

**184.** *Infrared Absorption Spectra of Alkali-metal, Silver, Thallous, and Ammonium Nitrate Dispersed in Some Silver and Thallous Halide Pressed Discs.*

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The infrared absorption spectra have been recorded of sodium, potassium, rubidium, caesium, silver, thallous and ammonium nitrate dispersed in silver bromide and iodide and in thallous chloride, bromide, and iodide pressed discs. The molecular structure of these dispersions is discussed in the light of the spectroscopic results. Two types of solid solution have been distinguished and in the ammonium nitrate-thallous chloride system both have been observed.

The spectra of crystalline silver and thallous nitrate are shown to be in agreement with their crystal structures and not to have a nitrate ion symmetry,  $D_{3h}$ , reported by other workers.

PREPARATION of metal halide pressed discs containing added inorganic ions may be expected to give one or more of three results. The spectrum of the finely dispersed crystals may be obtained; solid solution might occur such that guest cations and anions are on lattice cation and anion sites, respectively, which are either adjacent to, or remote from, one another. The latter event is synonymous with chemical reaction.

Among the first studies of such systems are those by Ketelaar,<sup>1,2</sup> Van der Elsken,<sup>3</sup> and Frevel,<sup>4</sup> but these were confined to alkali halide host lattices. The present work concerns the use of silver and thallous halides.

Upon dispersion as a solid solution, polyatomic ions display a narrowing of their fundamental absorption bands, partly owing to elimination of (a) coupling between identical molecular vibrations occurring in the pure crystalline form of the guest substance and (b) coupling of these molecular vibrations with lattice modes of the guest substance. However, sharpening of the bands may not be particularly marked, because combination with the lattice modes of the host substance may be considerable. Decius<sup>5</sup> has pointed out that introduction of foreign ions into a crystal lattice can lead to a breakdown of the selection rule, which otherwise permits absorption only in those modes which are in-phase. The symmetry of the substitution site in the host lattice may be such that it is a subgroup of the molecular symmetry of the free ion. The number of fundamental vibration frequencies for the ion will depend upon the site symmetry.

<sup>1</sup> Ketelaar, Haas, and Van Der Elsken, *J. Chem. Phys.*, 1956, **24**, 624.

<sup>2</sup> Ketelaar, Schutte, and Schram, *Spectrochim. Acta*, 1959, **13**, 336.

<sup>3</sup> Van der Elsken, Colloquium Spectroscopium Internationale Revue Universelle des Mines, 1959, No. 5, 445.

<sup>4</sup> Frevel, *Spectrochim. Acta*, 1959, **15**, 557.

<sup>5</sup> Decius, *J. Chem. Phys.*, 1954, **22**, 1941; 1955, **23**, 1290.

## EXPERIMENTAL

The spectra were recorded on a Unicam S.P. 100 infrared spectrophotometer fitted with a sodium chloride prism. Wave-number readings from the chart were accurate to  $\pm 1.5 \text{ cm.}^{-1}$  in the  $1400 \text{ cm.}^{-1}$  region, and to  $\pm 3 \text{ cm.}^{-1}$  for broad bands. Samples were prepared by grinding together 0.015–0.06% w/w of sample with disc material and pressing 1-g. discs. An agate mortar with two agate balls and a Unicam mark 1 vibrator mill were used for grinding. "Vigorous" grinding was that obtained with an amplitude, for the mill blade, of about 7 mm. for 0.5 hr. "Mild" grinding, that with an amplitude of about 2 mm. for 20 min. However, conditions vary from one mill to another.

*Preparation of Silver Bromide.*—"AnalaR" silver nitrate (45.2 g.) was heated in water (900 ml.) to  $70^\circ$ . Purified 47% hydrobromic acid was diluted to 2M with water and run slowly in subdued light into the silver nitrate solution, with stirring, at a constant temperature. When precipitation was complete (after addition of *ca.* 1329 ml.) an excess of bromide ions in the mother-liquor was ensured. After being stored in the dark for an hour and then filtered off in subdued light, the wet residue was transferred to a 1-l. flask containing 500 ml. of 1% hydrobromic acid, refluxed for 2 hr., filtered, and dried at  $130\text{--}150^\circ$ . The product (50 g.) was stored in a glass bottle painted on the outside.

