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Infrared Spectra of Ag_2BrNO_3 and Ag_2ClNO_3

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The infrared spectra of Ag_2BrNO_3 and Ag_2ClNO_3 are reported. Vibration assignments are proposed on the basis of the group theoretical analysis and D_{2h} symmetry. Factor group, site and TO–LO splittings are observed. The internal and external mode frequencies are correlated with those of $AgNO_3$ and KNO_3(II).

Introduction

Spectroscopic studies on crystalline $AgNO_3$ (*1*) and KNO_3 (*2*) have contributed to the knowledge of the magnitude of site and correlation field effects on the normal modes of vibration of the NO_3 species in a crystal lattice. $AgNO_3$ possesses the orthorhombic structure at room temperature with space group symmetry *Pbca* (D_{2h}^{15}) in a primitive cell containing 8 molecules with dimensions $a_0 = 6.995$, $b_0 = 7.328$, $c_0 = 10.118$ Å (*3*). The room-temperature stable KNO_3(II) also has the orthorhombic structure with space group *Pnma* (D_{2h}^{16}) containing 4 molecules in its unit cell of dimensions $a_0 = 5.414$, $b_0 = 9.164$, $c_0 = 6.431$ Å (*4*).

Recently, the crystal structures of Ag_2BrNO_3 and Ag_2ClNO_3 were determined to be isomorphous in the orthorhombic system, space group *Pnma* with $Z = 4$ and unit-cell dimensions $a_0 = 6.846$, $b_0 = 5.132$, $c_0 = 12.823$ Å for Ag_2BrNO_3 and $a_0 = 6.656$, $b_0 = 5.111$, $c_0 = 12.488$ Å for Ag_2ClNO_3 (*5*, *6*). The structure of each compound comprises a three-dimensional network of trigonal-bipyramidal Ag_5Cl or Ag_5Br units sharing Ag(2) corners and Ag(1)–Ag(1) edges with the NO_3 group encased in a cavity formed by seven Ag^+ ions (*6*). The Ag–O distances in Ag_2BrNO_3 and Ag_2ClNO_3 are comparatively longer, 2.65–2.91 Å, relative to their distances in $AgNO_3$, 2.48–2.58 Å. The NO_3 group is stated to possess close to perfect D_{3h} symmetry (*5*).

The prospect that the infrared spectra of crystalline Ag_2BrNO_3 and Ag_2ClNO_3 might provide additional information relating effects of possible interactions of NO_3 with the halide ion and cation and allow identification of the external lattice modes of Cl^- and Br^- on the basis of mass effect is the rationale for this study. The spectra are interpreted on the basis of factor group analysis.

Experimental

Ag_2BrNO_3 and Ag_2ClNO_3 crystals were grown according to the method described

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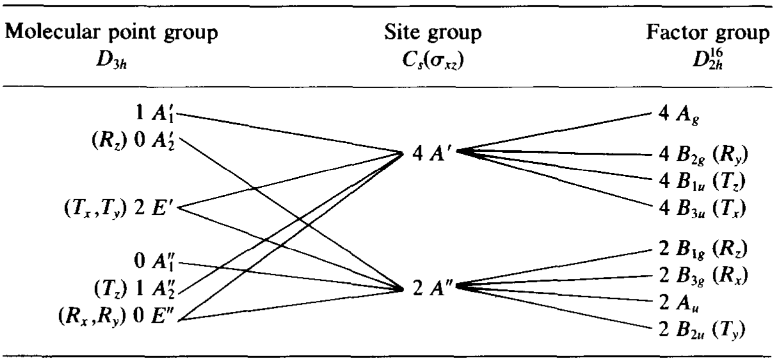
TABLE I

CORRELATION TABLE FOR INTERNAL MODES OF NO_3^- IN Ag_2XNO_3 (X = Br, Cl)



