These relations precisely parallel the corresponding quadrate expressions for the Φ functions, given in eq 8.

It should be kept in mind that the present Ψ^0 functions are only approximate wave vectors, which are not reliable near the octahedral origin. Nevertheless, the expressions in eq 22 perform reasonably well, as may be judged from Figure 6.

IIId. Discussion. All trigonal d^3 complexes have been shown to belong to only one emission class, which is characterized by an unequal orbital occupation of the trigonal t_{2g} orbitals. In consequence all trigonal emitters are expected to exhibit the characteristic spectral features, such as band broadening and solvent shifts, which in the study of Forster et al.[1] were associated with the ^2T emission class of strongly perturbed tetragonal complexes. The prominence of these effects will be proportional to the degree of charge anisotropy in the emitting state and thus will depend on the trigonal field strength as shown in Figure 6. For very weak trigonal fields, such as in the tris(ethylenediamine) complex, emission will of course still be matching the octahedral pattern, but even moderate trigonal fields should already give rise to observable effects. These predictions seem to meet Endicott's working hypothesis[24] that ligands with a tendency toward trigonal distortions might facilitate excited-state relaxation.

Broad absorption spectra and Stokes-shifted phosphorescence have certainly been observed for the Cr(acac)$_3$ compound in the crystalline study of Armendarez and Forster.[25] This spectral broadening is to a large extent due to solid-state interactions. In dilute matrices at temperatures below 10 K the Cr(acac)$_3$ emission spectrum is very narrow with the preponderance of the emission in the 0–0 bands,[26] but even under these circumstances many vibrational sidebands are present, indicating excited-state distortions. Hence, in Cr(acac)$_3$ the lowest electronic transition, with a band origin around 12 880 cm^{-1}, must be assigned to a ^2E state, of mixed ^2E_g, $^2T_{1g}$, and $^2T_{2g}$ parentage. In principle the vector composition of this state and the sign of the trigonal splitting can be obtained by Zeeman spectroscopy. However, so far such measurements have not resulted in conclusive assignments.[27]

For Cr(bpy)$_3^{3+}$ one expects on the basis of the Orgel effect a pronounced depletion of the a_1 orbital, which should be higher in energy than the e orbitals. In view of the angular form of the a_1 orbital as depicted in Figure 3, this charge flow should promote solvent attack along the direction of the threefold axis and eventually give rise to a photosubstitution reaction. Apparently this trigonal polarization must be quite pronounced since Cr(bpy)$_3^{3+}$ is one of the only Cr(III) complexes that is claimed to have a photoreactive doublet state.[28,29] Although the spectral reports of König and Herzog[30] do suggest a strong trigonal splitting for Cr(bpy)$_3^{3+}$, conclusive spectral evidence again is still lacking. Hopefully these issues can be clarified. The outcome of such studies may also necessitate a reassignment of the phosphorescent states[31] in Cr(III) tris(diimine) complexes.

The I^* bonding model, which was applied to tetragonal emitters in the previous section, can also be used to predict excited-state geometries in trigonal emitters. Here such calculations will not be pursued since no detailed empirical information with regard to the excited-state geometries in trischelated complexes is available. It should be pointed out though that, because of bidentate strain effects, excited-state charge redistributions in chelated complexes may not only affect the bond lengths but could also induce changes of the bite angles and the trigonal twist angle.

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IV. Appendix

In this Appendix we collect some useful parameter values for typical Cr(III) complexes. Racah's interelectronic repulsion parameters *B* and *C* were taken to be $B = 700$ cm^{-1} and $C = 4B$. The calculations of the orbital occupation numbers were based on the following values for the energy gaps between the doublet levels: $D(^2T_{2g} \leftrightarrow {}^2T_{1g}) = 7000$ cm^{-1}, $D'(^2T_{1g} \leftrightarrow {}^2E_g) = 700$ cm^{-1}.

AOM parameters for various ligands coordinated at the Cr(III) ion may be found in ref 15. As an example for the fluoride ligand one has $\sigma_F \approx 7630$ cm^{-1} and $\pi_F = 1880$ cm^{-1}. For the acac$^-$ ligand we assume that $\pi_\perp(\chi)$ is almost negligible while $\pi_\perp(\psi) \approx 1000$ cm^{-1}. For the bpy ligand no parameter values could be obtained.

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Bromine Nitrates

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The reaction of BrF$_5$ with a large excess of LiNO$_3$ at 0 °C produces LiF, BrONO$_2$, N$_2$O$_5$, and O$_2$ as the principal products. The infrared spectra of BrONO$_2$ in the gas and solid phases and in N$_2$ and Ne matrices and the Raman spectrum of the solid phase were recorded. With the exception of the N–OBr torsional mode, all fundamental vibrations of BrONO$_2$ can be assigned and support a planar structure for this molecule. The fundamental vibrations involving the NO$_2$ group exhibit pronounced frequency shifts on going from the gas to the solid, indicating association in the solid phase. With N$_2$O$_5$ the BrONO$_2$ molecule forms an unstable adduct, which was shown by Raman spectroscopy to possess the ionic structure NO$_2^+$[Br(ONO$_2$)$_2$]$^-$. On the basis of a comparison of our results with those found in the literature and in three unpublished dissertations, it is concluded that the previously reported compounds BrO$_2$·3NO$_2$, Br(NO$_3$)$_3$, and BrNO$_3$·N$_2$O$_5$ are all identical with our material and therefore must be assigned the composition NO$_2^+$[Br(ONO$_2$)$_2$]$^-$. For comparison, Cs$^+$[Br(ONO$_2$)$_2$]$^-$ was also prepared, and its vibrational spectra were recorded and assigned.

Introduction

In a recent study from our laboratory it was shown that the reactions of an excess of BrF$_5$ with the nitrates of Na, K, Rb, and Cs provide simple, high-yield, one-step syntheses for the corresponding BrF$_4$O$^-$ salts and FNO$_2$. Since lithium does not form a stable BrF$_4$O$^-$ salt, the use of LiNO$_3$ as a starting material in the above reaction afforded a direct, one-step synthesis of BrF$_3$O.[1] During the study of the LiNO$_3$–BrF$_5$ system, it was found that

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the use of an excess of $LiNO_3$ in this reaction dramatically altered its course and produced bromine nitrate containing material.

Very few papers dealing with bromine nitrates have previously been published. The first report on the existence of bromine nitrates was published in 1961 by Schmeisser and Taglinger.[2] From the reaction of BrF_3 with N_2O_5 they obtained a compound believed to be $Br(NO_3)_3$. By reaction with iodine this material was converted to $BrONO_2$, which was also prepared from BrCl and $ClONO_2$. Ozonization of $BrONO_2$ resulted in the formation of O_2BrONO_2.[2] The only other published reports on these compounds were a confirmation[3] of the $BrONO_2 + O_3$ reaction and a study of the stratospheric significance of $BrONO_2$ in which its gas-phase ultraviolet and infrared spectra and some physical properties were also reported.[4] In addition, the synthesis and a partial infrared spectrum were reported for $[N(CH_3)_4]^+[Br(ONO_2)_2]^-$, which was prepared from $[N(CH_3)_4]^+BrCl_2^-$ and $ClONO_2$.[5]

Toward the end of our study, Professor Naumann from the University of Dortmund, West Germany, kindly provided us with copies of three unpublished dissertations[6-8] that were carried out between 1963 and 1977 under the late Professor Schmeisser. The pertinent results of these studies are summarized in the following three paragraphs.

