Crystal Structure, and the Infrared and Raman Spectra, of Potassium Hydroxylamine-*N*,*O*-disulphonate, $K_2[O_3SONHSO_3]$. The Infrared and Raman Spectra of Potassium Hydroxylaminetrisulphonate Sesquihydrate, $K_3[O_3SON(SO_3)_2]\cdot 1.5H_2O$ †

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The crystal structure of $K_2[O_3SONHSO_3]$ has been determined using three-dimensional *X*-ray diffraction data with 1 097 observed reflections. Crystals are monoclinic, space group $P2_1/a$, with $Z = 4$ in a cell of dimensions $a = 11.009(3)$, $b = 10.040(2)$, $c = 7.483(3)$ Å, and $\beta = 109.49(2)°$. The structure was solved by the heavy-atom method and refined by full-matrix least squares to *R* 0.033. The N–S bond [1.704(3) Å] is markedly longer than found for $K_2[NH(SO_3)_2]$ in which both sulphonate groups are bound directly to nitrogen. The infrared (4 000—50 cm^{-1}) and Raman spectra of $K_2[O_3SONHSO_3]$ and $K_3[O_3SON(SO_3)_2]\cdot 1.5H_2O$ and their ^{15}N and ^2H derivatives at 77 K are reported and interpreted. Aqueous spectra have also been recorded. The following frequencies were assigned: ν(N–O), 925; ν(N–S), 808; and ν[S–O(N)], *ca.* 730 cm^{-1} for $K_2[O_3SONHSO_3]$; ν(N–O), 930; ν_{asym}(N–S), 820; ν_{sym}(N–S), 757; and ν[S–O(N)], 708 cm^{-1} for $K_3[O_3SON(SO_3)_2]\cdot 1.5H_2O$.

As part of a continuing investigation into the vibrational properties of the sulphonate derivatives of methane, ammonia, and hydroxylamine, we have recorded the i.r. and Raman spectra of polycrystalline potassium hydroxylamine-*N*,*O*-disulphonate, $K_2[O_3SONHSO_3]$, and potassium hydroxylaminetrisulphonate sesquihydrate, $K_3[O_3SON(SO_3)_2]\cdot 1.5H_2O$, at liquid nitrogen temperature. Spectra of the ^{15}N and ^2H derivatives have also been recorded. The i.r. spectra above 400 cm^{-1} of $K_2[O_3SONHSO_3]$, $K_2[O_3SONDSO_3]$, and $K_3[O_3SON(SO_3)_2]\cdot 1.5H_2O$ have previously been reported.[1] In order to have an adequate prediction of the spectra of $K_2[O_3SONHSO_3]$, the *X*-ray crystal structure of this salt has now been determined. However, the neutron structure of $K_3[O_3SON(SO_3)_2]\cdot 1.5H_2O$ has already been published.[2] To assist with the internal mode assignments, the aqueous solution spectra, including qualitative Raman polarization data, have been obtained. The lattice-water assignment of $K_3[O_3SON(SO_3)_2]\cdot 1.5H_2O$ is assisted by comparison with the i.r. spectra of partially deuteriated samples.

EXPERIMENTAL

Preparations.—$K_3[O_3SON(SO_3)_2]\cdot 1.5H_2O$ was prepared by the method described by Raschig [3,4] (Found: K, 28.0; N, 3.5; S, 23.5. Calc. for $H_3K_3NO_{11.5}S_3$: K, 28.3; N, 3.4; S, 23.2%). The ^{15}N derivative was prepared by the same procedure, starting with $Na[NO_2]$ of 99.8% ^{15}N enrichment (The British Oxygen Company Ltd.).

The compound $K_3[O_3SON(SO_3)_2]\cdot 1.5D_2O$ was converted by several recrystallizations of $K_3[O_3SON(SO_3)_2]\cdot 1.5H_2O$ in D_2O made weakly alkaline with dry $Li_2[CO_3]$ to prevent hydrolysis [5] to hydroxylamine-*N*,*O*-disulphonate. Exchange of the hydrogen atoms was estimated from i.r. spectra to be *ca.* 80% (Found: K, 27.8; N, 3.4. Calc. for $D_3K_3NO_{11.5}S_3$: K, 28.1; N, 3.4%).

Partially deuteriated samples were made using a previously reported method,[6] starting with $K_3[O_3SON(SO_3)_2]\cdot 1.5H_2O$ and recrystallizing from H_2O–D_2O mixtures made weakly alkaline with dry $Li_2[CO_3]$. The approximate concentrations of H_2O, HDO, and D_2O in the deuteriated samples were calculated.[7]

The compound $K_2[O_3SONHSO_3]$ was obtained by the acid-catalysed hydrolysis of hydroxylaminetrisulphonate using Raschig's method [8] (Found: K, 28.8; N, 5.0; S, 23.7. Calc. for $HK_2NO_7S_2$: K, 29.0; N, 5.2; S, 23.8%). The same procedure was used for the ^{15}N derivative.

The compound $K_2[O_3SONHSO_3]$ was deuteriated into $K_2[O_3SONDSO_3]$ by several recrystallizations from D_2O made weakly alkaline with dry $Li_2[CO_3]$ to prevent hydrolysis [5] to hydroxylamine-*O*-sulphonate, $NH_2OSO_3^-$. Exchange was estimated to be *ca.* 85% (Found: K, 28.8; N, 5.3. Calc. for $DK_2NO_7S_2$: K, 28.9; N, 5.2%).

Crystal Data.—$HK_2NO_7S_2$, $M = 269.4$, Monoclinic, $a = 11.009(3)$, $b = 10.040(2)$, $c = 7.483(3)$ Å, $\beta = 109.49(2)°$, $U = 779.7(4)$ Å^3, $D_m = 2.30$ g cm^{-3} (by flotation), $Z = 4$, $D_c = 2.29$ g cm^{-3}, $F(000) = 536$, space group $P2_1/a$ (variant of $P2_1/c$) (C_{2h}^5, no. 14), Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 16.7 cm^{-1}. A total of 1 097 reflections with $I > 3\sigma(I)$ were considered observed out of 1 369 unique reflections collected from one crystal (0.25 × 0.43 × 0.40 mm) mounted on a Syntex $P\bar{1}$ four-circle diffractometer ($2\theta_{max.} = 50°$) using a θ—2θ scanning mode. Graphite-monochromated Mo-K_α radiation was used and no absorption corrections were applied.

Structure Determination.—The structure was solved using the heavy-atom method and refined by full-matrix least squares with anisotropic temperature factors on all atoms except hydrogen. The hydrogen position was located in a difference-Fourier synthesis and its co-ordinates refined giving a final isotropic temperature factor (*U*) of 0.02 Å^2. The final $R(= \Sigma|F_o - F_c|/\Sigma F_o)$ was 0.033 and $R'(= \Sigma w|F_o - F_c|^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$ was 0.044. Reflections were given

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† The title compounds are more systematically named as potassium hydroxylamido-*N*,*O*-disulphate(2−) and potassium hydroxylamidotrisulphate(3−) sesquihydrate respectively.

the weights $w = [\sigma^2(F_o) + 0.000\,5(F_o)^2]^{-1}$. Neutral-atom scattering factors [9,10] were used while non-hydrogen atoms were corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[11] All computations were carried out on the University of Western Australia's CYBER 73 computer using the '*X*-RAY '76' system. Final atomic positional parameters are listed in Table 1 while structure factor amplitudes and anisotropic thermal parameters are deposited as Supplementary Publication No. SUP 22802 (9 pp.).*

Infrared Spectra.—Infrared spectra were recorded using Perkin-Elmer model 225 and Beckman-RIIC IR-720 spectrophotometers with low-temperature facilities.[12]

Raman Spectra.—Raman spectra were recorded on a Cary model 82 laser spectrometer using 514.5 nm exciting radiation and a power of *ca.* 600 mW at the sample.

