_3O (see Figure 3, traces B–D) association predominates, as expected.[12] For the symmetric F–Br–F stretching mode, only a weak Raman band occurred in the monomer region at 526 cm^{-1}, but a series of bands was observed at 511, 480, 457, and 447 cm^{-1} with increasing relative intensities which show infrared counterparts of medium intensities. Furthermore, the infrared frequency of the antisymmetric F–Br–F stretching mode has decreased by about 60 cm^{-1}, relative to the gas-phase value.

The above conclusions were further corroborated by the results from the matrix-isolation study. In addition to the bands due to monomeric BrF_3O, new bands were observed, particularly in the Ne spectra. These new bands had frequencies similar to those of neat solid BrF_3O and, therefore, are assigned to associated BrF_3O. In agreement with previous findings[12] for ClF_3O, the bands due to associated BrF_3O were observed on the high-frequency sides of ν(Br=O) and ν(Br–F′) and the low-frequency side of ν_{as}(F–Br–F) (see Figures 4 and 5 and the bands marked by P). For ν_{sym}(F–Br–F), the bands due to associated BrF_3O at 490 and 470 cm^{-1} (trace A, Figure 3) exhibited a large shift to lower frequencies and were more intense than that of the corresponding monomer band at 524 cm^{-1}. The higher intensities of the 490- and 470-cm^{-1} bands do not imply the presence of more associated than monomeric BrF_3O but are mainly due to a larger change of dipole moment involved in these modes. The ratio of monomer to oligomer can better be judged from the relative intensities of bands, such as ν(BrO), which do not participate in the bridge formation. In Figure 3, trace A, the appropriate bands are 998 cm^{-1} (monomer) and the shoulder on its high-frequency side (oligomer).

It should be noted that the spectra of neat liquid or solid BrF_3O did not show any evidence for bands due to BrF_2O^+[26-28] or BrF_4O^-.[2,10,36] This rules out extensive self-ionization according to $2BrF_3O \rightleftarrows BrF_2O^+BrF_4O^-$.

Additional support for the proposed association stems from the ^{19}F NMR spectra of BrF_3O which by analogy with those[26,34] of ClF_3O show an upfield shift with increasing concentration and decreasing temperature, conditions which favor association. For ClF_3O, the axial fluorine signal is observed[34] at higher field than that due to the equatorial fluorine. Since the axial fluorine bond is weaker than the equatorial one, an upfield shift is indicative of bond weakening, i.e., association.

Thermodynamic Properties. The thermodynamic properties of BrF_3O were computed with the molecular geometry given above and the vibrational frequencies of Table II, assuming an ideal gas at 1 atm and using the harmonic-oscillator-rigid-rotor approximation.[37] These properties are given for the range 0–2000 K in Table V.

Conclusion. Except for the ^{19}F NMR data, which in the absence of relaxation time measurements[34] are inconclusive, all of the data observed for BrF_3O are in excellent agreement with the predictions made for model I of symmetry C_s. Whereas gaseous, matrix-isolated, and $FClO_3$-dissolved BrF_3O is mainly monomeric, liquid, solid, and HF-dissolved BrF_3O shows pronounced association involving bridging through the axial fluorine atoms.[38]

Acknowledgment. K.O.C. is indebted to Mr. R. D. Wilson for experimental help, to Drs. L. R. Grant, C. J. Schack, and W. W. Wilson for helpful discussions, and to the Office of Naval Research, Power Branch, for financial support. R.B. is grateful to Mr. T. Bui Huy for experimental contributions.

Registry No. BrF_3O, 61519-37-7.