In 1963 Schuster[6] found that the interaction between Br_2 and $ClONO_2$ at room temperature can produce two different products. At short reaction times $BrONO_2$ was obtained in good yield, whereas at extended reaction times the principal product was $BrONO_2 \cdot N_2O_5$. The latter compound was also obtained by reaction 1 and found in the residue from the partial decomposition

$$BrONO_2 + N_2O_5 \rightarrow BrONO_2 \cdot N_2O_5 \qquad (1)$$

of Taglinger's "$Br(NO_3)_3$".[2] Furthermore, it was shown that the compound trinitrobromine dioxide, $BrO_2 \cdot 3NO_2$, reported in 1953 by Pflugmacher,[9] was identical with $BrONO_2 \cdot N_2O_5$. Although no structural information on $BrO_2 \cdot 3NO_2$ and $BrONO_2 \cdot N_2O_5$ was available, their compositions were firmly established by elemental analyses, and the possibility of the ionic structure $NO_2^+[Br(NO_3)_2]^-$ was suggested.

Holthausen[7] confirmed for $BrONO_2 \cdot N_2O_5$ the ionic $NO_2^+[Br(NO_3)_2]^-$ structure by low-temperature infrared spectroscopy and by the metathetical reaction 2. The $[N(CH_3)_4]^+[Br(NO_3)_2]^-$ salt was also prepared according to reactions 3, 4, and, interestingly, 5. Attempts to prepare $NO^+[Br(NO_3)_2]^-$ and $Cs^+[Br(NO_3)_2]^-$ were either unsuccessful or resulted in an impure product, respectively. The low-temperature infrared spectrum of $BrONO_2$ was also recorded and showed the following absorptions (cm^{-1}): 1655 s, 1615 vs, 1260 vs, 830 vs, 725 s, 630 s, 395 s.[7]

$$NO_2^+[Br(NO_3)_2]^- + [N(CH_3)_4]^+NO_3^- \rightarrow [N(CH_3)_4]^+[Br(NO_3)_2]^- + N_2O_5 \qquad (2)$$

$$[N(CH_3)_4]^+BrCl_2^- + 2ClONO_2 \rightarrow [N(CH_3)_4]^+[Br(NO_3)_2]^- + 2Cl_2 \qquad (3)$$

$$[N(CH_3)_4]^+NO_3^- + BrONO_2 \rightarrow [N(CH_3)_4]^+[Br(NO_3)_2]^- \qquad (4)$$

$$[N(CH_3)_4]^+NO_3^- + \text{“}Br(NO_3)_3\text{”} \rightarrow [N(CH_3)_4]^+[Br(NO_3)_2]^- \qquad (5)$$

Stosz[8] repeated the previous preparations[2,6,7] of $BrONO_2$, $NO_2^+[Br(NO_3)_2]^-$, and "$Br(NO_3)_3$", recorded their low-temperature Raman spectra, and redetermined some physical properties, such as melting points and vapor pressures ($BrONO_2$: mp −28 °C, $\Delta H_{vap} = 8.0$ kcal/mol).[8] He showed that the Raman spectra of $NO_2^+[Br(NO_3)_2]^-$ and "$Br(NO_3)_3$" were identical and concluded that $NO_2^+[Br(NO_3)_2]^-$ actually was $Br(NO_3)_3$. Attempts to prepare $K^+[Br(NO_3)_2]^-$ were unsuccessful.[8]

On the basis of the above data, the identity of $BrONO_2$ appeared well-established; however, serious doubts existed concerning the exact nature of $BrO_2 \cdot 3NO_2$, $BrONO_2 \cdot N_2O_5$, $NO_2^+[Br(NO_3)_2]^-$, or $Br(NO_3)_3$. The fact that all four compounds represent one single species has been well-established.[6-8] However, the recent Raman spectroscopic identification of this species as $Br(NO_3)_3$ by Stosz[8] could not explain the results of both Schuster[6] and Holthausen[7] and required a thorough reexamination.

Experimental Section

Materials. Commercial $LiNO_3$ (J. T. Baker, 99.7%) and CsBr (Aldrich, 99.9%) were dried in a vacuum oven at 120 °C for 1 day prior to their use. BrF_5 (Matheson) was treated with 35 atm of F_2 at 100 °C for 24 h and then purified by fractional condensation through traps kept at −64 and −95 °C, with the material retained at −95 °C being used. Br_2 (J. T. Baker, purified) was stored over P_2O_5 prior to its use. $CsBrCl_2$ was prepared from CsBr and Cl_2 in CH_3CN solution.[10] After addition of about the stoichiometric amount of Cl_2 to the CsBr–CH_3CN solution, a small amount of undissolved white solid was removed by filtration under a dry N_2 atmosphere. The clear, yellow filtrate was pumped to dryness at ambient temperature. The resulting yellow solid was identified as $CsBrCl_2$ by its strong Raman band at 294 cm^{-1}.[10] The synthesis of $ClONO_2$ has previously been described.[11]

Apparatus. Volatile materials used in this work were handled in a well-passivated (with BrF_5 until it was recovered as a white solid at −196 °C or with $ClONO_2$ when no fluoride coatings were desired) stainless steel Teflon FEP vacuum line.[12] Nonvolatile materials were handled under the dry nitrogen atmosphere of a glovebox.

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer. Spectra of solids were obtained by using dry powders pressed between AgCl or AgBr windows in an Econo press (Barnes Engineering Co.). Spectra of gases were obtained by using a Teflon cell of 5-cm path length equipped with AgCl windows. The low-temperature infrared spectra of solid and matrix-isolated materials were obtained with an Air Products Model DE202S helium refrigerator equipped with CsI windows. For the matrix isolation spectra of $BrONO_2$, the N_2 or Ne matrix gas was swept through a Teflon FEP U-tube containing $BrONO_2$ at −31 °C.

Raman spectra were recorded on either a Cary Model 83 or a Spex Model 1403 spectrophotometer using the 488-nm exciting line of an Ar ion laser or the 647.1-nm exciting line of a Kr ion laser, respectively. Sealed glass tubes were used as sample containers in the transverse-viewing–transverse-excitation mode. A previously described[13] device was used for recording the low-temperature spectra.

Preparation of $BrONO_2$. Since the reaction of BrCl with $ClONO_2$ gives only low yields of $BrONO_2$,[2,4,6] the reaction of Br_2 with $ClONO_2$ was used for its synthesis.[6,8] In a typical experiment, dry Br_2 (10.43 mmol) and $ClONO_2$ (31.82 mmol) were successively condensed into a prepassivated (with $ClONO_2$) 75-mL stainless steel cylinder. The cylinder was warmed from −196 to +25 °C and was kept at this temperature for 1.5 h with frequent agitation. It was then cooled to −196 °C and contained no noncondensible material (no O_2 evolution). The cylinder was allowed to slowly warm to 25 °C while the volatile material was separated by fractional condensation under an oil pump vacuum through a series of traps kept at −31 °C (bromobenzene slush), −45 °C (chlorobenzene slush), and −196 °C. The trap at −45 °C contained 3.90 mmol of a yellow solid, which was identified by its vibrational spectra as $BrONO_2$ (18.6% yield based on Br_2). The −196 °C trap contained the Cl_2 byproduct and the unreacted Br_2 and $ClONO_2$.

