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Crystal Structure, and the Infrared and Raman Spectra, of Tripotassium Methanetrisulphonate Hydrate, $K_3[CH(SO_3)_3]$ ·H₂O

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The crystal structure of the title compound has been determined using three-dimensional X-ray diffraction data, from 839 reflections; crystals are orthorhombic, space group $P2_12_12_1$, with unit-cell dimensions a = 9.405(1), b = 9.405(1), c = 12.321(1) Å, Z = 4. The structure has been solved using direct methods and refined by fullmatrix least squares to R 0.045. The S-C-S angles (*ca.* 113°) indicate an expansion from tetrahedral stereochemistry and the S-C bond lengths (*ca.* 1.81 Å) are appreciably longer than those for K₂[CH₂(SO₃)₂] (1.77 Å) and Ca[CH₃SO₃]₂ (1.75 Å). The i.r. ($4 000-50 \text{ cm}^{-1}$) and Raman spectra of K₃[CH(SO₃)₃]·H₂O and K₃[CD-(SO₃)₃]·D₂O at 77 K are reported and interpreted according to the crystal structure. To assist with the assignment, spectra of the anhydrous salt, K₃[CH(SO₃)₃], and of aqueous solutions of the soluble lithium salts, have also been recorded. The SO₃ groups show their characteristic group frequencies: v_{sym} (C-S) and v_{asym} (C-S) are assigned to 762 and 820 cm⁻¹, respectively; δ_{synn} (CS₃) and δ_{asym} (CS₃) to 170 and *ca.* 210 cm⁻¹, respectively. I.r. spectra of samples containing the isotopically dilute HDO species confirm the presence of two types of hydrogen bond per water molecule.

As part of an 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 tripotassium methanetrisulphonate hydrate, $K_3[CH(SO_3)_3] \cdot H_2O$ and $K_3[CD(SO_3)_3] \cdot D_2O$ at liquid nitrogen temperature. No vibrational data on the methanetrisulphonate ion have been published, although the spectrum of the methylsulphonate species, $[CH_3SO_3]^-$, has been reported.^{1,2} In order to have an adequate prediction of the spectra, the crystal structure of K₃[CH(SO₃)₃]·H₂O was determined. To assist with the internal mode assignment for $[CH(SO_3)_3]^{3-}$ and $[CD(SO_3)_3]^{3-}$, the aqueous solution spectra, including qualitative Raman polarization data of the soluble lithium salts, have been obtained. The lattice-water assignment is assisted by comparison with the spectra of the anhydrous salt $K_3[CH(SO_3)_3]$, and of partially deuteriated $K_3[CH(SO_3)_3]$ · H_2O samples.

EXPERIMENTAL

Preparations.---K₃[CH(SO₃)₃]·H₂O was prepared by the method described by Backer³ (Found: C, 3.0; K, 30.1; H₂O, 4.7. Calc. for CH₃K₃O₁₀S₃: C, 3.1; K, 30.2; H_2O , 4.6%). Anhydrous $K_3[CH(SO_3)_3]$ was obtained by heating $K_3[CH(SO_3)_3] \cdot H_2O$ at 410 K at 1 atm for 12 h (Found: C, 3.4; K, 31.1. Calc. for CHK_aO₉S_a: C, 3.2; K, 31.7%). $Li_3[CH(SO_3)_3]$ ·4H₂O was obtained by decomposing a suspension of the insoluble barium salt, Ba₃[CH-(SO₃)₃]₂·9H₂O^{4,5} {obtained by addition of BaCl₂·2H₂O solution to a boiling solution of K₃[CH(SO₃)₃]·H₂O} with lithium sulphate. The resulting precipitate of Ba[SO4] was filtered off and the volume of the filtrate reduced until crystals of $Li_3[CH(SO_3)_3]$ ·4H₂O ⁵ were deposited (Found: C, 3.7. Calc. for $CH_{9}Li_{3}O_{13}S_{3}$: C, 3.5%). $K_{3}[CD(SO_{3})_{3}]\cdot D_{2}O$ was prepared by several recrystallizations of $K_3[CH(SO_3)_3]$. H₂O from the minimum quantity of boiling D₂O. Exchange of the methane hydrogen was almost complete. Exchange of the water hydrogen atoms was estimated from i.r. spectra to be ca. 85% (Found: C, 3.1; K, 30.0; D₂O, 5.1. Calc. for $CD_3K_3O_{10}S_3$: C, 3.1; K, 30.0; D_2O , 5.1%). $Li_3[CD(SO_3)_3] \cdot 4D_2O$ was prepared by the same procedure.

