

# Comparative Multinuclear ( $^{35}\text{Cl}$ , $^{79}\text{Br}$ , $^{81}\text{Br}$ , $^{127}\text{I}$ and $^{17}\text{O}$ ) Magnetic Resonance Study of the Perhalate Anions $\text{XO}_4^-$ ( $\text{X} = \text{Cl}, \text{Br}$ or $\text{I}$ ) in Acetonitrile Solution

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The NMR spectra ( $^{35}\text{Cl}$ ,  $^{79}\text{Br}$ ,  $^{81}\text{Br}$ ,  $^{127}\text{I}$  and  $^{17}\text{O}$ ) of the tetrahedral perhalate anions  $\text{XO}_4^-$  ( $\text{X} = \text{Cl}, \text{Br}$  and  $\text{I}$ ) were compared for the first time in acetonitrile solution, a medium in which the resonances are relatively sharp and in which no oxygen exchange occurs. Relaxation studies of the quadrupolar nuclei in these solutions at  $24^\circ\text{C}$  are reported and show that excellent spectra may be obtained at 0.1 M concentration; thus the observation of separate resonances for  $\text{Cl}^{16}\text{O}_4^-$  and  $\text{Cl}^{18}\text{O}^{16}\text{O}_3^-$  represents the first reported instance of a  $^{35}\text{Cl}$  secondary isotopic shift [ $^{18}\text{O}$  shift ( $^{18,16}\text{O}$ ) =  $-0.090$  ppm]. Enrichment with  $^{17}\text{O}$  of all three ions was carried out and the  $^1J(^{127}\text{I}, ^{17}\text{O})$  coupling constant (489 Hz) has been observed for the first time. The chemical shifts and coupling constants are discussed, especially in connection with the anomalous properties of the perbromate ion. Halogen chemical shifts for  $\text{BrO}_3\text{F}$ ,  $\text{IF}_7$  and  $\text{IF}_6^+$   $\text{AsF}_6^-$  are reported for the first time.

KEY WORDS NMR  $^{35}\text{Cl}$   $^{79}\text{Br}$   $^{81}\text{Br}$   $^{127}\text{I}$   $^{17}\text{O}$  Perhalate anions Relaxation coupling constants

## INTRODUCTION

The perchlorate ( $\text{ClO}_4^-$ ) and metaperiodate ( $\text{IO}_4^-$ ) anions have been known for well over a century and their chemistries are well established and quite extensive.<sup>1–3</sup> In contrast, the perbromates ( $\text{BrO}_4^-$ ) were only synthesized for the first time 22 years ago,<sup>4,5</sup> ending many years of speculation and theories as to why they did not exist.<sup>6,7</sup> In fact, the  $\text{BrO}_4^-$  anion does exhibit anomalous properties when compared with  $\text{ClO}_4^-$  and  $\text{IO}_4^-$ .<sup>6</sup> The relative thermodynamic instability of  $\text{Br(VII)}$  is a property shared with the highest oxidation states of other post-3d transition series elements, e.g.  $\text{As(V)}$  and  $\text{Se(VI)}$ .<sup>8</sup>

The sensitivity of NMR chemical shifts and coupling constants to different electronic environments at the nucleus suggested that a comparative high-resolution multinuclear magnetic resonance study of  $\text{ClO}_4^-$ ,  $\text{BrO}_4^-$  and  $\text{IO}_4^-$  could provide new data pertinent to the unusual properties of the  $\text{BrO}_4^-$  anion. In fact, there have already been extensive  $^{35}\text{Cl}$  NMR studies on  $\text{ClO}_4^-$  in aqueous and non-aqueous solutions,<sup>9–11</sup> but only brief reports have appeared regarding NMR studies on  $\text{BrO}_4^-$  and  $\text{IO}_4^-$ .<sup>9,12</sup> Levason *et al.*<sup>13</sup> reported the  $^{81}\text{Br}$ ,  $^{127}\text{I}$  and  $^{17}\text{O}$  NMR spectra of  $\text{KBrO}_4$  and  $\text{NaIO}_4$  in concentrated aqueous solutions. The  $^{17}\text{O}$  NMR spectrum of  $\text{KBrO}_4$  displayed an average coupling to the two bromine nuclides ( $^{79,81}\text{Br}$ ),

but coupling between  $^{17}\text{O}$  and  $^{127}\text{I}$  was not observed in the  $^{17}\text{O}$  NMR spectrum of  $\text{NaIO}_4$ . This was thought to be due to rapid quadrupolar relaxation. Hitherto, however, no multinuclear magnetic resonance study of all three perhalates in non-aqueous solution has been carried out under comparable optimized conditions of measurement.

All the heavier halogens ( $\text{Cl}$ ,  $\text{Br}$  and  $\text{I}$ ) have NMR-active nuclides. The NMR properties of these and of oxygen-17 (Table 1) are such that all the nuclides have  $I > \frac{1}{2}$  and are therefore quadrupolar.  $^{35}\text{Cl}$ ,  $^{37}\text{Cl}$  and  $^{17}\text{O}$  have small quadrupole moments, i.e.  $< 0.1 \times 10^{-28} \text{ m}^2$ , whereas those of  $^{79}\text{Br}$ ,  $^{81}\text{Br}$  and  $^{127}\text{I}$  are classed as being of medium magnitude, i.e.  $0.1 \times 10^{-28} < Q < 1.0 \times 10^{-28} \text{ m}^2$ . Consequently, the relaxation of all these nuclides is invariably dominated by the efficient quadrupolar mechanism which, under the conditions of extreme narrowing, is described by the equation<sup>14</sup>

$$(\pi T_2)^{-1} \approx (\pi T_1)^{-1} = \Delta\nu_{1/2} \\ = (3\pi/10)\{(2I + 3)/[I^2(2I - 1)]\}(e^2 q_{zz} Q/h)^2(1 + \eta^2/3)\tau_c \quad (1)$$

where  $\Delta\nu_{1/2}$  is the linewidth at half-height,  $T_2$  is the transverse relaxation time,  $T_1$  is the longitudinal relaxation time,  $e$  is the charge on the electron,  $q$  is the tensor of the electric field gradient at the nucleus with  $q_{zz}$  as its largest component,  $\eta$  is the asymmetry parameter for  $q$  and  $\tau_c$  is the rotational correlation time (1–10 ps for mobile liquids). An indication of the susceptibility of the quadrupolar nuclide to extensive quadrupolar relaxation, and hence its suitability for NMR observation, is given by the linewidth function  $f(IQ)$  defined as

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Table 1. NMR properties of the halogens and oxygen-17<sup>a</sup>

Nucleus	<i>I</i> <sup>b</sup>	N.A. <sup>c</sup> (%)	<i>R</i> ( <sup>13</sup> C) <sup>d</sup>	<i>Q</i> <sup>e</sup> (10 <sup>-28</sup> m <sup>2</sup> )	<i>γ</i> <sup>f</sup> (10 <sup>7</sup> rad s <sup>-1</sup> T <sup>-1</sup> )	<i>Ξ</i> <sup>g</sup> (MHz)	<i>f</i> ( <i>Q</i> ) <sup>h</sup> (10 <sup>-59</sup> m <sup>4</sup> )
<sup>35</sup> Cl	3/2	75.53	20.2	8.2 × 10 <sup>-2</sup>	2.6242	9.809	9.0
<sup>37</sup> Cl		24.47	3.78	-6.5 × 10 <sup>-2</sup>	2.1844	8.165	5.6
<sup>79</sup> Br		50.54	2.28 × 10 <sup>2</sup>	0.33	6.7256	25.140	145
<sup>81</sup> Br		49.46	2.79 × 10 <sup>2</sup>	0.27	7.2498	27.100	97
<sup>127</sup> I	5/2	100	5.41 × 10 <sup>2</sup>	-0.79	5.3896	20.146	200
<sup>17</sup> O	5/2	0.037	6.11 × 10 <sup>-2</sup>	-2.6 × 10 <sup>-2</sup>	-3.6280	13.562	0.22

<sup>a</sup> Data taken from Ref. 15.<sup>b</sup> Nuclear spin quantum number.<sup>c</sup> Natural abundance.<sup>d</sup> Receptivity relative to <sup>13</sup>C.<sup>e</sup> Quadrupole moment.<sup>f</sup> Magnetogyric ratio.<sup>g</sup> Resonance frequency at 2.3488 T.<sup>h</sup> Linewidth factor, (2*I* + 3)*Q*<sup>2</sup>/*I*<sup>2</sup>(2*I* - 1).

$Q^2(2I + 3)/[I^2(2I - 1)]$ .<sup>15</sup> The values of this function for the halogen and <sup>17</sup>O nuclides, listed in Table 1, imply that resonances for all the halogen nuclides are likely to be readily observable only in symmetrical environments, such as at the centre of a cubic array of ligands in a tetrahedron or octahedron. The width factor for <sup>17</sup>O is small and <sup>17</sup>O resonances have been obtained for a range of oxygen chemical environments of low symmetry.<sup>16,17</sup> However, for studies in dilute solutions, the low receptivity of natural abundance <sup>17</sup>O necessitates the preparation of <sup>17</sup>O-enriched samples.

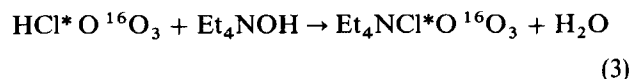
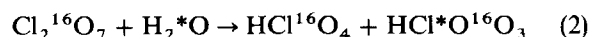
The tetrahedral structures of the perhalate anions make them ideally suited for study by halogen NMR spectroscopy. Our recent successes in obtaining high-resolution <sup>75</sup>As (*I* =  $\frac{3}{2}$ ), <sup>121</sup>Sb (*I* =  $\frac{5}{2}$ ) and <sup>123</sup>Sb (*I* =  $\frac{7}{2}$ ) NMR spectra from the salts Et<sub>4</sub>N<sup>+</sup>[MCl<sub>n</sub>F<sub>6-n</sub>]<sup>-</sup> (where M = As or Sb, and *n* = 0–6) dissolved in CH<sub>3</sub>CN<sup>18,19</sup> suggested that a similar approach would be favourable for a comparative multinuclear magnetic resonance study of the perhalate anions. To this end, we employed solutions of Et<sub>4</sub>N<sup>+</sup>XO<sub>4</sub><sup>-</sup> (X = Cl, Br or I) in CH<sub>3</sub>CN in this study. These salts have excellent solubility in the highly polar, mobile CH<sub>3</sub>CN, a solvent which circumvents the facile oxygen exchange,<sup>3</sup> which occurs with IO<sub>4</sub><sup>-</sup>, but not with ClO<sub>4</sub><sup>-</sup> or BrO<sub>4</sub><sup>-</sup>, in aqueous media, and also affords the opportunity to observe <sup>127</sup>I–<sup>17</sup>O spin-spin coupling in the IO<sub>4</sub><sup>-</sup> anion. Hence we are able to compare, for the first time, the NMR spectra of the quadrupolar halogen and <sup>17</sup>O nuclides in the perhalate anions under very favourable conditions in this solvent. The results of this study are reported here, together with a relaxation study of the perhalate anions in CH<sub>3</sub>CN solution. Additionally, the NMR data for the central heavy halogen nuclides in BrO<sub>3</sub>F, IF<sub>7</sub> and IF<sub>6</sub><sup>+</sup>AsF<sub>6</sub><sup>-</sup> were determined and are presented here for the first time.

## RESULTS AND DISCUSSION

### ClO<sub>4</sub><sup>-</sup>

The <sup>35</sup>Cl and <sup>17</sup>O NMR spectra of Et<sub>4</sub>NClO<sub>4</sub> in CH<sub>3</sub>CN were obtained from a sample enriched with <sup>17</sup>O and <sup>18</sup>O. Since ClO<sub>4</sub><sup>-</sup> does not exchange oxygen

with water,<sup>3</sup> it was not possible to prepare <sup>17</sup>O-enriched samples by this method. Consequently, enrichment was accomplished by hydrolysis of Cl<sub>2</sub>O<sub>7</sub> (natural abundance oxygen) with <sup>17,18</sup>O-enriched water (oxygen composition: <sup>16</sup>O, 12%; <sup>17</sup>O, 50%; <sup>18</sup>O, 38%) followed by conversion of the resulting enriched HClO<sub>4</sub> into Et<sub>4</sub>NClO<sub>4</sub> by neutralization with Et<sub>4</sub>NOH according to the reactions



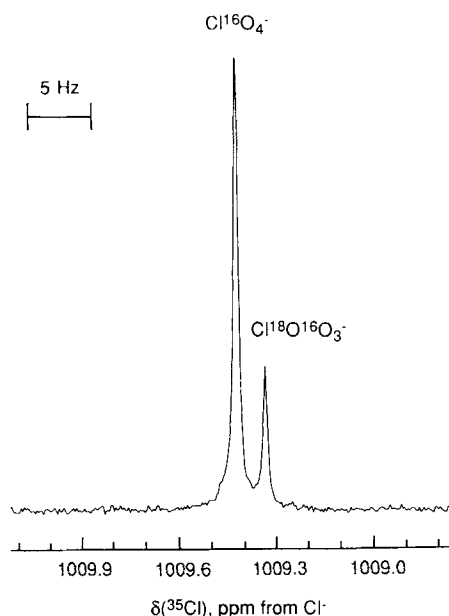
where \*O = <sup>16</sup>O, <sup>17</sup>O or <sup>18</sup>O. This method yields singly labelled isotopomers and a final sample composition of Cl<sup>16</sup>O<sub>4</sub><sup>-</sup> 56%, Cl<sup>17</sup>O<sup>16</sup>O<sub>3</sub><sup>-</sup> 25% and Cl<sup>18</sup>O<sup>16</sup>O<sub>3</sub><sup>-</sup> 19%.