When the reaction between Br_2 and $ClONO_2$ is carried out for prolonged time periods at room temperature, the main product becomes $NO_2^+[Br(ONO_2)_2]^-$.[6] Separation of $BrONO_2$ from $NO_2^+[Br(ONO_2)_2]^-$ can be achieved by pumping on a mixture of the two kept at −35 °C. $NO_2^+[Br(ONO_2)_2]^-$ is less volatile and remains as a white or very pale yellow residue, whereas $BrONO_2$ can be collected as a yellow sublimate.

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Preparation of $Cs^+[Br(ONO_2)_2]^-$. A prepassivated (with $ClONO_2$) 30-mL stainless steel cylinder was loaded in the drybox with $CsBrCl_2$ (2.432 mmol). On the vacuum line, $ClONO_2$ (19.68 mmol) was added at −196 °C. The cylinder was allowed to warm to 0 °C and was kept at this temperature for 4 h with occasional agitation. The cylinder was cooled to −196 °C and contained no noncondensible gas. The material volatile at 0 °C was pumped off and separated by fractional condensation through traps kept at −112 and −196 °C during warmup of the cylinder from −196 to 0 °C. The −196 °C trap contained Cl_2 (4.51 mmol), whereas the −112 °C trap had unreacted $ClONO_2$ (14.78 mmol). The cylinder contained 743 mg of a white solid, which on the basis of its vibrational spectra was $Cs^+[Br(ONO_2)_2]^-$ containing a small amount of $CsNO_3$. The latter was formed by slow decomposition of $Cs^+[Br(ONO_2)_2]^-$ at ambient temperature, which was shown to yield $CsNO_3$ and $BrONO_2$ as the primary products, followed by decomposition of $BrONO_2$ to Br_2, N_2O_5, NO_2, and O_2. Attempts to prepare $Cs^+[Br(ONO_2)_2]^-$ directly with CsBr and $ClONO_2$ at 0 °C were unsuccessful and produced only a product consisting of $CsNO_3$ and an unidentified cesium polyhalide, which was also obtained from the reaction of CsBr with Cl_2 in aqueous solution. Its solid-phase Raman spectrum showed bands at 340 vw, 230 sh, 215 s, 203 vs, 142 m, 126 w, 108 w, 80 m, and 62 mw cm^{-1} and resembled that of $CsIBr_2$,[14,15] except for significant shifts to higher frequencies.

The $LiNO_3$–BrF_5 System. A prepassivated (with BrF_5) 30-mL stainless steel cylinder was loaded in the drybox with $LiNO_3$ (20.065 mmol). On the vacuum line, BrF_5 (2.485 mmol) was added at −196 °C. The cylinder was kept at 0 °C for 3.5 days and then cooled to −196 °C. The material volatile at −196 °C consisted of O_2 (2.481 mmol). The cylinder was allowed to slowly warm to 25 °C while the volatile material was separated under a dynamic vacuum by fractional condensation through two traps kept at −142 and −196 °C. The −196 °C trap contained a trace of FNO_2, whereas the −142 °C trap had 894 mg of a white solid consisting of an equimolar mixture of $NO_2^+[Br(ONO_2)_2]^-$ and N_2O_5 (weight calculated for 2.485 mmol of $NO_2^+[Br(ONO_2)_2]^-$ and 2.485 mmol of N_2O_5, 889 mg). The white solid residue (851 mg) in the cylinder consisted of LiF and $LiNO_3$ (weight calculated for 12.423 mmol of LiF and 7.643 mmol of $LiNO_3$, 849 mg). Separation of $NO_2^+[Br(ONO_2)_2]^-$ from N_2O_5 was achieved by fractional condensation. $NO_2^+[Br(ONO_2)_2]^-$ was trapped at −35 °C whereas N_2O_5 slowly passed. Vibrational spectroscopy was used for the identification of the materials.

When the ratio of $LiNO_3$ to BrF_5 was less than 5, the formation of some free FNO_2 was observed together with a decreased yield of N_2O_5.

Results and Discussion

In this section, we will first present our results on the syntheses and characterizations of $BrONO_2$, $Cs^+[Br(ONO_2)_2]^-$, and $NO_2^+[Br(ONO_2)_2]^-$, followed by a critical review of the presently known bromine nitrate chemistry based on our data and the unpublished dissertations of Schuster,[6] Holthausen,[7] and Stosz.[8]

Syntheses. When BrF_5 is reacted with a threefold amount of $LiNO_3$, the main products are $BrONO_2$ and FNO_2 (eq 6). At a mole ratio of $LiNO_3$ to BrF_5 above 5, $BrONO_2$ and N_2O_5 (or their adduct, depending on the temperature) become the main products (eq 7). Subtraction of eq 6 from eq 7 implies reaction 8, which was experimentally verified and will be reported on separately.[16]

$$3LiNO_3 + BrF_5 \rightarrow 3LiF + BrONO_2 + 2FNO_2 + O_2 \quad (6)$$

$$5LiNO_3 + BrF_5 \rightarrow 5LiF + BrONO_2 + 2N_2O_5 + O_2 \quad (7)$$

$$2LiNO_3 + 2FNO_2 \rightarrow 2LiF + N_2O_5 \quad (8)$$

Furthermore, it was found that, in agreement with Schuster[6] and Holthausen,[7] $BrONO_2$ forms with N_2O_5 the 1:1 adduct $BrONO_2{\cdot}N_2O_5$ (eq 1), which has, as shown below, the ionic structure $NO_2^+[Br(ONO_2)_2]^-$. Since our vibrational spectra for $NO_2^+[Br(ONO_2)_2]^-$ (see below) were almost identical with those attributed by Stosz[8] to "$Br(NO_3)_3$", additional synthetic work was carried out to resolve some of the previously reported discrepancies. For example, $BrONO_2$ was prepared by Schuster's method[6] (eq 9) and was characterized. For the unambiguous identification of the $[Br(ONO_2)_2]^-$ anion, the $Cs^+[Br(ONO_2)_2]^-$ salt was prepared according to eq 10 and characterized.

$$Br_2 + 2ClONO_2 \rightarrow 2BrONO_2 + Cl_2 \quad (9)$$

$$CsBrCl_2 + 2ClONO_2 \rightarrow Cs^+[Br(ONO_2)_2]^- + 2Cl_2 \quad (10)$$

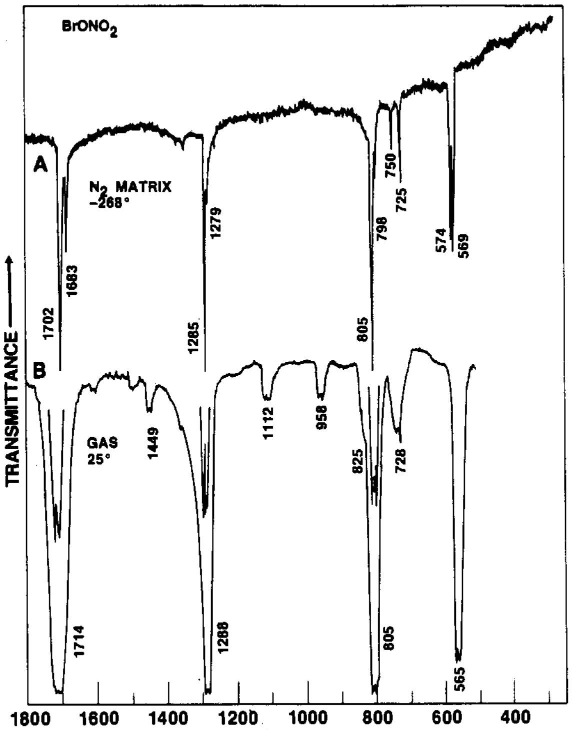

Figure 1. Infrared spectra of $BrONO_2$: (A) N_2 matrix (M_r = 300) isolated sample at 5 K; (B) sample of the gas at 120 and 10 mm pressure in a 5 cm path length cell.