References and Notes

(1) R. Bougon and T. Bui Huy, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **283**, 461 (1976).
(2) R. Bougon, T. Bui Huy, P. Charpin, and G. Tantot, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **283**, 71 (1976).
(3) J. Shamir and J. Binenboym, *Inorg. Chim. Acta*, **2**, 37 (1968).
(4) R. Bougon, P. Joubert, and G. Tantot, *J. Chem. Phys.*, **66**, 1562 (1977).
(5) R. Bougon, P. Charpin, J. P. DesMoulin, and J. G. Malm, *Inorg. Chem.*, **15**, 2532 (1976).
(6) K. O. Christe and D. Pilipovich, *J. Am. Chem. Soc.*, **93**, 51 (1971).
(7) K. O. Christe, *Spectrochim. Acta, Part A*, **27a**, 631 (1971).
(8) E. K. Plyler, A. Danti, L. R. Blaine, and E. D. Tidwell, *J. Res. Natl. Bur. Stand., Sect. A*, **64**, 841 (1960).
(9) International Union of Pure and Applied Chemistry, "Tables of Wavenumbers for the Calibration of Infrared Spectrometers", Butterworths, Washington, D.C., 1961.
(10) K. O. Christe, R. D. Wilson, E. C. Curtis, W. Kuhlmann, and W. Sawodny, *Inorg. Chem.*, **17**, 533 (1978).
(11) H. H. Claassen, H. Selig, and J. Shamir, *Appl. Spectrosc.*, **23**, 8 (1969).
(12) K. O. Christe and E. C. Curtis, *Inorg. Chem.*, **11**, 2196 (1972).
(13) T. Ueda and T. Shimanouchi, *J. Mol. Spectrosc.*, **28**, 350 (1968).
(14) R. A. Frey, R. L. Redington, and A. L. Khidir Aljibury, *J. Chem. Phys.*, **54**, 344 (1971).
(15) K. O. Christe, unpublished results.
(16) K. O. Christe, E. C. Curtis, and D. Pilipovich, *Spectrochim. Acta, Part A*, **27a**, 931 (1971).
(17) H. Selig, H. H. Claassen, and J. H. Holloway, *J. Chem. Phys.*, **52**, 3517 (1970).
(18) E. C. Curtis, *Spectrochim. Acta, Part A*, **27a**, 1989 (1971).
(19) D. W. Magnuson, *J. Chem. Phys.*, **27**, 223 (1957).
(20) E. A. Robinson, *Can. J. Chem.*, **41**, 3021 (1963).
(21) S. Siegel, B. Tani, and E. Appelman, *Inorg. Chem.*, **8**, 1190 (1969).
(22) L. C. Brown, G. M. Begun, and G. E. Boyd, *J. Am. Chem. Soc.*, **91**, 2250 (1969).
(23) H. H. Claassen and E. H. Appelman, *Inorg. Chem.*, **9**, 662 (1970).
(24) E. H. Appelman, B. Beagley, D. W. J. Cruickshank, A. Foord, S. Rustad, and V. Ulbrecht, *J. Mol. Struct.*, **35**, 139 (1976).
(25) K. O. Christe and C. J. Schack, *Adv. Inorg. Chem. Radiochem.*, **18**, 319 (1976).
(26) R. Bougon, unpublished results.
(27) M. Adelhelm and E. Jacob, Paper J 2, presented at the 6th European Symposium on Fluorine Chemistry, Dortmund, West Germany, April 1977.
(28) R. J. Gillespie and P. Spekkens, Paper J 1, presented at the 6th European Symposium on Fluorine Chemistry, Dortmund, West Germany, April 1977.
(29) G. C. Pimentel, *J. Chem. Phys.*, **10**, 446 (1951).
(30) R. J. Hach and R. E. Rundle, *J. Am. Chem. Soc.*, **73**, 4321 (1951).
(31) R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 112 (1963).
(32) D. Pilipovich, C. B. Lindahl, C. J. Schack, R. D. Wilson, and K. O. Christe, *Inorg. Chem.*, **11**, 2189 (1972).
(33) K. Züchner and O. Glemser, *Angew. Chem.*, **84**, 1147 (1972).
(34) M. Alexandre and P. Rigny, *Can. J. Chem.*, **52**, 3676 (1974).
(35) R. Rousson and M. Drifford, *J. Chem. Phys.*, **62**, 1806 (1975).
(36) R. J. Gillespie and P. Spekkens, *J. Chem. Soc., Dalton Trans.*, 2391 (1976).
(37) J. E. Mayer and M. G. Mayer, "Statistical Mechanics", Wiley, New York, N.Y., 1940.
(38) Note added in proof: After completion of this study, R. J. Gillespie and P. H. Spekkens, *J. Chem. Soc., Dalton Trans.*, 1539 (1977), have reported some spectroscopic properties of BrF_3O which are in good agreement with the results from this study.

Contribution from the Departments of Chemistry and Physics and the Laboratory for Research on the Structure of Matter,
University of Pennsylvania, Philadelphia, Pennsylvania 19104

Synthesis of Metallic Polythiazyl Halides from Tetrasulfur Tetranitride

MASUD AKHTAR, CHWAN K. CHIANG, ALAN J. HEEGER, JoANN MILLIKEN,
and ALAN G. MacDIARMID*

Received December 29, 1977

Powdered tetrasulfur tetranitride, S_4N_4, polymerizes at room temperature in the presence of Br_2 or ICl vapor to form a series of highly conducting metallic solid compounds of approximate composition $(SNBr_{0.4})_x$ and $[SN(ICl)_{0.4}]_x$, respectively. Carbon tetrachloride solutions of IBr also react with S_4N_4 at room temperature to give a conducting solid of composition $[SN(IBr)_{0.40}]_x$. When $(SNBr_{0.4})_x$ is heated with pumping at 80 °C, it is converted to a series of highly conducting copper-colored powders of composition $(SNBr_y)_x$ (y = 0.16–0.28). The conductivity at room temperature of compressed pellets of the compounds is in the range 10–400 Ω^{-1} cm^{-1} and is almost temperature independent down to 4.2 K.

Considerable interest has recently been shown in the synthesis and study of metallic covalent polymers such as polythiazyl, $(SN)_x$,[1] and the polythiazyl bromides, $(SNBr_y)_x$.[2] The synthesis of $(SN)_x$, from which $(SNBr_y)_x$ is made, first involves the preparation of disulfur dinitride, S_2N_2, from tetrasulfur tetranitride, S_4N_4, by a relatively complicated procedure, followed by its solid-state polymerization.

Recently, independent studies by ourselves[3] and by Street et al.[4] have shown that polycrystalline $(SNBr_y)_x$ and other metallic polythiazyl halides may be synthesized by a very simple procedure directly from S_4N_4. Thus, solid S_4N_4 reacts readily at room temperature with Br_2, ICl, and IBr vapor to give highly conducting black powders. We reported[3] that the metallic compound formed from bromine had the composition $(SNBr_{0.4})_x$ and that pumping at ca. 80 °C for ca. 4 h gave a copper-colored metallic powder of composition $(SNBr_{0.25})_x$. Street et al.[4] reported that heating $(SNBr_{0.4})_x$ at 80 °C for 18 h gave a copper-bronze-colored powder, $(SNBr_{0.07})_x$. The latter authors also stated that IBr and ICl gave conducting powders of unknown composition. In this communication we report experimental details of the synthesis of the products formed from S_4N_4 and Br_2, ICl, and IBr and some of their more important physical properties.

Experimental Section

Apparatus and Techniques. All operations were carried out under a dry argon atmosphere in a Vacuum Atmospheres Corp. Dri-Train

---

* To whom correspondence should be addressed at the Department of Chemistry.

0020-1669/78/1317-1539$01.00/0