The i.r. and Raman spectra recorded at ambient temperature showed little change from the 77 K spectra. Observed frequencies are considered accurate to ±2 cm^{-1} below 2 000 cm^{-1} and ±4 cm^{-1} above 2 000 cm^{-1}. Experimental conditions used have been previously described.[12]

TABLE 1

Atomic positional parameters for hydrogen ($\times 10^3$) and other atoms ($\times 10^4$) with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
K(1)	3 120(1)	933(1)	3 468(1)
K(2)	4 848(1)	2 525(1)	9 548(1)
S(1)	1 237(1)	2 448(1)	5 565(1)
S(2)	2 337(1)	−442(1)	9 097(1)
N(21)	1 568(4)	76(3)	6 831(5)
O(11)	948(2)	1 333(3)	6 958(4)
O(12)	668(3)	1 925(3)	3 663(4)
O(13)	2 610(2)	2 612(3)	6 123(4)
O(14)	555(3)	3 553(3)	6 009(4)
O(22)	1 489(3)	−183(3)	10 179(4)
O(23)	3 512(3)	310(3)	9 767(4)
O(24)	2 506(3)	−1 835(3)	8 787(4)
H(21)	90(4)	−35(4)	652(5)

RESULTS AND DISCUSSION

Crystal Structure.—Figure 1 illustrates the molecular conformation and atomic numbering scheme used for $K_2[O_3SONHSO_3]$. The observed bond distances and angles are given in Table 2. As in the case of imidosulphonate, $K_2[NH(SO_3)_2]$, in which *both* sulphonate groups are bound directly to nitrogen, the nitrogen atom has distorted tetrahedral stereochemistry. However, the sum of the interbond angles at nitrogen in $K_2[O_3SONHSO_3]$ (303.7°) is considerably less than that in $K_2[NH(SO_3)_2]$ (347.6°).[13] This is attributed mainly to reduced repulsion between the bulky sulphonate groups in the former species due to the presence of the bridging oxygen atom. Also, this increased deviation from planarity is accompanied by an increase in the N–S bond length {1.704(3) Å for $K_2[O_3SONHSO_3]$, 1.674(5) Å for $K_2[NH(SO_3)_2]$ [13]}. This is presumably due to the net effect of a decrease in the *s* character of the σ N–S bond and less efficient π overlap between the lone-pair orbital of nitrogen and the unfilled 3*d* orbitals of sulphur on the one hand, and delocalization of the nitrogen lone pair into only *one* set of sulphur *d* orbitals on the other hand. The N–S bond length observed for sulphamic acid, $[NH_3][SO_3]$ [1.76(2) Å] [14] is indicative of a single N–S bond since there are no lone-pair electrons on nitrogen available for π bonding. The single-bond value calculated from the Schomaker–Stevenson rules [15] is 1.74 Å. In $K_3[N(SO_3)_2]\cdot H_2O$, which has *two* π-bonding lone pairs on nitrogen, the N–S bond length is 1.609(3) Å.[16] Similar arguments can be used to rationalize the decrease in the sum of the interbond angles at nitrogen and the increase in the N–S bond length on going from nitrilosulphonate, $K_3[N(SO_3)_3]\cdot 2H_2O$ [360°, 1.71(2) Å] [17] to hydroxylaminetrisulphonate, $K_3[O_3SON(SO_3)_2]\cdot 1.5H_2O$ [330.6°, 1.750(2) Å].[2]

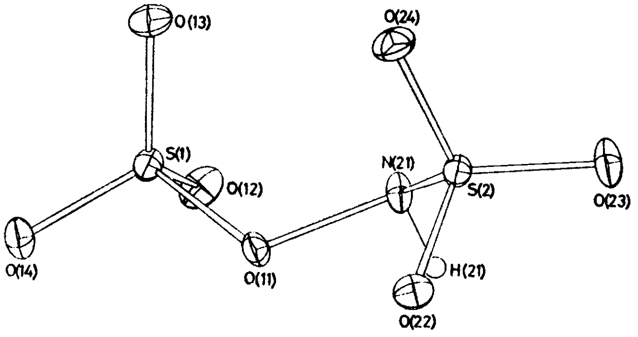

FIGURE 1 Molecular conformation and atomic numbering used for the $O_3SONHSO_3^{2-}$ ion

The N–O bond length [1.454(4) Å] is very close to the postulated σ-bond length (1.44 Å) [15] and that observed for $K_3[O_3SON(SO_3)_2]\cdot 1.5H_2O$ [1.434(1) Å] [2] and sulphoperamidic acid, $[NH_3][OSO_3]$ [1.48(4) Å].[18,*] The S–O (mean 1.442 Å) and S–O(N) [1.632(3) Å] bond lengths and the O–S–O (mean 114.1°), O–S–N (mean 104.8°), and O–S–O(N) (mean 104.0°) angles are generally similar to those found in other sulphonates of methane, ammonia, and hydroxylamine.

TABLE 2

Interatomic distances and angles with estimated standard deviations in parentheses

(*a*) Distances (Å)

N(21)–O(11)	1.454(4)	S(1)–O(14)	1.440(3)
N(21)–H(21)	0.82(4)	N(21)–S(2)	1.704(3)
O(11)–S(1)	1.632(3)	S(2)–O(22)	1.448(3)
S(1)–O(12)	1.448(3)	S(2)–O(23)	1.436(3)
S(1)–O(13)	1.437(3)	S(2)–O(24)	1.440(3)

(*b*) Angles (°)

O(11)–N(21)–S(2)	106.7(2)	N(21)–S(2)–O(22)	107.6(2)
O(11)–N(21)–H(21)	94(3)	N(21)–S(2)–O(23)	106.1(2)
S(2)–N(21)–H(21)	103(3)	N(21)–S(2)–O(24)	100.6(2)
N(21)–O(11)–S(1)	110.9(2)	O(22)–S(2)–O(23)	112.6(2)
O(11)–S(1)–O(12)	105.5(2)	O(22)–S(2)–O(24)	114.0(2)
O(11)–S(1)–O(13)	107.7(2)	O(23)–S(2)–O(24)	114.6(2)
O(11)–S(1)–O(14)	98.8(2)		
O(12)–S(1)–O(13)	113.3(2)		
O(12)–S(1)–O(14)	114.8(2)		
O(13)–S(1)–O(14)	114.8(2)		
O(13)–S(1)–O(14)	115.1(2)		

The torsion angles about the N(21)–O(11), N(21)–S(2), and O(11)–S(1) vectors in $O_3SONHSO_3^{2-}$ (1) and $O_3SON(SO_3)_2^{3-}$ (2) are compared in Table 3. The

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

* Systematic name: peroxoamidosulphuric acid.

presence of an additional sulphonate group on the nitrogen group in (2) appears to impose some strain on the system, where torsion angles are contracted (116.2, − 116.7°) compared with 132.5° for (1). This conformation results in subsequent distortion within the (OSO_3) group for (2) where the angle between N(21)–O(11) and S(1)–O(12) (27.0°) is considerably smaller than the value of 62.5° for (1) (Figure 2). For both compounds, reasonably regular staggered conformations are observed for the oxygens of sulphonate groups about the N–S vector.