Characterization of $BrONO_2$. Physical Properties. $BrONO_2$ is the best characterized bromine nitrate. It is a yellow solid with a melting point of −28 °C. This value agrees well with that reported by Stosz[8] but is significantly higher than those of −42 and −33 °C reported previously.[2,4] These low values were probably due to the presence of some impurities. It has a vapor pressure of 114 mm at 23 °C and slowly decomposes at ambient temperature to Br_2, N_2O_5, NO_2, and O_2.

Vibrational Spectra and Structure. Only limited data were previously available on the vibrational spectra and structure of $BrONO_2$. A partial infrared spectrum of the gas had been published,[4] and one of the dissertations contained a Raman spectrum of the solid[8] whose frequencies deviated significantly from the gas-phase values. No conclusions were reached whether the bromine atom is coplanar with or perpendicular to the O_2NO plane. For the closely related $ClONO_2$ molecule, the question concerning its planarity was hotly disputed[17-25] and finally settled in favor of a planar structure.[26-32] In view of the scarcity of data

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Table I. Vibrational Spectra of Gaseous, Matrix-Isolated, and Solid $BrONO_2$

obsd freq, cm^{-1} (rel intens)					
infrared				Raman	assignt in
gas	N_2 matrix	Ne matrix	solid	solid	point group C_s
3406 (vvw)					$2\nu_1$
2982 (vw)					$\nu_1 + \nu_2$
2565 (vvw)					$2\nu_2$
2273 (vvw)					$\nu_1 + \nu_5$
1719 1709 (vs)	1702 (vs)	1709 (vs)	1616 (vs)	1622 (10)	ν_1
	1683 (m)				$\nu_2 + \nu_6$
1610 (vvw)					$2\nu_3$
1449 (vw)			1468 (vw)	1468 (1)	$2\nu_8$
				1460 (0+)	$\nu_3 + \nu_5$
				1397 (0+)	$\nu_4 + \nu_5$
				1307 (0+)	
				1260 sh	$2\nu_5$ (solid)
1292 1288 (vs, PQR) 1281	1285 (vs) 1279 (w) [a]	1285 (vs)	1265 (vs)	1251 (29)	ν_2
1112 (vw)					$2\nu_5$ (gas)
958 (vw)					$\nu_5 + \nu_6$
825 (sh)					$\nu_5 + \nu_7$
810 806 (vs, PQR) 799	805 (vs) 798 (w) [a]	802 (vs)	839 (vs)	830 (2)	ν_3
	750 (w)	750 (w)	765 (vvw)	761 (18)	ν_4
738 728 (w)	725 (mw)	723 (vw)	735 (m)	738 (1)	ν_8
569 559 (s)	574 (s) 569 (s) [a]	563 (s)	642 (s) 637 (sh)	639 sh 635 (5)	ν_5
				413 (2)	
			400 (s)	397 (100)	ν_6
			365 (sh)	368 (2)	$\nu_7 + 122$
			245 (w)	244 (40)	ν_7
				198 (0+)	
				145 (2)	
				122 (5)	
				106 (10)	
				91 (12)	
				60 (20)	
				49 (9)	
				41 (38)	
				30 (0+)	

[a] The splittings observed for these three bands are attributed to matrix effects. In the neon matrix, for example, only a single band was observed for ν_5.

for $BrONO_2$, we have recorded its infrared spectra in the gas phase and in N_2 (see Figure 1) and Ne matrices, and the infrared and Raman spectra of the neat solid (see Figure 2). The observed frequencies are summarized in Table I.

Vibrational Assignments. A comparison of the fundamental vibrations of $BrONO_2$ with those of the closely related molecules $ClONO_2$,[17-22,27,28,30] $FONO_2$,[19-21] CH_3ONO_2,[33] and $HONO_2$[34] shows excellent agreement with respect to both frequencies and relative infrared and Raman intensities (see Table II). Since the planarity of $ClONO_2$,[26-32] CH_3ONO_2,[35] and $HONO_2$[36] is well-established, the data of Table II strongly support a planar structure for $BrONO_2$ as well.

The assignments of the observed fundamental vibrations to the individual modes are straightforward. A planar $BrONO_2$ molecule has the symmetry C_s. The irreducible representation for the intramolecular vibrations is $\Gamma = 7\,A' + 2\,A''$. The intense 1714-, 1288-, 806-, and 564-cm^{-1} infrared gas-phase bands are characteristic for all covalent nitrates and are due to the antisymmetric NO_2 stretching, the symmetric NO_2 stretching, the NO_2 scissoring, and the ONO_2 antisymmetric in-plane deformation vibrations, respectively.[21]

The N–O stretching mode has very high Raman intensities in all the covalent nitrates listed in Table II and occurs in $FONO_2$ and $ClONO_2$ at 457 and 436 cm^{-1}, respectively.[21] Therefore, this mode is assigned to the very intense Raman band at 397 cm^{-1} in solid $BrONO_2$.

A cursory inspection of Table II might raise questions of why the N–O stretching modes should be of such high Raman intensities, exhibit negligible ^{14}N–^{15}N isotopic shifts, and have surprisingly low frequencies. A comparison with the well-known and -analyzed vibrational spectra of FNO_2 provides the answer to these questions. The FNO_2 molecule is a good approximation to the ONO_2 part of the $XONO_2$ compounds but due to its higher symmetry and lower number of fundamental vibrations is much more amenable to a thorough normal-coordinate analysis. Thus, the A_1 block of FNO_2 contains only three fundamental vibrations at about 1308, 810, and 555 cm^{-1}, which are best assigned to the symmetric NO_2 stretching, the NO_2 scissoring, and the NF stretching modes, respectively.[21,37-39] The observed frequencies, intensities, and ^{14}N–^{15}N isotopic shifts are similar to those of the corresponding ONO_2 modes in $XONO_2$. The potential energy

