Characterisation of the Oxo-anions of Bromine BrO_x^- (x = 1—4) by Infrared, Raman, Nuclear Magnetic Resonance, and Bromine *K*-Edge Extended *X*-Ray Absorption Fine Structure Techniques†

William Levason,* J. Steven Ogden, Mark D. Spicer, and Nigel A. Young
Department of Chemistry, The University, Southampton SO9 5NH

The bromine oxo-anions BrO_x^- (x = 1—4) have been studied by vibrational and multinuclear n.m.r. spectroscopy and bromine *K*-edge extended *X*-ray absorption fine structure (EXAFS) measurements. Raman and/or i.r. data for BrO^- and BrO_2^- are presented, and conflicts in the literature for the latter resolved. Oxygen-17 n.m.r. data for the halogen oxo-anions have been recorded, and an increase in $\delta(^{17}O)$ with formal oxidation state of the halogen noted. Coupling to the halogen nucleus has been observed for ClO_4^-, $^1J(^{35/37}Cl-^{17}O)$ = 85, and for BrO_4^-, $^1J(^{79/81}Br-^{17}O)$ = 420Hz, but could not be resolved for IO_4^-. The ^{81}Br n.m.r. resonance of BrO_4^- (δ = 2 476) and the ^{127}I resonance of IO_4^- (δ = 4 090 p.p.m.) are reported. Bromine *K*-edge EXAFS data are presented for all four ions in solution, and for all but BrO^- in the solid state, and differences in bond lengths between solid state and solution found to be within experimental error. Bond lengths obtained are: BrO_4^- 1.61, BrO_3^- 1.65, BrO_2^- 1.72, and BrO^- 1.81 Å. This is the first bond length reported for the hypobromite ion.

The oxo-anions of bromine have a long history, with hypobromite (BrO^-) and bromate (BrO_3^-) both being prepared[1,2] soon after the discovery of bromine. However, until quite recently bromate was the only easily isolated and well characterised[3] member of the series. The perbromate ion (BrO_4^-) was for many years the subject of much speculation[4] until its eventual preparation by Appelman,[5] and considerable uncertainty remains concerning bromite (BrO_2^-) and hypobromite despite widespread use of their solutions in synthetic and industrial processes.[6,7] One reason for the lack of definitive spectroscopic and structural data for these particular ions undoubtedly arises from the difficulties encountered in obtaining pure samples of their salts in the solid state, and this is reflected in the discrepancies found in the literature.[8–10]

As part of a programme of spectroscopic and structural studies on the oxides and oxo-anions of bromine, we have recently reported the *X*-ray crystal structure of $NaBrO_2\cdot3H_2O$.[11] Here we describe an extension of this work in which characteristic i.r., Raman, and n.m.r. spectra and bromine *K*-edge extended *X*-ray absorption fine structure (EXAFS) data have been obtained for the complete series BrO_x^- (x = 1—4). The results are discussed in the light of previous studies on these systems, and are compared with data on related halogen oxo-anions.

Experimental

With the exception of $NaBrO_3$ which was obtained commercially (BDH 99.9%), synthetic routes to all of the bromine oxo-anions were explored. Hydrated sodium hypobromite was obtained by the method of Scholder and Krauss[12] involving treatment of 10 mol dm^{-3} aqueous NaOH with Br_2 at low temperatures. The product was a bright yellow solid, which must be handled with care since it melted in its own water of crystallisation below room temperature, and readily disproportionated.

