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# X-RAY INVESTIGATION OF THE STRUCTURE OF LIQUID

#### BROMINE TRIFLUORIDE

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Using x-ray methods appropriate to liquids we determined the nearest neighbor coordination in liquid bromine trifluoride at 298°K. We have proposed a model for the structure which takes into account the presence of associated and non-associated forms.

The structure of bromine trifluoride, a prospective non-aqueous solvent, has been studied in all states of aggregation [1-8]. At present we are hoping to establish the structure of the monomeric molecule in the gaseous phase, which, according to the most recent data from electron diffraction [3] confirming and refining earlier data [1], has a twisted T-form configuration with a shortened central bond  $Br-F_2(r_{Br}-F_{1,3}) = 1.809(17)$  $r_{Br}-F_2 = 1.728(15)$  Å,  $\alpha = 85(2)^{\circ}$ . This kind of structure agrees well with the IR spectroscopic data [2], the electric and dipole moments for gaseous  $BrF_3$ , and also with earlier data from microwave measurements [5]. In the solid state bromine trifluoride crystallizes in the ortho-

rhombic system [6], a = 5.34, b = 7.35, c = 6.61 Å, Z = 4, R = 21%, space group Cmc2<sub>1</sub>.

The liquid state of bromine trifluoride has been studied using Raman, IR, and NMR <sup>19</sup>F spectroscopy [2, 7-9]. From the Raman spectroscopic data for liquid  $BrF_3$ , whose appearance does not agree, (for a molecule with  $C_{2V}$  symmetry) with the IR spectra of a dimer ( $PBrF_3 = 8$  tor) [2], and also from the abnormality high Trouton constant [1], we could not exclude the possibility of the existence in liquid  $BrF_3$  of molecular associates [3]. At the same time the NMR <sup>19</sup>F spectrum of liquid  $BrF_3$  shows a single broadened signal with chemical signal  $\sqrt{451}$  ppm (relative to  $F_2$ ) which does not agree with the isolated T-form molecules with non-equivalent fluorine atoms which exist both in the gaseous and the solid state.

### STRUCTURAL ANALYSIS METHODS

The investigation was carried out on a DRON-2.0 x-ray diffractometer using an airtight cuvette of fluorplastic-4 whose construction is shown in Fig. 1. We used monochromatic  $MoK_{\alpha}$  radiation of wave length 0.711 Å.

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Fig. 1. Cuvette for x-ray investigation of corrosive liquids. 1) Sheet of fluoroplastic-4 (2-5 M). 2) Conical thickening washer (fluoroplastic-4). 3) Frame ring (Dural D16T), 4) Frame of the cuvette (fluoroplastic-4). 5) Holder (Dural D16T). 6) Sealing screw (fluoroplastic-4).

Bromine trifluoride was obtained by direct interaction of gaseous fluorine with liquid bromine of "ChDA" quality at 20-40°C (P = 766 torr) and melting, according to DTA data, at 8.8  $\pm$  0.1°C, which agrees with the data for pure BrF<sub>3</sub> [1]. The absence of HF, BrF and BrF<sub>5</sub> was checked using NMR <sup>1</sup>H and <sup>19</sup>F spectroscopy.

The operations of filling and sealing the cuvette were carried out in dry nitrogen container. The filled cuvette was placed in a GP-3 attachment provided with a GUP-5 goniometer and the cuvette was tested for airtightness with a layer of kerosene, and over a period of 24 hrs no seepage was detected.

