Raman Spectrum and Structure of Bromine Dioxide

By JEAN-LOUIS PASCAL and JACQUELINE POTIER*

(*Laboratoire des Acides Minéraux associé au CNRS n° 79, Université des Sciences et Techniques du Languedoc, Place Eugène Bataillon,* 34060 *Montpellier-Cédex*)

Summary The Raman spectrum of bromine dioxide is interpreted as indicating that it has the dimeric structure Br_2O_4 with a Br–Br bond.

ALTHOUGH the structures of oxides of chlorine Cl_2O_7,[1] Cl_2O_6,[2] ClO_2,[3] and Cl_2O[4] are quite well known this is not the case for oxides of bromine, and only Br_2O has been studied previously, by i.r. spectroscopy.[5]

Bromine dioxide was synthetised in crystalline form in a Raman tube (diam. 7 mm) by ozonising a solution of bromine in Freon 11 (1—6 g/l) at −50 °C.[6] P_2O_5 was not used as drying agent.[7] Iodometric and potentiometric analysis confirmed the composition BrO_2.

The Raman spectrum (Table 1) was recorded at −180 °C, in a sealed tube *in vacuo*. The spectrum shows five groups of lines in the internal vibration range and a very strong, sharp line at 205 cm^{-1}. Since for BrO$_2$ monomer only three groups of lines are expected, we conclude that the product is not a monomer, and we consider the following structures: (i) a chain or ring structure with bridging oxygen atoms as found previously for SeO$_2$[8] and IO$_2$;[9] (ii) a dimer with a central Br–Br bond; (iii) the ionic structures: BrO$^+$BrO$_3^-$ or Br$^+$BrO$_4^-$.

TABLE 1

Raman spectra of (BrO$_2$)$_2$

Frequencies cm^{-1}	Assignments
68sh	lattice and ρ_r
114sh	
125sh	
205vs	ν(Br–Br)
376br,w	δ(BrO$_2$)
428br,w	ρ_t(BrO$_2$)
485br,w	ρ_w(BrO$_2$)
861m	ν_s(Br–O)
878s	
882sh	
910s	ν_{as}(Br–O)
919s	

s: strong; m: medium; w: weak; sh: shoulder; b: broad; v: very.

The valence vibrations of the Br–O–Br group would presumably be close to those for Br$_2$O (504 and 587 cm^{-1})[5] and for the Se–O–Se group in (SeO$_2$)$_2$ (543 and 660 cm^{-1}),[8] *i.e.*, 600 cm^{-1}. An intense vibration would be expected for the Br–Br bond, at a lower frequency than that of Br$_2$ (300 cm^{-1}), because the Br–Br bond energy in Br$_2$O$_4$ is expected to be lower than that of Br$_2$. Ionic structures should show an intense line characteristic of BrO$_3^-$ and BrO$_4^-$ near 800 cm^{-1}.[10,11]

The absence of lines between 504 and 861 cm^{-1} eliminates hypotheses (i) and (iii). The presence of a very strong line at 205 cm^{-1} strongly favours the structure O$_2$Br–BrO$_2$. The symmetric N–N vibration in N$_2$O$_4$ has a similar high intensity.[12] It is difficult to assign this line to a lattice vibration, because ClO$_2$ lattice vibrations are in the range 174—40 cm^{-1} [3] and those of Br$_2$ are in the range 110—49 cm^{-1}.[13] Since each bromine has an unshared electron pair, it is reasonable that Br$_2$O$_4$ should have a structure similar to that of several other X$_2$Y$_4$ compounds (P$_2$I$_4$, P$_2$Cl$_4$, N$_2$F$_4$, N$_2$H$_4$) which have C_{2v} or C_2 symmetry. The number and width of the observed peaks are consistent with this hypothesis.

In this first analysis, in-phase and out-of-phase-splittings and crystal field effects were neglected. The bands at 861—882 cm^{-1} and 910—919 cm^{-1} may be assigned respectively to the symmetric and antisymmetric Br–O valence vibrations. Assignment of the deformation modes is somewhat more difficult but Yamaguchi[14] has shown that the deformation modes of a group X$_2$Y$_4$ may be correlated with the deformation modes of the group XY$_3$ as follows:

$$\delta_s \longrightarrow \rho_w$$

$$\delta_{as} \begin{array}{l} \nearrow \rho_t \\ \searrow \delta \end{array}$$

We have therefore assigned the deformation modes of Br$_2$O$_4$ by comparison with those of BrO$_3^-$ (see Table 2). Of the three lines at 68, 114, and 124 cm^{-1}, one could possibly be the rocking mode and the others must be assigned as lattice vibrations.

TABLE 2. (*Frequencies in* cm^{-1}).

BrO$^-$		Br$_2$O$_4$	
$\delta_s(A_1)$	418 $\rightarrow \rho_w$	(A,B)	485
	$\nearrow \rho_t$	(A,B)	428
$\delta_{as}(E)$	350		
	$\searrow \delta$	(A,B)	376

This preliminary study of the structure of BrO$_2$ shows the considerable differences between the oxides of the halogens in the solid state. ClO$_2$ is a monomer (as shown previously), BrO$_2$ is a dimer with a Br–Br bond, while IO$_2$ is a polymer containing I–O–I bridges.

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