TABLE 3

Comparative torsion angles (°) for $O_3SONHSO_3^{2-}$ (1) and $O_3SON(SO_3)_2^{3-}$ (2). The primed atoms O(22′), O(23′), O(24′), and S(2′) are from the second sulphonate group in (2)

Vector	Torsion angle	(1) $O_3SONHSO_3^{2-}$	(2) $O_3SON(SO_3)_2^{3-}$
N(21)–O(11)	S(2)–S(1)	132.5	116.2
	S(2′)–S(1)		−116.7
N(21)–S(2)	O(11)–O(22)	41.5	−69.9
	O(11)–O(22′)		−67.1
	O(11)–O(23)	−79.2	48.9
	O(11)–O(23′)		52.5
	O(11)–O(24)	159.9	171.4
	O(11)–O(24′)		171.8
O(11)–S(1)	N(21)–O(13)	−58.7	−86.4
	N(21)–O(12)	62.5	27.0
	N(21)–O(14)	178.7	146.6

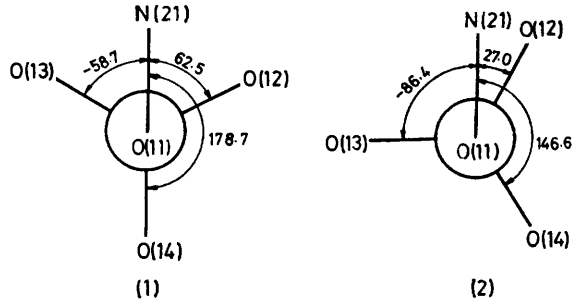


FIGURE 2 Newman projections down the O(11)–S(1) vector for $O_3SONHSO_3^{2-}$ (1) and $O_3SON(SO_3)_2^{3-}$ (2)

The potassium cations are surrounded by seven [K(1)] and six [K(2)] oxygens from sulphonate groups (Figure 3) with K · · · O distances less than 3.1 Å [range 2.701—3.008 Å, mean 2.831(3) Å]. This mean compares closely with those found for $K_3[N(SO_3)_2]\cdot H_2O$ [16] (2.863 Å) and $K_2[NH(SO_3)_2]$ [13] (2.89 Å). Full details of the potassium environments are provided in Table 4. Only one close H · · · O contact interpreted as a hydrogen bond could be found [H(21) · · · O(12)($\bar{x}$, $\bar{y}$, 1 − z), 2.30(4) Å].

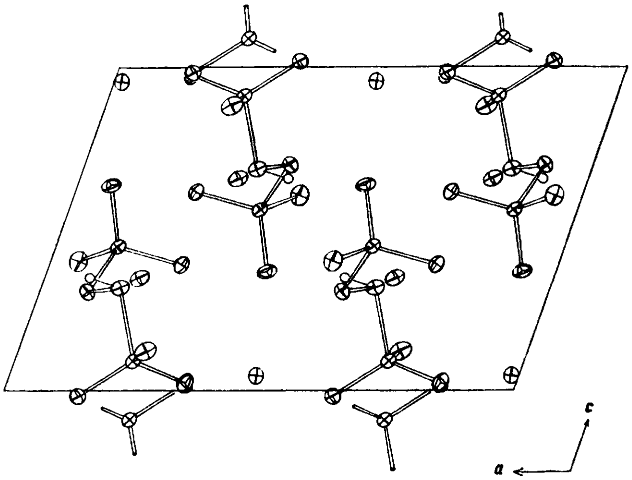


FIGURE 3 Perspective view of the packing in the cell viewed perpendicular to the *ac* plane

Vibrational Investigation.—The isolated $O_3SONHSO_3^{2-}$ ion is devoid of symmetry (C_1) and hence the 27 normal modes of vibration (symmetry species A) are both i.r. and Raman active. Approximate descriptions of these modes in terms of internal co-ordinate contributions are given in Table 5. Considerable mixing of these motions is expected in the actual normal modes. In the crystal, all atoms occupy general positions and hence factor-

TABLE 4

Cation environment about K(1) and K(2) indicating K · · · O contacts [r(K–O)] (Å) less than 3.1 Å. The other entries in the matrices are the angles (°) subtended by the two numbered atoms at the potassium

(*a*) K(1)

	r	O(13)	O(22^{I})	O(23^{I})	O(24^{II})	O(14^{III})	O(14^{IV})
O(12)	2.926(3)	49.71(7)	81.14(9)	122.33(8)	72.96(10)	137.79(10)	126.89(9)
O(13)	2.801(3)		130.79(9)	154.49(9)	82.91(10)	129.97(9)	77.18(9)
O(22^{I})	2.755(3)			48.96(9)	80.09(9)	86.00(9)	151.93(10)
O(23^{I})	3.008(4)				71.82(9)	73.66(9)	105.54(10)
O(24^{II})	2.751(3)					143.59(11)	104.88(9)
O(14^{III})	2.759(3)						73.68(8)
O(14^{IV})	2.769(3)						

(*b*) K(2)

	r	O(23)	O(24^{V})	O(22^{VI})	O(12^{VII})	O(11^{IV})
O(13)	2.904(3)	76.07(8)	146.82(10)	74.06(8)	141.96(9)	79.36(8)
O(23)	2.701(3)		105.76(9)	111.40(10)	94.24(9)	137.46(9)
O(24^{V})	2.845(3)			121.33(8)	71.18(9)	77.91(9)
O(22^{VI})	2.776(3)				75.73(8)	94.18(9)
O(12^{VII})	2.958(3)					128.62(8)
O(11^{IV})	2.846(3)					

Roman numeral superscripts refer to the following transformations of the asymmetric unit:

I ($x,y,z-1$); II ($\frac{1}{2}-x, \frac{1}{2}+y, 1-z$); III ($\frac{1}{2}-x, y-\frac{1}{2}, 1-z$); IV ($\frac{1}{2}+x, \frac{1}{2}-y, z$); V ($1-x, \bar{y}, 2-z$); VI ($\frac{1}{2}-x, \frac{1}{2}+y, 2-z$); VII ($\frac{1}{2}+x, \frac{1}{2}-y, 1+z$)

group analysis gives the vibrational representation shown in Table 6(*a*) (acoustic modes omitted). The A_g and B_g modes are Raman active only whereas the A_u and B_u modes are i.r. active only. The correlation between point, site, and unit-cell symmetry species is given in Table 7(*a*).

TABLE 5

Approximate internal co-ordinate contributions to the vibrational modes of $O_3SONHSO_3^{2-}$ (C_1) and $O_3SON(SO_3)_2^{3-}$ (C_s)

$O_3SONHSO_3^{2-}$	$O_3SON(SO_3)_2^{3-}$	
A		N–H stretch
A	$A' + A''$	N–S stretches
A	A'	N–O stretch
$3A$	$3A' + 3A''$	(N)S–O stretches
$3A$	$2A' + A''$	(O)S–O stretches
A	A'	S–O(N) stretch
A		HNS deformation
A		HNO deformation
	A'	NS_2 deformation
A	$A' + A''$	SNO deformations
A	A'	NOS deformation
$3A$	$3A' + 3A''$	(N)SO_3 deformations
$3A$	$2A' + A''$	(O)SO_3 deformations
$2A$	$2A' + 2A''$	(N)SO_3 rocks
$2A$	$A' + A''$	(O)SO_3 rocks
A	$A' + A''$	(N)SO_3 torsions
A	A''	(O)SO_3 torsion
A	A''	OSO_3 torsion*

* About the O–N bond.

