The Raman Spectrum and Structure of Bromyl Fluoride

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Summary The Raman spectra of solid and liquid BrO_2F have been obtained and show that in both states BrO_2F is monomeric with a pyramidal structure, like ClO_2F but differing from polymeric IO_2F.

THE Raman spectrum of liquid ClO_2F and the i.r. spectrum of the gas show that it is monomeric and has a pyramidal structure.[1] In contrast the Raman spectrum of IO_2F together with its lack of volatility strongly suggests that it has a polymeric structure.[2] Schmeisser and Pammer[3,4] have reported the preparation of BrO_2F by several reactions but no analytical or spectral data has been reported, and there is no information available about the structure of BrO_2F.

TABLE

Raman spectra of BrO_2F, ClO_2F and SeO_2F^-/cm^{-1}

ClO_2F[a]	SeO_2F^-[b]	solid BrO_2F (−75 °C)	BrO_2F in BrF_5 solution[c] (room temp.)	liquid BrO_2F (−10° C)	assignment
1253(40)[d] dp[e]	888(45)	963(5) }	962(8) dp	953(14 dp	ν_5; ν_{BrO} asym
		940(20) }			
1097(100 p	903(100	908(100) }	916(100) p	908(100) p	ν_1;ν_{BrO} sym
	450(sh) } (25)	524(sh) } (25)			
602(20) p	424 } v.br.	496 } v.br.		506(36) p	ν_2; ν_{BrF}
	408(sh) }	487(sh)			
533(50) p	324(10)	400(sh) } (10)		394(14) p	ν_3; δ_{OBrO}
		386 }			
398(30) p(?)	283(10)	305 } (20)		305(21) p	ν_4; δ_{OBrF} sym
		294(sh) }			
351(O+)[f]	238(2)	267(15)		271(16) dp	ν_6; δ_{OBrF} asym

[a] Ref. 1. [b] Unpublished results; our results and interpretation are not in complete agreement with those of Paetzold and Aurich Ref. 10. This will be discussed in more detail in a future publication. [c] The BrO_2F spectrum below 900 cm^{-1} is obscured by the very intense BrF_5 lines. [d] Numbers in parentheses give relative intensities. [e] dp: depolarized; p: polarized; sh: shoulder; v.br.: very broad. [f] Intensity too small to be measured.

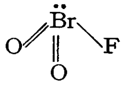
We have now prepared BrO_2F by the reaction of $KBrO_3$ and BrF_5 at room temperature. Although this reaction was previously reported[4] to occur at −50°C we were unable to obtain any reaction at this low temperature. The product (**1**) was a white solid which was obtained by dynamic distillation of the reaction mixture through a trap kept at −48 °C. The product melted at *ca.* −10°C, and the melt was stable even at room temperature when kept in a well-passivated Kel-F tube.

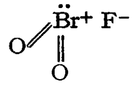
The n.m.r. spectrum of (**1**) in BrF_5 at −35° consisted of a single sharp line at −210 ± 4 p.p.m. from $CFCl_3$. The chemical shift depended slightly on the concentration, composition and temperature of the solution. It was comparable to the chemical shifts of the two resonances of BrF_5 which are at −135 and −275 p.p.m. from $CFCl_3$, thus confirming that the product is a Br^V species.

The Raman spectra of (**1**) in the solid and liquid states and the partial Raman spectrum of (**1**) in BrF_5 solution are given in the Table. For a pyramidal BrO_2F molecule of C_s symmetry, six fundamental vibrations are expected, all of which are Raman active. Of these six, four are totally symmetric A′ modes, and two are asymmetric A″ modes. The six lines observed in the spectrum of the liquid (**1**), of which four are polarized and two are depolarized may be satisfactorily assigned to a monomeric pyramidal BrO_2F molecule, by analogy with the known spectrum of ClO_2F.[1] The solid state spectrum is essentially similar to the liquid state spectrum, the major differences being that the asymmetric BrO stretching mode is split into two peaks and that shoulders appear on some of the peaks. We conclude, therefore, that the reaction of $KBrO_3$ with BrF_5 produces BrO_2F, that it has a monomeric pyramidal structure like ClO_2F, and that it is not polymeric like IO_2F.

The BrO_2F frequencies are lower than those of ClO_2F, which is consistent with the expected greater bond strength in ClO_2F due to the greater electronegativity of chlorine. There is also reasonable agreement with the spectrum of the isoelectronic SeO_2F^-, the frequencies of the latter being slightly lower than those of BrO_2F because of the negative charge of the anion.

The BrF stretching frequency of BrO_2F (506 cm^{-1}) is relatively low compared with the mean values of the Br–F stretching motions of some other Br^{III}, Br^V and Br^{VII} species, *e.g.*, BrO_3F (605 cm^{-1}),[5] BrF_5 (615 cm^{-1}),[6] BrF_3 (606 cm^{-1}),[7] BrF_4^- (492 cm^{-1}),[7] and BrF_6^- (487 cm^{-1}).[8] A force constant calculation for ClO_2F has revealed a very low Cl–F stretching force constant which indicated a rather weak Cl–F bond, and was attributed to a large ionic character in the Cl–F bond.[1,9] A similar unexpectedly low stretching frequency for the Se–F bond in SeO_2F^- was also attributed, at least in part, to a large ionic character of the Se–F bond.[10] Our results indicate that the Br–F bond in BrO_2F is similarly rather weak, and presumably this may be attributed partly to an important contribution from the ionic resonance structure (**2**) in addition to the covalent structure (**1**). The mean of the BrO stretching frequencies in liquid BrO_2F (931 cm^{-1}) is similar to that for BrO_3F (941 cm^{-1}),[5] but higher than those of other related species,


(**1**)


(**2**)

BrO_2^- (695 cm^{-1}),[11] BrO_3^- (829 cm^{-1})[12] and Br_2O_4 (893 cm^{-1}).[13] As the stretching frequency for a Br^{VII} compound is expected to be significantly higher than that for a similar Br^V compound, it appears that the BrO stretching frequencies in BrO_2F are abnormally high. This is also consistent with an important contribution from structure (**2**) which places a positive charge on bromine, thereby increasing the BrO stretching frequencies.

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