Various attempts were made to prepare bromites, including $NaBrO_2$ (Fuchs and Landsberg[13]), $Ba(BrO_2)_2$ (Noszticzius *et al.*[14]), and $[NBu^n_4][BrO_2]$ (Kageyama and Yamamoto[15]). Solutions of $NaBrO_2$ and $Ba(BrO_2)_2$ were readily obtained, and shown by Raman and ^{17}O n.m.r. spectroscopy to contain the required BrO_2^- ion, with only small amounts of bromate impurity. However, attempts to crystallise the solid bromites led to extensive decomposition to bromate. In our hands, attempts to make the alkylammonium salt yielded only bright orange $[NBu^n_4]^+[Br_3]^-$. Ironically, during the course of this work $NaBrO_2\cdot3H_2O$ became commercially available (Fluka >95%), and this product not only proved to be relatively stable and crystalline, but was found by solution Raman and n.m.r. studies to have only minimal amounts of BrO_3^- impurity. Finally $KBrO_4$ was prepared[5] as a white crystalline solid by fluorine oxidation of basic solutions of $KBrO_3$.

Commercial samples (BDH) of $NaClO_3$, $NaClO_4$, $NaClO_2\cdot3H_2O$, $NaIO_4$, and $NaIO_3$ of the highest purity available were used for the n.m.r. studies, and sodium hypochlorite was made by the method of Underwood and Mack.[16]

Instrumental Techniques.—Raman spectra were obtained using a Spex 1401D instrument equipped with argon-ion laser excitation (514.5 nm), i.r. spectra were recorded in Nujol mulls on Perkin-Elmer 580B and 983G spectrometers. Oxygen-17 n.m.r. spectra were recorded at room temperature from saturated solutions in H_2O–D_2O (5:1 v/v) on a Bruker AM 360 spectrometer operating at 48.8 MHz, and are referenced to external H_2O (δ = 0); ^{81}Br and ^{127}I n.m.r. spectra were obtained similarly at 97.3 and 72.3 MHz, and referenced to the corresponding KX in water (1 mol dm^{-3}), and the values corrected to 'infinite dilution' using published data.[17]

Bromine *K*-edge EXAFS data were recorded at the Daresbury Synchrotron Radiation Source on station 9.2 using a double-crystal silicon 220 monochromator. The operating energy was 2 GeV with an average current of 180 mA. Solid samples were diluted with boron nitride (*ca.* 10% by weight of Br) and held between Sellotape strips in 1-mm aluminium spacers. Solution studies used an aluminium cell for aqueous $KBrO_4$ or $NaBrO_3$, whilst samples of aqueous BrO_2^- and BrO^- were run in a polytetrafluoroethylene cell. In each case the path length was 3 mm, both cells being fitted with Mylar

---

† *Non-S.I. unit employed:* eV ≈ 1.60 × 10^{-19} J.

Table 1. Selected i.r. and Raman spectroscopic data (cm^{-1}) for the ions BrO^- and BrO_2^-

	Vibrational fundamentals					
	Previous studies			This work		Assignment
	Ref. 9		Ref. 10			
	Raman			Raman		
BrO^- solution	620			618		ν(Br–O)
	Raman	Raman	Raman	Raman	Raman, I.r.	
BrO_2^- solution*	709	(728)	711	710	(728, 721)	ν(Br–O) A_1
	324	(330)	340	320	(327, 328)	δ(Br–O_2) A_1
	680	(680)	—	—	(680, 682)	ν(Br–O) B_1

* Values for $NaBrO_2 \cdot 3H_2O$ in parentheses.

Table 2. Oxygen-17 n.m.r. data for halogen oxo-anions[a]

	δ/p.p.m. ($W_{\frac{1}{2}}$/Hz)		
Ion	X = Cl	Br	I
XO^-	+14 (220)	+8 (100)	
XO_2^-	+147 (330)	+145 (570)	
XO_3^-	+287 (95) lit. 289	+296.5 (146) lit. 297	210 (700) lit. 206
XO_4^-	+292[b] lit. 290	+357.5[c] lit. 352[d]	254 (3 000)

[a] In H_2O–D_2O solutions (5:1 v/v) referenced to external H_2O (δ = 0). Literature data from R. K. Harris and B. E. Mann (eds.), 'N.M.R. and the Periodic Table,' Academic Press, New York, 1978 and J. Mason (ed.), 'Multinuclear N.M.R.,' Plenum, New York, 1987 unless otherwise indicated. [b] 1:1:1:1 Quartet $^1J(^{35/37}Cl–^{17}O)$ = 85 Hz. [c] 1:1:1:1 Quartet $^1J(^{79/81}Br–^{17}O)$ = 420 Hz. [d] Ref. 23.