The NMR data for Et<sub>4</sub>NClO<sub>4</sub> (Table 2) are in good agreement with previous measurements.<sup>9–11,16,17</sup> A 0.1 M solution of the <sup>17,18</sup>O-enriched Et<sub>4</sub>NClO<sub>4</sub> in CH<sub>3</sub>CN gave a <sup>35</sup>Cl NMR spectrum (Fig. 1) consisting of two very sharp lines ( $\Delta\nu_{1/2}$  = 0.4 Hz). At high gain, a partially quadrupole-collapsed sextet arising from coupling to <sup>17</sup>O was observed. The resonance was 'square-topped' with no multiplet lines resolved: the sharp central lines are assigned to Cl<sup>16</sup>O<sub>4</sub><sup>-</sup> and Cl<sup>18</sup>O<sup>16</sup>O<sub>3</sub><sup>-</sup>. The line due to Cl<sup>18</sup>O<sup>16</sup>O<sub>3</sub><sup>-</sup> has an intensity approximately one third that of the Cl<sup>16</sup>O<sub>4</sub><sup>-</sup>

Table 2. NMR data for the perhalate anions

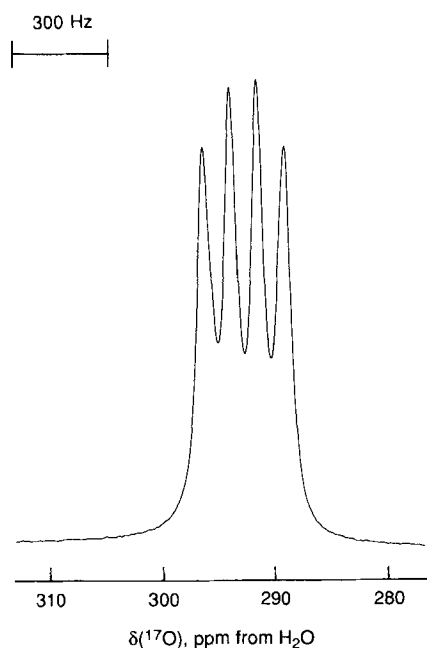
Sample XO <sub>4</sub> <sup>-</sup>	Solvent	Chemical shift (ppm)		Coupling constant <sup>1</sup> J(X, <sup>17</sup> O) (Hz)
		<i>δ</i> (X) <sup>a</sup>	<i>δ</i> ( <sup>17</sup> O) <sup>b</sup>	
Et <sub>4</sub> N <sup>35</sup> ClO <sub>4</sub> <sup>c</sup>	CH <sub>3</sub> CN	1009.3	292.6	83 ± 3
Et <sub>4</sub> N <sup>79</sup> BrO <sub>4</sub> <sup>c</sup>	CH <sub>3</sub> CN	2488.7	360.9	408 ± 6
Et <sub>4</sub> N <sup>81</sup> BrO <sub>4</sub> <sup>c</sup>	CH <sub>3</sub> CN	2488.7		440 ± 6
Et <sub>4</sub> N <sup>127</sup> IO <sub>4</sub> <sup>c</sup>	CH <sub>3</sub> CN	4121.3	242.9	489 ± 6
H <sup>81</sup> BrO <sub>4</sub> <sup>d</sup>	H <sub>2</sub> O	2478	358.8	433 <sup>e</sup>
Na <sup>127</sup> IO <sub>4</sub> <sup>f</sup>	H <sub>2</sub> O	4089	238.1	— <sup>g</sup>

<sup>a</sup> Relative to X<sup>-</sup> at infinite dilution.<sup>b</sup> Relative to H<sub>2</sub>O.<sup>c</sup> 0.1 M solution.<sup>d</sup> 2.3 M solution.<sup>e</sup> Average coupling <sup>1</sup>J(<sup>79,81</sup>Br,<sup>17</sup>O).<sup>f</sup> 0.88 M solution.<sup>g</sup> Coupling not observed.



**Figure 1.**  $^{35}\text{Cl}$  NMR spectrum (24.508 MHz) of 0.1 M  $\text{Et}_4\text{NClO}_4$  in  $\text{CH}_3\text{CN}$  at 24 °C. The isotopomeric composition of the sample was  $\text{Cl}^{16}\text{O}_4^-$  (56%),  $\text{Cl}^{17}\text{O}^{16}\text{O}_3^-$  (25%) and  $\text{Cl}^{18}\text{O}^{16}\text{O}_3^-$  (19%). The broad resonance due to the  $\text{Cl}^{17}\text{O}^{16}\text{O}_3^-$  isotopomer is not visible at the gain level shown.

line, in good agreement with the calculated isotopomer ratios and, in addition, is shifted to low frequency of the  $\text{ClO}_4^-$  line by 0.090 ppm. The observation of separate resonances for  $\text{Cl}^{16}\text{O}_4^-$  and  $\text{Cl}^{18}\text{O}^{16}\text{O}_3^-$  represents the first reported instance of a  $^{35}\text{Cl}$  secondary isotopic shift [ $\Delta^{35}\text{Cl}(^{18,16}\text{O}) = -0.090$  ppm]. The  $^{17}\text{O}$  spectrum (Fig. 2) consists of a well resolved equal-intensity quartet arising from spin coupling of  $^{17}\text{O}$  to  $^{35}\text{Cl}$  ( $I = \frac{3}{2}$ , 75.53%) and  $^{37}\text{Cl}$  ( $I = \frac{3}{2}$ , 24.47%); however, owing to the much smaller natural abundance of  $^{37}\text{Cl}$ , only  $^1J(^{35}\text{Cl}, ^{17}\text{O})$  is resolved (Table 1). The component



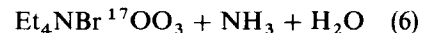
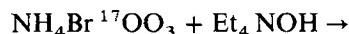
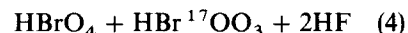
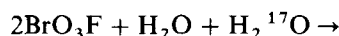
**Figure 2.**  $^{17}\text{O}$  NMR spectrum (33.909 MHz) of 0.1 M  $\text{Et}_4\text{NClO}_4$  (containing 25%  $\text{Cl}^{17}\text{O}^{16}\text{O}_3^-$ ) in  $\text{CH}_3\text{CN}$  at 24 °C.

linewidths of the  $^{17}\text{O}$  resonance were approximately 50 Hz.

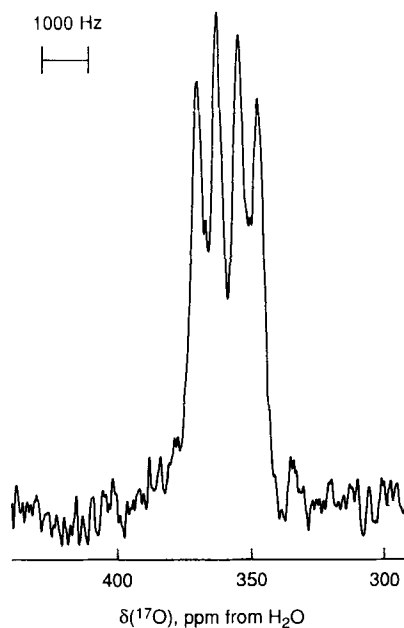
### $\text{BrO}_4^-$

For the sake of completeness, the  $^{81}\text{Br}$  and  $^{17}\text{O}$  NMR spectra of aqueous perbromic acid were recorded, since they have not been reported previously. The  $^{81}\text{Br}$  NMR spectrum of 2.3 M aqueous  $\text{HBrO}_4$  shows a singlet ( $\Delta\nu_{1/2} = 79$  Hz) shifted 2478 ppm to high frequency of infinitely dilute aqueous  $\text{Br}^-$ . The natural-abundance  $^{17}\text{O}$  NMR spectrum yields an equal-intensity quartet (Fig. 3) arising from the spin coupling of  $^{17}\text{O}$  to  $^{81}\text{Br}$  ( $I = \frac{3}{2}$ , 49.46%) and  $^{79}\text{Br}$  ( $I = \frac{3}{2}$ , 50.54%). However, owing to the large  $^{17}\text{O}$  linewidths ( $\Delta\nu_{1/2} = 379$  Hz) and the similar magnetogyric ratios and natural abundances of the two bromine isotopes, only an average coupling constant  $J(^{79,81}\text{Br}, ^{17}\text{O})$  (Table 2) can be measured from the spectrum. These results are in good agreement with the  $^{81}\text{Br}$  and  $^{17}\text{O}$  data obtained recently for aqueous  $\text{KBrO}_4$  solutions.<sup>13</sup>

The perbromate ion, like  $\text{ClO}_4^-$ , does not exchange oxygen atoms with water,<sup>3</sup> so an alternative means of preparing  $^{17,18}\text{O}$ -enriched  $\text{Et}_4\text{NBrO}_4$  was necessary. The enrichment was carried out by the hydrolysis of  $\text{BrO}_3\text{F}$  in  $^{17,18}\text{O}$ -enriched  $\text{H}_2\text{O}$  (oxygen composition:  $^{16}\text{O}$ , 12%;  $^{17}\text{O}$ , 50%;  $^{18}\text{O}$ , 38%) followed by neutralization with  $\text{NH}_3$  and precipitation as  $\text{Et}_4\text{NBrO}_4$  according to the reactions



The  $^{81}\text{Br}$  NMR spectrum of a 0.1 M solution of the  $^{17,18}\text{O}$ -enriched  $\text{Et}_4\text{NBrO}_4$  in  $\text{CH}_3\text{CN}$  demonstrates

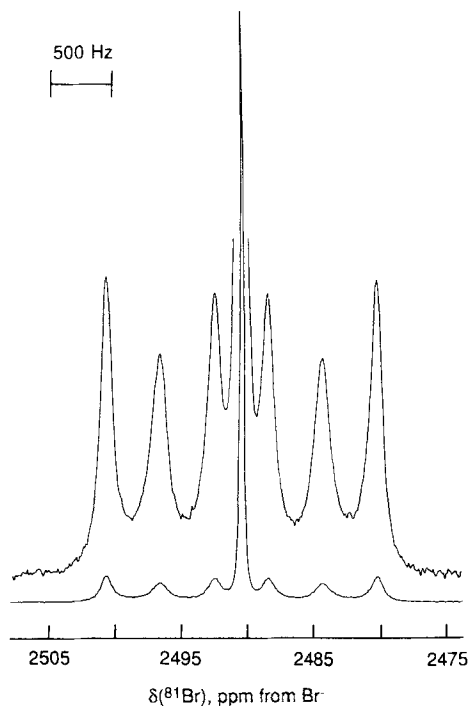


**Figure 3.**  $^{17}\text{O}$  NMR spectrum (54.204 MHz) of 2.3 M aqueous  $\text{HBrO}_4$  at 24 °C.

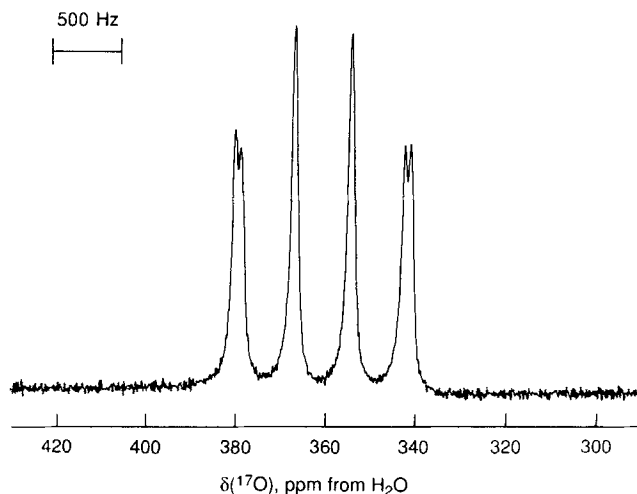
the dramatic improvement in resolution obtained by using CH<sub>3</sub>CN as a solvent instead of H<sub>2</sub>O (see discussion on relaxation studies); accordingly the <sup>81</sup>Br NMR spectrum yields a narrow central singlet ( $\Delta\nu_{1/2} = 12$  Hz) assigned to Br<sup>16</sup>O<sub>4</sub><sup>-</sup> and Br<sup>18</sup>O<sup>16</sup>O<sub>3</sub><sup>-</sup>, and also a well resolved equal-intensity sextet assigned to Br<sup>17</sup>O<sup>16</sup>O<sub>3</sub><sup>-</sup> (Fig. 4). The integrated areas of the resonances are in agreement with the calculated composition of the sample: 50% Br<sup>17</sup>O<sup>16</sup>O<sub>3</sub><sup>-</sup>, 38% Br<sup>18</sup>O<sup>16</sup>O<sub>3</sub><sup>-</sup> and 12% Br<sup>16</sup>O<sub>4</sub><sup>-</sup>. Separate resonances are not observed for Br<sup>16</sup>O<sub>4</sub><sup>-</sup> and Br<sup>18</sup>O<sub>3</sub><sup>-</sup>, even at high field (9.395 T), as they were for Cl<sup>16</sup>O<sub>4</sub><sup>-</sup> and Cl<sup>18</sup>O<sup>16</sup>O<sub>3</sub><sup>-</sup>, owing to the greater <sup>81</sup>Br linewidth and the lower intensity of the Br<sup>16</sup>O<sub>4</sub><sup>-</sup> resonance.