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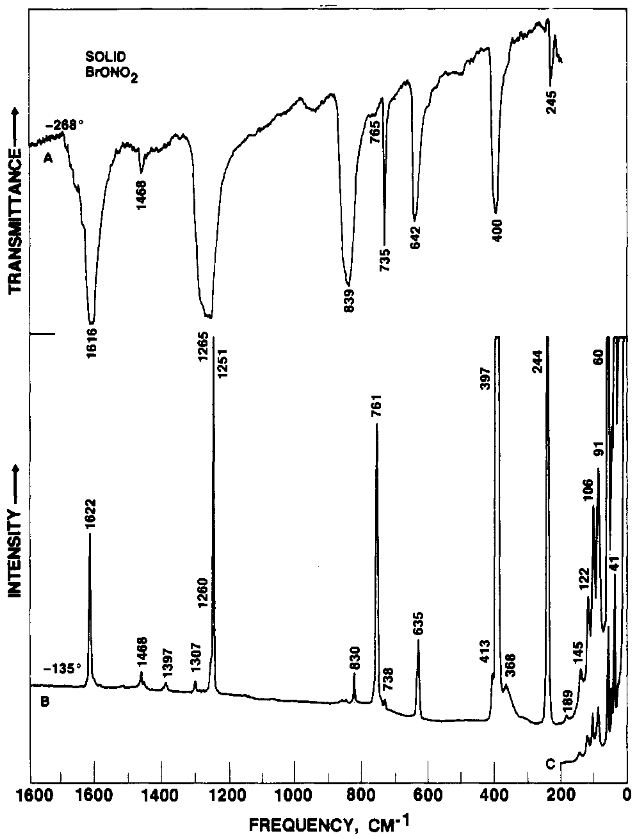


Figure 2. Vibrational spectra of solid $BrONO_2$: (A) infrared spectrum of the neat solid on a CsI window at 5 K; (B, C) Raman spectra of the neat solid in a glass tube at −135 °C, recorded at two different sensitivity settings.

distribution (set I in Table VII of Mirri et al.)[38] shows that the highest frequency is almost pure NO_2 stretching and the intermediate frequency is mainly an antisymmetric combination of the NO_2 scissoring motion and the NF stretching motion with some contribution from NO_2 stretching, while the lowest frequency is best described as a symmetric combination of NF stretching and some NO_2 stretching. These results account nicely for the experimental observations and should be directly transferable to the $XONO_2$ molecules of this study. A normal-coordinate analysis for $BrONO_2$, however, would be of little value in view of the grossly underdetermined nature of the problem (28 symmetry force constants from 7 frequencies in the A′ block) and the expected strong coupling effects.

It should be noted that in the infrared spectrum of solid $BrONO_2$ the N–O stretching mode becomes quite intense (see the 400-cm^{-1} band in trace A of Figure 2). This increase in intensity for the neat solid is attributed to pronounced association effects (see below).

The N–O–Br in-plane bending mode should result in an intense Raman band between 300 and 200 cm^{-1} and therefore can readily be assigned to the strong Raman band at 244 cm^{-1}. The N–OBr torsional mode should occur below 140 cm^{-1} and cannot be assigned with confidence on the basis of the available data.

The only two fundamental vibrations yet unaccounted for are the ONO_2 out-of-plane deformation and the O–Br stretching modes. The O–Br stretching mode should be of high Raman and low infrared intensity, whereas the $\delta(ONO_2)$ out-of-plane mode should be of medium IR and low Raman intensity and occur in the 700–770-cm^{-1} region. On the basis of these predictions, the intense Raman band at 761 cm^{-1} with a weak matrix infrared counterpart at 750 cm^{-1} is assigned to ν(O–Br) and the medium-strong matrix infrared band at 725 cm^{-1} with a very weak Raman counterpart at 738 cm^{-1} to the δ out-of-plane ONO_2 mode. This accounts for all the nine fundamental vibrations of $BrONO_2$ and provides consistent frequency and intensity trends for the series $HONO_2$, CH_3ONO_2, $FONO_2$, $ClONO_2$, and $BrONO_2$ (see Table

Table II. Fundamental Vibrations of Covalent Nitrates

obsd freq, cm^{-1} (rel intens)													
$HONO_2$[a]			CH_3ONO_2[d]		$FONO_2$[e]		$ClONO_2$[e]		$BrONO_2$[f]				assignts in point group C_s and approx descripn of mode
IR		Ra	IR	Ra	IR	Ra	IR	Ra	IR			Ra	
gas	solid	liquid	gas	liquid	gas	liquid	gas	liquid	gas	matrix	solid	solid	
[36.2][b] 1708 (vs)	1646 (vs)	1675 (w) dp	1669 (vs)	1634 (w) dp	[39] 1759 (vs)	1760 (3) dp	[41] 1735 (vs)	1728 (4) dp	1714 (vs)	1702 (vs)	1616 (vs)	1622 (10)	A′ ν_1 $\nu_{as}(NO_2)$
[4.3] 1325 (vs)	1256 (vs)	1303 (vs) p	1287 (s)	1283 (s) p	[10] 1301 (vs)	1302 (59) p	[12] 1292 (vs)	1290 (30) p	1288 (vs)	1285 (vs)	1265 (vs)	1251 (29)	ν_2 $\nu_s(NO_2)$
[7.8] 879 (s)	958 (s)	926 (s) p	854 (s)	860 (s) p	[12] 804 (s)	800 (17) p	[7] 780 (ms)[g]	779 (6) p	806 (vs)	805 (vs)	839 (vs)	830 (2)	ν_3 $\delta_{sciss}(NO_2)$
[0] 3550 (m)	3106 (m)	3410 (w) p	1017 (s)	993 (w) p	[0] 928 (m)	929 (67) p	[6] 809 (s)[g]	810 (49) p		750 (w)	765 (vvw)	761 (18)	ν_4 $\nu(OX)$
[1] 579 (w)	707 (s)	612 (m) dp	657 (m)	664 (m) p	[1] 633 (m)	636 (31) dp	[3] 560 (s)	561 (20) dp	564 (s)	572 (s)	642 (s)	635 (5)	ν_5 $\delta_{as}(ONO_2)$ in plane
[0] 647 (w)	722 (s)	677 (s) p	(578)	578 (s) p	[0] 454 (m)	457 (100) p	[2] 434 (m)	436 (100) p	(394)	(398)	400 (s)	397 (100)	ν_6 $\nu(N{-}O)$
[3.7] 1331 (s)	1420 (m)	1395 (w) p	(340)	351 (w) p	[1] 303 (vw)	304 (33) p	270 (vvw)	267 (47) p			245 (w)	244 (40)	ν_7 $\delta(NOX)$ in plane
[18.6] 762 (s)	773 (s)	(771)[c]	759 (m)	(761)	[18] 708 (m)	708 (0.6)	[17] 711 (mw)	710 (1)	728 (mw)	725 (mw)	735 (m)	738 (1)	A″ ν_8 $\delta(ONO_2)$ out of plane
[0] 456 (m)	737 (m)	485 (w)			152 (vvw)	165 (4) dp		140 (2) dp					ν_9 $\tau(N{-}OX)$

[a] Reference 34. [b] Numbers in brackets are $^{14}N-^{15}N$ isotopic shifts. [c] Frequencies in parentheses are calculated from overtones. [d] Reference 33. [e] References 19–21; the previously reported polarization data for ν_8 are questionable due to the extremely low Raman intensities of this mode. [f] This work. [g] On the basis of the observed $^{14}N-^{15}N$ and $^{35}Cl-^{37}Cl$ isotope shifts,[19,31] these two vibrations are strongly mixed.