Silver iodide was prepared in an analogous manner.

Hydrobromic and hydriodic acid were of analytical reagent quality and freshly distilled, in the former case from lead bromide to remove sulphuric acid.

*Purification of Thallous Halides.*—Commercial thallous chloride was recrystallised from 1% hydrochloric acid. Thallous bromide (20 g.) was refluxed for 2–3 hr. with water (200 ml.) and 47% hydrobromic acid (3 ml.). Thallous iodide was treated similarly to the bromide but with hydriodic acid. All were washed until acid-free. Thallous chloride and bromide were heated to  $300^\circ$  for 2–3 hr. and stored in brown bottles in a desiccator containing phosphorus pentoxide. Thallous iodide was dried at  $120^\circ$ .

The silver and thallous salts so prepared were free from significant absorption except in the region  $1000\text{--}1100 \text{ cm.}^{-1}$  where the intensity of a broad absorption varied from batch to batch. The absorption was greatest in the silver halides and reached a maximum intensity after prolonged grinding.<sup>6</sup> In all but the worst batches, use of a compensating pressed disc was feasible. A trace of water was always present in the silver salts. The spectra of silver and thallous nitrate were obtained from the powders supported on Teflon film, with compensation for the latter.

## RESULTS AND DISCUSSION

The unperturbed nitrate ion has six fundamental modes of vibration. The totally symmetric N–O stretching mode ( $\nu_1$ ) active in Raman only, the doubly degenerate anti-symmetric N–O stretching mode ( $\nu_3$ ), the out-of-plane bending mode ( $\nu_2$ ) active in infrared only, and the doubly degenerate in-plane bending mode ( $\nu_4$ ).

Table I lists the fundamental absorptions and some overtone and combination bands, together with assignments of these for the range of dispersions studied.

*Alkali-metal Nitrates.*—Except for caesium nitrate,  $\nu_1$  and  $\nu_4$  were not observed in any of the spectra at normal concentrations. Caesium nitrate is apparently insoluble in silver and thallous halide crystals, the resulting spectra being virtually identical with that of crystalline caesium nitrate. It was considered unlikely that the  $\text{Cs}^+$  ion would be incorporated in the above host lattices because of its relative size. Rubidium nitrate was found to be insoluble in thallous iodide. All the remaining spectra showed increased sharpness of the  $\nu_3$  absorption compared with that for the crystalline materials (Table 2), which suggests that the substances are in solid solution. For sodium nitrate the relative intensity of the combination  $\nu_1 + \nu_4$  near  $1900 \text{ cm.}^{-1}$  is very much less in all the pressed-disc spectra than in the spectrum of crystalline sodium nitrate. For potassium nitrate  $2\nu_4$  occurs near  $1435 \text{ cm.}^{-1}$  and  $\nu_1 + \nu_4$  near  $1765 \text{ cm.}^{-1}$  in the disc spectra. The absence or extreme weakness of  $\nu_1$  and retention of the two degenerate modes of the nitrate ion in the

<sup>6</sup> Milkey, *Analyt. Chem.*, 1958, **30**, 1931.

TABLE I.  
Infrared spectra of discs (data in  $\text{cm}^{-1}$ ).