The equal-intensity sextet arises from spin coupling of <sup>81</sup>Br to one <sup>17</sup>O in the isotopomer Br<sup>17</sup>O<sup>16</sup>O<sub>3</sub><sup>-</sup> (Table 2). The intensity pattern and variation in component linewidths (100, 160, 125, 125, 160 and 100 Hz) of the multiplet are in accord with those expected for the <sup>17</sup>O nucleus undergoing relatively slow quadrupolar relaxation.<sup>20</sup> The <sup>79</sup>Br NMR spectrum is virtually identical with the <sup>81</sup>Br spectrum except that all the lines are broader, as expected from the slightly larger quadrupole moment of <sup>79</sup>Br, and the equal-intensity sextet assigned to Br<sup>17</sup>O<sup>16</sup>O<sub>3</sub><sup>-</sup> arises from the spin coupling of <sup>79</sup>Br to one <sup>17</sup>O (Table 2). The ratio  $^1J(^{81}\text{Br}, ^{17}\text{O})/^1J(^{79}\text{Br}, ^{17}\text{O}) = 1.078$  is in excellent agreement with the value calculated from the two bromine magnetogyric ratios  $\gamma(^{81}\text{Br})/\gamma(^{79}\text{Br}) = 1.0779$ .

The <sup>17</sup>O NMR spectrum shows two overlapping 1:1:1:1 quartets which are assigned to <sup>81</sup>Br<sup>17</sup>O<sup>16</sup>O<sub>3</sub><sup>-</sup> and <sup>79</sup>Br<sup>17</sup>O<sup>16</sup>O<sub>3</sub><sup>-</sup> (Fig. 5). The quartet patterns arise from spin coupling of <sup>17</sup>O to <sup>79</sup>Br and <sup>81</sup>Br (Table 2)



**Figure 4.** <sup>81</sup>Br NMR spectrum (108.060 MHz) of 0.1 M <sup>17,18</sup>O-enriched Et<sub>4</sub>NBrO<sub>4</sub> in CH<sub>3</sub>CN at 24°C. The central line arises from Br<sup>16</sup>O<sub>4</sub><sup>-</sup> (12%) and Br<sup>18</sup>O<sup>16</sup>O<sub>3</sub><sup>-</sup> (38%); the equal-intensity sextet is from Br<sup>17</sup>O<sup>16</sup>O<sub>3</sub><sup>-</sup> (50%). The vertical expansion reveals the variation in linewidth of the sextet components.



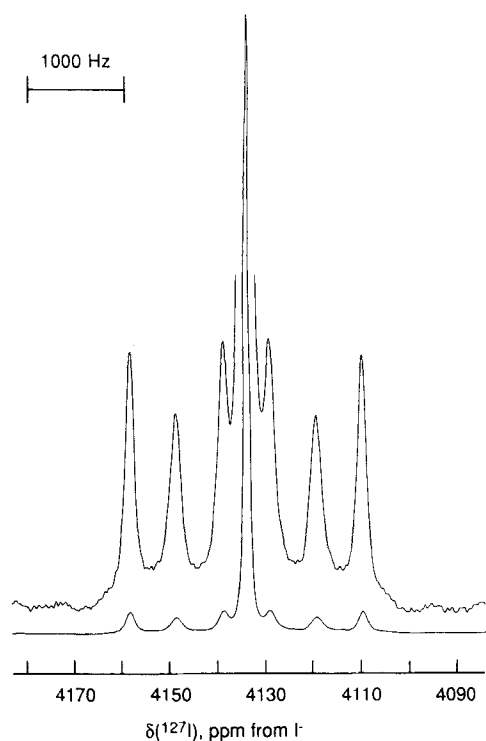
**Figure 5.** <sup>17</sup>O NMR spectrum (33.909 MHz) of 0.1 M Et<sub>4</sub>NBrO<sub>4</sub> (containing 50% Br<sup>17</sup>O<sup>16</sup>O<sub>3</sub><sup>-</sup>) in CH<sub>3</sub>CN at 24°C. Coupling to the two bromine isotopes (<sup>79,81</sup>Br) is clearly resolved in the outer components of the multiplet.

and the equal intensities of the two resonances are in agreement with the natural abundances of the two bromine isotopes (<sup>79</sup>Br, 50.57%; <sup>81</sup>Br, 49.43%). The <sup>17</sup>O linewidths are *ca.* 60 Hz.

#### IO<sub>4</sub><sup>-</sup>

In order to make a comparison between the spectra obtained from aqueous solution and those obtained from CH<sub>3</sub>CN solution, the <sup>127</sup>I and <sup>17</sup>O NMR spectra of NaIO<sub>4</sub> dissolved in water were measured. The <sup>127</sup>I NMR spectrum of a 0.88 M aqueous solution of NaIO<sub>4</sub> showed a broad singlet ( $\Delta\nu_{1/2} = 1000$  Hz) shifted 4089 ppm to high frequency of infinitely dilute aqueous I<sup>-</sup> and in good accord with earlier reports.<sup>9,13,21,22</sup> The natural-abundance <sup>17</sup>O NMR spectrum showed a broad almost completely quadrupole-collapsed sextet due to coupling with <sup>127</sup>I (Table 2). The linewidth ( $\Delta\nu_{1/2} = 1945$  Hz) is *ca.* 100 Hz narrower than that reported.<sup>13</sup>

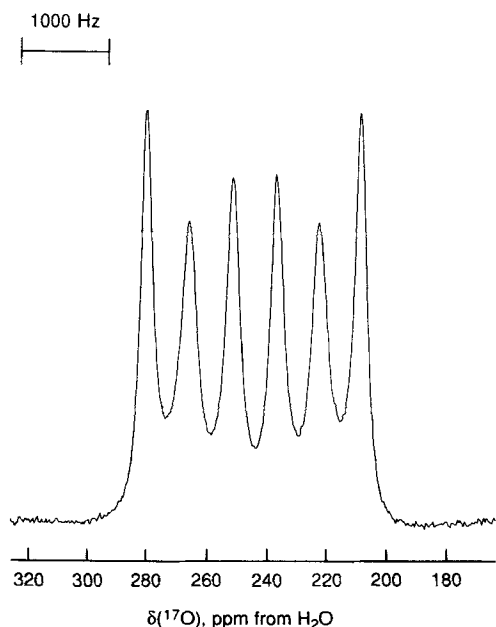
Enrichment of IO<sub>4</sub><sup>-</sup> with <sup>17</sup>O was achieved by oxygen exchange between Et<sub>4</sub>NIO<sub>4</sub> and enriched H<sub>2</sub>O(<sup>16</sup>O, 82.4%; <sup>17</sup>O, 10.0%; <sup>18</sup>O, 7.6%) followed by dehydration to yield a dry product. As for Et<sub>4</sub>NClO<sub>4</sub> and Et<sub>4</sub>NBrO<sub>4</sub>, a dramatic decrease in the halogen linewidth was observed using CH<sub>3</sub>CN as the solvent instead of H<sub>2</sub>O (see later discussion on relaxation). A 0.1 M solution of the enriched Et<sub>4</sub>NIO<sub>4</sub> in CH<sub>3</sub>CN gives a <sup>127</sup>I NMR spectrum (Fig. 6) which consists of a central singlet ( $\Delta\nu_{1/2} = 60$  Hz) arising from the I<sup>16</sup>O<sub>4</sub><sup>-</sup> and I<sup>18</sup>O<sup>16</sup>O<sub>3</sub><sup>-</sup> isotopomers, and an equal-intensity sextet, which arises from the I<sup>17</sup>O<sup>16</sup>O<sub>3</sub><sup>-</sup> and I<sup>17</sup>O<sup>18</sup>O<sup>16</sup>O<sub>2</sub><sup>-</sup> isotopomers. As for perbromate, separate resonances from the I<sup>16</sup>O<sub>4</sub><sup>-</sup> and I<sup>18</sup>O<sup>16</sup>O<sub>3</sub><sup>-</sup> ions could not be distinguished, even at 9.395 T, owing to the inherent breadth. The sextet pattern derives from the spin coupling of <sup>127</sup>I to one <sup>17</sup>O and represents the first observation of an <sup>127</sup>I-<sup>17</sup>O coupling constant (Table 2). Again the intensity pattern and variation in the component linewidths of the multiplet are consistent



**Figure 6.**  $^{127}\text{I}$  NMR spectrum (50.051 MHz) of 0.1 M  $^{17,18}\text{O}$ -enriched  $\text{Et}_4\text{NIO}_4$  in  $\text{CH}_3\text{CN}$  at  $24^\circ\text{C}$ . The central line arises from  $\text{I}^{16}\text{O}_4^-$  (46%) and  $\text{I}^{18}\text{O}^{16}\text{O}_3^-$  (17%); the equal-intensity sextet from  $\text{I}^{17}\text{O}^{16}\text{O}_3^-$  (29%) and  $\text{I}^{17}\text{O}^{18}\text{O}^{16}\text{O}_2^-$  (6%). The vertical expansion reveals the variation in linewidth of the sextet components.

with a relatively slow  $^{17}\text{O}$  relaxation rate.<sup>20</sup> The integrated areas of the two resonances are in agreement with the calculated statistical distribution of isotopomers.

The  $^{17}\text{O}$  NMR spectrum of the same sample shows a well resolved equal-intensity sextet (Fig. 7) arising from spin coupling of  $^{17}\text{O}$  to  $^{127}\text{I}$  ( $I = \frac{5}{2}$ ) in the anions



**Figure 7.**  $^{17}\text{O}$  NMR spectrum (33.909 MHz) of 0.1 M  $\text{Et}_4\text{NIO}_4$  (containing 25%  $\text{I}^{17}\text{O}^{16}\text{O}_3^-$  and  $\text{I}^{17}\text{O}^{18}\text{O}^{16}\text{O}_2^-$ ) in  $\text{CH}_3\text{CN}$  at  $24^\circ\text{C}$ .

$\text{I}^{17}\text{O}^{16}\text{O}_3^-$  and  $\text{I}^{17}\text{O}^{18}\text{O}^{16}\text{O}_2^-$  (Table 2). The component linewidths, which range from 170 to 260 Hz, and the intensity pattern of the sextet are indicative of a relatively slow  $^{127}\text{I}$  relaxation.<sup>20</sup>

### Halogen chemical shifts of the perhalates

Only for  $^{35}\text{Cl}$  have a reasonable number of chemical shifts been measured. These include those of a wide variety of covalent main group and transition element chlorides, which were studied using wide-line and pulse techniques.<sup>9,23</sup> It was found that most of the shielding variations could be attributed to differences in the paramagnetic contribution  $\sigma^p$ , although some anomalies in the shifts of chlorocarbons and chlorosilanes were thought to arise from medium effects.<sup>9,23</sup> Further, with the exception of  $\text{ClO}_3^-$  and  $\text{ClO}_4^-$ , the absolute paramagnetic contribution to the shielding was smaller than the diamagnetic contribution. A study of a similar range of covalent bromine and iodine compounds by  $^{81,79}\text{Br}$  and  $^{127}\text{I}$  NMR has not been undertaken, since the larger quadrupole moments of these nuclides give rise to much shorter relaxation times and hence very large linewidths compared with the corresponding chlorine values for analogous compounds. Therefore, information on  $^{79,81}\text{Br}$  and  $^{127}\text{I}$  chemical shifts is minimal.

The  $^{35}\text{Cl}$ ,  $^{81}\text{Br}$  and  $^{127}\text{I}$  chemical shifts for the perchlorate anions are presented in Table 2. The halogen nuclei in the perchlorate anions,  $\text{ClO}_4^-$ ,  $\text{BrO}_4^-$  and  $\text{IO}_4^-$ , are strongly deshielded with respect to the appropriate halide reference at infinite dilution, as is consistent with the increased formal oxidation state of the halogen in the perchlorate anion.<sup>24</sup> These high-frequency shifts are indicative of a large paramagnetic contribution  $\sigma^p$  to the shielding constant and can be ascribed to the double bond character of the halogen-oxygen bond, since contributions such as  $\text{X}=\text{O}$  and  $\text{X}^+-\text{O}^-$  can increase the electron imbalance terms  $P_\mu$  and  $D_\mu$  in the expression for  $\sigma^p$ .<sup>24,25</sup> The extent to which the halogen nucleus of a perchlorate anion is deshielded with respect to halide increases considerably on going from  $\text{ClO}_4^-$  to  $\text{IO}_4^-$ ; this is in accord with the general trend for increasing shielding ranges on descending a group in the Periodic Table, which can be attributed, in part, to the heavier elements having valence electrons in orbitals, such as p, d and f orbitals, with non-zero angular momentum and also to the greater polarizability of these valence electrons.<sup>24</sup>

The halogen chemical shifts of  $\text{Et}_4\text{NXO}_4$  in  $\text{CH}_3\text{CN}$  show only a very small concentration dependence ( $<1$  ppm) over the range 1.5–0.1 M. The  $^{79,81}\text{Br}$  shifts of aqueous perbromic acid also show a very small concentration dependence (0.4 ppm) over the range 2.3–0.1 M. Dilution produces a shift to higher frequency in both  $\text{CH}_3\text{CN}$  and  $\text{H}_2\text{O}$ . This weak dependence of shielding on concentration has previously been observed for  $\text{ClO}_4^-$  and results from the effective isolation of the halogen atom by the tetrahedral arrangements of the surrounding oxygen ligands.<sup>26</sup>

The  $^{18,16}\text{O}$ -induced secondary isotope shift observed in the  $^{35}\text{Cl}$  NMR spectrum of  $^{18}\text{O}$ -enriched  $\text{ClO}_4^-$  has a value [ $^1\Delta^{35}\text{Cl}(^{18,16}\text{O}) = -0.090$  ppm] which is larger than the theoretical prediction ( $-0.03$  ppm) of Jameson

and Osten.<sup>27</sup> Small chemical shift differences between the X<sup>16</sup>O<sub>4</sub><sup>−</sup> and X<sup>17</sup>O<sup>16</sup>O<sub>3</sub><sup>−</sup> isotopomers in BrO<sub>4</sub><sup>−</sup> and IO<sub>4</sub><sup>−</sup> have also been measured in the <sup>81</sup>Br and <sup>127</sup>I NMR spectra, respectively. These correspond to the secondary isotope shifts <sup>1</sup>Δ<sup>81</sup>Br(<sup>17,16</sup>O) = −0.06 ppm and <sup>1</sup>Δ<sup>127</sup>I(<sup>17,16</sup>O) = −0.19 ppm. Assuming these shifts are linearly dependent on mass, then <sup>1</sup>Δ<sup>81</sup>Br(<sup>18,16</sup>O) = −0.12 ppm and <sup>1</sup>Δ<sup>127</sup>I(<sup>18,16</sup>O) = −0.38 ppm. These values are again larger than those predicted theoretically, i.e. <sup>1</sup>Δ<sup>81</sup>Br(<sup>18,16</sup>O) = −0.09 ppm and <sup>1</sup>Δ<sup>127</sup>I(<sup>18,16</sup>O) = −0.16 ppm,<sup>27</sup> although it should be pointed out that the experimental values could not be measured very accurately because of the inherently broader linewidths of the <sup>81</sup>Br and <sup>127</sup>I resonances.

