251. *The Infrared Absorption of ^{18}O-Labelled Salts. Part I. Silver Nitrite and Potassium Nitrate.*

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The infrared absorption of normal and O^{18}-labelled silver nitrite and potassium nitrate was measured in the solid phase. The ν_1, ν_2, and ν_3 frequencies of the labelled nitrite ion appear at about 1365, 817, and 1227 cm.$^{-1}$, respectively. These values are only partly in agreement with the isotopic relations. In the case of the nitrate, only the ν_2 frequency was found to be practically unaffected by lattice forces.

THE infrared spectra of various compounds labelled with ^{18}O have recently been reported.[1] Except for a brief report [1f] on the absorption of the partially labelled $BaSO_3{}^{18}O$, the effect of such a substitution on the infrared absorption bands of an ionic crystal, where the lattice forces are quite strong, has not yet been investigated. The similar effect of substituting ^{15}N for ^{14}N in sodium and silver nitrites has, however, been studied,[2] and in the former case the isotopic product rule was found to hold in respect to the $\nu_3(b_1)$ frequencies (of potassium bromide pellets).

This paper describes the infrared absorption of mulls of normal and O^{18}-labelled silver nitrite in Nujol and in perfluorokerosene (Fluorolube), and Nujol mulls of normal and labelled potassium nitrate. The infrared spectrum of normal silver nitrite has already been reported several times.[2,3,4]

EXPERIMENTAL

The normal silver nitrite and potassium nitrate used were C.P. commercial products.

^{18}O-Labelled silver nitrite was prepared by dissolving sodium nitrite (6·9 g.) in $D_2{}^{18}O$ (25 ml., 90 atom % of ^{18}O) and acidifying it with 70% perchloric acid (0·5 ml.) with vigorous stirring. The solution (pH 4·9) was kept overnight,[5] and a neutralised solution of anhydrous silver perchlorate (18·5 g.) in $D_2{}^{18}O$ (15 ml.) was added to it slowly (stirring), the resulting precipitate being centrifuged off after each portion. The silver nitrite (10·5 g.) was washed with normal distilled water, centrifuged, and dried at 70° in a vacuum. Its ^{18}O content was estimated to be well over 60% on the basis of the ^{18}O content of the nitromethane prepared from it (58%; see following paper).

^{18}O-*Labelled Potassium Nitrate*.—A mixture of nitric acid (5 ml.; *d* 1·48) and $D_2{}^{18}O$ (15 ml.; 90 atom % of ^{18}O) was kept in a glass-stoppered flask at room temperature for four days, then neutralised with potassium hydroxide in $D_2{}^{18}O$. The bulk of the enriched water was recovered by distillation at normal pressure. The potassium nitrate crystallised on cooling, and was

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[1] (*a*) Braude and Turner, *Chem. and Ind.*, 1955, 1223; (*b*) Halmann and Pinchas, *J.*, 1958, 1703; (*c*) *Idem, J.*, 1958, 3264; (*d*) Pinchas and Halmann, *Bull. Res. Counc. Israel*, 1958, **7**, *A*, 231; (*e*) Eggers and Arends, *J. Chem. Phys.*, 1957, **27**, 1405; (*f*) Spencer, *Biochem. J.*, 1959, **71**, 19p.

[2] Weston and Brodansky, *J. Chem. Phys.*, 1957, **27**, 683.

[3] Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.

[4] Newman, *J. Chem. Phys.*, 1952, **20**, 444.

[5] Anbar and Taube, *J. Amer. Chem. Soc.*, 1954, **76**, 6243.

filtered off by suction and dried in a vacuum (yield, 8·0 g.). Its ^{18}O content was determined by introducing a few crystals of it into an ampoule with a break-seal, evacuating to less than 1 micron, and sealing off. The crystals were decomposed by gentle heating, producing oxygen. This was analysed mass-spectrometrically (Found: ^{18}O, 42·6; ^{17}O, 0·56%).

Further enrichment in ^{18}O was achieved by sealing in an ampoule 1 g. of the above potassium nitrate, 4 ml. of $D_2{}^{18}O$ (90% of ^{18}O), and 0·1 ml. of fuming nitric acid. The ampoule was kept in an oven at 70° for 38 hr. The tube was then opened, and the water recovered by distillation into a cold trap in a vacuum-system. The remaining potassium nitrate was analysed as above; it contained 84·2 atom % of ^{18}O and 1·1% of ^{17}O.

The instrument used was a Perkin–Elmer spectrophotometer Model 12C, equipped with a sodium chloride prism. Capillary layers of the mulls were measured and the spectrum of the mulling agent was recorded immediately before each measurement. Each measurement was carried out at least twice.

RESULTS AND DISCUSSION

Normal silver nitrite mulled in Nujol showed an absorption band at 1374 cm.$^{-1}$ (on top of the 1380 cm.$^{-1}$ Nujol band), a strong and diffuse absorption with a peak at 1251 cm.$^{-1}$, and two bands at 846 and 829 cm.$^{-1}$, the former being appreciably stronger. In order to check the reality of the band at 1374 cm.$^{-1}$, a mull of the nitrite in perfluorokerosene (which is transparent in the 1390—1360 cm.$^{-1}$ region) was also examined. This showed a weak yet definite band at 1363 cm.$^{-1}$ together with a strong broad band centred at about 1243 cm.$^{-1}$. The lower bands appeared in this case at about 844 and 828 cm.$^{-1}$, respectively.