The survey of the diffraction records was carried out using a system with a Soller slit (beam divergence  $\leq 1.5^{\circ}$ ) and a diaphragm thickness of 0.5 mm. Recording of the diffracted radiation was carried out five times using a set of 2000 impulses with 0.2° steps across the diffraction angle of 20° in the region of the diffraction maximum and with 0.5-1.0° steps in the shallow region of the diffraction peak. From the diffractogram obtained we calculated the corresponding diffractogram for the foreground of the fluorolayer sheet in the empty cuvette and we found  $I_S$  (observed) where  $s = 4\pi \sin\theta/\lambda A^{-1}$ . For the experimental diffraction curve thus obtained we carried out corrections for the dispersion from the heavy bromine nuclei using the method of [10] and a correction for the polarization of the radiation by the liquid and the monochromator using the formula  $P(20^{\circ}) = 0.5(1 + \cos^2 20^{\circ} + \cos^2 2\alpha^{\circ})$ , where  $\alpha$  is the monochromator angle. Absorption of the radiation for the survey of the reflection was constant and did not depend on the 20° angle [11]. We converted the experimental diffraction curve  $I_S$  (observed) to electron units using Weinstein's method [12]. We determined the coefficient of standardization using the formula

$$k = \int_{s_{\min}}^{s_{\max}} \sum_{i} n_{i} f_{i}^{2}(s) s^{2} ds \left( \int_{s_{\min}}^{s_{\max}} I_{experimental}^{corrected}(s) s^{2} ds \right)$$
(1)

where  $\sum_{i} n_i f_i^2(s)$  is the independent gaseous scattering by fluorine and bromine atoms in one molecular unit of BrF<sub>3</sub>, n<sub>1</sub> is the number of atoms of each type in the formula unit of the solution (3 for fluorine and 1 for bromine), f<sub>1</sub> are the atomic scattering factors (form factors) using the data of [13], and I<sup>corrected</sup>(s) is the intensity corrected for the effects described above. It should be noted that the use of atomic scattering factors for F<sup>-</sup> and Br<sup>3+</sup> rather than for fluorine and bromine atoms is not of prime importance and does not have any bearing on the nature of the molecular scattering and the radial distribution because the sum of the radii of fluorine and bromine atoms for covalent and ionic bonds are virtually identical [20]. r<sub>F</sub>- + r<sub>Br</sub><sup>3+</sup> = 1.82; r<sub>Br</sub> + r<sub>F</sub> = 1.78 Å, giving a mean bond length of 1.80 ± 0.02 Å, which is close to the experimental data [1, 3]. We expressed the stand-

of 
$$1.80 \pm 0.02$$
 Å, which is close to the experimental data [1, 3]. We expressed the stand-  
dardized intensity in the following manner:

$$I_{experimental}^{standardized}(s) = k I_{experimental}^{corrected}(s).$$
(2)

After the experimental diffraction curve has been standardized we calculated the molecular scattering function i(s) from the equation:

$$\mathbf{i(s)} = \mathbf{I}_{\text{experimental}}^{\text{standardized}}(\mathbf{s}) - \sum_{i} u_{i} \left\{ \left[ f_{i}(s) + \Delta f_{i}'(s) \right]^{2} + \left[ \Delta f_{i}''(s) \right]^{2} \right\}$$
(3)

It was necessary to carry out corrections on the ordinate and abscissa of the background beginning with the requirement for equality of area between the standardized curve and the curve of independent gaseous scattering, i.e., an equal oscillation of the maximum and minimum interference functions (2) relative to the zero axis as per reference [14]. From the functions obtained in this way i(s) previously corrected for the dispersions  $\Delta f'_i(s)$ ,  $\Delta f''_i(s)$  [10], we calculated the radial distribution function (rdf) using the Fourier transform as per method

$$D(R) = \int_{R_{1}}^{R_{2}} 4\pi R^{2} \rho(R) \, dR = D_{0} + \sum_{i} n_{i} \cdot k_{i}^{2} \cdot \frac{2R}{\pi} \int_{s_{\min}}^{s_{\max}} i(s) \sin(sR) \, ds, \tag{4}$$

where  $\rho(R')$  is the mean value of the atomic density in time and space (in a spherical layer of width dR),  $D_0$  is the mean distribution of atoms

$$D_0 = 4\pi R^2 \left( \sum_i n_i k_{\beta_i}^2 \right) \cdot d/M \cdot m_1, \tag{5}$$