Guest ions	Host lattice					Symmetry species	Assignment
	AgBr	AgI	TlI	TlCl	TlBr		
$\text{Na}^+\text{NO}_3^-$ .....	840m	840m	840m	840m	840m	$A_2$	$\nu_2$
	1374vs	1374vs	1370vs	1370vs	1367	$E$	$\nu_3$
	1452w	1452w	?	?	?	$E$	$\nu_4$
	1789vw	1792w	?	1790vw	1790vw	$E''$	$\nu_1 + \nu_4$
$\text{K}^+\text{NO}_3^-$ .....	829m	829m	829m	829m	829m	$A_2$	$\nu_2$
	1389vs	1389vs	1388vs	1386vs	1386vs	$E$	$\nu_3$
	1433m	1433m	—	—	—	$E$	$\nu_4$
	1763vw	1763vw	—	—	—	$E''$	$\nu_1 + \nu_4$
$\text{Rb}^+\text{NO}_3^-$ .....	839m	839m	841m	841m	841m	$A_2$	$\nu_2$
	1365vs	1365vs	1373vs	1362vs	1373vs	$E$	$\nu_3$
	839m	839m	839m	838m	838m	$A_2$	$\nu_2$
	1377s	1377s	1373s	1372s	1372s	$E$	$\nu_1$
$\text{Cs}^+\text{NO}_3^-$ .....	1746w(b)	—	—	—	—	$E$	$\nu_3$
	806w	722vw	825m	815w	817w	$A_2$	$\nu_2$
	w?	806w	1046w	1056w	1056w	$A_1$	$\nu_1$
	1340vs	1310vs ( $A_1$ ) 1374vs ( $B_1$ )	~1358vs ~1385s	1334vs	1336vs	$E$	$\nu_2$
$\text{Ti}^+\text{NO}_3^-$ .....	826m	826m	—	816m	818m	$A_2$	$\nu_2$
	1048w?	1048w	—	—	—	$A_1$	$\nu_1$
	1310vs ( $A_1$ )	1303s ( $A_1$ )	—	1336vs	1330vs	$E$	$\nu_3$
	1393vs ( $B_1$ )	1390s ( $B_1$ )	—	1740w(b)	1740vw(b)	$E''$	$\nu_1 + \nu_4$
$\text{NH}_4^+\text{NO}_3^-$ .....	719w	719w	720w	718w	818m	$A_2$	$\nu_2$
	830m	830m	832m	831w-m	834m	$A_1$	$\nu_1$
	1048m	1048m	~1340vs b ( $A_1$ )	1050m	1055w-m	$E$	$\nu_3$
	~1380vs b ( $B_1$ )	~1340vs b ( $A_1$ )	~1375vs b ( $B_1$ )	~1340vs b ( $A_1$ )	—	$A_2$	$\nu_2$
	~1380vs b ( $B_1$ )	~1380vs b ( $B_1$ )	~1375vs b ( $B_1$ )	1340vs	1347vs	$A_1$	$\nu_1$
	1430vs b	1430vs b	1440vs b	1419vs	1407vs	$E$	$\nu_3$
	3100m b	—	—	2850w-m	2810w-m	$F_2$	$\nu_4$
	3270m b	—	—	3060s	3020m-s	$F_2$	$\nu_4$
	—	—	—	3160s	3020m-s	$F_2$	$\nu_4$
	—	—	—	3290s	3150s	$F_2$	$\nu_4$
$\text{NH}_4^+$ .....	—	—	—	—	—	$F_2$	$\nu_3$
	—	—	—	—	—	$F_2$	$\nu_3$
	—	—	—	—	—	$F_2$	$\nu_3$
	—	—	—	—	—	$F_2$	$\nu_3$

alkali-metal nitrate dispersions, where solid solution is possible, indicate that the nitrate ion is not far from planar in these lattices. This is particularly noteworthy in the case of rubidium nitrate which has a crystal site symmetry of  $C_{3v}$  for the nitrate ion and a weak  $\nu_1$  absorption in the spectrum of the crystalline solid. Repeated grinding and pressing of the discs increased the intensity of  $\nu_2$  and  $\nu_3$  to a maximum, but not  $\nu_1$  which was very weak indeed.