For an isolated $O_3SON(SO_3)_2^{3-}$ ion of C_s symmetry, the 36 normal modes of vibration belong to the symmetry species $20A' + 16A''$. Both species are i.r. and Raman active. Approximate descriptions of these modes are compared with those of $O_3SONHSO_3^{2-}$ in Table 5. Crystals of $K_3[O_3SON(SO_3)_2]\cdot1.5H_2O$ have the space symmetry $I2/c$ (standard space group $C2/c$) with eight formula units per monoclinic unit cell.[2] The oxygen atoms of one type of water molecule [$H_2O(1)$] lie on two-fold rotation axes (C_2 sites) whereas all other atoms are on general sites. Therefore, factor-group analysis gives the vibrational representation shown in Table 6(*b*). Also, the correlation between point, site, and unit-cell symmetry species is shown in Table 7(*b*). The i.r. and Raman spectra of polycrystalline $K_2[O_3SONHSO_3]$ and $K_3[O_3SON(SO_3)_2]\cdot1.5H_2O$ at 77 K are shown in Figures 4 and 5 respectively. The observed frequencies (including those for the ^{15}N and ^2H derivatives) and their assignments are given in Table 8. Frequencies observed for aqueous solutions of $K_2[O_3SONHSO_3]$, $K_2[O_3SONDSO_3]$, and $K_3[O_3SON(SO_3)_2]\cdot1.5H_2O$ are also given in Table 8. Symmetry species given in the table refer to vibrations of the $O_3SON(SO_3)_2^{3-}$ ion.

TABLE 6

Vibrational representations for (*a*) $K_2[O_3SONHSO_3]$ and (*b*) $K_3[O_3SON(SO_3)_2]\cdot1.5H_2O$

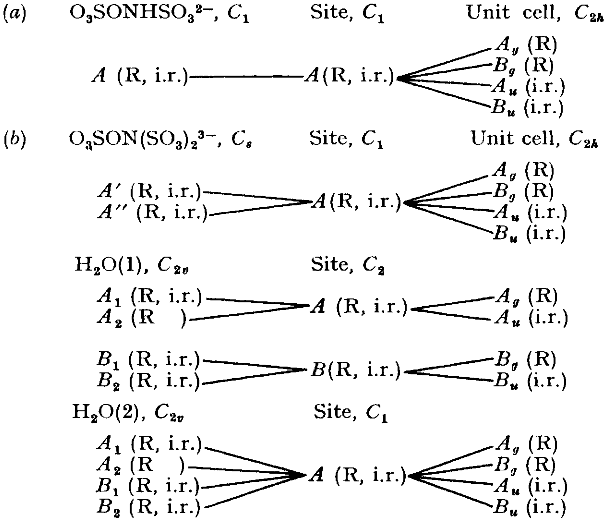
(*a*)	Γ(internal modes)	$27\,A_g + 27\,B_g + 27\,A_u + 27\,B_u$
	Γ(rotatory modes)	$3\,A_g + 3\,B_g + 3\,A_u + 3\,B_u$
	Γ(translatory modes)	$9\,A_g + 9\,B_g + 8\,A_u + 7\,B_u$
(*b*)	Γ[internal $OS_3ON(SO_3)_2^{3-}$ modes]	$36\,A_g + 36\,B_g + 36\,A_u + 36\,B_u$
	Γ(internal H_2O modes)	$5\,A_g + 4\,B_g + 5\,A_u + 4\,B_u$
	Γ(rotatory modes)	$7\,A_g + 8\,B_g + 7\,A_u + 8\,B_u$
	Γ(translatory modes)	$16\,A_g + 17\,B_g + 15\,A_u + 15\,B_u$

N–H Modes. The N–H stretching-mode assignment for $K_2[O_3SONHSO_3]$ is straightforward [$\nu(H)/\nu(D) = 1.35$]. The 1 433 cm^{-1} band in the aqueous solution i.r. spectrum is assigned to the NHS deformation on the basis of its isotopic (D) frequency ratio (1.41) and by analogy with the frequency of the substantially HNS bending mode of hydroxylamine-*N*-sulphonate, $K[HONHSO_3]$ (1 450 cm^{-1}).[19] These assignments are in agreement with those reported.[1] Bands at *ca.* 1 060 cm^{-1} in the polycrystalline spectrum which shift to *ca.* 820 cm^{-1} on deuteriation [$\nu(H)/\nu(D) = 1.30$] can then be assigned to the HNO deformation. The i.r. band (1 061 cm^{-1}) assigned to this mode was attributed to S–O stretching.[1]

Skeletal stretching modes. In the aqueous solution Raman spectrum of the trisulphonate, four bands are observed in the 700—1 000 cm^{-1} region which may only be ascribed to the skeletal stretching modes, ν(N–O) (A'), ν[S–O(N)] (A'), ν(N–S) (A'), and ν(N–S) (A''). Three of these bands (930, 757, and 708 cm^{-1}) are definitely polarized and hence the feature of uncertain polarization at 820 cm^{-1} may confidently be assigned to the antisymmetric N–S stretch (A''). Both A_u and B_u components are observed in the polycrystalline i.r. spectrum and a frequency shift of 25 cm^{-1} is observed on ^{15}N substitution. The 757 cm^{-1} band is assigned to the symmetric N–S stretch (A'), which is expected to occur at a lower frequency than the antisymmetric mode [*cf.* $N(SO_3)_2^{3-}$ [16]]. The 708 cm^{-1} band, which appears as a doublet in the polycrystalline i.r. spectrum has a counterpart in the i.r. spectrum of $[NH_3][OSO_3]$ (712 cm^{-1})[1] and is assigned to S–O(N) stretching by analogy with the assignment made for the S–O(S) stretching modes of disulphate, $S_2O_7^{2-}$ (ν_{sym} 730, ν_{asym} 790 cm^{-1}).[20] The S–O(S) bond length of $K_2[S_2O_7]$ [1.645(5) Å][21] is similar to that found for $K_3[O_3SON(SO_3)_2]\cdot1.5H_2O$ [1.644(2) Å][2] and $K_2[O_3SONHSO_3]$ [1.632(3) Å]. Therefore, the 930 cm^{-1} band, which splits into two components in the poly-

TABLE 7

Correlation schemes for (*a*) $K_2[O_3SONHSO_3]$ and (*b*) $K_3[O_3SON(SO_3)_2]\cdot1.5H_2O$



crystalline Raman spectrum (A_g, B_g), is assigned to the N–O stretch. This assignment is supported by a shift of 17 cm^{-1} on ^{15}N substitution.

Bands in the 700—1 000 cm^{-1} region of the disulphonate spectrum are assigned by analogy with those discussed above. The S–O(N) stretch, which appears as a doublet at 732—742 cm^{-1} (A_u, B_u) in the i.r. spectrum of the solid, shifts by 8—9 cm^{-1} on ^{15}N substitution. On deuteriation the shift is greater (*ca.* 17 cm^{-1}), probably because of coupling with the DNO deformation. The N–S stretch, which splits into two components (792—810 cm^{-1}) (A_g, B_g) in the polycrystalline Raman spectrum, shifts by 6 cm^{-1} on ^{15}N substitution. The skeletal stretching mode assignments are in agreement with those proposed [1] although these workers did not assign symmetry species to any vibrations.