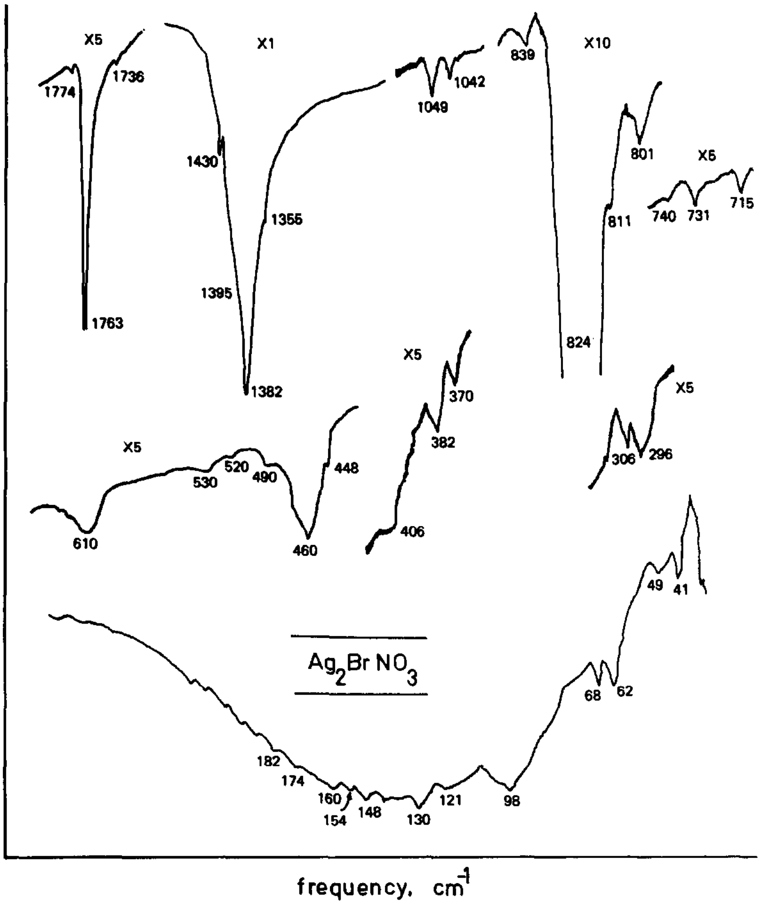


FIG. 1. Infrared spectrum of Ag_2BrNO_3; percentage transmission intensity versus frequency (cm^{-1}) with expansion factors indicated.

earlier (*5*, *6*) using stock reagents of stated purity ≥ 99.9% supplied by Alfa Ventron Corporation and distilled water. The crystal dimensions, <0.1 mm thickness and 0.5 mm length did not permit single-crystal studies.

The infrared transmittance spectra were recorded with a Perkin–Elmer 180 spectrophotometer using the standard KBr disk technique in the region 250–2000 cm^{-1}. Far infrared spectra, region 40–250 cm^{-1}, were obtained on samples in Nujol mull between polyethylene windows. The characteristic peaks of polystyrene film and $K_3[Fe(CN)_6]$ in Nujol mull between polyethylene windows were used for frequency calibration.

Factor Group Analysis

In both Ag_2BrNO_3 and Ag_2ClNO_3 [D_{2h}^{16} – *Pnma*, $Z = 4$], the halogen, silver, and $NO_3(\sigma_{xz})$ species are located in the mirror planes $y = \frac{1}{4}$ and $\frac{3}{4}$. Using standard correlation mapping procedures (*7*) it is found that the internal modes of the NO_3 group consists of $4A'$ and $2A''$ species as illustrated in Table I; therefore, four NO_3 groups will have $16A'$ and $8A''$ internal modes. The ex-