### Oxygen-17 chemical shifts of the perhalates

The <sup>17</sup>O chemical shifts for the perhalate anions (Table 2) show an interesting phenomenon in that they decrease in the order BrO<sub>4</sub><sup>−</sup> > ClO<sub>4</sub><sup>−</sup> > IO<sub>4</sub><sup>−</sup>, which is contrary to the order predicted on the basis of halogen electronegativity considerations alone (i.e. ClO<sub>4</sub><sup>−</sup> > BrO<sub>4</sub><sup>−</sup> > IO<sub>4</sub><sup>−</sup>). Such considerations do, in fact, correctly predict the <sup>19</sup>F shifts of the hexafluorohalogen(VII) cations to decrease in the order ClF<sub>6</sub><sup>+</sup> > BrF<sub>6</sub><sup>+</sup> > IF<sub>6</sub><sup>+</sup>.<sup>28</sup> Also, the <sup>17</sup>O chemical shifts of the transition element tetraoxo species (see Table 3) decrease on passing down a group from 3d element to the 4d and 5d congeners.<sup>17</sup> However, it is interesting that, as for BrO<sub>4</sub><sup>−</sup>, the SeO<sub>4</sub><sup>2−</sup> and AsO<sub>4</sub><sup>3−</sup> anions also display <sup>17</sup>O chemical shifts which occur to high frequency of those of their corresponding third-row congeners, i.e. SO<sub>4</sub><sup>2−</sup> and PO<sub>4</sub><sup>3−</sup>. Unfortunately TeO<sub>4</sub><sup>2−</sup> and SbO<sub>4</sub><sup>3−</sup> do not exist as discrete anions in solution, and therefore confirmation of their expected lower frequency <sup>17</sup>O shifts, with respect to their third- and fourth-row analogues, is not possible (see Table 3).

A linear correlation between the <sup>17</sup>O chemical shift and the reciprocal of the lowest energy, fully allowed, electronic transition has been found for the tetraoxo species of the transition metals.<sup>29</sup> This correlation stems from the average excitation energy term, ΔE<sup>−1</sup>, in the expression for the paramagnetic contribution to the shielding constant, σ<sup>p</sup>. For a closed-shell XO<sub>4</sub><sup>n−</sup> species, these lowest energy electronic transitions result from excitations from the <sup>1</sup>A<sub>1</sub>(*t*<sub>1</sub><sup>6</sup>) ground state to terms arising from configurations such as (*t*<sub>1</sub><sup>5</sup>*e*<sup>1</sup>), which

provide a mechanism for introducing orbital angular momentum about the oxygen nuclei. Nonetheless, the use of an average excitation energy is an approximation, since the lowest-energy electronic transition does not necessarily make the dominant contribution to σ<sup>p</sup>; for an accurate calculation of σ<sup>p</sup>, a knowledge of all possible excited states is required, although, in practice, this is rarely possible for molecules containing heavy atoms.<sup>30</sup> However Figgis *et al.*<sup>29</sup> have performed a detailed calculation of σ<sup>p</sup> (<sup>17</sup>O) for MnO<sub>4</sub><sup>−</sup>, which, despite the approximate values of the excitation energies used, gives a result in reasonable agreement with the experimentally observed <sup>17</sup>O shift. More importantly, the calculation demonstrates that in MnO<sub>4</sub><sup>−</sup> the main contribution to σ<sup>p</sup> comes from the transition *t*<sub>1</sub><sup>6</sup> → *t*<sub>1</sub><sup>5</sup>*t*<sub>2</sub><sup>1</sup>, which does not correspond to the lowest energy electronically allowed transition *t*<sub>1</sub><sup>6</sup> → *t*<sub>1</sub><sup>5</sup>*e*<sup>1</sup>, and therefore the observed correlation between this transition and the <sup>17</sup>O shift in this instance is a fortunate coincidence.

Interestingly, when the <sup>17</sup>O chemical shifts of the perhalates are plotted against the respective lowest energy, fully allowed electronic transitions, it is apparent that the correlation observed for transition metal tetraoxo species is not valid here. This is because the lowest energy electronic transitions for the perhalates, <sup>1</sup>A<sub>1</sub>(*t*<sub>1</sub><sup>6</sup>) → <sup>1</sup>T<sub>2</sub>(*t*<sub>1</sub><sup>5</sup>*t*<sub>2</sub><sup>1</sup>), increase in the order ClO<sub>4</sub><sup>−</sup> (<185 nm) < BrO<sub>4</sub><sup>−</sup> (187 nm) < IO<sub>4</sub><sup>−</sup> (222.5 nm), whereas the <sup>17</sup>O chemical shifts decrease in the order BrO<sub>4</sub><sup>−</sup> > ClO<sub>4</sub><sup>−</sup> > IO<sub>4</sub><sup>−</sup>. This suggests that other transitions are probably more important in providing the dominant contributions to σ<sup>p</sup> in these anions. More specifically, the elements following the 3d transition series have a particularly strongly bound 4s orbital owing to the ineffective screening of the nuclear charge provided by the filled 3d orbitals.<sup>8,31</sup> This leads to a greater s-p promotion energy and consequently to a greater instability of the highest oxidation states of As, Se and Br, which is borne out by the enhanced oxidizing power of AsO<sub>4</sub><sup>3−</sup>, SeO<sub>4</sub><sup>2−</sup> and BrO<sub>4</sub><sup>−</sup> compared with their group congeners. As a result of the larger s-p promotion energy, the LUMO in these anions, which is probably *a*<sub>2</sub><sup>\*</sup>, would be expected to be lowered in energy relative to the *t*<sub>1</sub><sup>6</sup> HOMO and thus the energy of the transition *t*<sub>1</sub><sup>6</sup> → *t*<sub>1</sub><sup>5</sup>*a*<sub>1</sub><sup>\*</sup> would also be lowered. If this transition makes an important contribution to σ<sup>p</sup> (<sup>17</sup>O) in the main group tetraoxo species, it can be expected that σ<sup>p</sup> (<sup>17</sup>O) will be greater in AsO<sub>4</sub><sup>3−</sup>, SeO<sub>4</sub><sup>2−</sup> and BrO<sub>4</sub><sup>−</sup>, and hence the <sup>17</sup>O nuclei in these anions will be deshielded relative to those of their group homologues.

### Halogen-oxygen spin-spin coupling in the perhalates

The halogen-oxygen spin-spin coupling constants, <sup>1</sup>J(X, <sup>17</sup>O), for the perhalate anions are summarized in Table 4. It is normally assumed that spin-spin coupling between heavy nuclides is dominated by the Fermi contact mechanism,<sup>32</sup> and if this is the case, then such couplings can be discussed using the expressions developed by Pople and Santry<sup>33</sup> for the contact term:

$$^1J(AB) = (16\pi^2/9h)(g\beta h/2\pi)^2 \gamma_A \gamma_B |\psi_{ns, A}(0)|^2 |\psi_{ns, B}(0)|^2 \pi_{AB} \quad (7)$$

Table 3. <sup>17</sup>O chemical shifts of main group and transition element tetraoxo species<sup>a</sup>

VO <sub>4</sub> <sup>3−</sup> 568	CrO <sub>4</sub> <sup>2−</sup> 835	MnO <sub>4</sub> <sup>−</sup> 1230	—	PO <sub>4</sub> <sup>3−</sup> 99 <sup>b</sup>	SO <sub>4</sub> <sup>2−</sup> 167	ClO <sub>4</sub> <sup>−</sup> 292 <sup>d</sup>
	MoO <sub>4</sub> <sup>2−</sup> 831	TcO <sub>4</sub> <sup>−</sup> 748	RuO <sub>4</sub> 1106	AsO <sub>4</sub> <sup>3−</sup> 108 <sup>c</sup>	SeO <sub>4</sub> <sup>2−</sup> 204	BrO <sub>4</sub> <sup>−</sup> 360 <sup>d</sup>
—	WO <sub>4</sub> <sup>2−</sup> 420	ReO <sub>4</sub> <sup>−</sup> 569	OsO <sub>4</sub> 796	—	—	IO <sub>4</sub> <sup>−</sup> 243 <sup>d</sup>

<sup>a</sup> All <sup>17</sup>O chemical shifts taken from Ref. 17, unless stated otherwise.

<sup>b</sup> Na<sub>2</sub>HPO<sub>4</sub> in H<sub>2</sub>O at 66 °C; from Ref. 79.

<sup>c</sup> NaHAsO<sub>4</sub> in H<sub>2</sub>O at 25 °C; this work.

<sup>d</sup> This work.

**Table 4. Halogen–oxygen coupling constants and reduced coupling constants for  $\text{XO}_4^-$  ( $\text{X} = \text{Cl, Br or I}$ )**

$\text{XO}_4^-$	$^1J(\text{X}, ^{17}\text{O})$ (Hz)	$^1K(\text{X}, \text{O})$ ( $10^{21} \text{ T}^2 \text{ J}^{-1}$ ) <sup>a</sup>	$^1K(\text{X}, \text{O})_{\text{RC}}$ ( $10^{21} \text{ T}^2 \text{ J}^{-1}$ ) <sup>a,b</sup>
$^{35}\text{ClO}_4^-$	83	5.2	5.2
$^{79}\text{BrO}_4^-$	408	9.97	8.50
$^{81}\text{BrO}_4^-$	440	9.97	8.50
$^{127}\text{IO}_4^-$	489	14.9	10.6

<sup>a</sup> Units recommended for reduced coupling constants.<sup>80</sup> Other equivalent SI units are  $\text{N A}^{-2} \text{ m}^{-3}$ .

<sup>b</sup> Relativistically corrected reduced coupling constants,  $^1K(\text{X}, \text{O})_{\text{RC}}$ , as defined in Eqn (10).

$$\pi_{\text{AB}} = 4 \sum_i^{\text{occ}} \sum_j^{\text{unocc}} (E_j - E_i)^{-1} C_{is, \text{A}} C_{is, \text{B}} C_{js, \text{A}} C_{js, \text{B}} \quad (8)$$

All symbols in these equations have their standard meanings or values:  $|\psi_{ns, \text{A}}(0)|^2$  and  $|\psi_{ns, \text{B}}(0)|^2$  are the s-electron densities for the  $ns$  valence orbitals at the nuclei of atoms A and B;  $\pi_{\text{AB}}$  is the mutual polarizability of the  $ns$  orbitals on A and B;  $C_{n, \text{A}}$  and  $C_{n, \text{B}}$  are the LCAO coefficients of the s-type atomic orbitals centred on A and B, and  $E_i$  and  $E_j$  are the energies of the occupied and unoccupied molecular orbitals, respectively.

Equation (7) demonstrates that the coupling constant is dependent on the electronic properties of the two coupled nuclei [i.e.  $|\psi_{ns, \text{A}}(0)|$ ,  $|\psi_{ns, \text{B}}(0)|$  and  $\pi_{\text{AB}}$ ]. In order to compare the coupling constants of a series of structurally related species and obtain information about the electronic environments in the molecules, it is necessary to remove the nuclear dependence of  $^1J(\text{AB})$ . This is done by using the reduced coupling constant,  $^1K(\text{AB})$ :

$$^1K(\text{AB}) = (2\pi/\gamma_{\text{A}})(2\pi/\gamma_{\text{B}})^{1/2} J(\text{AB})/h \quad (9)$$

The reduced coupling constant,  $^1K(\text{X}, \text{O})$ , for the perchlorate anions are listed in Table 4 and, for comparison, the reduced coupling constants,  $^1K(\text{X}, \text{F})$ , for the hexafluorohalogen(VII) cations ( $\text{ClF}_6^+$ ,  $\text{BrF}_6^+$  and  $\text{IF}_6^+$ ) are presented in Table 5. First, it may be noted that  $^1K(\text{X}, \text{O})$  is consistently larger than  $^1K(\text{X}, \text{F})$ , which indicates that the X–O bonds have more s-character than the X–F bonds. This can be accounted for qualitatively since the halogen atom in  $\text{XO}_4^-$  ( $T_d$  symmetry) is  $\text{sp}^3$  hybridized (ie ca. 25% s-character), whereas in  $\text{XF}_6^+$  ( $h_h$  symmetry) it is  $\text{sp}^3\text{d}^2$  hybridized (ie ca. 17% s-character). Second, the values of  $^1K(\text{X}, \text{O})$  and  $^1K(\text{X}, \text{F})$

**Table 5. Halogen–fluorine coupling constants and reduced coupling constant for  $\text{XF}_6^+$  ( $\text{X} = \text{Cl, Br or I}$ )**

$\text{XF}_6^+$	$^1J(\text{X}, ^{19}\text{F})$ (Hz)	$^1K(\text{X}, \text{F})$ ( $10^{21} \text{ T}^2 \text{ J}^{-1}$ )	$^1K(\text{X}, \text{F})_{\text{RC}}$ ( $10^{21} \text{ T}^2 \text{ J}^{-1}$ ) <sup>a</sup>
$^{35}\text{ClF}_6^+$	340 <sup>b</sup>	3.07	3.07
$^{37}\text{ClF}_6^+$	283 <sup>b</sup>	3.07	
$^{79}\text{BrF}_6^+$	1587 <sup>c</sup>	5.585	4.756
$^{81}\text{BrF}_6^+$	1709 <sup>c</sup>	5.579	
$^{127}\text{IF}_6^+$	2740 <sup>d</sup>	12.046	

<sup>a</sup> Relativistically corrected reduced coupling constants,  $^1K(\text{X}, \text{O})_{\text{RC}}$ , as defined in Eqn (10).