According to Weston and Brodansky [2] a usual silver nitrite mull shows only a broad absorption at about 1250 cm.$^{-1}$ and a sharp band at 846 cm.$^{-1}$. They state that after the mull had been rubbed with sodium chloride plates the spectrum obtained was identical with that of sodium nitrite (bands at 1328, 1261, and 828 cm.$^{-1}$).

Miller and Wilkins [3] report, however, for a Nujol mull of silver nitrite, the following bands: 1380 (very strong), 1250 848 (weak), 833 cm.$^{-1}$. It is true that Weston and Brodansky [2] assumed that these results had been obtained after the cell plates had been rubbed with the nitrite but our results were definitely obtained with a usual mull and still showed an appreciable absorption band at 829 cm.$^{-1}$ and a definite band at about 1374 cm.$^{-1}$. It seems therefore that the bands at about 1374 and 829 cm.$^{-1}$ appear as *weak* peaks even in the spectrum of the usual mull of silver nitrite, being however sometimes obliterated because of the high light-scattering of ionic crystals. The high intensity of the 1380 cm.$^{-1}$ band reported by Miller and Wilkins [3] seems to be due to a too low correction for the absorption of the methyl groups present in the mulling agent (Nujol). These bands must be assigned as follows: [2] the 1374 cm.$^{-1}$ band to the ν_1 frequency (symmetrical stretching) of the nitrite ion, that centred at 1251 cm.$^{-1}$ to its ν_3 (antisymmetrical stretching) frequency, and the two bands at 846 and 829 cm.$^{-1}$ to the ν_2 bending frequency, split and modified by lattice forces, as in the case of crystalline potassium nitrite [2] (836, 804). The corresponding bands in the spectrum of aqueous solutions of sodium nitrite were found [2] at 1345 ± 20, 1236 ± 15, and 816 ± 2 cm.$^{-1}$. The somewhat higher mean bending frequency in the case of the silver salt than of sodium and potassium salts may be the result of the tendency of the silver cation to form bonds of a partial covalent character with anionic oxygen atoms.[6]

A Nujol mull of silver [^{18}O]nitrite showed a shoulder at about 1365 cm.$^{-1}$, a broad band centred at 1227 cm.$^{-1}$ (s), and bands at 847, 827, and 807 cm.$^{-1}$, the intensity of the last being highest. It was also observed that the relative intensity of the 847 cm.$^{-1}$ band increased with the ^{16}O content of the measured sample. When the labelled nitrite was measured as a mull in Fluorolube, fully developed bands appeared at about 1367, 1225, 848, 827, and 806 cm.$^{-1}$, the last being the strongest of the triplet. The 827 cm.$^{-1}$ band is also quite strong.

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[6] Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, 1940, 243; Bergmann, Littauer, and Pinchas, *J.*, 1952, 847.

It is clear that the ν_1 and ν_3 frequencies of crystalline $AgN^{18}O_2$, which was probably the main constituent of the labelled sample measured, are at about 1365 and 1227 cm.$^{-1}$, respectively. It seems also that the band which appears in the normal spectrum at about 846 cm.$^{-1}$ is shifted in the case of $AgN^{18}O_2$ to about 827 cm.$^{-1}$, while the normal band at about 829 cm.$^{-1}$ moved to 807 cm.$^{-1}$. If the mean value of the doublet frequencies is taken as the value of the ν_2 frequency, this is thus shifted from about 838 cm.$^{-1}$ in the normal nitrite to about 817 cm.$^{-1}$ in $AgN^{18}O_2$. According to this interpretation the relative absorption intensity of the two ν_3 branches is inverted on substituting ^{18}O for ^{16}O, and although the higher band (846 cm.$^{-1}$) is stronger in the normal spectrum, the lower (807 cm.$^{-1}$) branch is stronger in that of $AgN^{18}O_2$.

If the symmetry of the nitrite ion in crystalline silver nitrite [2] is indeed taken as C_{2v}, the following ratios are obtained for the isotopic zero-frequencies by using the appropriate equations [7] and taking [8] $2\alpha = 126°$:

$$\omega_3{}^i/\omega_3 = 0{\cdot}9801 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

and

$$\omega_1{}^i\omega_2{}^i/\omega_1\omega_2 = 0{\cdot}9267 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

When the actual vibration frequencies are substituted for the ω_n's, the values obtained must be close to these ratios if the effect of the lattice forces can be neglected. After this is done one obtains:

$$\nu_3{}^i/\nu_3 = 0{\cdot}9808 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

and

$$\nu_1{}^i\nu_2{}^i/\nu_1\nu_2 = 0{\cdot}9685 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

It is evident that, while (3) is in an excellent agreement with (1), the agreement between (4) and (2) is very poor. It is possible that this is so because the value of 1365 cm.$^{-1}$ for $\nu_1{}^i$ is in error owing to the near broad band of $\nu_2{}^i$ and the difficult experimental conditions (a mull of ionic crystals). It seems, however, more reasonable to assume that the lattice forces in this case are too strong to be neglected in calculating the isotopic frequencies.