Comparison of the alkali-metal nitrate solid solutions with those of silver and thallous nitrates in the same halide media shows that the former solutes occupy adjacent cation and anion sites respectively in the host lattice.

*Silver and Thallous Nitrate.*—The infrared absorption spectrum of crystalline silver nitrate has been observed by a number of workers<sup>7,8</sup> of whom two<sup>8</sup> assigned a symmetry of  $D_{3h}$  to the nitrate ion. Crystalline thallous nitrate has been examined by Halford and his colleagues<sup>9</sup> who observed in the  $1350\text{ cm.}^{-1}$  region only one absorption band. Silver nitrate crystals are orthorhombic with space group  $D_2$  and eight molecules per unit cell. Thallous nitrate is orthorhombic with space group  $D_2^3$  and four molecules per unit cell. For these nitrates the anions can occupy sites of symmetry  $D_2$  and  $C_2$ , respectively. Consequently all degeneracy for the vibrations will be removed.

The spectrum of finely ground silver nitrate (Table 2) shows broad absorption in the  $1350\text{ cm.}^{-1}$  region, which easily could be two moderately broad overlapping  $\nu_3(A_1)$ ,  $\nu_3(B_1)$

TABLE 2.  
Infrared bands ( $\text{cm.}^{-1}$ ).

Crystal	$\nu_1$	$\nu_2$	$\nu_3$ and $\nu_3^-$	$\nu_1 + (\nu_4 \text{ and } \nu_4^-)$
$\text{AgNO}_3$ .....	1040w	805m	1320—1390sb	—
$\text{TlNO}_3$ .....	1045w	824m	1316vs, 1378vs	1731vw, 1743vw
$\text{NaNO}_3$ * .....	—	836	1409	1785
$\text{KNO}_3$ † .....	1052vvw	826vvw	1383s	1767vvw
$\text{RbNO}_3$ .....	1060w	840s	1382vs vb	1772vw
$\text{CsNO}_3$ .....	1057w	839m	1378s	?

\* From Höfele (*Z. Phys.*, 1957, **148**, 262). † From Buijs and Schutte (*Spectrochim. Acta*, 1962, **18**, 307).

absorptions. In Table 1, the spectrum of silver nitrate in a silver iodide disc is probably that of highly dispersed silver nitrate microcrystals. Small frequency differences might arise through contributions from the reflection spectra, for crystals finely dispersed in a pressed disc when compared with the spectrum from larger crystals.<sup>10</sup>

Finely ground thallous nitrate exhibits a spectrum (Table 2) in full agreement with the crystal structure.

Silver nitrate in silver bromide gives a sharp very strong absorption peak at  $1340\text{ cm.}^{-1}$  ( $\nu_3$ ) with broad inflections at *ca.*  $1315\text{s}$  and *ca.*  $1372\text{s cm.}^{-1}$ . These shoulders do not decrease in intensity relative to the central band when the concentration of silver nitrate is halved. Consequently the shoulders are unlikely to belong to finely dispersed silver nitrate crystals as distinct from a solid solution, and they are tentatively attributed to sum and difference combinations with lattice-vibration frequencies.

Silver nitrate in thallous chloride and bromide evidently forms solid solutions in which the silver and nitrate ions are not on adjacent cation and anion sites, respectively, since the spectrum obtained is that of thallous nitrate in thallous chloride or bromide.

Thallous nitrate in silver bromide and iodide yields spectra suggesting fine dispersion of guest crystals. The difference in frequencies between these spectra and that of crystalline thallous nitrate may be analogous to that of silver nitrate in silver iodide. For

<sup>7</sup> Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.

<sup>8</sup> Ferraro, *J. Mol. Spectroscopy*, 1960, **4**, 99; Vratny, *Appl. Spectroscopy*, 1959, **13**, 59.

<sup>9</sup> Keller and Halford, *J. Chem. Phys.*, 1949, **17**, 26; Newman and Halford, *ibid.*, 1950, **18**, 1276.