S–O (*Sulphonate*) *stretching modes*. The $O_3SON(SO_3)_2^{3-}$ ion may, for the purpose of the following discussion, be considered to be comprised of a disulphonate [$-N(SO_3)_2$] and a monosulphonate ($-OSO_3$) fragment. Two polarized bands (1 062 and 1 091 cm^{-1}) are observed in the S–O stretching region for this species and are accordingly assigned to A' modes. Also, the very weak band at 1 043 cm^{-1} and the intense band at 1 046 cm^{-1} in the Raman and i.r. spectra respectively of the solid may be assigned to an A' mode since all S–O stretches below 1 100 cm^{-1} in the disulphonate $N(SO_3)_2^{3-}$ (C_{2v}) [16] and the monosulphonate $NH_2SO_3^-$ (C_s) [22] are totally symmetric. The remaining six S–O stretches of $O_3SON(SO_3)_2^{3-}$ ($2A' + 4A''$) are crowded together in the 1 200—1 300 cm^{-1} region and hence no distinction can be made between the polarized and depolarized components in the aqueous solution spectrum. However, the six modes can be distinguished in the polycrystalline spectrum and the

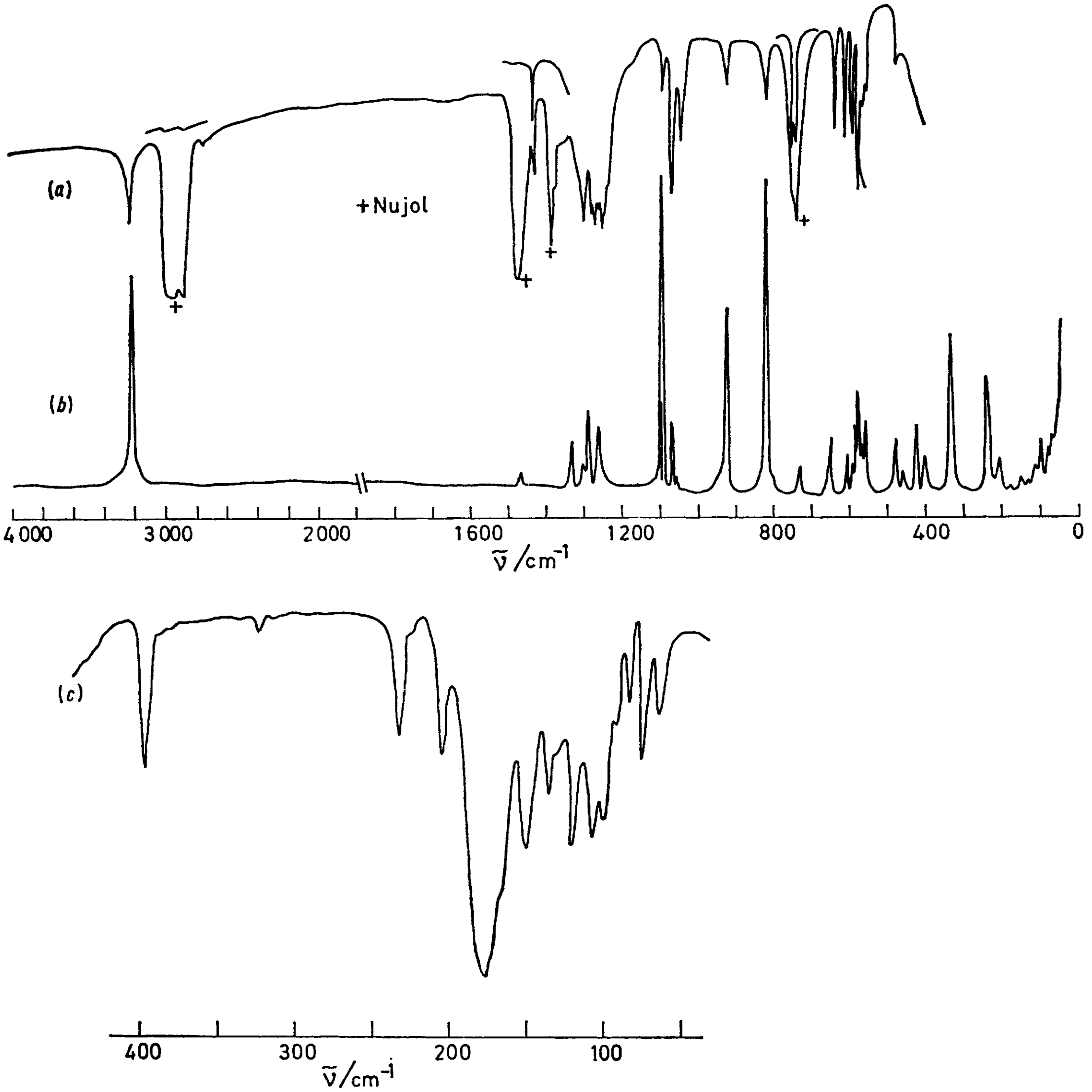


FIGURE 4 Infrared (400—4 000 cm^{-1}) (*a*), Raman (*b*), and far-i.r. (*c*) spectra of $K_3[O_3SONHSO_3]$ at 77 K

two at lowest frequency are tentatively assigned to the *A'* modes. One of the latter gives a doublet in the i.r. and the mode of highest frequency gives doublets in both the i.r. and Raman. The assignment of the bands to the six S–O stretches of $K_2[O_3SONHSO_3]$ is straightforward. In the polycrystalline spectrum, two of these give doublets in the i.r. and two give doublets in both the i.r. and Raman. For both species, all bands in the 1 000—1 300 cm^{-1} region have been assigned to S–O stretches.[1]