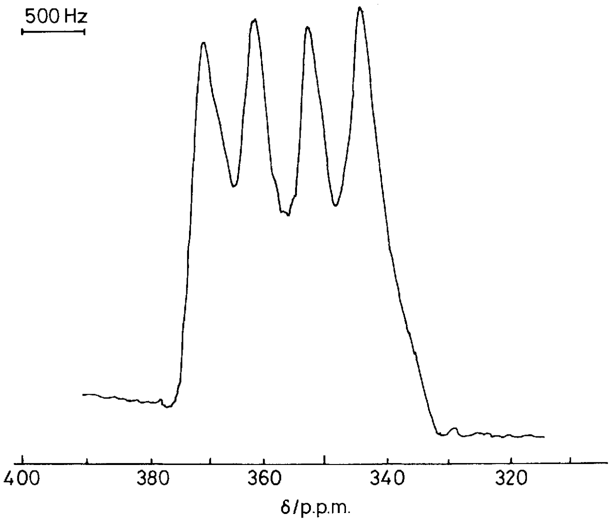

Figure 1. The ^{17}O n.m.r. spectrum of saturated aqueous $KBrO_4$ solution

windows. All data were collected in transmission mode, and calibrated to the Au L_{II} edge at 13.731 keV. Data treatment was performed using the programs PAXAS[18] and EXCURVE.[19] Phase shifts and back-scattering factors were calculated by the normal *ab initio* methods[19] and gave satisfactory results without further modification.

Results and Discussion

I.R. and Raman Studies.—Infrared spectra were obtained for solid samples of $KBrO_4$, $NaBrO_3$, and $NaBrO_2 \cdot 3H_2O$ in Nujol mulls at room temperature, whilst Raman studies were carried out on powdered samples contained in thin glass capillaries. Raman spectra were also obtained for aqueous solutions of NaBrO and $NaBrO_2 \cdot 3H_2O$ contained in small glass cells.

The spectra for the BrO_3^- and BrO_4^- salts were in very close agreement with previous work.[5,20,21] For NaBrO there appears to be only one previous report, by Evans and Lo[9] who observed a prominent Raman feature in aqueous solution at 620 cm^{-1}, which was assigned to the BrO^- ion. Our solution Raman data on this system yielded a similar prominent band at 618 cm^{-1}, together with a very weak feature at *ca.* 820 cm^{-1}, which is assigned as the most intense Raman fundamental of BrO_3^-. This latter feature did not measurably increase in intensity over a period of *ca.* 1 h.

Previous spectroscopic studies on BrO_2^- salts, however, are in disagreement regarding both the positions and assignments of the three fundamentals of this ion. An early paper by Tanguy *et al.*[8] identified the modes ν_1, ν_2, and ν_3 at 775, 400, and 800 cm^{-1} respectively from i.r. studies on solid samples of $Ba(BrO_2)_2$, whilst Evans and Lo[9] quote values of 709, 324, and 680 cm^{-1} from Raman studies on aqueous solutions of $NaBrO_2$. The disparity between these two assignments would seem to be too great to be attributed to the different cations present, or to solid-solution shifts. Evans and Lo also report i.r. and Raman data on solid $NaBrO_2 \cdot 3H_2O$ consistent with their assignment. A subsequent study by Djeda-Mariadassou *et. al.*[10] on these systems assigned the fundamentals ν_1—ν_3 at 630, 360, and 680 cm^{-1} in the i.r. spectrum of the solid barium salt, and identified ν_1 and ν_2 at 711 and 340 cm^{-1} respectively from Raman studies of aqueous $NaBrO_2$ solutions.