<sup>10</sup> Bovey, *J. Opt. Soc. Amer.*, 1951, **41**, 836.

thallous nitrate in thallous chloride and bromide the presence of one symmetrical  $\nu_3$  absorption and apparent absence of the  $\nu_1$  band show that the nitrate ion is situated in the halide ion lattice in an analogous manner to that postulated for the alkali-metal nitrate solid solutions. Thallous nitrate did not disperse well in thallous iodide.

Examination of a Table given by Halford<sup>11</sup> shows that for a NaCl-type lattice, space group  $O_h^5$ , to which AgCl and AgBr belong, the following site groups exist,  $O_h, T_d, V_h, C_{4v}, C_{3v}, C_{2v}, C_s$ ; and for a CsCl-type structure, to which thallous chloride bromide and iodide belong (space group  $O_h^1$ ),  $O_h, D_{4h}, C_{4v}, C_{3v}, C_{2v}, C_s$ . The site group must be a sub-group of the molecular group and for the nitrate ion of molecular group  $D_{3h}$  the only acceptable site groups, of those above, are  $C_{3v}, C_{2v}$  and  $C_s$ . Further selection of the site group from a knowledge of the number of molecules in the unit cell is not applicable for the solid solutions. Apparent retention of the doubly degenerate modes, however, indicates that the nitrate ion in silver and thallous halide media is on site  $C_{3v}$ , but the apparent absence of  $\nu_1$  shows that the ion is little removed from planar.

*Ammonium Nitrate in Silver Bromide and Iodide.*—Dispersions of ammonium nitrate in silver bromide and iodide and in thallous iodide gave spectra resembling that of crystalline ammonium nitrate, but with somewhat narrower bands. In these cases the ammonium nitrate is probably present as finely dispersed microcrystals.

*Ammonium Nitrate in Thallous Chloride and Bromide.*—Mild grinding before pressing gave, for ammonium nitrate in thallous chloride, spectrum (1) of Table I, and for ammonium nitrate in thallous bromide a spectrum which was predominantly that of crystalline ammonium nitrate.

Vigorous grinding followed by pressing gave, for the chloride, spectrum (2) and, for the bromide, spectrum (3). The corresponding absorptions of the ammonium ion in crystalline ammonium chloride and bromide are given in Table 3.

The ammonium nitrate spectra (1) and (3) possess extra N-H stretching absorptions at frequencies which suggest that one of the hydrogen atoms is involved in weaker hydrogen bonding than the other three. The possibility that these high-frequency bands belong to crystalline ammonium nitrate (*ca.* 3180 and 3270  $\text{cm}^{-1}$ ) is excluded because of the absence of a strong  $\nu_1$  absorption and the presence of a symmetric moderately broad  $\nu_3$  absorption for the nitrate ion, in place of the very broad unsymmetric  $\nu_3\nu_3'$  band of ammonium nitrate crystals.

An ammonium ion situated on a cation site in a thallous halide (CsCl-type) lattice should give an infrared spectrum which is free from perturbations by neighbouring ammonium ions. Similar considerations might be applicable to this system with regard to the orientation of the ammonium ion, as were applied to ammonium chloride and bromide crystals.<sup>12-15</sup> From Tables I and 3 it can be seen that these spectra are sensibly similar.

TABLE 3.

	Crystal type	$\nu_4$ ( $\text{cm}^{-1}$ )	$2\nu_4$ ( $\text{cm}^{-1}$ )	$\nu^*$ ( $\text{cm}^{-1}$ )	Site symmetry
$\text{NH}_4\text{Cl}$	CsCl	1403	2870	3044, 3138	$T_d$
$\text{NH}_4\text{Br}$	„	1401	2833	3031, 3137	$T_d$

Data are taken from Waddington (*J.*, 1958, 4340).