where d is the peak metric density of bromine trifluoride which equals  $2.804 \text{ g/cm}^3$  at  $298^{\circ}$ K, M is the molecular weight of the formula unit of the solution which equals 137 for one molecule of bromine trifluoride, m is the mass of the lightest atom in the formula unit, r and k are the effective scattering characteristics of the atoms of the formula unit of the solution determined by the formula

$$k_{i} = \int_{0}^{s_{\text{max}}} s^{2} f_{i}^{2}(s) \, ds \, \left/ \int_{0}^{s_{\text{max}}} s^{2} f_{1}^{2}(s) \, ds, \right. \tag{6}$$

where  $f_i$  is the atomic scattering factor of the lightest atom.

The procedure for calculating the function (4) which we have described was carried out on a BESM-6 minicomputer using the programs of reference [14]. From the position of the maximum in the radial distribution function D(R) we determined the interatomic distances  $R_{ij}$  and from the values of the areas under the peaks of the rdf we found the coordination number  $(CN_{A-B})$  of the atom A relative to atoms B,

$$\operatorname{CN}_{\mathbf{A}-\mathbf{B}} = Q/2k_{\mathbf{A}} \cdot k_{\mathbf{B}} \cdot n_{\mathbf{A}},\tag{7}$$

where Q is the measured area of the coordination peak on the curve D(R) expressed in units of the space  $n_A$  where the number of atoms of type A in the formula unit were chosen as central and surrounded by atoms of type B. Where the coordination maximum was not solvable at the extreme of large R values its reverse side was transformed by symmetry to the front one. The accuracy of the determination of the position of the first maximum (depending on the 'sharpness' of the peaks of function (4)) was no worse than  $\pm 0.02 - 0.05$  Å. The value of the error in the calculation of the area of the peak was determined essentially by the precision of measurement of  $I_{obs}^{obs}(s)$ , by the precision of the graphic division of this maximum and particularly by the propertionality constant  $N^{-1/2}$ , which, where N = 2000 corresponds to an error in the area of the peak of  $\pm 3\%$ . The error in the determination of the graphic area was  $\pm 3-5\%$ . Thus, the total error does not exceed  $\pm 6-8\%$ .

### EXPERIMENTAL ATOMIC RADIAL DISTRIBUTION FUNCTION

In Fig. 2 we give the rdf of atoms for liquid bromine trifluoride obtained using the procedure described above. In this function peaks can clearly be seen whose maxima are situated at 1.80, 2.80, 4.90, and 6.20 Å and correspond to the intermolecular and intramolecular distances and interactions in the liquid.

The first maximum at  $1.80 \pm 0.05$  Å corresponds to the intra-molecular distances, i.e., to bond lengths Br-F, and is situated in accordance with the appropriate data (mean bond length for Br-F in the BrF<sub>3</sub> molecule equals 1.75 Å in the gas and 1.83 Å in the solid state [1-3, 5, 6]). The coordination number for bromine, determined by the area of the first peak using equation (7) is  $3.5 \pm 0.2$  i.e., in the liquid each bromine atom probably has in its

[12]



Fig. 2. Radial distribution function of liquid bromine trifluoride at 298°K.

closest environment on the average rather more than three fluorine atoms at a distance of  $\sim 1.8$  Å. The interatomic distances between fluorine and bromine atoms, situated in a series of ordered molecules at distances of 2.5 to 3.2 Å (Br-Br, Br-F, and F-F respectively) contribute to the area of the second peak at 2.8 ± 0.10 Å. This corresponds to molecular arrangements with diameters between 5.0 and 6.4 Å. We based this conclusion on the agreement of the calculated values of the areas with possible scattering interatomic distances for various models and this is discussed below. The third peak at 4.9 ± 0.1 Å results from intermolecular distances in the second coordination sphere. Both the distances between the individual BrF<sub>3</sub> molecules in the third and fourth coordination spheres and the distances which determine the dimensions of the normal molecular arrangements in liquids are determined by the first diffraction peak in the function  $i_{exp}(s)$  (see Fig. 4, curve 10). Such regular arrangements can be associated bromine trifluoride molecules.