In view of these uncertainties we recorded both i.r. and Raman spectra for solid $NaBrO_2 \cdot 3H_2O$ and Raman spectra for its aqueous solution. The results of these experiments are contained in Table 1, which also summarises previous work. It is clear that our spectra of the sodium salt are in very satisfactory agreement with those obtained by Evans and Lo[9] and Djeda-Mariadassou *et al.*[10] Some problems would appear to remain regarding the assignment of ν_1 in the solid barium salt, but we believe that the bands reported by Tanguy *et al.*[8] arise from the presence of BrO_3^- impurity.

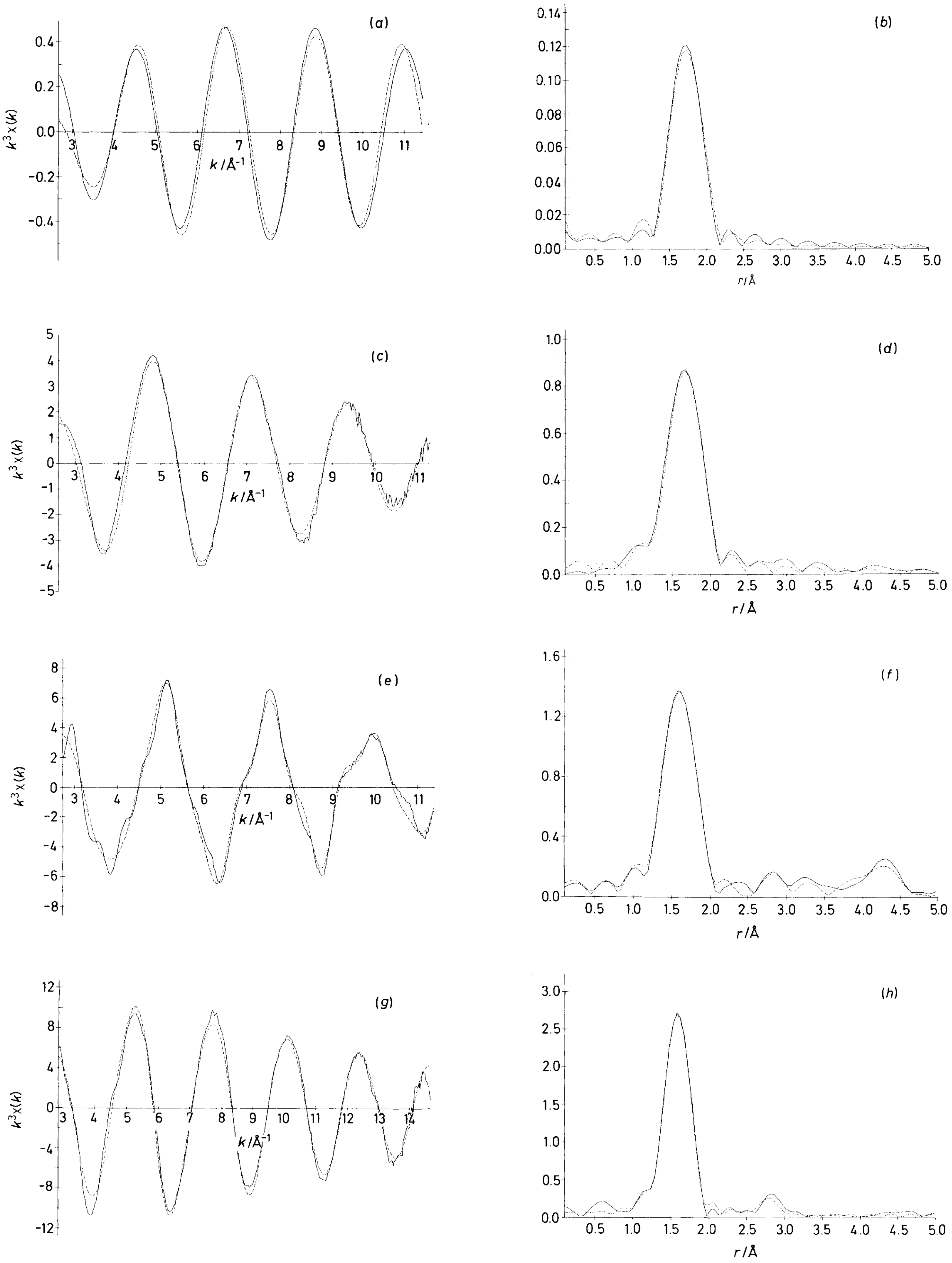

Figure 2. Background-subtracted EXAFS (——, observed; - - -, curved wave theory; both × k^3) and Fourier transforms (——, experimental; - - -, theoretical) for aqueous NaBrO [(*a*) and (*b*)] solid $NaBrO_2 \cdot 3H_2O$ [(*c*) and (*d*)], $NaBrO_3$ [(*e*) and (*f*)], and $KBrO_4$ [(*g*) and (*h*)]

Table 3. Comparison of bromine *K*-edge EXAFS and *X*-ray crystallographic data

Compound	Technique	d(Br–O) [a]/Å	$2\sigma^2$ [b]/Å^2	E_0/eV	F.I.[c]	R[d]	Ref.[e]
$KBrO_4$	*X*-Ray	1.59(1), 1.61(1) 1.62(1)	—	—	—	—	*f*
$KBrO_4$	EXAFS	1.61	0.004	11.93	1.37	10.5	—
$KBrO_4$ (aq)[g]	EXAFS	1.62	0.004	13.98	4.17	13.2	—
$NaBrO_3$	*X*-Ray	1.648(4)	—	—	—	—	25
$NaBrO_3$	EXAFS	1.65	0.008	14.45	0.21	13.2	—
$NaBrO_3$ (aq)	EXAFS	1.65	0.005	13.86	1.54	12.7	—
$NaBrO_2{\cdot}3H_2O$	*X*-Ray	1.702(2), 1.731(2)	—	—	—	—	11
$NaBrO_2{\cdot}3H_2O$	EXAFS	1.75	0.013	11.23	0.04	11.9	—
$NaBrO_2$ (aq)	EXAFS	1.72	0.009	11.80	0.20	11.4	—
NaBrO (aq)	EXAFS	1.81	0.008	13.27	0.01	12.4	—

