

524. The Infrared Absorption of ^{18}O -Labelled Salts. Part II.¹ Sodium Sulphite.

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The infrared absorptions of Nujol mulls of normal and enriched [^{18}O ; 57 atom %] sodium sulphite in the 3700—400 cm^{-1} region are reported. The assignment of ν_3 of the SO_3^{2-} ion is discussed and the frequency of 1164 cm^{-1} suggested for it. The ν_3 and ν_4 bands of $\text{S}^{16}\text{O}_3^{2-}$ are split in the case of $\text{S}^{16}\text{O}^{18}\text{O}_2^{2-}$ as a result of its lower symmetry. The observed ratios of the $\text{S}^{16}\text{O}^{18}\text{O}_2^{2-}$ frequencies to the corresponding $\text{S}^{16}\text{O}_3^{2-}$ frequencies are compared with the theoretically calculated ratios; agreement is only moderate.

THE effect of ^{18}O -labelling on the $\text{X}-\text{O}_n^m$ frequencies of an ionic crystal is interesting both as a criterion of the specific lattice forces and as a ready indication for the extent of such labelling in an "unknown" sample. This paper reports the infrared absorption of Nujol mulls of normal and enriched [^{18}O ; 57 atom %] sodium sulphite in the 3700—400 cm^{-1} region.

Experimental.—Normal sodium sulphite was a C.P. commercial product.

^{18}O -Labelled sodium sulphite. Normal sodium sulphite was dissolved in a large excess of enriched [^{18}O ; ~90 atom %] water at room temperature. After 24 hr. the water was distilled off *in vacuo* and the salt dried in a desiccator. The isotopic content, determined by Anbar and Guttman's method,² was 57.3 atom % ^{18}O .

The instrument used was a Perkin-Elmer spectrophotometer, model 12 C, equipped with a sodium chloride prism (down to 670 cm^{-1}) or a potassium bromide prism (in the 670—400 cm^{-1} region). Capillary layers of the mulls were measured (usually more than once) and the spectrum of the mulling agent was run before each measurement.

Results and Discussion.—The frequencies of the bands observed are given in Table I. They agree quite well with those reported previously³ for the normal salt. The 965, 630.

TABLE I.

The infrared absorption bands (cm^{-1}) of normal and labelled sodium sulphite.

Normal salt:	2515vw, 2435vw, 1987sh, 1930s ($2\nu_1$), 1214m ($2\nu_2$), 1164m (ν_3), 965bs (ν_1), 889w, 847m, 762w, 630s (ν_2), 494m (ν_4), 471sh
Labelled salt:	3470w (? traces of H_2O), 2090w (995 \perp 1115, 1190 \perp 951, etc.), 1190bs, 1115bs, 995sh, 951s ν_1 , 878w, 620bs (ν_2), 494w, 471w

and 494 cm^{-1} bands belong to the ν_1 , ν_2 , and ν_4 vibrations of the pyramidal 4,5 SO_3^{2-} ion of C_{3v} symmetry, respectively.⁵ The ν_3 vibration seems to be correlated with the 1164 cm^{-1} band (observed for the sodium, potassium, and barium salt³) rather⁵ than with that appearing for various sulphites³ at 930 cm^{-1} , since it is difficult to see why the ν_3 frequency should drop so much from its 1330 cm^{-1} value⁶ in the SO_3 molecule while the ν_1 , ν_2 and ν_4 vibrations remain well within 10% of their values in SO_3 and the β angle (between the C_3 -axis and an S—O direction) is as high⁵ as 68.5° . The absence of an 1164 cm^{-1} band in the observed Raman spectrum⁵ seems to be due to the asymmetry of the ν_3 vibration which makes its activity in this spectrum much weaker than that of ν_1 .

The weak infrared band at 762 cm^{-1} , observed with normal sodium sulphite, may be a branch of the ν_2 absorption which is possibly split as a result of the interaction between

¹ Part I, Anbar, Halmann, and Pinchas, *J.*, 1960, 1242.

² Anbar and Guttmann, *Internat. J. Appl. Radiation Isotopes*, 1959, **3**, 233.

³ Rocchiccioli, *Ann. Chim. (France)*, 1960, **5**, 999; *Compt. rend.*, 1957, **244**, 2704; Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253; *Spectrochim. Acta*, 1960, **16**, 135; Anderson and Woodall, *Analyt. Chem.*, 1953, **25**, 1908.

⁴ Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York, Chap. VII, p. 18.

⁵ Simon and Waldmann, *Z. phys. Chem. (Leipzig)*, 1955, **204**, 235.

⁶ Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, 1945, p. 178.

the two SO_3^{2-} ions in the unit cell.⁴ The 847 and the 889 cm^{-1} band may be similar branches of the ν_1 frequency, split possibly further by the lattice.