Table III. Vibrational Spectra of Solid $Cs^+[Br(ONO_2)_2]^-$ and $NO_2^+[Br(ONO_2)_2]^-$

obsd freq, cm^{-1} (rel intens)				
$Cs^+[Br(ONO_2)_2]^-$		$NO_2^+[Br(ONO_2)_2]^-$		assignts for NO_2^+ and $[Br(ONO_2)_2]^-$
Ra	IR	Ra	IR	
			2370 (m)	$\nu_{as}(NO_2^+)$
		1569 (1)		
1530 (12)	1520 (vs)	1529 (26)	1530 (vs)	$\nu_{as}(NO_2)$ out of phase
		1493 (1)		
		1395 (35)		$\nu_s(NO_2^+)$
		1308 (2)		
1283 (14)	1285 (vs)	1283 (21)	1265 (vs)	$\nu_s(NO_2)$ in phase
		1130 (2)		
		1118 (3)		$\nu_{as}(NO_2)$ in phase
		1103 (5)		
975 (4)		982 (4)		
960 sh	955 (s)	964 (14)	965 sh	$\nu_s(NO_2)$ out of phase
	935 (vs)		930 (vs)	
791 (2)	786 (s)	787 (1)	782 (s)	$\delta_{sciss}(NO_2)$
732 (63)	735 (s)	747 (100)	750 (s)	$\delta_{as}(ONO_2)$ in plane
697 (1)	699 (s)	700 (4)	706 (s)	$\delta(ONO_2)$ out of plane
			566 (ms)	
			551 (ms)	$\delta(NO_2^+)$
460 (0+, br)		480 (0+, br)		ν_{as}(O–N)
400 (0+, br)		400 (2, br)		$\nu_{as}(BrO_2)$
317 (71)		315 (63)		ν_s(O–N)
298 (35)				$\nu_s(BrO_2)$
230 (10)				
		175 (33)		
157 (47)		162 (32)		
128 sh		126 (21)		
110 (64)		105 (100)		
87 (100)		93 (5)		
		80 (57)		
53 sh				

II). Essentially all of the observed weak bands can be assigned in terms of overtones and combination bands of these fundamental vibrations (see Table I).

Association in the Solid Phase. As mentioned above, some of the fundamental vibrations in solid $BrONO_2$ significantly deviate from those of the gas and the matrix-isolated molecule. From the fundamental vibrations involved and the magnitudes and directions of the shifts, conclusions can be drawn concerning the nature of the association. The involvement of the NO_2 group in the bridging is indicated by a lowering of its stretching frequencies ($\Delta\nu_{as} = -98$ cm^{-1}, $\Delta\nu_s = -23$ cm^{-1}) and an increase of its in-plane deformation frequencies ($\Delta\delta_{as} = 77$ cm^{-1}, $\Delta\delta_s = 34$ cm^{-1}). The fact that the δ out-of-plane ONO_2 frequency is essentially unshifted suggests that the bridging occurs in the ONO_2 plane and does not directly involve the nitrogen atom. Hence, the NO_2 group should bridge to either the bromine or the oxygen atom of the O–Br group of another $BrONO_2$ molecule. Of these two alternatives, bromine definitely is the better acceptor as shown by the existence of the $[Br(ONO_2)_2]^-$ anion. Since in this anion the nitrate ligands are monodentate, we prefer for solid $BrONO_2$ a model involving intermolecular $BrON(O)O \rightarrow BrONO_2$ bridges that are also monodentate.

Characterization of $Cs^+[Br(ONO_2)_2]^-$ and $NO_2^+[Br(ONO_2)_2]^-$. Physical Properties. $Cs^+[Br(ONO_2)_2]^-$ is a white crystallinic solid. It is only marginally stable at room temperature and dissociates to $CsNO_3$ and $BrONO_2$ with the latter decomposing further to Br_2, N_2O_5, NO_2, and O_2. Therefore, it is difficult to obtain samples that are completely free of $CsNO_3$.

$NO_2^+[Br(ONO_2)_2]^-$ is a white crystallinic solid that can be purified by vacuum sublimation. It is stable at −35 °C and can be trapped at this temperature. At 23 °C it has a dissociation pressure of about 130 Torr and decomposes to $BrONO_2$ and N_2O_5, which can then undergo further slow decomposition to $Br_2 + N_2O_5 + O_2$ and $N_2O_4 + O_2$, respectively. It melts at about 46 °C with decomposition.

Vibrational Spectra. The vibrational spectra of $Cs^+[Br(ONO_2)_2]^-$ and $NO_2^+[Br(ONO_2)_2]^-$ are shown in Figures 3 and 4, respectively. The observed frequencies and their assignments are summarized in Table III. A cursory inspection of Figures 3 and 4 reveals that the main features in the spectra of both materials are very similar, except for three extra bands in $NO_2^+[Br(ONO_2)_2]^-$. These extra bands occur at 1395 cm^{-1} in

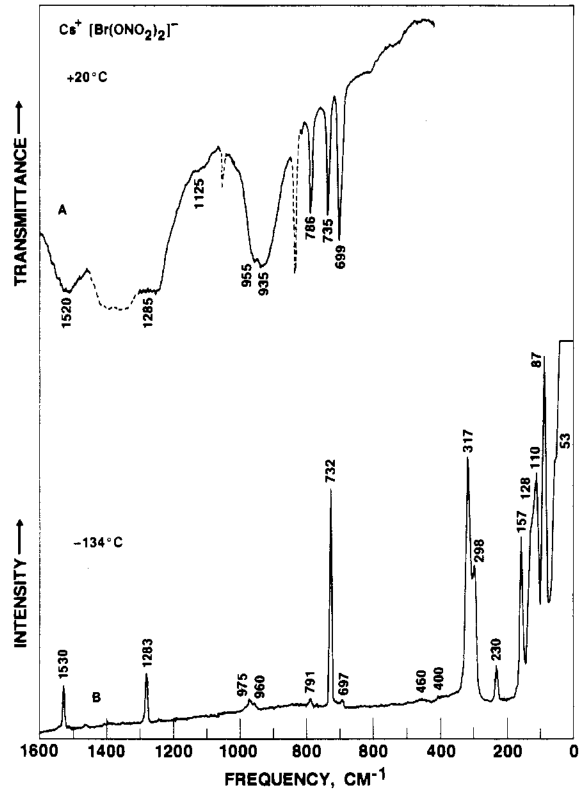


Figure 3. Vibrational spectra of solid $Cs^+[Br(ONO_2)_2]^-$: (A) infrared spectrum of the solid as an AgCl disk at 20 °C (absorptions shown with a broken line are due to $CsNO_3$ formed by slow decomposition of the compound at this temperature); (B) Raman spectrum of the solid at −134 °C.