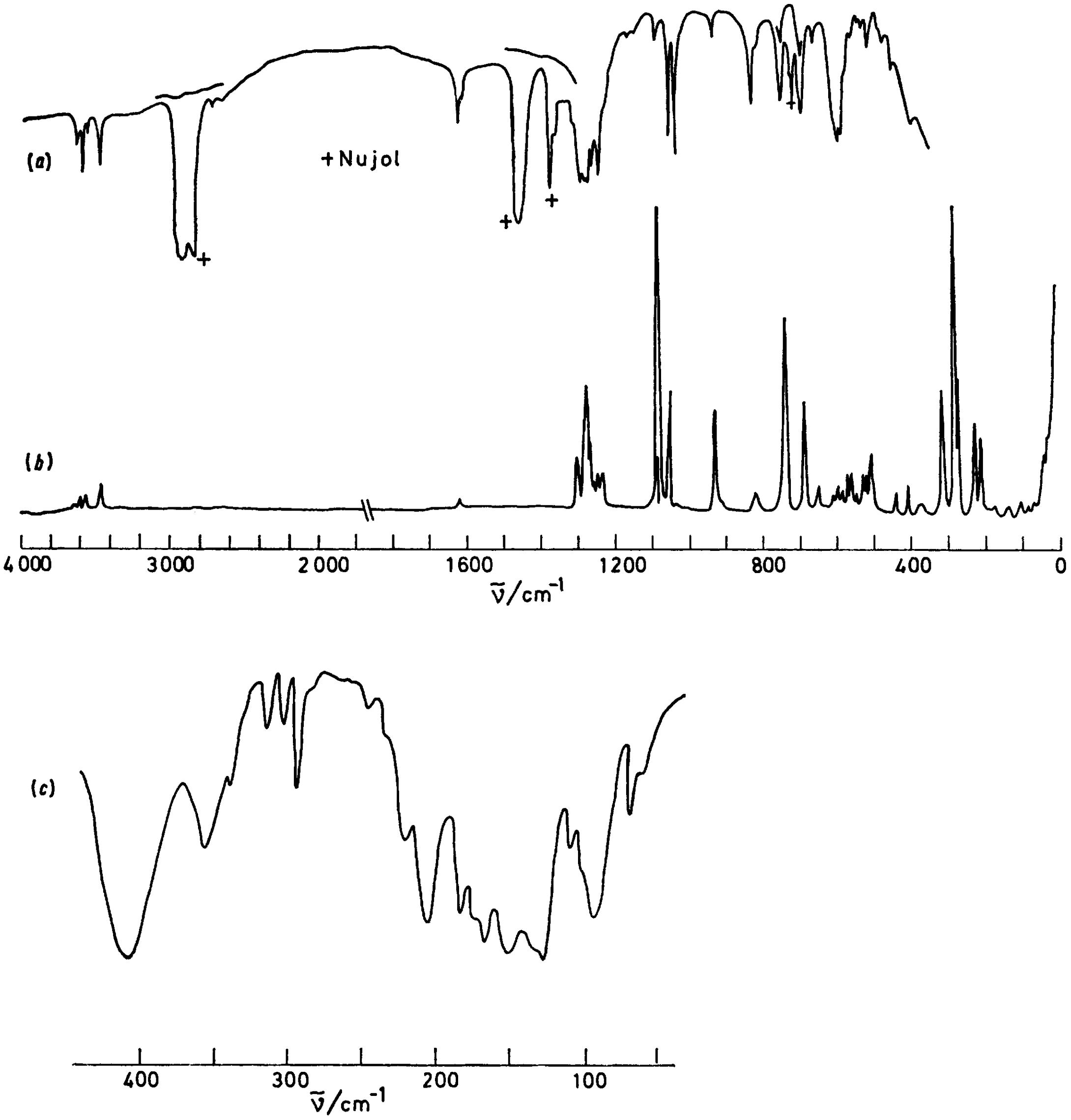


FIGURE 5 Infrared (400—4 000 cm^{-1}) (*a*), Raman (*b*), and far-i.r. (*c*) spectra of $K_3[O_3SON(SO_3)_2]\cdot 1.5H_2O$ at 77 K

Other modes of the anionic species. The SO_3 and skeletal bending and the SO_3 rocking modes are located below 700 cm^{-1}. Although considerable vibrational coupling between these vibrations is expected, modes having predominantly SO_3 bending character probably occur at higher frequencies than predominantly SO_3 rocking modes [*cf.* $NH_2SO_3^-$ (C_s): $\delta(SO_3)$ 586 (*A'*), 599 (*A''*), 504 cm^{-1} (*A'*); $\rho(SO_3)$ 403 (*A''*), 363 cm^{-1} (*A'*)].[22] Also, modes involving mainly skeletal deformations are expected to occur below those involving mainly SO_3 group motion, as in the case of the stretching modes. Aqueous solution polarization data could be obtained for less than half of the modes below 700 cm^{-1} for both species and hence some bands are tentatively assigned to particular symmetry species by analogy with the spectrum of $N(SO_3)_2^{3-}$.[16]

In the 450—700 cm^{-1} region of the polycrystalline trisulphonate spectrum, bands ascribable to the full complement of nine SO_3 deformations are observed. Three of these can be assigned symmetry species on the basis of their polarizations [522 (*A'*), 545 (*A''*), 594 (*A''*)]. The 522 cm^{-1} band gives doublets in both the i.r. and Raman

TABLE 8

Observed frequencies and assignments for the $O_3SONHSO_3^{2-}$, $O_3SONDSO_3^{2-}$, and $O_3SON(SO_3)_2^{3-}$ ions, and polycrystalline $K_2[O_3SONHSO_3]$ and $K_3[O_3SON(SO_3)_2]\cdot 1.5H_2O$ and their ^{15}N and ^2H derivatives at 77 K (p = polarized, dp = depolarized)