<sup>b</sup> Ref. 34.

<sup>c</sup> Ref. 28.

<sup>d</sup> This work.

increase in magnitude for the heavier congeners of the two respective series. These differences in  $^1K$  values between the members of each series are expected to be dominated by the s-electron density terms in Eqn (7). Relativistic effects in the heavier halogens result in s-orbital contractions, which substantially increase the s-electron density to the nucleus, and hence the Fermi contact term for  $^1K$  also increases.<sup>32,35</sup> A method for removing these relativistic effects give a relativistically corrected reduced coupling constant,  $^1K(\text{AB})_{\text{RC}}$ :

$$^1K(\text{AB})_{\text{RC}} = ^1K(\text{AB}) R_{\text{A}}^f R_{\text{B}}^f \quad (10)$$

has been illustrated previously,<sup>36</sup> where the correction factors ( $R^f$ ) for each element are derived from the ratio  $|\psi_{ns, \text{A}}(0)|_{\text{non-rel}}^2 / |\psi_{ns, \text{A}}(0)|_{\text{rel}}^2$  for that element. Values for the relativistic and non-relativistic s-electron densities were taken from the work of Pyykkö and Wiesenfeld<sup>37</sup> and gave the following correction ratios:  $R^f(\text{O})$ , 1;  $R^f(\text{F})$ , 1;  $R^f(\text{Cl})$ , 1;  $R^f(\text{Br})$ , 0.852; and  $R^f(\text{I})$ , 0.701. These ratios show that relativistic effects are negligible for O, F and Cl, but significant for Br and I. The relativistically corrected coupling constants,  $^1K(\text{X}, \text{O})_{\text{RC}}$  for the perchlorates and  $^1K(\text{X}, \text{F})_{\text{RC}}$  for the related hexafluorohalogen(VII) cations, are given in Table 4 and 5. In a homologous series of molecules such as the  $\text{XO}_4^-$  anions and the  $\text{XF}_6^+$  cations ( $\text{X} = \text{Cl, Br or I}$ ) where the spin–spin coupling is assumed to be dominated by the Fermi contact mechanism, the individual  $^1K(\text{AB})_{\text{RC}}$  values should be approximately equal to one another, provided that the geometry and bonding are the same in all the molecules in the series.<sup>38</sup> It can be seen from the  $^1K(\text{X}, \text{O})_{\text{RC}}$  and  $^1K(\text{X}, \text{F})_{\text{RC}}$  values in Tables 4 and 5 that this is not the case; rather, the values increase on passing from  $\text{ClO}_4^-$  to  $\text{IO}_4^-$  and from  $\text{ClF}_6^+$  to  $\text{IF}_6^+$ . An analogous trend is also observed for  $^2K(\text{M}, \text{Te})_{\text{RC}}$  in  $\text{M}(\text{OTeF}_5)_6^-$  (where  $\text{M} = ^{75}\text{As}$ ,  $^{121}\text{Sb}$  and  $^{209}\text{Bi}$ ).<sup>39</sup> This would indicate an increase in the s-character of the bonds passing down each series. However, this interpretation may be oversimplistic because of the possibility of non-contact contributions to the coupling constants, which could obfuscate any unambiguous interpretation solely in terms of the Fermi contact interaction. Recent experimental results suggest that the spin–orbital and spin–dipolar contributions to the coupling constant can be substantial for couplings involving heavy nuclei.<sup>40,41</sup> Indeed, this is especially likely to be the case where multiple bonding exists between the two coupled nuclei,<sup>32</sup> as in the X–O bonds of the perchlorate anions. Consequently, it is not possible to make any unequivocal interpretation of the trends in  $^1K(\text{X}, \text{O})_{\text{RC}}$  and  $^1K(\text{X}, \text{F})_{\text{RC}}$  with the present data.

It has been shown previously that the values of  $^1K(\text{Cl}, \text{F})$  and  $^1K(\text{Br}, \text{F})$  for  $\text{ClF}_6^+$  and  $\text{BrF}_6^+$ , respectively, do not follow the empirical rule relating  $[^1K(\text{X}, \text{F})]^{1/2}$  to the atomic number of a series of isoelectronic hexafluorides.<sup>28</sup> Gillespie and Schrobilgen<sup>28</sup> suggested that this may be the result of crowding of electron pairs in the small valence shells of chlorine and bromine, which gives rise to Cl–F and Br–F bonds that are longer than would be expected for the +VII oxidation state and, as a consequence, the halogen–fluorine reduced coupling constants are smaller than expected. It has also been demonstrated that the established relationship<sup>42</sup> between  $[^1K(\text{AB})]^{1/2}$  and the

atomic number,  $Z_A$ , of the changing nucleus, A, is valid for  $^1K(X,O)$  in the series of tetrahedral molecules  $XO_4^-$ ,<sup>43</sup> although, owing to the difficulties inherent in measuring coupling constants involving  $^{17}O$ , relatively few experimental values have been reported. In view of this, Yarzhemskii *et al.*<sup>44</sup> used a combination of experimental and calculated  $^1K(X,O)$  values to predict the  $^1J(X,^{17}O)$  values for  $XO_4^-$  which have not, hitherto, been determined experimentally. The  $^1J(X,^{17}O)$  values were obtained by extrapolating the data obtained from plots of  $[^1K(X,O)]^{1/2}$  vs.  $Z_X$  and converting the new  $^1K(X,O)$  values back to  $^1J(X,^{17}O)$  in Hz. The value of  $^1J(^{127}I,^{17}O)$  for  $IO_4^-$  determined in this way is 554 Hz, which is larger than the experimental value (489 Hz) obtained in the present study. The plot of the reduced halogen–oxygen coupling constants,  $^1K(X,O)$ , for the perhalate anions vs. the atomic number of the halogen  $Z_X$  is shown in Fig. 8. Contrary to the behaviour of the  $XF_6^+$  cations, the plot displays the expected variation on passing down a group in the Periodic Table.<sup>28,42</sup>

#### Halogen and oxygen-17 NMR relaxation study of $Et_4NXO_4$ (X = Cl, Br or I) in CH<sub>3</sub>CN

The relaxation of  $^{35}Cl$ ,  $^{79}Br$ ,  $^{81}Br$ ,  $^{127}I$  and  $^{17}O$  nuclei in most compounds is dominated by the efficient quadrupolar mechanism [Eqn (1)]. An indication of the suitability of a quadrupolar isotope for NMR observation is given by the isotope  $f(IQ)$  factor; the smaller this factor is, the sharper the resonances should be, and hence the easier they will be to detect.<sup>36</sup> The  $f(IQ)$  values for  $^{35}Cl$ ,  $^{37}Cl$ ,  $^{79}Br$ ,  $^{81}Br$ ,  $^{127}I$  and  $^{17}O$  are listed in Table 1 and show that resonances for  $^{79}Br$ ,  $^{81}Br$  and  $^{127}I$  are likely to be observable only in those environments in which  $q$  approaches zero, e.g. in the most symmetrical environments.

In theory, the halogen nuclei at the centre of the unperturbed tetrahedral anions  $ClO_4^-$ ,  $BrO_4^-$  and  $IO_4^-$  are subject to a vanishing electric field gradient; thus the quadrupolar relaxation mechanism is quenched and very narrow resonances should result. However, in solution electric field gradients can arise in two main ways. First, the polarization of the electrons surround-

ing the nucleus by ionic charges or solvent dipoles induces field gradients at the nucleus. This effect is known as Sternheimer antishielding and, according to Reimarsson *et al.*,<sup>45</sup> it is difficult to account for properly in a tetrahedral molecule as both external field gradients and external electric fields are capable of inducing field gradients at the central nucleus. Second, the field gradients along the covalent halogen–oxygen bonds become effective if the molecule is distorted from  $T_d$  symmetry and even small distortions can have a pronounced effect on relaxation. Such distortions may arise, for example, from asymmetric vibrational motions of the anion,<sup>46</sup> molecular collisions,<sup>47</sup> ion-pair formation or complexation with other species.<sup>48</sup> Accordingly, the NMR resonance of the central nucleus has a finite linewidth, which can be fairly large, despite the cubic symmetry of the environment surrounding the nucleus.<sup>36</sup>

Since quadrupolar relaxation is the dominant factor in determining the quality of the halogen and  $^{17}O$  spectra required for the comparative study, it was first necessary to determine the optimum experimental conditions such that quadrupolar relaxation could be minimized without prohibitive use of instrument time. To this end, CH<sub>3</sub>CN was chosen as the solvent partly because of its high polarity and low viscosity. The latter minimizes the correlation time,  $\tau_c$ , which is the only factor in Eqn (1) over which some experimental control can be exerted.<sup>36</sup> The tetraethylammonium perhalates all have excellent solubilities ( $>1$  mol dm<sup>-3</sup>) in CH<sub>3</sub>CN, which allowed the concentration dependence of the halogen  $T_1$ s to be investigated in order to ascertain the optimum concentration to be used in the high-resolution comparative study on the  $^{17}O$ -enriched materials. In addition, the  $^{17}O$  relaxation times were obtained from the  $^{17}O$ -enriched samples at the optimum concentration determined from the halogen relaxation study.

The  $T_1$  spin–lattice relaxation times of  $^{35}Cl$ ,  $^{79}Br$ ,  $^{81}Br$  and  $^{127}I$  for  $Et_4NXO_4$  in CH<sub>3</sub>CN were determined over a range of molarities (1.4, 1.0, 0.56 and 0.1 for X = Cl and Br; 1.0, 0.56, 0.1 and 0.05 for X = I) by the inversion–recovery method; the results are given in Table 6. No attempts were made to study the temperature dependence of the halogen  $T_1$ s because of the hazards involved in heating solutions of perhalates in organic solvent.<sup>49</sup> Plots of  $T_1$  against concentration [Fig. 9(a)–(d)] clearly show the expected steady increase in  $T_1$  as the solute concentration decreases. It can also be seen that the  $T_1$  values decrease in the order  $^{35}Cl > ^{81}Br > ^{79}Br > ^{127}I$  as expected from the increase in the magnitudes of the quadrupole moments of these nuclei in the order  $^{35}Cl < ^{81}Br < ^{79}Br < ^{127}I$ . The approximate infinite dilution relaxation times,  $T_1^0$ , can be obtained by extrapolation of the data to zero concentration in CH<sub>3</sub>CN. The  $T_1$  data for the three perhalate salts:

$$\begin{array}{ccc} ClO_4^- & BrO_4^- & IO_4^- \\ T_1^0 (^{35}Cl) = 1190 \text{ ms} & (^{79}Br) = 24.2 \text{ ms} & (^{127}I) = 6.3 \text{ ms} \\ & (^{81}Br) = 33.8 \text{ ms} & \end{array}$$

suggested that a concentration of 0.1 mol dm<sup>-3</sup> should yield high-resolution halogen spectra within a reason-

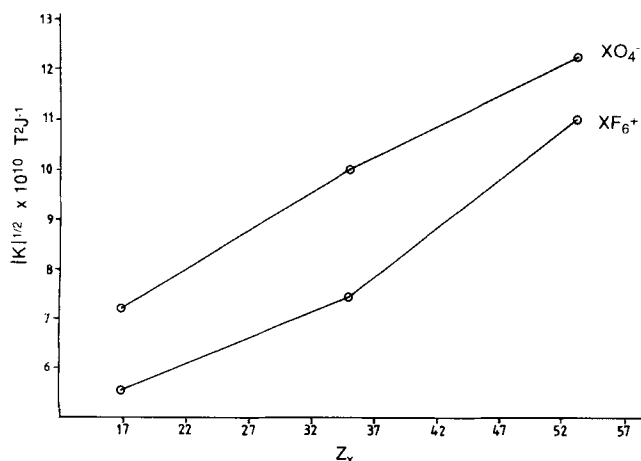


Figure 8. Plot of the variation of  $|K|^{1/2}$  with atomic number ( $Z_X$ ) for  $XO_4^-$  and  $XF_6^+$ , where X = Cl, Br and I.



**Table 6. Halogen spin-lattice relaxation times for Et<sub>4</sub>NXO<sub>4</sub> (X = Cl, Br, I) in CH<sub>3</sub>CN**

Nucleus X	[Et <sub>4</sub> NXO <sub>4</sub> ] (mol dm <sup>-3</sup> )	$T_1$ (ms)	$R_1$ <sup>a</sup> (s <sup>-1</sup> )	$\Delta\nu_{1/2}$ <sup>b</sup> (Hz)	$\Delta\nu_{1/2}(\text{obs})$ <sup>c</sup> (Hz)
<sup>35</sup> Cl	1.4	810	1.24	0.39	0.9
	1.0	890	1.12	0.36	0.6
	0.56	990	1.01	0.32	0.5
	0.1	1150	0.87	0.28	0.4
<sup>79</sup> Br	1.4	13.3	75.2	23.9	25
	1.0	15.1	66.7	21.1	22
	0.56	18.1	55.2	17.6	18
	0.1	22.8	43.9	13.9	15
<sup>81</sup> Br	1.4	18.7	53.5	17.0	18
	1.0	21.1	47.4	15.1	16
	0.56	25.2	39.7	12.6	14
	0.1	31.9	31.3	10.2	12
<sup>127</sup> I	1.0	3.9	256.4	81.6	83
	0.56	4.5	222.2	70.7	71
	0.1	5.8	172.4	54.9	54
	0.05	6.1	163.9	52.2	51

<sup>a</sup> Relaxation rate  $T_1^{-1}$ .<sup>b</sup> Calculated half-height linewidth  $1/\pi T_1$ .<sup>c</sup> Experimentally observed linewidth.

able time period; the NMR spectra of the <sup>17</sup>O-enriched samples were also recorded at this concentration.