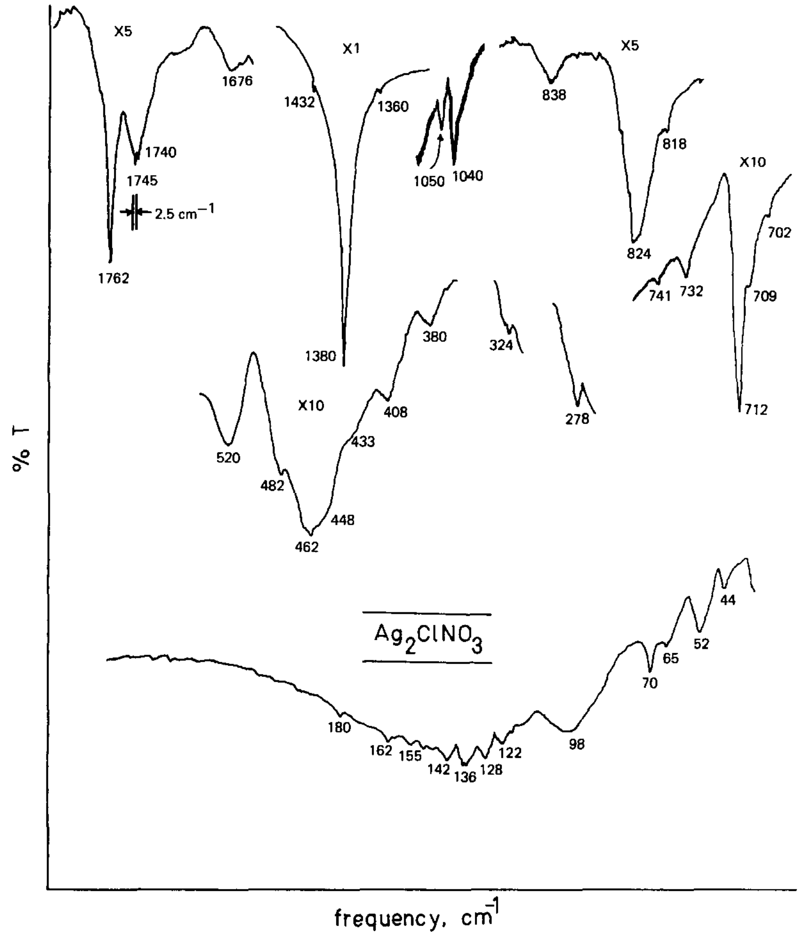


FIG. 2. Infrared spectrum of Ag_2ClNO_3; percentage transmission intensity versus frequency (cm^{-1}) with expansion factors indicated.

ternal modes obtained in a similar manner are subdivided into $4A'$ and $8A''$ for NO_3 rotations along with $8A'$ and $4A''$ for translations of NO_3, Cl, or Br and $16A'$ and $8A''$ for translations of Ag. The total number of modes for Ag_2BrNO_3 and Ag_2ClNO_3 crystals consists of $52A'$ and $32A''$ species, i.e., 84 modes. The complete infrared spectrum is expected, therefore, to exhibit a total of 31 modes, viz. $12B_{1u} + 7B_{2u} + 12B_{3u}$, of which $4B_{1u} + 2B_{2u} + 4B_{3u}$ are NO_3 internal modes.

Results and Discussion

The fundamental vibration frequencies for NO_3^- of D_{3h} symmetry have been reported (*8*) as ~1050(A_1'), 830(A_2''), ~1400(E'), and ~700(E') where the E' and A_2'' modes are infrared active. Since the selection rules are relaxed in the crystal, it is possible to observe all four fundamentals in the infrared spectrum (*8*).

The infrared transmittance spectra recorded for Ag_2BrNO_3 and Ag_2ClNO_3 are given in Figs. 1 and 2, respectively. The fundamental vibrational frequencies of Ag_2BrNO_3 and Ag_2ClNO_3 from the spectra are tabulated along with their assignments in Table II; the external mode frequencies are given in Table III. Also included in Tables II and III for comparison purposes are

TABLE II

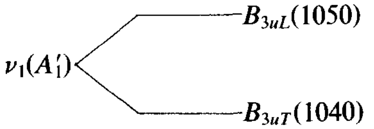
INFRARED INTERNAL MODE FREQUENCIES OF Ag_2BrNO_3 AND Ag_2ClNO_3 (cm^{-1})

Ag_2BrNO_3		Ag_2ClNO_3	$KNO_3(II)$[a]	$AgNO_3$[a]	Assignment
				1848	$\nu_1 + \nu_2$
				1843	
1774				1773	$\nu_1 + \nu_4$
1763		1762			
		1745		1753	
1736		1740			
		1676			$2\nu_2$
1430	B_{3uL}	1432	$(B_{2uL})1441$ $1440(B_{3uL})$		ν_3
1395(?)	B_{3uT}				
1382	B_{2uL}	1380	$(B_{2uT})1376$ $1375(B_{3uT})$	1382	
1355	B_{2uT}	1360			
				1328	
				1313	
				1067	ν_1
1049	B_{3uL}	1050	1052		
1042	B_{3uT}	1040		1043	
				1015	
				948	
				930	
839	B_{1uL}	838			ν_2
824	B_{1uT}	824	823		
811	B_{3uL}	818	820		
				804	
801	B_{3uT}			801	
740	B_{1uL}	741		732	ν_4
731	B_{2uL}	732		729	
715	B_{2uT}	712	716	715	
710	B_{1uT}	709		711	
		702			

[a] Literature values (Refs. (*1*, *2*)).

the literature values for $AgNO_3$ and KNO_3(II).

The four fundamental vibration modes for NO_3^- are observed in Ag_2BrNO_3 and Ag_2ClNO_3. The splitting of the $\nu_1(A_1')$ and $\nu_2(A_2'')$ modes and the extra components in addition to the predicted factor group splitting of the $\nu_3(E')$ and $\nu_4(E')$ modes are attributed to the separation of the transverse (T) and longitudinal (L) optic modes as typified in the scheme below.



The tentative transverse and longitudinal assignments are made in accordance with parallel assignments for KNO_3(II) (*2*) which are based on dipolar coupling factors for vibrational multiplet of internal optic modes in crystals (*9, 10*).