[a] Systematic errors in data collection and analysis give rise to errors of 0.02—0.03 Å in the first-shell distances determined by EXAFS. [b] Debye–Waller factor. [c] Fit Index (F.I.) = $\Sigma_i[(\chi_i^{T} - \chi_i^{E})k_i^{3}]^2$. [d] R = $(\int|\chi^{T} - \chi^{E}|k^3 dk/\int|\chi^{E}|k^3 dk) \times 100\%$. [e] This work unless indicated otherwise. [f] S. Siegel, B. Tani, and E. H. Appelman, *Inorg. Chem.*, 1968, **7**, 1190. [g] aq = Aqueous solution of compound.

N.M.R. Studies.—Oxygen-17 n.m.r. spectra of the BrO_x^- ions, and some chlorine and iodine analogues, were recorded in concentrated aqueous solutions, and the results are listed in Table 2. The low natural abundance of ^{17}O (0.037%) required long accumulations to obtain good signal-to-noise levels, typically 12—16h, and in this period the more unstable anions (ClO^-, BrO^-, and BrO_2^-) partially decomposed to the corresponding XO_3^- ions which were also observed in the spectra. The resonances of ClO^- and BrO^- were also very close to the water resonance, especially if D_2O was present as internal lock (^{17}O resonance of D_2O is +3 p.p.m. from H_2O[22]), and some care was necessary to obtain adequate resolution. Our results are compared with available literature data in Table 2, and overall the agreement is satisfactory. As can be seen there is a progressive shift to high frequency in $\delta(^{17}O)$ as the formal oxidation state of the halogen increases, with generally parallel shifts for each halogen. The sole exception to this is ClO_4^- where the resonance frequency is little different from that of ClO_3^-.