#### Halogen relaxation in Et<sub>4</sub>NXO<sub>4</sub> (X = Cl, Br or I)

The quadrupolar relaxation of <sup>35</sup>Cl in ClO<sub>4</sub><sup>-</sup> has been extensively studied for both aqueous and non-aqueous solutions.<sup>9-11</sup> As expected from the quadrupolar mechanism, the <sup>35</sup>Cl relaxation has been shown to be dependent on the solvent properties, on the concentration and on the cation.<sup>50</sup> <sup>35</sup>Cl NMR studies on LiClO<sub>4</sub> in acetone, methanol and acetonitrile yielded narrow linewidths which remained relatively narrow even at high concentrations. However, in other solvents, e.g. nitromethane, tetrahydrofuran and tetramethylguanidine, the linewidths increase rapidly with increasing solute concentration; this has been ascribed to ion-pair formation, although increases in viscosity may also be important.<sup>51</sup> The high sensitivity of the <sup>35</sup>Cl relaxation rate to molecular distortions has been exploited by using ClO<sub>4</sub><sup>-</sup> in the study of anion binding sites in proteins.<sup>52</sup> The <sup>35</sup>Cl relaxation times for Et<sub>4</sub>NClO<sub>4</sub> dissolved in CH<sub>3</sub>CN are longer than those obtained for either ClO<sub>4</sub><sup>-</sup> in aqueous solution or for LiClO<sub>4</sub> in CH<sub>3</sub>CN and represent the lowest <sup>35</sup>Cl relaxation rates yet reported. This fact is also reflected in the infinite dilution relaxation times for aqueous ClO<sub>4</sub><sup>-</sup> ( $T_1^0 = 0.27$  s)<sup>45</sup> and Et<sub>4</sub>NClO<sub>4</sub> in CH<sub>3</sub>CN ( $T_1^0 = 1.19$  s), which correspond to linewidths of 1.2 and 0.27 Hz, respectively. Moreover, the <sup>35</sup>Cl relaxation rate is so low in these solutions that it can be expected that at higher temperatures, i.e. > 50 °C, the spin-rotation relaxation mechanism may become important, as has been found for other low- $Q$  nuclei in small symmetric molecules.<sup>53</sup> The slower <sup>35</sup>Cl relaxation in CH<sub>3</sub>CN solutions of Et<sub>4</sub>NClO<sub>4</sub> cannot be attributed solely to the lower vis-

cosity of CH<sub>3</sub>CN compared with that of H<sub>2</sub>O, since CH<sub>3</sub>CN solutions of LiClO<sub>4</sub> of comparable concentrations have shorter <sup>35</sup>Cl relaxation times.<sup>51</sup> It can be inferred that there is less of a tendency towards ion-pair formation in CH<sub>3</sub>CN solutions of Et<sub>4</sub>NClO<sub>4</sub> than for CH<sub>3</sub>CN solutions of LiClO<sub>4</sub> on account of the weaker electrostatic attraction of Et<sub>4</sub>N<sup>+</sup> for the ClO<sub>4</sub><sup>-</sup> ion as compared with solvated Li<sup>+</sup>.

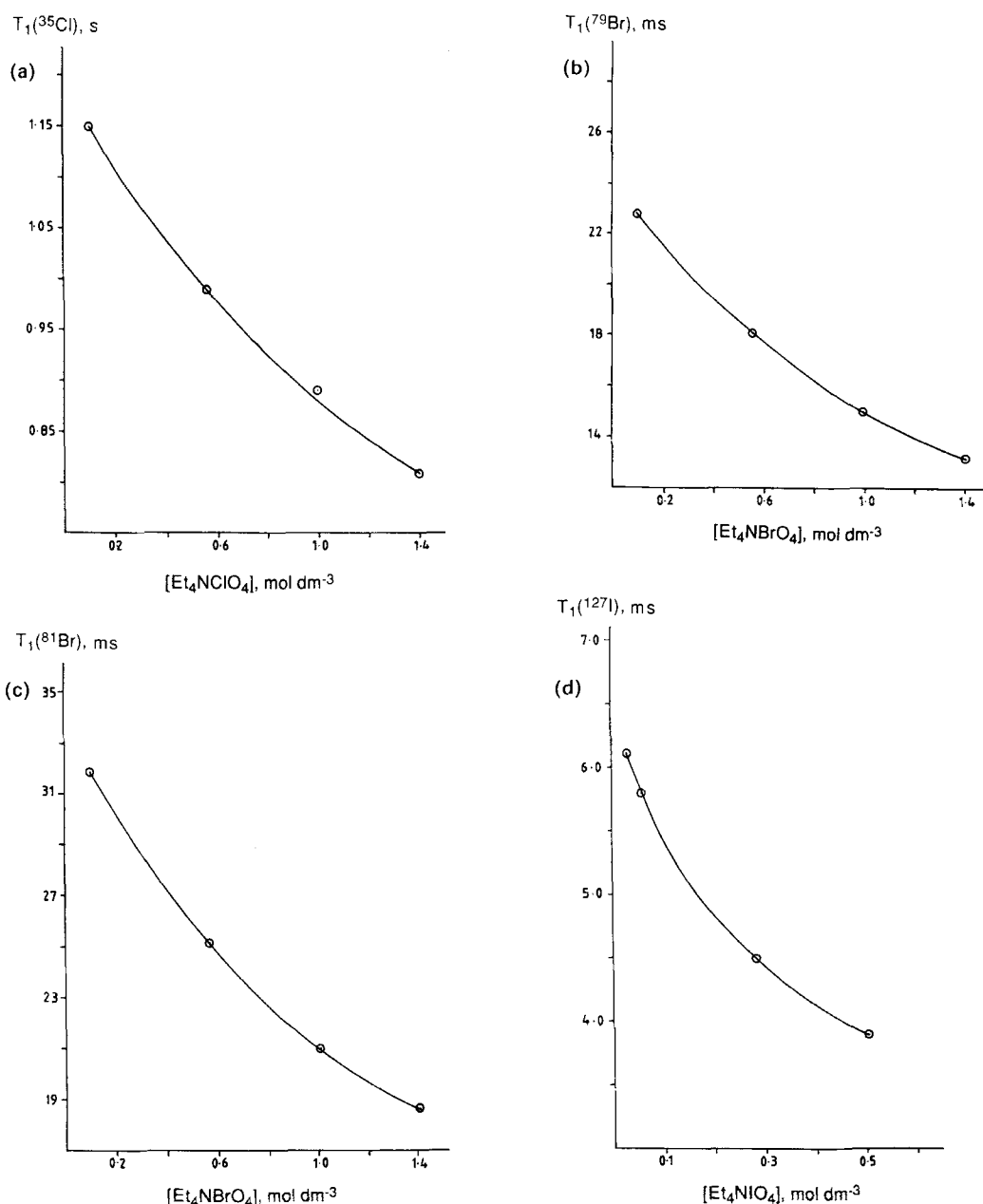
Similarly, solutions of Et<sub>4</sub>NBrO<sub>4</sub> and Et<sub>4</sub>NIO<sub>4</sub> in CH<sub>3</sub>CN have <sup>79,81</sup>Br and <sup>127</sup>I spin-lattice relaxation times, respectively, that are much longer than those measured for aqueous solutions of BrO<sub>4</sub><sup>-</sup> and IO<sub>4</sub><sup>-</sup> of comparable concentration. For example, a 1 M solution of Et<sub>4</sub>NBrO<sub>4</sub> in CH<sub>3</sub>CN has a <sup>81</sup>Br relaxation time of 21.1 ms, corresponding to a linewidth of 15 Hz, whereas a 1 M aqueous solution of HBrO<sub>4</sub> show a <sup>81</sup>Br relaxation time of 4.5 ms and a corresponding linewidth of 70 Hz. The low <sup>79,81</sup>Br and <sup>127</sup>I relaxation rates in CH<sub>3</sub>CN solutions of Et<sub>4</sub>NBrO<sub>4</sub> and Et<sub>4</sub>NIO<sub>4</sub>, respectively, probably result from the low viscosity of the solvent and the lower tendency of Et<sub>4</sub>NXO<sub>4</sub> to form ion pairs in CH<sub>3</sub>CN, as was postulated for the low <sup>35</sup>Cl relaxation rates for CH<sub>3</sub>CN solutions of Et<sub>4</sub>NClO<sub>4</sub>. However, as the concentration of Et<sub>4</sub>NXO<sub>4</sub> increases, so the halogen (X) relaxation time decreases; this is probably due to the formation of ion pairs or increase in solution viscosity, or both.

The <sup>127</sup>I resonance of aqueous IO<sub>4</sub><sup>-</sup> obtained in the present work is very broad ( $\Delta\nu_{1/2} = 1000$  Hz), and although this is expected from the large quadrupole moment of <sup>127</sup>I, it is possible that oxygen exchange with the solvent is making a contribution to the linewidth. This exchange has been shown to occur via expansion of the coordination sphere of the iodine from tetrahedral to octahedral, IO<sub>6</sub><sup>5-</sup>.<sup>21</sup> Therefore, the dramatic narrowing of the <sup>127</sup>I resonance for IO<sub>4</sub><sup>-</sup> in CH<sub>3</sub>CN solutions may be attributed, in part, to the absence of oxygen exchange in this solvent. An earlier continuous-wave study of the <sup>127</sup>I resonance of aqueous IO<sub>4</sub><sup>-</sup> yielded an infinite dilution relaxation time of 0.2 ms, corresponding to a linewidth of 1590 Hz.<sup>45</sup> However, more recent studies on saturated solutions of NaIO<sub>4</sub> in H<sub>2</sub>O and (CH<sub>3</sub>)<sub>2</sub>SO have yielded <sup>127</sup>I linewidths for IO<sub>4</sub><sup>-</sup> of 850 and 500 Hz, respectively.<sup>22</sup> This also seems to corroborate the idea that the large linewidth observed for IO<sub>4</sub><sup>-</sup> in aqueous solution is in part due to oxygen exchange.

Although no temperature-dependence relaxation studies were undertaken in the present work, Tarasov *et al.*<sup>54</sup> have studied the temperature dependence of the <sup>35,37</sup>Cl and <sup>79,81</sup>Br quadrupolar relaxation rates in aqueous solutions of NaClO<sub>4</sub> (1.02 mol kg<sup>-1</sup>) and NaBrO<sub>4</sub> (0.95 mol kg<sup>-1</sup>). As expected, the relaxation rates decrease with increasing temperature owing to the shortening of the correlation times; however, no evidence for spin-rotation relaxation at the higher temperatures was observed.

#### Oxygen-17 relaxation in Et<sub>4</sub>NXO<sub>4</sub> (X = Cl, Br or I)

The <sup>17</sup>O spin-lattice relaxation times for 0.1 M solutions of <sup>17</sup>O-enriched Et<sub>4</sub>NXO<sub>4</sub> (X = Cl, Br, I) in CH<sub>3</sub>CN were also determined by the inversion-recovery



**Figure 9.** Variation of halogen  $T_1$  values with concentration for solutions of  $\text{Et}_4\text{NXO}_4$  ( $X = \text{Cl, Br or I}$ ) in  $\text{CH}_3\text{CN}$  at  $24^\circ\text{C}$ ; (a)  $^{35}\text{Cl}$ ; (b)  $^{79}\text{Br}$ ; (c)  $^{81}\text{Br}$ ; (d)  $^{127}\text{I}$ .

method; the results are listed in Table 7 along with the observed linewidths. The imperfect agreement between the calculated and observed linewidths for the  $\text{XO}_4^-$  ions is attributed to partial quadrupolar collapse. The  $^{17}\text{O}$  spin-lattice relaxation times for  $\text{ClO}_4^-$ ,  $\text{BrO}_4^-$  and  $\text{IO}_4^-$  in  $\text{CH}_3\text{CN}$  are typical of those for terminal oxygen atoms;<sup>16,17</sup> it is interesting that these values are two orders of magnitude smaller than those measured for  $\text{MoO}_4^{2-}$ ,  $\text{TcO}_4^-$ ,  $\text{RuO}_4$  and  $\text{OsO}_4$  in the more viscous solvents  $\text{H}_2\text{O}$  and  $\text{CCl}_4$  (see Table 8).

#### Halogen and $^{17}\text{O}$ nuclear quadrupole constants ( $\chi$ ) in $\text{Et}_4\text{NXO}$ ( $X = \text{Cl, Br or I}$ )

The halogen and oxygen quadrupole coupling constants in the perhalate anions may be calculated by substitut-

ing the  $^{35}\text{Cl}$ ,  $^{79}\text{Br}$ ,  $^{81}\text{Br}$ ,  $^{127}\text{I}$  and  $^{17}\text{O}$  spin-lattice relaxation times, measured from 0.1 M solutions of  $\text{Et}_4\text{NXO}_4$  ( $X = \text{Cl, Br, I}$ ) in  $\text{CH}_3\text{CN}$ , and the appropriate values of the rotational correlation time  $\tau_c$  for  $\text{ClO}_4^-$ ,  $\text{BrO}_4^-$

**Table 7.**  $^{17}\text{O}$  spin-lattice relaxation times for  $\text{Et}_4\text{NXO}_4$  ( $X = \text{Cl, Br, I}$ ) in  $\text{CH}_3\text{CN}$

$\text{XO}_4^-$ <sup>a</sup>	$T_1(^{17}\text{O})$ (ms) <sup>a</sup>	$\Delta\nu_{1/2}$ (Hz) <sup>b</sup>	$\Delta\nu_{1/2}(\text{obs})$ (Hz) <sup>c</sup>
$\text{ClO}_4^-$	$9.7 \pm 0.2$	33	50
$\text{BrO}_4^-$	$6.6 \pm 0.2$	48	70
$\text{IO}_4^-$	$8.1 \pm 0.2$	39	170

<sup>a</sup> 0.1 M  $\text{Et}_4\text{NXO}_4$  in  $\text{CH}_3\text{CN}$ .