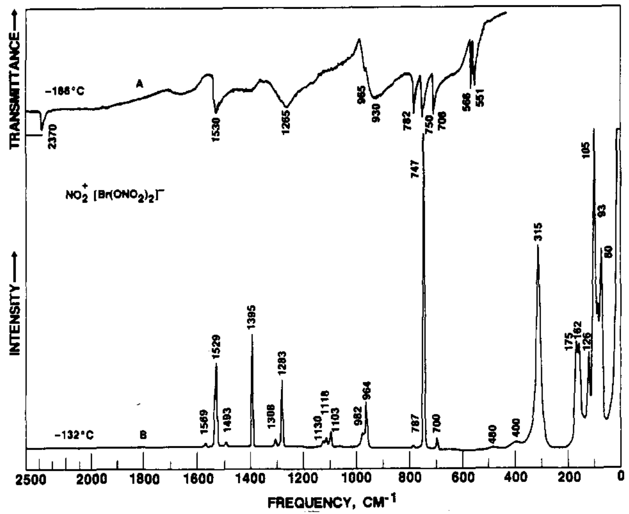


Figure 4. Vibrational spectra of solid $NO_2^+[Br(ONO_2)_2]^-$: (A) infrared spectrum of the solid at −186 °C between CsI windows; (B) Raman spectrum of the solid at −132 °C.

Table IV. Summary of the 21 Fundamental Vibrations Expected for $[Br(ONO_2)_2]^-$ in Point Group C_2

NOBrON Skeletal Modes
$\nu_{as}(BrO_2)$ (B)
$\nu_s(BrO_2)$ (A)
ν(O–N) in phase (A)
ν(O–N) out of phase (B)
δ(BrON) in plane, in phase (A)
δ(BrON) in plane, out of phase (B)
δ(OBrO) out of plane (B)
τ(Br–O) in phase (A)
τ(Br–O) out of phase (B)
NO_2 Modes
$\nu_{as}(NO_2)$ in phase (A)
$\nu_{as}(NO_2)$ out of phase (B)
$\nu_s(NO_2)$ in phase (A)
$\nu_s(NO_2)$ out of phase (B)
$\delta_{sciss}(NO_2)$ in phase (A)
$\delta_{sciss}(NO_2)$ out of phase (B)
$\delta(ONO_2)$ out of plane, in phase (A)
$\delta(ONO_2)$ out of plane, out of phase (B)
$\delta_{as}(ONO_2)$ in plane, in phase (A)
$\delta_{as}(ONO_2)$ in plane, out of phase (B)
τ(O–N) in phase (A)
τ(O–N) out of phase (B)

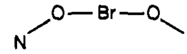
the Raman and at 2370 and 566–551 cm^{-1} in the infrared spectra. These bands are characteristic for the NO_2^+ cation[40,41] and establish the ionic structure $NO_2^+[Br(ONO_2)_2]^-$ for this $BrONO_2 \cdot N_2O_5$ adduct.

The first question that must be answered with respect to the $[Br(ONO_2)_2]^-$ anion is the nature of the nitrato groups. These groups could be either ionic or covalent. From the complexity of the observed spectra and the absence of bands characteristic for a free NO_3^- anion,[40] it can be concluded that the nitrato groups must be covalent.

A covalent nitrato ligand could be either mono- or bidentate. On the basis of previous thorough vibrational analyses,[42,43] covalent bidentate nitrato ligands should exhibit in the 900–1700-cm^{-1} range three groups of Raman bands at about 1600 (ν(N=O)), 1200 ($\nu_{as}(NO_2)$), and 1000 cm^{-1} ($\nu_s(NO_2)$) with their intensities decreasing in the order $I_{1600} > I_{1000} > I_{1200}$. On the other hand, covalent monodentate nitrato groups should exhibit two bands in the 900–1700-cm^{-1} frequency range at about 1700 ($\nu_{as}(NO_2)$) and 1300 cm^{-1} ($\nu_s(NO_2)$) with the 1300-cm^{-1} band being more intense in the Raman spectrum.[17-22] For molecules containing more than one nitrato ligand, coupling of the vibrations of these ligands is expected, which should result in splittings due to in-phase and out-of-phase motions. Furthermore, the formal negative charge in the ion is predicted to increase the polarity of the nitrogen–oxygen bands, thereby lowering their frequencies somewhat. Inspection of Figures 3 and 4 shows that the observed spectra are in accord with these predictions for strongly coupled monodentate ligands and therefore will be assigned in this manner.

The next question is as follows: how are the two nitrato ligands in $[Br(ONO_2)_2]^-$ most likely arranged with respect to each other? If the $-ONO_2$ group is treated as a pseudohalide, the O–Br–O part of $[Br(ONO_2)_2]^-$ is expected to be, for practical purposes, linear. Since the N–O–Br angle should be close to tetrahedral (109°), the two nitrato ligands could be either cis or trans to each other or form a dihedral angle. If the nitrato ligands were trans to each other, the $[Br(ONO_2)_2]^-$ anion would possess a symmetry center and the infrared and Raman bands should either be mutually exclusive or at least differ dramatically in intensity. Since this is not the case, a trans configuration can be ruled out. Since mutual repulsion arguments mitigate against a cis isomer, we prefer a configuration with a dihedral angle. Such an anion would possess the symmetry C_2, with the twofold rotation axis passing through the Br atom at a right angle to the O–Br–O axis and splitting the dihedral angle in half.

The irreducible representation for the intramolecular vibrations of $[Br(ONO_2)_2]^-$ of symmetry C_2 is $\Gamma = 10\ A + 11\ B$, where the A modes are symmetric and the B modes antisymmetric to the twofold axis. Of these 21 modes, 9 belong to the



skeleton and 12 involve motions of the nitrato ligands. A breakdown into the individual modes is given in Table IV. Since the unit cells of these $[Br(ONO_2)_2]^-$ salts might contain more than one molecule, additional splittings might be observed in the actual spectra due to ion coupling and anion–cation interactions. Tentative assignments for some of the fundamental vibrations of $[Br(ONO_2)_2]^-$ can be made on the following basis. The four groups of bands between 900 and 1600 cm^{-1} should represent the four NO_2 stretching modes. Of these, the symmetric, in-phase NO_2 stretch should be very strong in both the Raman and the infrared spectra and therefore must be assigned to either the 1280- or the 1530-cm^{-1} group. Since in $BrONO_2$ (see above) the symmetric NO_2 stretch is about 370 cm^{-1} lower than the antisymmetric one, the 1280-cm^{-1} group in the spectra of $[Br(ONO_2)_2]^-$ is assigned to the symmetric, in-phase NO_2 stretch. This leaves the 1530-cm^{-1} group for assignments to one of the two antisymmetric NO_2 stretches. From these two, the out-of-phase mode should be of much higher infrared intensity than the in-phase mode and therefore the 1530-cm^{-1} group is assigned to the antisymmetric, out-of-phase NO_2 stretch. On the basis of its low infrared intensity, the 1100-cm^{-1} group is assigned to the antisymmetric, in-phase NO_2 stretch, leaving the 950-cm^{-1} group for assignment to the symmetric, out-of-phase NO_2 stretch.

Two comments are required with respect to these NO_2 stretching bands: (i) For $NO_2^+[Br(ONO_2)_2]^-$ the Raman bands show additional splittings into three components for the antisymmetric and two components for the symmetric modes and also their frequencies significantly deviate in most cases from those of their infrared counterparts. This is attributed to the influence of the NO_2^+ counterion, which is less symmetrical than Cs^+, thus causing stronger cation–anion interactions in the solid. (ii) For $Cs^+[Br(ONO_2)_2]^-$ the failure to observe a Raman band around 1130 cm^{-1} might be due to the lower signal to noise ratio in the spectrum.