The labelled salt is a mixture of four species: $\text{Na}_2\text{S}^{16}\text{O}_3$, $\text{Na}_2\text{S}^{16}\text{O}_2^{18}\text{O}$, $\text{Na}_2\text{S}^{16}\text{O}^{18}\text{O}_2$, and $\text{Na}_2\text{S}^{18}\text{O}_3$. Calculation on the basis of a simple statistical approach shows that it contains these species in the approximate percentages, 7.7, 18.5, 41.7, 32.1%. Since the bands of the fully labelled sulphite ion and those of the monolabelled ion will probably be spaced almost equally on both sides of the parallel $\text{S}^{16}\text{O}^{18}\text{O}_2^{2-}$ bands, one can expect the bands of this labelled salt almost to coincide with those of pure $\text{Na}_2\text{S}^{16}\text{O}^{18}\text{O}_2$ (in view of the considerable width of such bands). As can be seen from Table 1, only one set of bands was indeed observed for the labelled salt mixture.

The ν_4 frequency which is located in the normal-salt spectrum at 494 cm^{-1} (the 471 cm^{-1} absorption forming there only a shoulder) seems to be split in the spectrum of the labelled salt into two bands of almost equal intensity, at 494 and 471 cm^{-1} . This appears to be the result of loss of its symmetry owing to formation of the $\text{S}^{16}\text{O}^{18}\text{O}_2^{2-}$ ion, which can be expected to split this degenerate frequency into two branches. The 620 cm^{-1} band is due to the symmetrical ν_2 frequency, shifted from its 630 cm^{-1} location in the normal salt as a result of isotopic substitution. The ν_1 frequency seems to give rise both to the strong band at 951 cm^{-1} and to its weak branch at 878 cm^{-1} , possibly as a result of interaction in the unit cell. The pair of strong and broad bands at about 1115 and 1190 cm^{-1} , respectively, appears to be due to the degenerate ν_3 frequency of the sulphite ion, shifted from its original position at 1164 cm^{-1} by isotopic substitution and split into two branches as a result of the destruction of the SO_3^{2-} symmetry.

In order to be able to compare the isotopic shifts with those expected theoretically, both as a check on the assignment of the ν_3 frequencies and for evaluating the extent of

TABLE 2.

	ν_1	ν_2	ν_3	ν_4
$\text{S}^{16}\text{O}_3^{2-}$	965	630	1164	494
$\text{S}^{16}\text{O}^{18}\text{O}_2^{2-}$	951	620	1152	482

the interaction between lattice forces and ionic vibrations, the mean values of the ν_3 and ν_4 frequency pairs of $\text{S}^{16}\text{O}^{18}\text{O}_2^{2-}$ are taken as its ν_3 and ν_4 counterparts. For comparing the ν_1 and ν_2 frequencies of the normal and labelled sulphite ions, only the main bands were taken into account. The values (cm^{-1}) in Table 2 for the four fundamentals were thus obtained.

It can be shown⁷ that for a pyramidal XY_3 molecule

$$\nu_{i1}\nu_{i2}/\nu_1\nu_2 = \sqrt{(1 + 3m_{iY}/m_X) m_Y^2 / (1 + 3m_Y/m_X) m_{iY}^2}$$

and

$$\nu_{i3}\nu_{i4}/\nu_3\nu_4 = \sqrt{\frac{(1 + \cos^2\beta + 3m_{iY}\sin^2\beta/m_X)m_Y^2}{(1 + \cos^2\beta + 3m_Y\sin^2\beta/m_X)m_{iY}^2}}$$

where the subscript *i* denotes that the respective symbol refers to the XY_3 molecule isotopic in Y or to the isotopic Y atom. Solving these equations for $\text{S}^{16}\text{O}_3^{2-}$ and $\text{S}^{18}\text{O}_3^{2-}$ [with $\beta = 68.5^\circ$ (ref. 5)] yields the solutions: $\nu_{i1}\nu_{i2}/\nu_1\nu_2 = 0.922$; $\nu_{i3}\nu_{i4}/\nu_3\nu_4 = 0.917$. For $\text{S}^{16}\text{O}_3^{2-}$ and $\text{S}^{16}\text{O}^{18}\text{O}_2^{2-}$ only about two-thirds of these shifts are expected and the theoretical ratios are therefore very near to 0.948 and 0.945, respectively. Using above values for the various fundamentals gives the observed ratios as: $\nu_{i1}\nu_{i2}/\nu_1\nu_2 = 951 \times 620/965 \times 630 = 0.970$; and $\nu_{i3}\nu_{i4}/\nu_3\nu_4 = 1152 \times 482/1164 \times 494 = 0.966$.

The fair agreement between the observed values and the calculated ones is therefore good enough to support the assignments of the ν_3 bands but still shows that the single SO_3^{2-} ions are kept strongly in place in the crystalline lattice; if the lattice forces were weak one would expect an even better agreement between these ratios.

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⁷ Ref. 6, p. 188.