<sup>b</sup> Calculated linewidth  $\Delta\nu_{1/2} = (1/\pi)T_1(^{17}\text{O})$ .

<sup>c</sup> Observed linewidth measured for central components of quartet for  $\text{ClO}_4^-$  and  $\text{BrO}_4^-$ , and for outer components of the sextet for  $\text{IO}_4^-$ .

**Table 8.**  $^{17}\text{O}$  spin-lattice relaxation times in tetraoxo species  $\text{XO}_4^-$ 

$\text{XO}_4^-$	$T_1$ (ms)	$\text{XO}_4^-$	$T_1$ (ms)
$\text{MoO}_4^{2-}$ <sup>a</sup>	220	$\text{ClO}_4^-$ <sup>d</sup>	9.7
$\text{TcO}_4^-$ <sup>b</sup>	202	$\text{BrO}_4^-$ <sup>d</sup>	6.6
$\text{RuO}_4^-$ <sup>c</sup>	100	$\text{IO}_4^-$ <sup>d</sup>	8.1
$\text{OsO}_4^-$ <sup>c</sup>	130		

<sup>a</sup> 2 M  $\text{Na}_2\text{MoO}_4$  in  $\text{H}_2\text{O}$ .<sup>55</sup><sup>b</sup> 0.24 M  $\text{NH}_4\text{TcO}_4$  in  $\text{H}_2\text{O}$ .<sup>56</sup><sup>c</sup> 1.02 M in  $\text{CCl}_4$ .<sup>57</sup><sup>d</sup> 0.1 M  $\text{Et}_4\text{NXO}_4$  in  $\text{CH}_3\text{CN}$  (this work).

and  $\text{IO}_4^-$  into the quadrupolar relaxation expression [Eqn (1)]. This method has been used previously to calculate the  $^{17}\text{O}$  quadrupole coupling constant in  $\text{RuO}_4^-$ ,  $\text{OsO}_4^-$  and  $\text{MoO}_4^{2-}$ .<sup>55,57</sup> The  $\tau_c$  values for  $\text{ClO}_4^-$ ,  $\text{BrO}_4^-$  and  $\text{IO}_4^-$  were calculated using the modified Stokes-Einstein-Debye equation  $\tau_c = 4\pi[r(\text{XO}_4^-)]^3 f\eta / (3kT)$ .<sup>58</sup> The radii of the anions  $r(\text{XO}_4^-)$  were taken to be equal to the sum of the halogen-oxygen bond length<sup>3</sup> plus the ionic radius of oxygen.<sup>55</sup> The viscosities  $\eta$  of the solutions were taken to be equal to the viscosity of pure  $\text{CH}_3\text{CN}$  (i.e. 0.34 cP), and the microviscosity coefficients  $f(\text{XO}_4^-)$  were calculated by the method of Gierer and Wirtz.<sup>59</sup> The values of  $\tau_c$  obtained were  $\text{ClO}_4^- = 2.0 \times 10^{-12}$  s,  $\text{BrO}_4^- = 2.4 \times 10^{-12}$  s and  $\text{IO}_4^- = 3.0 \times 10^{-12}$  s. Substituting these values along with the halogen and oxygen  $T_1$  values into the quadrupolar relaxation equation yielded estimates of the  $^{35}\text{Cl}$ ,  $^{79}\text{Br}$ ,  $^{81}\text{Br}$ ,  $^{127}\text{I}$  and  $^{17}\text{O}$  quadrupole coupling constants, and these are given in Table 9. It should be noted that these values are approximate owing to the assumptions made in the calculation of  $\tau_c$ , i.e. the value of  $r(\text{XO}_4^-)$  and  $\eta$ . As expected, the halogen  $\chi$  values increase in the order  $^{35}\text{Cl} < ^{81}\text{Br} < ^{79}\text{Br} < ^{127}\text{I}$  in accordance with the magnitude of the product  $f(IQ)$  for these nuclides. The  $^{17}\text{O}$  quadrupole coupling constants are considerably larger than those for  $\text{MoO}_4^{2-}$ ,  $\text{RuO}_4^-$  and  $\text{OsO}_4^-$ .<sup>17</sup> In the case of  $\text{MoO}_4^{2-}$ , the small value of  $\chi(^{17}\text{O}) = 720$  kHz has been taken to indicate that the electronic distribution around oxygen in this anion is close to spherical symmetry with almost complete filling of the oxygen 2p orbitals.<sup>55</sup> Despite their approximate nature, the  $\chi(^{17}\text{O})$  values for the perhalates do show a distinct variation within the series, the smallest and largest values being those for  $\text{IO}_4^-$  and  $\text{BrO}_4^-$ , respectively. This indicates that, as might be expected, the

**Table 9.** Halogen and oxygen quadrupole coupling constants ( $\chi$ ) in the perhalate anions

$\text{XO}_4^-$ <sup>a</sup>	$\chi(\text{X})$ (MHz) <sup>b</sup>	$\chi(^{17}\text{O})$ (MHz)
$^{35}\text{ClO}_4^-$	0.3	7.4
$^{79}\text{BrO}_4^-$	2.1	8.0
$^{81}\text{BrO}_4^-$	1.8	
$^{127}\text{IO}_4^-$	7.7	6.5

<sup>a</sup> 0.1 M  $\text{Et}_4\text{NXO}_4$  in  $\text{CH}_3\text{CN}$  at 24 °C.<sup>b</sup>  $\chi = e^2qQ/h$ .

I—O bond is more polar than either the Cl—O or Br—O bonds, which results in a more spherical electronic symmetry around the oxygen in  $\text{IO}_4^-$ . However, on this basis the  $\chi(^{17}\text{O})$  value for  $\text{BrO}_4^-$  might be expected to be less than that of  $\text{ClO}_4^-$ , since the Br—O bond should be more polar than the Cl—O bond; that this is not the case tends to suggest a different electronic distribution in the Br—O bond.

### $^{19}\text{F}$ , $^{81}\text{Br}$ and $^{127}\text{I}$ NMR spectra of $\text{BrO}_3\text{F}$ , $\text{IF}_7$ and the $\text{IF}_6^+$ cation

**$\text{BrO}_3\text{F}$ .** The  $^{81}\text{Br}$  NMR spectrum of a 2 M solution of  $\text{BrO}_3\text{F}$  in anhydrous HF shows one exceedingly broad resonance ( $\Delta\nu_{1/2} = 8$  kHz) at high frequency (see Table 10). The  $^{19}\text{F}$  NMR spectrum shows a broad singlet ( $\Delta\nu_{1/2} = 390$  Hz) at high frequency (Table 10) and also an intense resonance due to the HF solvent, in agreement with the results of Gillespie and Spekkens.<sup>60</sup> Dilution of the solution with more HF had a negligible effect on the linewidth. The  $^{19}\text{F}$  NMR spectrum of  $\text{BrO}_3\text{F}$  dissolved in  $\text{CH}_3\text{CN}$  yields a narrower singlet ( $\Delta\nu_{1/2} = 135$  Hz) only slightly shifted ( $\delta = 279$  ppm) from that of  $\text{BrO}_3\text{F}$  in HF. The spectrum also shows a number of sharp resonances that are probably due to products of attack on the solvent by the highly reactive  $\text{BrO}_3\text{F}$ .

In contrast to the  $^{19}\text{F}$  spectrum of  $\text{ClO}_3\text{F}$ ,<sup>61</sup> where spin coupling between  $^{35,37}\text{Cl}$  and  $^{19}\text{F}$  is clearly observed, the  $^{19}\text{F}$  spectrum of  $\text{BrO}_3\text{F}$  shows no resolved spin coupling between  $^{79,81}\text{Br}$  and  $^{19}\text{F}$ . Although  $\text{ClO}_3\text{F}$  and  $\text{BrO}_3\text{F}$  both have distorted tetrahedral geometries,<sup>62,63</sup> the larger quadrupole moments of the bromine isotopes produce a larger quadrupole coupling constant in  $\text{BrO}_3\text{F}$ , and consequently the bromine relaxation in  $\text{BrO}_3\text{F}$  is much faster than the chlorine relaxation in  $\text{ClO}_3\text{F}$ . This is consistent with an almost complete quadrupolar collapse of the  $^{19}\text{F}$  resonance for  $\text{BrO}_3\text{F}$ , which precludes the observation of the bromine-fluorine spin coupling.

**$\text{IF}_7$ .** The previously unrecorded  $^{127}\text{I}$  NMR spectrum of neat  $\text{IF}_7$  shows a very broad singlet ( $\Delta\nu_{1/2} = 8800$  Hz) at high frequency (Table 10); in agreement with previous measurements, the  $^{19}\text{F}$  NMR spectrum shows a

**Table 10.** NMR data for  $\text{BrO}_3\text{F}$ ,  $\text{IF}_7$  and  $\text{IF}_6^+$ 

Species	$\delta$ (ppm) <sup>a</sup>		
	$^{81}\text{Br}$	$^{127}\text{I}$	$^{19}\text{F}$
$\text{BrO}_3\text{F}$ <sup>b</sup>	2499 (8000)		272 (390)
$\text{IF}_7$ <sup>c</sup>		3095 (8800)	172
$\text{IF}_6^+$ <sup>d</sup>		3361 (70)	73 (135)
			2740

<sup>a</sup> Chemical shifts with linewidths in parentheses.<sup>b</sup> 2 M solution in anhydrous liquid HF.<sup>c</sup> Neat liquid.<sup>d</sup> 0.5 M solution of  $\text{IF}_6^+\text{AsF}_6^-$  in anhydrous HF.<sup>e</sup> Not resolved owing to almost complete quadrupole collapse of resonance.<sup>f</sup> Resonance is partially quadrupole collapsed with no multiplet components resolved.

partially quadrupole-collapsed octet,<sup>64–66</sup> arising from coupling to <sup>127</sup>I. The widths of both the <sup>127</sup>I and <sup>19</sup>F resonances are due to the quadrupolar relaxation of the <sup>127</sup>I nucleus and to unresolved iodine–fluorine spin coupling. IF<sub>7</sub> has a fluxional pentagonal bipyramidal structure which results in a time-averaged electric field gradient at the iodine nucleus such that the quadrupolar relaxation of the iodine nucleus becomes slower, allowing the observation of partially resolved <sup>127</sup>I–<sup>19</sup>F spin coupling. Using computer-simulated <sup>19</sup>F line-shapes, Gillespie and Quail<sup>64</sup> were able to extract the iodine–fluorine coupling constant  $J(^{127}\text{I}, ^{19}\text{F}) = 2100$  Hz and the <sup>127</sup>I spin–lattice relaxation  $T_1 = 0.057$  ms from the experimentally observed <sup>19</sup>F spectrum of IF<sub>7</sub>. The half-height linewidth of the <sup>127</sup>I resonance of IF<sub>7</sub> measured in this study is in good accord with these values. Recent <sup>125</sup>Te and <sup>19</sup>F NMR studies on the iso-electronic TeF<sub>7</sub><sup>–</sup> anion have shown that this species is also fluxional in solution.<sup>67–69</sup>

IF<sub>6</sub><sup>+</sup>. The <sup>19</sup>F NMR spectrum of the IF<sub>6</sub><sup>+</sup> cation was obtained from a 0.5 M solution of IF<sub>6</sub><sup>+</sup>AsF<sub>6</sub><sup>–</sup> in anhydrous HF containing a threefold of AsF<sub>5</sub>. The excess AsF<sub>5</sub> helps to solubilize the IF<sub>6</sub><sup>+</sup>AsF<sub>6</sub><sup>–</sup> salt in the HF and also to suppress any exchange between the cation and the solvent, as described previously.<sup>70</sup> In agreement with the report of Brownstein and Selig,<sup>70</sup> the <sup>19</sup>F NMR spectrum of this solution shows, in addition to the solvent peak, a well resolved equal-intensity sextet (Table 10) assigned to the IF<sub>6</sub><sup>+</sup> cation. A resonance due to AsF<sub>6</sub><sup>–</sup> is not observed, presumably owing to rapid exchange with HF via AsF<sub>5</sub> and As<sub>2</sub>F<sub>11</sub><sup>–</sup>. The sextet arises from the spin coupling of the six equivalent <sup>19</sup>F's to central <sup>127</sup>I in the octahedral IF<sub>6</sub><sup>+</sup> cation (Table 10) and shows the classical intensity pattern and variation in component linewidth (134, 215, 178, 178, 215 and 134 Hz) expected for an  $I = \frac{1}{2}$  nucleus coupled to a slowly relaxing  $I = \frac{5}{2}$  nucleus.<sup>20</sup>

The <sup>127</sup>I NMR spectrum is a well resolved binomial septet (Fig. 10) at high frequency (see Table 10). The iodine–fluorine coupling constant agrees exactly with that measured from the <sup>19</sup>F spectrum  $^1J(^{127}\text{I}, ^{19}\text{F}) = 2740$  Hz. The narrow linewidths ( $\Delta\nu_{1/2} = 70$  Hz) and well resolved spin coupling displayed in both the <sup>19</sup>F and <sup>127</sup>I result from the cubic symmetry of the electric field at the iodine nucleus in the octahedral IF<sub>6</sub><sup>+</sup> cation which dramatically reduces the efficiency of the quadrupolar relaxation of this nucleus and yields a well resolved multiplet.