0.3 mol dm^{-3} $O_3SONHSO_3^{2-}$ Raman (and i.r.)	0.3 mol dm^{-3} $O_3SONDSO_3^{2-}$ Raman (and i.r.)	$K_2[O_3SONHSO_3]$				0.6 mol dm^{-3} $O_3SON(SO_3)_2^{3-}$ Raman (and i.r.)	$K_3[O_3SON(SO_3)_2]\cdot 1.5H_2O$				Assignment
		Raman		I.r.			Raman		I.r.		
		$^{14}N(^{15}N)$ [a]	^2H	$^{14}N(^{15}N)$ [a]	^2H		$^{14}N(^{15}N)$ [a]	^2H	$^{14}N(^{15}N)$ [a]	^2H	lattice modes
			41w								
			52w							55 (sh)	
			61w				57vw	55vw	63 (sh)	62 (sh)	
		70w	71w	66w	66w		66w	66w	69w	67w	
		81w	83w	77w	78w						
				86w	86w						
		96w	96w	94w	94w		91vw		91m	92m	
		105 (sh)	108w	102w	102w				99 (sh)	99 (sh)	
				110w	109w		110vw		108w	107w	
				122w	122w				126m	126m	
		129vw	129vw	132 (sh)	133 (sh)		133w	131w	131 (sh)	132 (sh)	
			144 (sh)	138w	138w						
		148w	149w	152w	151w				149m	150m	
		171vw	170vw	168 (sh)			161w	165w	165m	163m	
				179m	176m,br				171 (sh)	169 (sh)	
									181m	181m	$\delta(NS_2)(A')$
		205w	205w	206w	205w		200w	197vw	205m	204m	$\delta(SNO)(A'')$
							220 (sh)		220w	216 (sh)	$\rho(SO_3)(A'')$
		231m	231m	234w	233w	220m,p	237m	237w	232 (sh)	232 (sh)	$\delta(NOS)\ (A')$
							252m	253w	246vw	246vw	$\delta(SNO)\ (A')$
										275w	$D_2O(1)$ rock (B_2)
						298m,p	296m	297m	286 (sh)	293w	$\rho(SO_3)\ (A')$
									294w		
										300m	$D_2O(2)$ rock (B_2)
324w,p	320w,p	328s	329m	325vw	326vw		306s	306s	304w	304 (sh)	$\rho(SO_3)\ (A')$
							310 (sh)	311 (sh)	315w	317w	
		393w	371w	397w	376w	322w,dp	339m	339w	339w	339 (sh)	$\rho(SO_3)\ (A'')$
									355w		$H_2O(1)$ rock (B_2)
										348 (sh)	$HDO(2)$ rock (A')
										357m	$D_2O(1)$ wag (B_1)
							399w,br		407w,br	407w	$H_2O(2)$ rock (B_2)
418w,p		418m	417m				430w	430w			$\rho(SO_3)$ (A' and A'')
		471m	468m	471w	466w						
								ca. 450w, br		440w	$D_2O(2)$ wag (B_1)
							461w	466w	460w	461w	$\delta(SO_3)\ (A')$
									486w	486w	$H_2O(1)$ wag (B_1)
						522w, p	527w	526w	527w	527w	$\delta(SO_3)\ (A')$
							539w	538w	541w	537w	
553w,p	557w,p	549m	542m	542m	543w	545,wdp	549w	552w	549vw	554w	$\delta(SO_3)\ (A'')$
		557 (sh)	550m	558w	554m						
		559w	556w				565w	565w	569w	570 (sh)	$\delta(SO_3)\ (A')$
		568m	564m	568s	567s						
580 (sh), p		577m	577m				580w	581w	583 (sh)	581 (sh)	$\delta(SO_3)\ (A'')$
		584w	584w	586m	586m	594w,dp	589w	589w	594m	592s	$\delta(SO_3)\ (A'')$
		599w	598m	606m	603m		604w	601w	603m	601s	$\delta(SO_3)\ (A'')$
							617w	615w	610 (sh)	609 (sh)	
636w,p	635w,p	641w	638m	632m	630m		622w		620 (sh)	621 (sh)	$\delta(SO_3)\ (A')$
		643 (sh)	640 (sh)								
							671w (665w)	671w	670w (665w)	670w	$\delta(SO_3)\ (A')$
	(707m)	720w (712w)	703w	732s (723s)	713s	708m,p	708m	708m	702m	702m	$\nu(S{-}O)(N)\ (A')$
									708(sh)	707 (sh)	
				742s (733s)	733s						
808m,p	805m,p	792 (sh)	801 (sh)			757m,p	758s	757s	759m	758m	$\nu(N{-}S)\ (A')$
		810s (804s)	808s	809m (803m)	807w						
			802m		818w						$\delta(DNO)$
						820 (sh), dp?			822 (sh)	821 (sh)	$\nu(N{-}S)\ (A'')$
							840w (815w)	840w	835m (810m)	834m	
925w,p	943w,p (943w)	908s (899m)	940m	913w (901w)	946m	930w,p	929 (sh)				$\nu(N{-}O)\ (A')$
							940m (923m)	940m	942w (925w)	942w	
	1 036 (sh), p (1 038m)	1 044vw (1 035vw)	1 040vw	1 037m (1 032m)	1 040m	(1 042s)	1 043vw	1 045vw	1 046s	1 047s	$\nu(S{-}O)\ (A')$
1 052 (sh), p (1 052s)		1 053w		1 061s	1 059m [b]						$\delta(HNO)$
						1 062 (sh), p	1 063m	1 063m	1 063s	1 064s	$\nu(S{-}O)\ (A')$
1 076s,p (1 079w)	1 074s,p (1 073m)	1 079vs	1 070vs	1 085w	1 077s	1 091vs,p	1 095vs	1 096vs	1 098w	1 099w	$\nu(S{-}O)\ (A')$
	(1 084w)		1 091s		1 085s						$\delta(DNS)$
									1 160w	1 165 (sh)	565 + 594 (= 1 159)
									1 174w	1 179 (sh)	580 + 594 (= 1 174)
								1 197w		1 201w	$\delta(DOD)\ (A')$ [$H_2O(1)$ and $H_2O(2)$]
[1 241 (sh)]		1 230 (sh)	1 227vw	1 230 (sh)	1 231 (sh)	1 215 (sh), p/dp			1 225(sh)		$\nu(S{-}O)\ (A')$
		1 243m	1 241m	1 238 (sh)	1 241 (sh)		1 244w	1 243w	1 235 (sh)	1 237 (sh)	
1 250w,br,p		1 245 (sh)	1 245m	1 245s	1 245s		1 258w	1 257w	1 251s	1 253s	$\nu(S{-}O)\ (A')$
		1 259m	1 270m	1 252s	1 252s						
(1 265s)				1 263s	1 267s		1 266w	1 270w	1 268s	1 269s	$\nu(S{-}O)\ (A'')$
	[c]	1 279w	1 277w	1 274s	1 276s						
						1 275w,p/dp	1 276m	1 276w	1 279s	1 280s	$\nu(S{-}O)\ (A'')$
						(1 285s)	1 286m	1 284m	1 286s	1 291s	$\nu(S{-}O)\ (A'')$
				1 292s	1 298s		1 291m	1 291w	1 299s	1 300s	$\nu(S{-}O)\ (A'')$
		1 313m	1 317m	1 306 (sh)			1 309w	1 308w	1 319 (sh)	1 323 (sh)	

TABLE 8 (*Continued*)

0.3 mol dm^{-3} $O_3SONHSO_3{}^{2-}$ Raman (and i.r.)	0.3 mol dm^{-3} $O_3SONDSO_3{}^{2-}$ Raman (and i.r.)	$K_2[O_3SONHSO_3]$				0.6 mol dm^{-3} $O_3SON(SO_3)_2{}^{3-}$ Raman (and i.r.)	$K_3[O_3SON(SO_3)_2]\cdot1.5H_2O$				Assignment
		Raman		I.r.			Raman		I.r.		
		$^{14}N(^{15}N)$ [a]	^2H	$^{14}N(^{15}N)$ [a]	^2H		$^{14}N(^{15}N)$ [a]	^2H	$^{14}N(^{15}N)$ [a]	^2H	lattice modes
(1 433w,br)		1 447w		1 421m	1 425w [b]						δ(HNS)
										1 426w	δ(HOD) (*A′*)
										1 441w	δ(HOD) (*A′*)
										1 455 (sh)	δ(HOD) (*A′*)
							1 625w		1 623 (sh)	1 625 (sh)	δ(HOH) (A_1) [$H_2O(1)$]
									1 631m	1 633w	δ(HOH) (A_1) [$H_2O(2)$]
			2 382s		2 391m						ν(N–D)
								2 559m		2 560w	ν(O–D) (A_1) [$D_2O(2)$]
										2 583w	ν(O–D) (*A′*) (HDO)
								2 603m		2 613w	ν(O–D) (B_2) [$D_2O(2)$]
								2 642w		2 644w	ν(O–D) (*A′*) (HDO)
										2 653w	ν(O–D) (*A′*) (HDO)
								2 665w		2 669w	ν(O–D) (A_1) [$D_2O(1)$]
								2 696w		2 702w	ν(O–D) (B_2) [$D_2O(1)$]
		3 206s (3 200s)	3 212vw [b]	3 213m	3 217w [b]						ν(N–H)
							3 482w		3 488m	3 489w	[d] ν(O–H) (A_1) [$H_2O(2)$]
										3 499 (sh)	
							3 561w		3 569w	3 567w	ν(O–H) (B_2) [$H_2O(2)$]
							3 592w		3 598m	3 591 (sh)	ν(O–H) (A_1) [$H_2O(1)$]
										3 600w	
							3 620w		3 633w	3 634w	ν(O–H) (B_2) [$H_2O(1)$]

[a] ^{15}N Frequencies given where they differ by >4 cm^{-1}. [b] Isotopically dilute $O_3SONHSO_3{}^{2-}$ species. [c] Region masked by δ(DOD) of solvent. [d] Contains contribution from ν(O–H) (*A′*) (HDO).

spectra of the solid. This band, and those at 461 and 671 cm^{-1} in the Raman spectrum of the solid, correspond to $N(SO_3)_2{}^{3-}$ bands at 529 (A_1), 456 (B_1), and 687 cm^{-1} (A_1) respectively * and therefore may be assigned to symmetric (*A′*) modes of the disulphonate fragment. The remaining two symmetric modes arise from the $-(O)SO_3$ group. Bands at 614, 574, and 567 cm^{-1} in the i.r. spectrum of $[NH_3][OSO_3]$ (C_s) have been ascribed to SO_3 deformations but symmetry species have not been assigned.[1] However, the $O_3SON(SO_3)_2{}^{3-}$ bands at 622 and 565 cm^{-1} in the Raman spectrum of the solid are tentatively given to the *A′* modes. The frequencies of bands assigned to *A″* modes (545, *ca.* 580, 594, *ca.* 610 cm^{-1}) are similar to other $\delta(SO_3)$ modes of $N(SO_3)_2{}^{3-}$ [545 (B_2), *ca.* 580 (A_2), 610 cm^{-1} (B_2)] and $[NH_3][OSO_3]$ (574 cm^{-1}). The highest frequency *A″* mode gave doublets in both the i.r. and Raman spectrum of the solid. In all, nine Raman and six i.r. features belonging to six SO_3 deformations were observed in the spectrum of polycrystalline $K_2[O_3SONHSO_3]$.