We note that the mean value of the volume for one molecule of  $BrF_3$  in the liquid at 298°K is 81.13 Å<sup>3</sup> in the rigid rotator approximation and it follows that the mean radius is  $\sim 2.7$  Å. This corresponds to its dimensions of approximately 5.4 Å i.e., to the calculated mean interatomic distance for a liquid of the molecular type.

## THEORETICAL DIFFRACTION MAP OF LIQUID BROMINE TRIFLUORIDE

For an explanation of the observed diffraction map and an assessment of the nature of the interatomic distances  $R_{ij}$  with regard to their contribution to the peaks of the rdf, various models of the structure of bromine trifluoride in the liquid state were looked at and these can be proposed as explanations for several well known properties of liquid  $BrF_3$ . These are: a) the electrolytic dissociation [3] of bromine trifluoride into square planar bromine tetra-fluoride anions  $[BrF_4]^-$  and angular bromine difluoride cations  $[BrF_2]^+$ ;

$$2BrF_3 \rightleftharpoons [BrF_2]^+ + [BrF_4]^-; \tag{8}$$

b) the presence in the NMR <sup>19</sup>F spectrum of bromine trifluoride of a single broadened signal; c) the high Trouton constant whose value is characteristic of associated liquids; d) IR and other data. The structures of the  $[BrF_2]^+$  cations and the  $[BrF_4]^-$  anions are precisely defined in the solid compounds  $K[BrF_4]$ ,  $[BrF_2][SbF_6]$  and  $[BrF_2]_2[GeF_6]$  [15-17], and this was taken into account in selecting the type of model. The models considered are shown in Fig. 3. The theoretical functions of the molecular distances i<sup>theor</sup>(s) were calculated using the equation

$$i^{\text{theor}(s)} = \frac{I_{i}^{\text{theor}(s)}(s)}{\sum_{i}^{n} n_{i} f_{i}^{2}(s)} - 1,$$
(9)



Fig. 3. Calculated models of the structure of bromine trifluoride in the liquid state. 1) Monomer [1]. 2) Ionic model  $[BrF_2]^+[BrF_4]^-$  using data from reference [15-17]. 3) Trimer, a = 1.72, b = 3.62, c = 4.68,  $\gamma = 90^{\circ}$ . 4) Dimer, a = b = 1.81 Å 5) Tetramer, a = b = c = 1.81 Å. 6) Unit cell of solid bromine trifluoride using data from reference [6], a = 5.34, b = 7.35, c = 6.61,  $\gamma = 90^{\circ}$ .



Fig. 4. Molecular scattering functions for model bromine trifluoride structures which were studied. 1) Monomer (molecule). 2) Ionic model (see Fig. 3, 2). 3) Trimer (see Fig. 3, 3). 4) Dimer (see Fig. 3, 4). 5) Double tetramer a = c = 2.3, b = 1.85 Å,  $\gamma = 90^{\circ}$ . 6) Tetramer a = b = c = 1.81 Å,  $\gamma = 90^{\circ}$  (see Fig. 3, 5). 7) Tetramer, a = c = 2.46 Å, b = 1.88 Å,  $\gamma = 90^{\circ}$ . 8) Unit cell of solid bromine trifluoride (see Fig. 3, 6). 9) Model of simultaneous coexistence in the liquid of various associated forms (50% curve 8, 10% curve 7, and 40% curve 4). 10) Experimental molecular scattering function.