The nuclei of chlorine $[I(^{35/37}Cl) = \frac{3}{2}]$, bromine $[I(^{79/81}Br) = \frac{3}{2}]$, and iodine $[I(^{127}I) = \frac{5}{2}]$ have appreciable quadrupole moments, and spin–spin coupling is unlikely to be resolved except in cubic symmetry environments.[17] In fact the XO^-, XO_2^-, and XO_3^- ions have broad ^{17}O resonances with the approximate linewidths in the order $XO_3^- < XO^- < XO_2^-$ (Table 2). Spin–spin coupling to halogen nuclei is observed for the tetrahedral XO_4^- ions as 1:1:1:1 quartets for ClO_4^- and BrO_4^- (Figure 1). The coupling to the different isotopes of bromine was not resolved $[\gamma(^{79}Br)/\gamma(^{81}Br) = 0.9277]$. For IO_4^- the coupling to iodine was not resolved; only a very broad resonance was observed, presumably due to fast relaxation. The ^{81}Br n.m.r. resonance of BrO_4^- was observed as a single line ($W_{\frac{1}{2}}$ = 130 Hz) at +2 476 p.p.m. (relative to infinitely dilute aqueous Br^-), which is in good agreement with the reported ^{79}Br resonance of +2 484 p.p.m.[23] Despite the broad nature of the ^{17}O n.m.r. resonance, the ^{127}I resonance of IO_4^- was relatively sharp at +4 090 p.p.m. ($W_{\frac{1}{2}}$ = 1 400 Hz), relative to infinitely dilute aqueous I^-.

Bromine K-*Edge EXAFS.*—Data were obtained for all four ions in aqueous solution, and for all but BrO^- in the solid state. The background-subtracted k^3 weighted EXAFS was used for curve fitting without further treatment, except in the case of NaBrO solution which exhibited a further shell at *ca.* 3.2Å thought to arise from neighbouring solvent molecules. Attempts to fit this were unsuccessful, but since the first shell did not overlap with this feature, the data were Fourier-filtered with a window of 0—2.2Å, and the single shell fitted in the usual way. The bond lengths and the related EXAFS parameters are listed in Table 3 along with *X*-ray crystallographic data for comparison, and the background-subtracted EXAFS and the Fourier transforms are shown in Figure 2.

Data for solid $KBrO_4$ and $NaBrO_3$ gave first-shell distances in excellent agreement with crystallographic data, and the data for solid $NaBrO_2{\cdot}3H_2O$ are in similarly good agreement with our own subsequent *X*-ray study.[11] These data suggest that bond lengths derived from the bromine *K*-edge EXAFS studies may be viewed with some confidence. The solution studies of these three ions gave essentially the same bond lengths. Hydrated sodium hypobromite was extremely difficult to handle as a solid due to its tendency to melt below room temperature, and in the light of the good agreement between solution- and solid-phase data for the other ions the BrO^- data were obtained in aqueous solution. From Table 3 it can be seen that as the formal oxidation state of the bromine decreases the Br–O bond length increases, BrO_4^- (1.61) < BrO_3^- (1.65) < BrO_2^- (1.72) < BrO^- (1.81Å). There is a similar trend in the structural data for the chlorine oxo anions: ClO_4^- (1.436)[24] < ClO_3^- (1.485)[25] < ClO_2^- (1.56Å).[26] No *X*-ray structural data appear to be available for hypochlorite ions, but the bond length in gaseous HOCl has been determined by rotational spectroscopy as 1.69Å,[27] which may be taken as an approximately comparable system, and clearly fits the expected trend.

Acknowledgements

We thank the S.E.R.C. for support, the Director of the Daresbury Laboratory for the provision of facilities, Dr. T. R. Gilson for recording the Raman data, and Dr. J. Evans for assistance with the halogen n.m.r. data collection.