The Raman band at 430 cm^{-1} in the trisulphonate spectrum has a counterpart in the $[NH_3][OSO_3]$ spectrum (442 cm^{-1}) and is given to both the *A′* and *A″* rocking modes of the $-(O)SO_3$ group. The assignment of the polarized band at 298 cm^{-1} and the depolarized band at 332 cm^{-1} to 2*A′* and *A″* SO_3 rocking modes respectively is straightforward. The former gives a doublet and a singlet in the Raman and two doublets in the i.r. spectrum of the solid, while the latter gives a doublet in the Raman. Assignments made for the remaining *A″* rocking mode of the trisulphonate, the four rocking modes of the disulphonate, and the skeletal deformation modes of both species are based mainly on a comparison of the spectra. The assignment of the i.r. band at 181 cm^{-1} to the NS_2 deformation of the trisulphonate is consistent with the comparable mode of $N(SO_3)_2{}^{3-}$ (190 cm^{-1}). No assignment is made for the SO_3 or OSO_3 torsional modes, which are expected to occur below 50 cm^{-1}. All bands below 700 cm^{-1} have been assigned to SO_3 deformations.[1]

Internal water modes of $K_3[O_3SON(SO_3)_2]\cdot1.5H_2O$. Bands are assigned to the internal modes of H_2O on the basis of their isotopic (D) frequency shifts. In the O–H stretching region, four Raman and four i.r. bands are observed. The two bands of lower frequency in each spectrum are tentatively given to $H_2O(2)$ modes (A_1 and B_2) on the basis of the greater involvement in hydrogen bonding than $H_2O(1)$.[2] The hydrogen atoms of the latter, related by a crystallographic two-fold axis through the molecule, are involved in weak bifurcated hydrogen bonds with $H-O(SO_3)$ distances of 2.30 and 2.37 Å. For $H_2O(2)$ however, one hydrogen atom forms a normal hydrogen bond [$H-O(SO_3)$ distance 2.02 Å] while the other is involved in a very weak bifurcated bond [$H-O(SO_3)$ distances 2.49 and 2.46 Å].

The two i.r. features observed in the HOH deformation region persist in the $K_3[O_3SON(SO_3)_2]\cdot1.5D_2O$ spectrum where the concentration of the H_2O species is estimated to be 4 mol %. Significant correlation coupling cannot occur at this concentration and hence these bands may be ascribed to different types of H_2O molecules. The

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* A_1 and B_1 modes become *A′*, and A_2 and B_2 modes become *A″* when the symmetry of $N(SO_3)_2{}^{3-}$ (C_{2v}) is lowered to C_s. The representation for $\delta(SO_3)$ of $N(SO_3)_2{}^{3-}$ is $2A_1 + A_2 + B_1 + 2B_2$.

higher frequency component is assigned to $H_2O(2)$ on the basis of its greater involvement in hydrogen bonding.

In the O–D stretching region, five Raman and seven i.r. bands are observed. However, owing to incomplete deuteriation, some of these are probably due to the HDO species. Therefore, the assignment of bands in this region is assisted by the changes which occur for samples having varying degrees of deuteriation.

The i.r. spectra of partially deuteriated samples of $K_3[O_3SON(SO_3)_2]\cdot1.5H_2O$ at 77 K in the O–D stretching region are shown in Figure 6. In the spectrum of the least deuteriated sample (*a*) there are three features (2 650, 2 641, and 2 580 cm^{-1}) which can only be ascribed to the isotopically dilute HDO species (7.7 mol %). The D_2O concentration in this sample is 0.1 mol %. The presence of three bands is indicative of three types of HDO molecules in this sample and hence three types of hydrogen atoms in $K_3[O_3SON(SO_3)_2]\cdot1.5H_2O$. With further deuteriation [(*b*) and (*c*)], four new bands are observed. These bands increase in intensity relative to those of HDO and are accordingly assigned to D_2O modes.

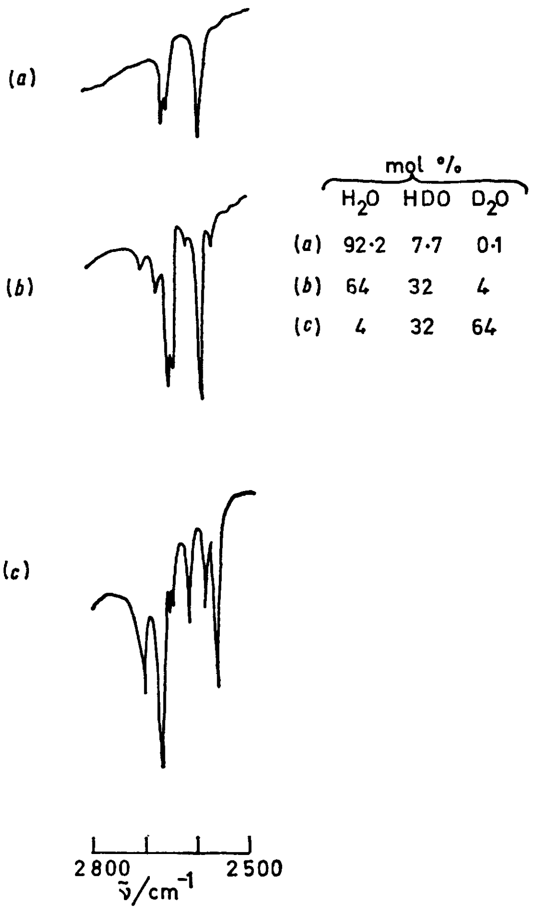

FIGURE 6 Infrared spectra (KBr discs) of partially deuteriated $K_3[O_3SON(SO_3)_2]\cdot1.5H_2O$ at 77 K in the O–D stretching region

Lattice modes. 16 lattice vibrations of $K_3[O_3SON(SO_3)_2]\cdot1.5H_2O$ are found below 200 cm^{-1}. Some of the lower lying modes may have some SO_3 or OSO_3 torsional character. Above 200 cm^{-1}, the assignment of i.r. bands to the wagging (B_1) (486 cm^{-1}) and rocking modes (B_2) (355 cm^{-1}) of $H_2O(1)$ and to the rocking mode (407 cm^{-1}) of the more strongly bound $H_2O(2)$ molecule is based on their isotopic (D) frequency ratios, 1.36, 1.29, and 1.36 respectively. The $H_2O(2)$ rocking mode is also observed in the Raman spectrum. The $H_2O(2)$ wagging mode is not observed, probably because of masking by bands in the 550—600 cm^{-1} region. However, the corresponding D_2O mode is observed in both the i.r. (440 cm^{-1}) and Raman (*ca.* 450 cm^{-1}) spectra. The twisting modes (A_2) are not observed. The shoulder at 348 cm^{-1} in the i.r. spectrum of the deuteriated sample is assigned to the HDO(2) rocking mode (A') since it is approximately midway between those of $H_2O(2)$ and $D_2O(2)$. Of the 93 lattice modes predicted for $K_3[O_3SON(SO_3)_2]\cdot1.5H_2O$, 20 are observed. For $K_2[O_3SONHSO_3]$, 19 of the predicted 45 lattice modes are observed.

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