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Position of peak	Boundaries of peak	Model (see Fig. 3)	Center atom	Atom closest to center atom	Coord, num. between atoms	Distance between• atoms, A	calc. area, diff- ractometer dist., area units	Peak area, area units	Experimental peak area, area units
1,80±0,05	0,82,6	Molecule Dimer Tetramer	pr 2	मि सि सि	n44	1,81 1,81 1,81	29,4 39,2 39,2	29,4 39,2 39,2	34土2
		Cell of Solid BrF3 Coexistence of	ňň	۴.۶.	n ⊶	$1,85 \\ 2,49$	29,4 9,8	39,2	
$2,80 \pm 0,10$	1,83,8	different assoc, forms Molecule	Ē.	يتر 	2	2,52	4,0	39,2 6,0	
		Dimer	ы Б.	는 면 다.	रूम रूम [२०	3,60 2,61	$     \frac{2,0}{14,00} $	70,02	
		Tetramer	~ n n i	- ää	N. 44 44 1	3,7 3,20 3,20 3,20	8,00 48,02 48,02 30 50	76 264	88+6
				I, II, II,	4 % %	2,61 2,61	36,00 16,00		-
	(1)	Cell of solid BrF <sub>3</sub>	ኯ፝ዹዾኯ፟	یو بن نیز ایر	≪4∞∞ <del>-</del>	2,52 2,52 2,70 2,52	39,20 16,00 9,80	81,00	
		Coexistence of	different	t associated	forms (50% of	cell of sc	vid BrF3 plus 40%	dimer plus	10% tetramers)
4,90	3,25,6	Cell of solid BrF3	Br Br	Br	6 18	4,1-4,54 3,8-5,6	288,2 176,5	00.2 454,6	
			Distance summary	e F - F are intensity.	not included	due to thei	r small contributio	on to the	
		Intermolecular interactions	Br	P.P.	6 18	4,54 3,2-5,6	288,2 176,4	454,6	460±30
			Distance calculat F-F dis	es between a ted from dif tances not i	ttoms of the br fraction peak included.	comine trifl i(s) = 1.55	uoride molecule		
	•								

(6.4 H = 1.0; kp. Radial Distribution Function D(R) for Models of  $BrF_{c}$  (kp TABLE 1.

65

where  $I^{\text{theor}}(s) = \sum_{i} \sum_{j} f_i(s) \cdot f_j(s) \cdot \sin(sR)$ . The calculations using equation (9) were carried out on a

BESM-6 minicomputer using the programs of reference [18]. These functions for the models in Fig. 3 are shown in Fig. 4 (curves 1-9) where the functions  $i_{exp}(s)$  for liquid BrF<sub>3</sub> (curve 10) are also given for comparison. There is a sharp initial maximum at  $s_1 = 1.55$  Å<sup>-1</sup> for this curve, which corresponds to the mean molecular distance in the liquid as determined from the empirical formula given in reference [19].

$$R_i = \frac{7.73}{s_i} - 0.3, \quad \text{Å}^{-1}.$$
 (10)

Taking the above value for  $s_1$ , the value of  $R_1$  is 4.54 Å, which is substantially less than the value of  $\sim$ 5.4 Å calculated by the rigid rotator approximation for a liquid of molecular type and points to the possibility of association of the  $BrF_3$  molecules in the liquid state. The value of  $s_1$  corresponds to curve 8 in Fig. 4 which was calculated for a unit cell of solid bromine trifluoride. However, the second and third peaks of the theoretical curve for i<sup>theor</sup>(s) on curve 8 do not agree with the analogous maxima on curve 10. The peaks corresponding most closely to these are those calculated for the trimer and tetramer structures (curves 2 and 7). In the trimer under consideration there are neighboring molecules of bromine trifluoride at distances of 2.34 Å from each other and in the tetramer, as can be seen from Fig. 3, there are two dimers of  $BrF_3$  molecules rotated along the screw axis and separated from each other along the axis at a distance of 2.46 Å. In curves 2 and 7 there are no important peaks at  $s_1(exp)$ , the experimental molecular scattering function (curve 10) but this peak would have been present in the curve itheor(s) where the number of intermolecular distances is increased in the more complex model. For this reason it was suggested that in liquid bromine trifluoride there can exist simultaneously both fragments of quasicrystallites of solid  $BrF_3$  (on the level of the unit cell) or associated molecules of  $BrF_3$  in the form of dimers, trimers or tetramers, and nonassociated free molecules. Their simultaneous existence is also expressed in curve 10 for the function  $i_{exp}(s)$ .