Akiyama *et al.* (*2*) have carried out a lattice dynamics analysis of KNO_3(II) crystals. They calculated the optically active vibrational frequencies using a slightly modified method developed by Shimanouchi *et al.* (*11*). Their calculations, based on a rigid ion model of NO_3^- did not correlate with the large TO–LO splittings observed for the B_{2u} and B_{3u} modes. The disparity between the observed and calculated values was attributed to the inadequacy of the rigid ion model as pointed out earlier by Yamamoto *et al.* (*12, 13*). The number of large TO–LO splittings reported in Table II for Ag_2BrNO_3 and Ag_2ClNO_3 is in strong contrast to the KNO_3(II) and $AgNO_3$ data. These results emphasize the fact that lattice dynamics analysis relating to optically active vibrational frequency calculations is not fully developed.

TABLE III

INFRARED EXTERNAL MODE FREQUENCIES OF Ag_2BrNO_3 AND Ag_2ClNO_3 (cm^{-1})

Ag_2BrNO_3		Ag_2ClNO_3	KNO_3(II)[a]	$AgNO_3$[a]
610				
530				
520		520		
490		482		
460		462		
448		448		
		433		
406		408		
382		380		
370				
		324		
306				195(B_{2g})
296		278	189(B_{3u})	191(B_{1g} + B_{3g})
182	B_{2u}	180	186(B_{2u})	
174	B_{3u}			175(B_{2g})
			166(B_{1u})	169(A_g)
160	B_{1u}	162	160(A_g)	
154	B_{2u}	155	150(B_{1g})	
148	B_{2u}	142	145(B_{2u})	146(B_{1g} + B_{2g})
		136	135(B_{1g})	136(A_{1g} + B_{1g}
			134(B_{3u})	+ B_{2g} + B_{3g})
130	B_{1u}	128	125(B_{2g})	126(B_{3g})
			124(B_{3g})	
121	B_{1u}	122		120(B_{2g} + B_{3g})
			112(B_{1u})	110(B_{2g})
			107(A_g)	107(A_g + B_{1g})
98	B_{3u}	98	104(B_{3g})	100(B_{3g})
				96(A_g)
			83(B_{3u})	
			75(A_g)	73(B_{2g})
68	B_{1u}	70	67(B_{1g})	
62	B_{3u}	65	63(B_{3u})	65(B_{3g})
				61(B_{1g})
			54(A_g)	54(B_{3g})
49	B_{1u}	52	51(B_{2g})	51(B_{2g})
				47(B_{1g})
41	B_{3u}	44		44(B_{1g} + A_g
				+ B_{2g} + B_{3g})

[a] Literature values (Refs. (*1, 2*)).

Of the 10 internal modes predicted by factor group splitting, at least 7 modes are observed and identified; it is most likely that the remaining 3 modes are masked by overlapping. It is interesting to note that the internal modes' infrared activity of Ag_2BrNO_3 and Ag_2ClNO_3 have more in common with $AgNO_3$ than KNO_3(II).

The external and lattice modes of NO_3^-, Br^-, Cl^-, and Ag^+ species fall within the frequency range 40–620 cm^{-1} as given in Table II whose 23 and 21 peaks are identified for Ag_2BrNO_3 and Ag_2ClNO_3, respectively. There are 21 infrared-active external modes predicted, i.e., $8B_{1u}$, $5B_{2u}$, $8B_{3u}$. The two additional frequencies in Ag_2BrNO_3, viz. 610 and 530 cm^{-1}, may be attributed to combinations (490 + 121) and (370 + 160) or (382 + 148), respectively.

There is no evidence among the data to suggest a clear distinction between Cl^- and Br^- external modes. Thus the interpretation that the 21 observed peaks represent the 21 predicted external modes is suspect. The alternate interpretation that the frequencies above 278 cm^{-1} are combinations leaving 12 observed fundamental external modes is a more plausible one. These latter external modes are identified with the factor group assignments taken from KNO_3(II) along with additional suggested assignments. In general the rotational modes are expected to appear at higher frequencies with higher intensities relative to the translational modes. Furthermore, the external mode frequencies are expected to decrease in the sequence $Cl^- > NO_3^- > Br^- > Ag^+$ on the basis of the mass factor alone.

Comparison of the external mode frequencies from this work with those of $AgNO_3$ and KNO_3(II) shows a high degree of agreement which is interpreted to involve the NO_3^- group. The striking contrast in Table III is the absence of any infrared activity in the region 278–610 cm^{-1} for $AgNO_3$ and KNO_3(II).

In summary, we observed 7 of the 10 internal modes predicted by factor group analysis for NO_3^- in Ag_2BrNO_3 and Ag_2ClNO_3 along with a multiplet structure arising from internal optic modes. Also recorded were 12 of the 21 predicted external modes for NO_3^-, Cl^-, Br^-, and Ag^+.

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