In any case the characteristic absorption band of $AgN^{18}O_2$ at about 807 cm.$^{-1}$ can be used for its easy identification in mixtures.

The absorption bands of the two modifications of potassium nitrate mulled in Nujol are given in the Table.

Infrared absorption bands (cm.$^{-1}$) of ^{18}O-labelled and normal potassium nitrate

Labelled compound		2010m	1755w	1073w	1028vw	969w	817m	705w [a]
Normal compound	2460s [b]	2060m	1768w	1072vw	1049w	974w	828m	716w [a]

m = medium, w = weak, v = very.

[a] Measured on a mull in decalin; 705 is only an approximate value. [b] The corresponding band in the case of the labelled nitrate is possibly obscured by the absorption of atmospheric carbon dioxide.

For the normal potassium nitrate Nujol mull Miller and Wilkins [3] report an absorption near 2400 cm.$^{-1}$ and bands at 1380, 1767, and 824 cm.$^{-1}$ (m; sharp). It seems, however, that the band observed by them at 1380 cm.$^{-1}$ was due to the mulling agent (Nujol), since no such absorption could be observed when the mulling agent was decalin or hexachlorobutadiene.

The four fundamental frequencies of the planar XY_3 nitrate ion are located [9] at 1050 (ν_1), 831 (ν_2), 1390 (ν_3), and 720 (ν_4) cm.$^{-1}$. It seems therefore that the 1049 cm.$^{-1}$ frequency of the normal crystalline potassium nitrate corresponds to ν_1 (symmetrical stretching) of

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[7] Herzberg, " Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, 1945, pp. 228, 229.

[8] Ketelaar, *Z. Krist.*, 1936, **95**, *A*, 383.

[9] Ref. 6, p. 178.

the free ion, that of 828 cm.$^{-1}$ to its ν_2 (out-of-plane bending), while the 716 cm.$^{-1}$ band parallels the ν_4 band (in-plane-bending) of the ion. It seems, further, that its degenerate ν_3 frequency at 1390 cm.$^{-1}$ is split in the potassium nitrate crystal, under the effect of the lattice forces, into two branches, at 974 and 1768 cm.$^{-1}$ (the sum of which, 2742, is very nearly equal to $2 \times 1390 = 2780$).

It is similarly very reasonable to assume that the closely related frequencies of the labelled potassium nitrate, at 1028, 817, and 705 cm.$^{-1}$, also belong to vibrations similar to the ν_1, ν_2, and ν_4 vibrations of the free nitrate ion, respectively, while the two bands at 1755 and 969 cm.$^{-1}$ are again connected with its ν_3 frequency.

Valency forces being assumed, the ratios of the NO_3^- isotopic frequencies must be: [9]

$$\nu_1^i/\nu_1 = \sqrt{\frac{16}{18}} = 0{\cdot}943; \quad \nu_2^i/\nu_2 = \sqrt{\frac{(1 + 54/14)16}{18(1 + 48/14)}} = 0{\cdot}987;$$

$$\nu_3^i\nu_4^i/\nu_3\nu_4 = \sqrt{\frac{(1 + 54/14)16^2}{18^2(1 + 48/14)}} = 0{\cdot}931$$

The ν_3 frequency being taken as the mean value of the two frequencies at about 1760 and 970 cm.$^{-1}$, the observed ratios are:

$$\nu_1^i/\nu_1 = 1028/1049 = 0{\cdot}980; \quad \nu_2^i/\nu_2 = 817/828 = 0{\cdot}987$$

$$\nu_3^i\nu_4^i/\nu_3\nu_4 = 1362 \times 705/1371 \times 716 = 0{\cdot}977$$

It is seen again that, while the agreement for one ratio (ν_2^i/ν_2) is excellent, yet that for other ratios is very poor. It seems thus that, although the lattice forces (including the electrostatic forces between the cations and the anions) can be neglected in respect to some modes of vibration of certain ionic groups in crystals, this is generally not the case. It is noteworthy that the vibration (ν_2) which is not much affected by lattice forces in the case of the nitrate ion, is the one which changes practically only the z (perpendicular to the nitrate ion plane) co-ordinates. This is remarkable, since it has been shown that in the case of the potassium salt the nitrate ions of different layers are coupled in this vibration.[10]

That this coupled vibration is not split in this case in analogy to the case of 50% and even 20% of potassium [^{15}N]nitrate [10] is probably the result of the much smaller difference between the frequencies of the isotopic modifications in this instance (of mainly $KN^{16}O^{18}O_2$ and $KN^{18}O_3$) than in that of the $K^{14}NO_3$–$K^{15}NO_3$ mixture. With the silver nitrite such a vibration is the one (ν_3) in which the stretching of one N–O bond is compensated by an equal and simultaneous shrinking of the other N–O bond, so that the mean N–O bond length remains constant during the whole of its period.

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[10] Decius, *J. Chem. Phys.*, 1955, **23**, 1290.