\* These two absorptions arise from the interaction of ( $\nu_2 + \nu_4$ ) and  $\nu_3$  in Fermi resonance.<sup>13</sup>

For ammonium nitrate in thallous chloride there appear to be two possibilities: solid-solution formation, where the ammonium and nitrate ions are on adjacent cation and anion sites, respectively, spectrum (1) of Table I; or solid-solution formation where the ions occupy cation and anion sites which are remote one from the other, spectrum (2).

<sup>11</sup> Halford, *J. Chem. Phys.*, 1946, **14**, 8.

<sup>12</sup> Levy and Peterson, *J. Amer. Chem. Soc.*, 1953, **75**, 1536.

<sup>13</sup> Wagner and Hornig, *J. Phys. Chem.*, 1950, **18**, 296.

<sup>14</sup> Gutowski, Pake, and Bersohn, *J. Chem. Phys.*, 1954, **22**, 643.

<sup>15</sup> Vedder and Hornig, *J. Chem. Phys.*, 1961, **35**, 1560.

The latter spectrum is that of thallous nitrate and ammonium chloride in solid solution in thallous chloride.

Ammonium nitrate in thallous bromide gives a spectrum (3) analogous to spectrum (1).

By analogy with the models suggested by Levi and Peterson<sup>12</sup> for ammonium chloride and bromide it is suggested that solid solutions giving spectra (1) and (3) have structures in which three hydrogen atoms of the ammonium ion are directed towards halide ions and one toward the nitrate ion along the mutual cube-nitrate ion three-fold rotation axis. This lowering of symmetry to  $C_{3v}$  should lead to a loss of triple degeneracy for  $\nu_3$  and  $\nu_4$  ammonium ion vibrations. Table 4 lists the suggested fundamental frequencies and symmetry species of the free ammonium ion which is tetrahedral, point group  $T_d$ .

TABLE 4.

Symmetry species	Raman active	Infrared active	Assignment (cm. <sup>-1</sup> )
$F_2$	a	a	$\nu_4$ ~1400
$E$	a	a	$\nu_2$ ~1700
$A_1$	a	ia	$\nu_1$ ~3250 *
$F_2$	a	a	$\nu_3$ ~3350 *

\* Mathieu and Poulet.<sup>16</sup>

The vibrational frequencies of the free ion are uncertain, but Mathieu and Poulet<sup>16</sup> have reviewed the situation.

Possible assignments are given in Table 1. Splitting of the triply degenerate bending frequency near 1400 cm.<sup>-1</sup> is uncertain, because the high-frequency inflection on the 1400 cm.<sup>-1</sup> band would contain the  $2\nu_4$  absorption of the nitrate ion.

In the spectra discussed above the nitrate ion shows a moderately intense  $\nu_1$  absorption, which with the single symmetrical  $\nu_3$  bands indicates a  $C_{3v}$  site group and, therefore, may be situated on the corner of the anion unit cell of the b.c.c. lattice with the threefold rotation axis of the nitrate ion directed along the cube diagonal. This model was postulated by Frevel<sup>4</sup> for solid solutions of alkali-metal nitrates in the f.c.c. lattices of the alkali halides, but for the ammonium nitrate-thallous chloride and -thallous bromide systems [spectra (1) and (3)] the nitrate ion must deviate from planar configuration to a much greater extent.

The dispersions examined demonstrate the three effects described in the first paragraph. Where solid solution occurred, the width of the absorption band was very much greater than expected, in contrast to solid solutions of nitrates in alkali-metal halide pressed discs. A similar observation concerning band widths was made by Price *et al.*<sup>17</sup>

For substances which do not enter into solid solution the band widths are sometimes a little less than those for spectra obtained from the free crystalline powders. This fact, when coupled with the lack of chemical reactivity relative to the alkali halides, makes silver halides a useful medium for the examination of inorganic nitrates.

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<sup>16</sup> Mathieu and Poulet, *Spectrochim. Acta*, 1960, **16**, 696.

<sup>17</sup> Price, Sherman, and Wilkinson, *Spectrochim. Acta*, 1960, **16**, 663.