There is a group of three distinct bands in the 690–790-cm^{-1} region, which are assigned by analogy with the spectra of solid $BrONO_2$ (see above) to the scissoring, the out-of-plane, and the antisymmetric in-plane deformation modes of the NO_2 groups (see Table III). No detectable splittings due to in-phase and out-of-phase coupling were observed for these modes.

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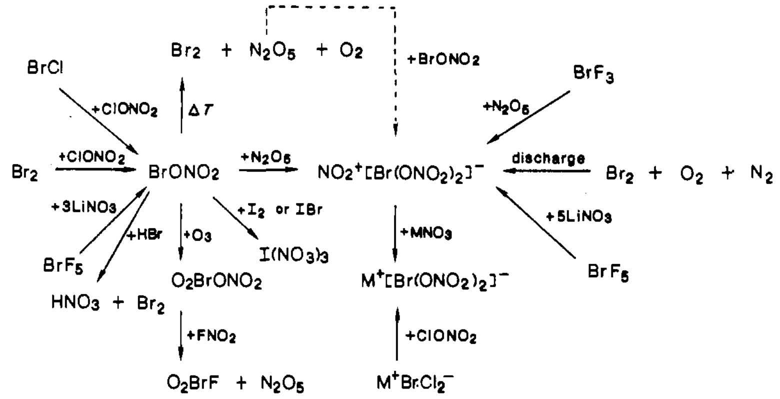
Scheme I. Reaction Chemistry of Bromine Nitrates



The O–N torsional mode is expected to be of low frequency and to occur in the frequency range of the skeletal modes. Therefore, no attempt was made to assign this mode.

The assignments for the NOBrON skeletal modes are more difficult because few data are available for comparable systems. If the nitrato group is treated as a pseudohalide, the known spectra of certain $[Br(Hal)_2]^-$ species will give us an estimate for the frequency range to be expected for the OBrO vibrations. In BrF_2^-, $BrCl_2^-$, and Br_3^- the symmetric stretching vibration has frequencies of 442,[44] 272,[45] and 162 cm^{-1},[45] respectively. Furthermore, the N–O stretching vibration in the halogen nitrates occurs between 390 and 460 cm^{-1} (see Table II). Therefore, it seems reasonable to assume that the NOBrON skeletal modes should occur in similarly low frequency ranges and should not be assignable to the bands observed in the 700–800-cm^{-1} range. On the basis of these comparisons, we tentatively assign the strong Raman bands at 317 and 298 cm^{-1} in $Cs^+[Br(ONO_2)_2]^-$ to the symmetric in-phase N–O stretch and the symmetric BrO_2 stretch, respectively, and the weak Raman bands at about 460 and 400 cm^{-1} to the corresponding antisymmetric stretching motions, respectively. Due to the overlap of the frequency ranges of the skeletal deformation modes and the lattice vibrations, no assignments are proposed at this time for the lower frequency bands.

Critical Review of Bromine Nitrate Chemistry. A combination of our results with those of Taglinger,[2] Schuster,[6] Holthausen,[7] Stosz,[8] and Pflugmacher[9] allows the following conclusions concerning the presently known bromine nitrates: (i) The compound obtained originally from BrF_3 and N_2O_5 and ascribed to "$Br(NO_3)_3$"[2] is actually $NO_2^+[Br(ONO_2)_2]^-$. Stosz[8] repeated the original synthesis[2] and recorded a low-temperature Raman spectrum that is identical with that obtained by us for $NO_2^+[Br(ONO_2)_2]^-$. Furthermore, the physical and chemical properties reported[2,8] for "$Br(NO_3)_3$" are practically identical with those of $NO_2^+[Br(ONO_2)_2]^-$. Schuster had previously shown[6] that Pflugmacher's "$BrO_2{\cdot}3NO_2$"[9] is identical with "$BrNO_3{\cdot}N_2O_5$", which has been shown by this study to be $NO_2^+[Br(ONO_2)_2]^-$. *Therefore, the previously reported compounds "$Br(NO_3)_3$", "$BrO_2{\cdot}3NO_2$", and "$BrNO_3{\cdot}N_2O_5$" are all one and the same compound, i.e. $NO_2^+[Br(ONO_2)_2]^-$.* (ii) On the basis of the fact that "$Br(NO_3)_3$" is actually $NO_2^+[Br(ONO_2)_2]^-$, we have critically reviewed the known reaction chemistry of the bromine nitrates. The most important reactions are presented in Scheme I. The formation of $NO_2^+[Br(ONO_2)_2]^-$ from BrF_3 and N_2O_5 in the original "$Br(NO_3)_3$" preparation[2] can readily be explained in terms of reactions 11–14. Experimental support for this sequence was

$$BrF_3 + N_2O_5 \rightarrow 2FNO_2 + BrFO \qquad (11)$$

$$2BrFO \rightarrow FBrO_2 + BrF \qquad (12)$$

$$BrF + N_2O_5 \rightarrow BrONO_2 + FNO_2 \qquad (13)$$

$$BrONO_2 + N_2O_5 \rightarrow NO_2^+[Br(ONO_2)_2]^- \qquad (14)$$

obtained by Stosz,[8] who demonstrated the formation of $FBrO_2$ as a byproduct in this system. Similarly, $BrONO_2$ does not disproportionate according to (15)[8] but produces $NO_2^+[Br(ONO_2)_2]^-$ according to (16) and (17). The formation of

$$3BrONO_2 \not\rightarrow Br(ONO_2)_3 + Br_2 \qquad (15)$$

$$2BrONO_2 \rightarrow Br_2 + N_2O_5 + {}^1/_2O_2 \qquad (16)$$

$$BrONO_2 + N_2O_5 \rightarrow NO_2^+[Br(ONO_2)_2]^- \qquad (17)$$

$NO_2^+[Br(ONO_2)_2]^-$ from Br_2 and $ClONO_2$ at room temperature and extended reaction times can similarly be explained by (9), followed by (16) and (17), resulting in (18) as the overall reaction.

$$Br_2 + 6ClONO_2 \rightarrow 2NO_2^+[Br(ONO_2)_2]^- + 3Cl_2 + O_2 \qquad (18)$$

If the reaction time of (9) is limited to about 1 h, the thermal decomposition of $BrONO_2$ (eq 16) and $NO_2^+[Br(ONO_2)_2]^-$ formation (eq 17) can be minimized and (9) becomes a useful $BrONO_2$ synthesis.

From a historical point of view it is interesting to note that the original misidentification[2] of "$Br(NO_3)_3$" was not recognized inspite of all the experimental evidence by Schuster, Holthausen, and Stosz. None of them questioned the correctness of the claim for "$Br(NO_3)_3$".

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Registry No. $BrONO_2$, 40423-14-1; Br_2, 7726-95-6; $ClONO_2$, 14545-72-3; $NO_2^+[Br(ONO_2)_2]^-$, 107556-54-7; $CsBrCl_2$, 13871-03-9; $Cs^+[Br(NO_3)_2]^-$, 107574-46-9; $LiNO_3$, 7790-69-4; BrF_5, 7789-30-2; N_2O_5, 10102-03-1.

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