#### <sup>81</sup>Br and <sup>127</sup>I NMR chemical shifts of BrO<sub>3</sub>F, IF<sub>7</sub> and IF<sub>6</sub><sup>+</sup>

The <sup>81</sup>Br chemical shift of BrO<sub>3</sub>F cannot be determined very accurately because of the large linewidth of the resonance. The resonance does occur close to that of BrO<sub>4</sub><sup>–</sup>, as might be expected by analogy with previous determinations of the <sup>35</sup>Cl shifts of ClO<sub>3</sub>F and ClO<sub>4</sub><sup>–</sup>.<sup>71</sup>

The <sup>127</sup>I chemical shift of the IF<sub>6</sub><sup>+</sup> cation is strongly deshielded ( $\delta = 3361$  ppm) with respect to iodide,

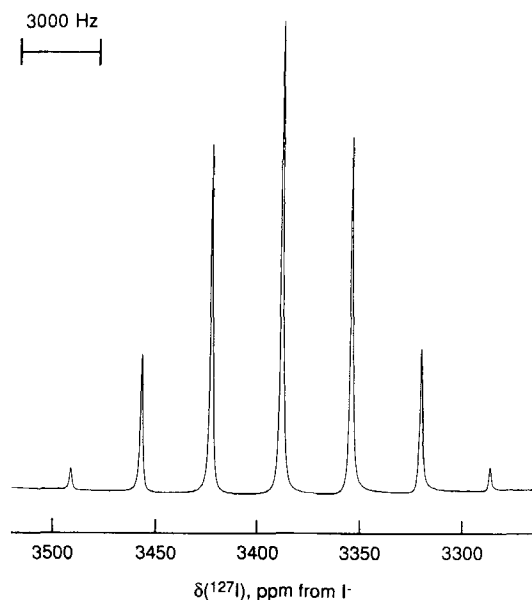


Figure 10. <sup>127</sup>I NMR spectrum (80.060 MHz) of 0.5 M IF<sub>6</sub><sup>+</sup>AsF<sub>6</sub><sup>–</sup> in anhydrous HF containing a threefold molar excess of AsF<sub>5</sub> at 24 °C.

although less so than IO<sub>4</sub><sup>–</sup> ( $\delta = 4121$  ppm). A similar phenomenon is observed for related tetraoxo and hexafluoro species (e.g. SO<sub>4</sub><sup>2–</sup>, SF<sub>6</sub>; SeO<sub>4</sub><sup>2–</sup>, SeF<sub>6</sub>; AsO<sub>4</sub><sup>3–</sup>, AsF<sub>6</sub><sup>–</sup>; PO<sub>4</sub><sup>3–</sup>, PF<sub>6</sub><sup>–</sup>)<sup>15,72</sup> and it can be expected that the <sup>35,37</sup>Cl shifts of ClF<sub>6</sub><sup>+</sup> and the <sup>79,81</sup>Br shifts of BrF<sub>6</sub><sup>+</sup> will also conform with this observation. In addition, it may be noted that the <sup>127</sup>I chemical shift for IF<sub>6</sub><sup>+</sup> occurs 266 ppm to high frequency of that for IF<sub>7</sub>; this effect is also observed for other fluoro species, e.g. the <sup>77</sup>Se shifts of SeF<sub>3</sub><sup>+</sup> and SeF<sub>4</sub>,<sup>38,73</sup> the <sup>125</sup>Te shifts of TeF<sub>3</sub><sup>+</sup> and TeF<sub>4</sub>,<sup>38</sup> and the <sup>129</sup>Xe shifts of XeOF<sub>3</sub><sup>+</sup> and XeOF<sub>4</sub>.<sup>74</sup> The higher frequency shifts of the cationic species are in accord with the increased positive charge on the cations.<sup>24</sup>

## EXPERIMENTAL

Volatile, moisture-sensitive materials were handled in Kel-F or FEP polymer reaction tubes, fitted with Kel-F needle valves, on a copper–fluoroplastic vacuum manifold; non-volatile, moisture-sensitive materials were transferred in the dry N<sub>2</sub> atmosphere of a glove-box.

#### Standard reagents

The following materials were used as supplied: tetraethylammonium hydroxide (40% aqueous solution, Fluka), perchloric acid (60%, AnalaR, BDH), anhydrous ammonia (Air Products) and <sup>17,18</sup>O-enriched water (oxygen composition: <sup>16</sup>O, 12%; <sup>17</sup>O, 50%; <sup>18</sup>O, 38%; Amersham). Aqueous HBrO<sub>4</sub>, BrO<sub>3</sub>F, AsF<sub>5</sub>, IF<sub>7</sub> and

$\text{IF}_6^+\text{AsF}_6^-$  were prepared by literature methods.<sup>70,74–77</sup> Anhydrous HF (ICI fluorine cell grade) was purified and dried as described previously. Acetonitrile (Rathburn Chemicals, HPLC grade) was purified by the multi-stage procedure developed by Winfield.<sup>78</sup> Natural-abundance tetraethylammonium perchlorate and perbromate were prepared by neutralization of 40% aqueous  $\text{Et}_4\text{NOH}$  with the perhalic acids. The precipitates were recrystallized from hot water to yield white crystalline solids; yields 75 and 71%, respectively. Commercial tetraethylammonium periodate (Fluka), supplied moistened with 10% water, was dissolved in the minimum quantity of  $\text{CH}_2\text{Cl}_2$  and the water was removed by filtration on paper. Anhydrous  $\text{Et}_4\text{NIO}_4$  was precipitated by the addition of dry diethyl ether, filtered and dried *in vacuo* at 70 °C for 12 h.

#### Tetraethylammonium perchlorate, $^{17}\text{O}$ -enriched

Aqueous perchloric acid (60%, 1.5 cm<sup>3</sup>, 33 mmol  $\text{H}_2\text{O}$ ) was mixed with oleum (30%  $\text{SO}_3$ , 6 cm<sup>3</sup>, 43 mmol  $\text{SO}_3$ ) in a Kel-F tube cooled in ice and then degassed. After standing at room temperature for 24 h, the anhydrous perchloric acid was distilled off under high vacuum and collected in an FEP tube at –196 °C; yield *ca.* 0.7 cm<sup>3</sup>, 12 mmol, 100%. Dichlorine heptoxide was prepared from the anhydrous perchloric acid as follows. Phosphorus(V) oxide (2.0 g, 7 mmol) was loaded into a Kel-F tube and degassed on a vacuum line. Anhydrous  $\text{HClO}_4$  (0.7 g, 12 mmol) was condensed on to the  $\text{P}_4\text{O}_{10}$  at –198 °C and the contents of the tube were held at –25 °C for 6 h. The product was distilled in vacuum into an FEP tube; it melted at *ca.* –90 °C to a pale green liquid. Pumping on the liquid at –90 °C removed the green colouration, which was probably due to  $\text{Cl}_2$  or lower chlorine oxides. The  $\text{Cl}_2\text{O}_7$  was a colourless, oily liquid (*ca.* 0.2 cm<sup>3</sup>, 2.2 mmol, 36%). It was converted into the labelled acid by reaction with excess  $^{17}\text{O}$ -enriched water (0.46 g) frozen at –196 °C in an FEP tube; the mixture was allowed to warm slowly to 0 °C when the  $\text{Cl}_2\text{O}_7$  sank and hydrolysed slowly at room temperature. After neutralization of the perchloric acid with anhydrous ammonia at –106 °C, the excess water was recovered *in vacuo* from the solid ammonium salt. Addition of  $\text{Et}_4\text{NOH}$  solution (40%, 1.7 cm<sup>3</sup>, 4.6 mmol) to the resulting solution of the ammonium perchlorate precipitated the tetraethylammonium salt: this was recrystallized from boiling water and dried in vacuum to give white fluffy crystals (0.5 g, 60%).

#### Tetraethylammonium perbromate, $^{17}\text{O}$ -enriched

Perbromyl fluoride (1.0 mmol) was condensed on to  $^{17,18}\text{O}$ -enriched water (0.5 cm<sup>3</sup>) in an FEP tube held at –196 °C; the mixture was allowed to warm spontaneously whilst being vigorously agitated. Excess anhydrous  $\text{NH}_3$  was added at –106 °C to neutralize the HF and  $\text{HBrO}_4$ . The white solid, which had separated at

room temperature, was taken up in the minimum volume of water and treated with excess  $\text{Et}_4\text{NOH}$  (40%). After cooling to –10 °C the perbromate salt was centrifuged off and recrystallized from water. The product (0.085 g, 31% yield) was a white crystalline powder containing 50%  $\text{Et}_4\text{NBr } ^{17}\text{O } ^{16}\text{O}_3$ , 38%  $\text{Et}_4\text{NBr } ^{18}\text{O } ^{16}\text{O}_3$  and 12%  $\text{Et}_4\text{NBr } ^{16}\text{O}_4$ .

#### Enriched tetraethylammonium periodate, $^{17}\text{O}$ -enriched

Anhydrous tetraethylammonium metaperiodate (0.45 g) was dissolved in  $^{17}\text{O}$ -enriched water (composition:  $^{17}\text{O}$ , 10%;  $^{18}\text{O}$ , 7.6%) and held at 50 °C for 2 days. After this equilibration time the water was distilled off under vacuum and the hydrated residue treated as described for the  $\text{Et}_4\text{NI } ^{16}\text{O}_4$  salt to give a white, hygroscopic powder (0.4 g). The calculated isotope composition is  $\text{I } ^{16}\text{O}_4^-$ , 46;  $\text{I } ^{16}\text{O}_3 ^{18}\text{O}^-$ , 17;  $\text{I } ^{16}\text{O}_3 ^{17}\text{O}^-$ , 29;  $\text{I } ^{16}\text{O}_2 ^{17}\text{O } ^{18}\text{O}^-$ , 6; others, <2%.

#### Samples for NMR spectroscopy

Samples of  $\text{Et}_4\text{NXO}$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ) in  $\text{CH}_3\text{CN}$  were prepared in 10 mm precision-glass NMR tubes (Wilmad). Solids were weighed into the tubes, the solvent was distilled under vacuum onto the solid at –78 °C and the tubes were sealed. Samples of  $\text{BrO}_3\text{F}$  and  $\text{IF}_7$  were sealed *in vacuo* in 4 mm diameter FEP tubing, pre-passivated with  $\text{F}_2$  gas. Anhydrous HF and  $\text{CH}_3\text{CN}$  were used as solvents for the  $\text{BrO}_3\text{F}$  samples. The sample of  $\text{IF}_6\text{AsF}_6$  was prepared in the 8 mm diameter FEP NMR tube from  $\text{IF}_7$  (0.37 g, 1.42 mmol), anhydrous HF (2.5 cm<sup>3</sup>) and a threefold excess of  $\text{AsF}_5$  (4.3 mmol). A white crystalline solid formed, which dissolved on warming to room temperature to give a colourless solution. These samples were kept at –196 °C until required and then placed in precision-bore (Wilmad 5 or 10 mm diameter) glass tubes prior to insertion in the NMR probe.

#### Multinuclear magnetic resonance spectroscopy

All  $^{17}\text{O}$ ,  $^{35}\text{Cl}$ ,  $^{79,81}\text{Br}$  and  $^{127}\text{I}$  NMR spectra were recorded on Bruker WM250 and/or WH400 pulse spectrometers. Spectra were generally recorded unlocked (field drift <0.1 Hz h<sup>–1</sup>) using 10 mm probes broadbanded over the frequency ranges 12–101 MHz (5.8719 T) and 18–164 MHz (9.395 T), respectively. The observing frequencies on the WM250 were 33.909 ( $^{17}\text{O}$ ), 24.508 ( $^{35}\text{Cl}$ ), 62.674 ( $^{79}\text{Br}$ ), 67.553 ( $^{81}\text{Br}$ ) and 50.051 MHz ( $^{127}\text{I}$ ). Free induction decays were typically accumulated in 16K memories. Spectral width settings of 5–25 kHz were employed, yielding data point resolutions of 0.18–2.5 Hz and acquisition times of 2.81–0.34 s, respectively. The number of transients accumulated ranged from 60 to 15000, depending on factors such as the nucleus involved and its isotopic abundance.

Pulse widths were typically 12–20 (WM250) and 10–20  $\mu$ s (WH400). Line broadening parameters used in the exponential multiplication of the free induction decays were 1–5 Hz.

Fluorine-19 NMR spectra were obtained on the WM250 at 235.341 MHz using a 10 mm dedicated probe; the key parameters were 16K memory, 50 kHz spectral width, 6.104 Hz data point resolution, acquisition time 0.164 s and 2000–8000 transients collected. The respective nuclei were referenced to the following standards at 24°C: H<sub>2</sub>O (<sup>17</sup>O); CFCl<sub>3</sub> (<sup>19</sup>F); 1 M aqueous NaCl (<sup>35</sup>Cl); 1 M aqueous NaBr (<sup>79,81</sup>Br); 1 M aqueous NaI (<sup>127</sup>I). The measured halogen chemical shifts were corrected to infinite dilution using literature data.<sup>9</sup> The chemical shift convention used was that a positive shift signifies to high frequency of the reference compound.

The halogen  $T_1$  measurements were carried out on a Jeol FX90 (2.1139 T) spectrometer at the City of

London Polytechnic (now the City University); the <sup>17</sup>O  $T_1$  measurements were made on a Bruker WH400 spectrometer at Warwick University. The halogen  $T_1$  results were obtained from deuterium-locked studies using the standard inversion–recovery pulse sequence (180°– $\tau$ –90°) with accumulation of the FID after the 90° pulse. The <sup>17</sup>O  $T_1$  measurements were made using the same pulse sequence but unlocked, in order to avoid frequency interference from the <sup>2</sup>D locking channel. The  $T_1$  values were calculated by exponential or linear fitting to the experimental data, using routines provided in the spectrometer software.

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