

Raman Spectrum and Structure of Bromine Dioxide

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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 synthesised 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 BrO₂ 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 SeO₂⁸ and IO₂⁹; (ii) a dimer with a central Br-Br bond; (iii) the ionic structures: BrO⁺BrO₂⁻ or Br⁺BrO₄⁻.

TABLE 1
Raman spectra of (BrO₂)₂
Frequencies of Assignments
cm⁻¹

68sh	} lattice and ρ_r
114sh	
125sh	
205vs	
376br,w	
428br,w	} $\nu(\text{Br-Br})$
485br,w	
861m	
878s	} $\nu_s(\text{Br-O})$
882sh	
910s	
919s	} $\nu_{as}(\text{Br-O})$

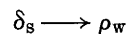
s: strong; m: medium; w: weak; sh: shoulder; b: broad; v: very.

The valence vibrations of the Br-O-Br group would presumably be close to those for Br₂O (504 and 587 cm⁻¹)⁵ and for the Se-O-Se group in (SeO₂)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 Br₂ (300 cm⁻¹), because the Br-Br bond energy in Br₂O₄ is expected to be lower than that of Br₂. Ionic structures should show an intense line characteristic of BrO₃⁻ and BrO₄⁻ 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 O₂Br-BrO₂. The symmetric N-N vibration in N₂O₄ has a similar high intensity.¹² It is difficult to assign this line to a lattice vibration, because ClO₂ lattice vibrations are in the range 174-40 cm⁻¹³ and those of Br₂ are in the range 110-49

cm⁻¹.¹³ Since each bromine has an unshared electron pair, it is reasonable that Br₂O₄ should have a structure similar to that of several other X₂Y₄ compounds (P₂I₄, P₂Cl₄, N₂F₄, N₂H₄) which have C_{2v} or C₂ 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 Yamaguchi¹⁴ has shown that the deformation modes of a group X₂Y₄ may be correlated with the deformation modes of the group XY₃ as follows:



We have therefore assigned the deformation modes of Br₂O₄ by comparison with those of BrO₃⁻ (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
$\delta_{as}(E)$	350 $\begin{cases} \nearrow \rho_t \\ \searrow \delta \end{cases}$	(A,B) 428
		(A,B) 376

This preliminary study of the structure of BrO₂ shows the considerable differences between the oxides of the halogens in the solid state. ClO₂ is a monomer (as shown previously), BrO₂ is a dimer with a Br-Br bond, while IO₂ is a polymer containing I-O-I bridges.

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