References

1 A. J. Ballard, *Ann. Chim. Phys.*, 1834, **57**, 225.
2 A. J. Ballard, *Ann. Chim. Phys.*, 1826, **32**, 337.
3 Z. E. Jolles (ed.), 'Bromine and Its Compounds,' Academic Press, New York, 1966.
4 L. Pauling, *Chem. Eng. News*, 1947, **25**, 2920.
5 E. H. Appelman, *J. Am. Chem. Soc.*, 1968, **90**, 1900; *Inorg. Chem.*, 1969, **8**, 223.
6 T. Kageyama, Y. Ueno, and M. Okawara, *Synthesis*, 1983, 815; S. Kajigaeshi, T. Nakagawa, S. Fujisaka, T. Nishida, and M. Noguchi, *Chem. Lett.*, 1983, 713; T. Kageyama, S. Kawahara, K. Kitamura, Y. Ueno, and M. Okawara, *ibid.*, p. 1097.
7 R. Bloch, K. Goldschmidt, P. Goldschmidt, and J. Schnerb, B.P. 596 193/1948. Societe d'Etudes Chimiques pour L'Industrie et L'Agriculture, B.P. 843 559/1960.

8 B. Tanguy, B. Frit, G. Turrell, and P. Hagenmuller, *C.R. Acad. Sci., Ser. C*, 1967, **264**, 301.

9 J. C. Evans and G.Y-S. Lo, *Inorg. Chem.*, 1967, **6**, 1483.

10 G. Djeda-Mariadassou, R. Kirchner, R. Diament, J. Breiss, F. Gans, and G. Pannetier, *Bull. Soc. Chim. Fr.*, 1968, 2726.

11 W. Levason, J. S. Ogden, M. D. Spicer, M. Webster, and N. A. Young, *J. Am. Chem. Soc.*, 1989, **111**, 6210.

12 R. Scholder and K. Krauss, *Z. Anorg. Allg. Chem.*, 1952, **268**, 279.

13 H. Fuchs and R. Landsberg, *Z. Anorg. Allg. Chem.*, 1970, **372**, 127.

14 Z. Noszticzius, E. Noszticzius, and Z. A. Schelly, *J. Phys. Chem.*, 1983, **87**, 510.

15 T. Kageyama and T. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 1175.

16 W. F. Underwood and E. Mack, jun., *J. Phys. Chem.*, 1931, **35**, 2650.

17 B. Lindman and S. Forsen, 'Chlorine, Bromine, and Iodine NMR,' Springer, Berlin, 1976.

18 N. Binsted, PAXAS, A microcomputer program for pre- and post-edge background subtractions, University of Southampton, 1988.

19 S. J. Gurman, N. Binsted, and I. Ross, *J. Phys. C*, 1984, **17**, 143; 1986, **19**, 1845.

20 W. Sterzel and W. D. Schnee, *Z. Anorg. Allg. Chem.*, 1971, **383**, 231.

21 L. C. Brown, G. M. Begun, and G. E. Boyd, *J. Am. Chem. Soc.*, 1969, **91**, 2250.

22 H. A. Christ, P. Diehl, H. R. Schneider, and H. Dahn. *Helv. Chim. Acta*, 1961, **44**, 866.

23 V. A. Shcherbakov, Yu. K. Gusev, L. G. Mashirov, L. L. Shcherbakova, V. Vodovatov, and V. V. Gavrilov. *Radiokhimiya.*, 1984, **26**, 700.

24 G. B. Johansson and O. Linquist, *Acta Crystallogr., Sect. B*, 1977, **33**, 2918.

25 S. C. Abrahams and J. L. Bernstein, *Acta Crystallogr., Sect. B*, 1977, **33**, 3601.

26 C. Tarimci, E. Schempp, and S. C. Chang, *Acta Crystallogr., Sect. B*, 1975, **31**, 2146.

27 C. M. Deely, *J. Mol. Spectrosc.*, 1987, **122**, 481.

Received 17*th April* 1989; *Paper* 9/01550G