In the model which we considered comprising the simultaneous existence of associated and monomeric forms, the coordination number of bromine is close to four, which corresponds to the data of other diffraction experiments (see Fig. 2, and see Table I). The structural components which make up this model, shown in Fig. 3, readily permit the formation of ions of bromine difluoride and bromine tetrafluoride, and data from the measured areas of the rdf peaks (experimental) (see Table I) do not contradict the corresponding values calculated using Eq. (7).

Thus the model of the structure of liquid bromine trifluoride, taking into account the simultaneous existence in the liquid of the monomer BrF<sub>3</sub> and of molecules associated in various ways, resulting in approximately equivalent environments for each bromine atom, namely of four fluorine atoms, can be compared with the presence in the NMR <sup>19</sup>F spectrum of liquid  $BrF_3$  of a single signal [8, 9], which suggests the absence in the liquid of bromine-fluorine bonds of unequal values. The disappearance of the nonequivalence in the Br-F bonds in the liquid is the consequence of association which can be related to the rapid exchange of bromine and fluorine atoms between neighboring molecules of the bromine trifluoride, which is the deciding factor in the existence in liquid bromine trifluoride of stable molecular associations.

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DIRECT IDENTIFICATION OF METAL-METAL BONDS IN POLYCRYSTALLINE SPECIMENS OF INORGANIC HEAVY-METAL CLUSTER COMPOUNDS FROM RADIAL DISTRIBUTIONS

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UDC 539.264+646.719

It is shown that one can detect bonds between heavy-metal atoms directly and measure their lengths from the radial distributions (RD) derived from powder patterns. Model substances of known structure have been used to elucidate and demonstrate the scope and limitations of this method. Model RD calculations provide direct tests on proposed structures. The structures have been established for two rhenium dimers not previously examined.

At present, the main observational criterion for a bond between metal atoms is the distance between them, which is determined directly in x-ray structure analysis (XSA) for single crystals. If the substance can be made only as a polycrystalline powder, the question of the interatomic distances and bonding usually remains open. However, the scope for measuring these directly is not exhausted by classical XSA. For example, interatomic distances and even coordination numbers can in principle be extracted from radial distributions (RD) [1, 2]. The RD G(r) is the one-dimensional spectrum of the interatomic distances for a macroscopically isotropic specimen. Each pair of atoms corresponds to a peak at r equal to the distance between them, so it can be measured. The RD method is quite often used with liquids and amorphous substances [1, 2], and it is in principle applicable to polycrystalline materials [3], although hardly any use has been made of it there.

The RD is derived from the diffraction pattern, which is a powder pattern for a polycrystalline material. One often uses x-ray diffraction, where the main difficulty lies in interpreting the RD, since the contributions for different interatomic distances overlap. Here I point out that this difficulty can be largely avoided for certain classes of compound containing heavy atoms. I consider that the most promising chemical application may be to cluster compounds, where one of the major structural problems lies in detecting metal-metal bonds and measuring their lengths, as well as the geometry of the metal core in the cluster. The distances between the heavy-metal atoms should give the strongest peaks on the RD, which are readily identified, so one can detect the metal-metal bonds and measure the distances without growing single crystals. Theoretical calculations can be made on the RD from models, which provides for teting of cluster geometries in a fashion more direct than that from spectral or other indirect evidence.

Here I examine inorganic rhenium clusters, mainly simple dimers. Initially, I examine the effects of ReRe bonds on the RD and the interfering factors by means of model powders of known structure. Then I consider two compounds assumed to have ReRe bonds, which have been made by A. S. Kotel'nikova and others, and whose structures cannot be examined by XSA because of the difficulty in growing single crystals.

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