Partially deuteriated samples. These were prepared by the procedure previously described,⁶ starting with 0.2 g of $K_3[CH(SO_3)_3]$ ·H₂O and recrystallizing from neutral H₂O-D₂O mixtures. The approximate concentrations of H₂O, HDO, and D₂O in the deuteriated samples were calculated by the method described by Seidl and Knop.⁷

Crystal Data.—CH₃K₃O₁₀S₃, M = 388.5, Orthorhombic, a = 9.405(1), b = 9.405(1), c = 12.321(1) Å, U = 1.090.0Å³, $D_m = 2.40$ g cm⁻³ (by flotation), Z = 4, $D_c = 2.38$ g cm⁻³, F(000) = 776, space group $P2_12_12_1$ (D_2^4 , No. 19); Mo- K_{α} radiation, $\lambda = 0.710$ 7 Å, μ (Mo- K_{α}) = 18.16 cm⁻¹.

Structure Determination .--- Crystal and intensity data were obtained from a single crystal mounted about the b axis on a Hilger and Watts four-circle diffractometer. A total of 839 unique reflections with $F > 2.5\sigma(F)$ were considered observed out of 995, for an octant of the limiting sphere up to $\theta = 22^{\circ}$. Absorption corrections were not applied. The structure was solved using the TANG-non-centrosymmetric direct-methods approach incorporated in the X-ray crystallographic program set SHELX.⁸ The oxygen atoms were located from the first weighted difference-Fourier. The methane hydrogen atom was found in a later difference map, and given the isotropic temperature factor of C(1) and included in the calculation, but its parameters were not refined. Full-matrix least-squares refinement, with anisotropic temperature factors for potassium and sulphur only, reduced R from an initial value of 0.42to 0.045; unit weights were used. A final difference-Fourier revealed no peaks greater than $0.3 \text{ e} \text{ Å}^{-3}$. The two hydrogens attached to the water oxygen could not be located from the difference map. Atomic parameters are listed in Table 1. Neutral element scattering factors were used,⁹ and correction was applied for anomalous dispersion.¹⁰ Observed and calculated structure amplitudes and atomic thermal parameters are listed in Supplementary Publication, No. SUP 22579 (7 pp.).†

I.r. Spectra.—I.r. spectra in the 4 000—400 cm⁻¹ region were recorded on a Perkin-Elmer model 225 spectrophotometer and calibrated with polystyrene film. Solution samples were examined as thin films between KRS5 plates; solid samples were examined as Nujol mulls between CsI

† See Notices to Authors No. 7, J.C.S. Dalton, 1979, Index issue.

TABLE 1

Atomic co-ordinates $(\times 10^4)$ and isotropic thermal parameters $(\times 10^3)$ with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	$U(\text{\AA}^2)$
K(1)	7 504(3)	1616(3)	$6\ 691(2)$	
$\mathbf{K}(2)$	9 842(3)	$5\ 028(4)$	5632(2)	
$\mathbf{K}(3)$	2895(4)	2 354(4)	7 134(3)	
S(1)	-842(3)	6 159(4)	$10\ 013(3)$	
S(2)	1264(4)	3776(4)	10.383(3)	
S(3)	-417(3)	3884(4)	8 287(3)	
O(11)	-2395(9)	$6\ 200(10)$	9 925(7)	21(2)
O(12)	-353(10)	6 474(10)	$11\ 133(7)$	21(2)
O(13)	-157(9)	7 042(10)	9 202(7)	15(2)
O(21)	2 253(10)	4 933(11)	10 257(8)	24(2)
O(22)	842(11)	3 537(12)	11 513(8)	31(3)
O(23)	1 669(10)	2 468(12)	9 853(9)	30(3)
O(31)	952(9)	4 311(10)	7 828(7)	17(2)
O(32)	-639(9)	2 346(10)	8 288(8)	17(2)
O(33)	-1605(10)	4 648(10)	7 796(8)	22(4)
O(H)	40(13)	326(14)	1 707(10)	49(3)
C(1)	-402(13)	4 345(13)	9 711(9)	9(4)
H(1)	1 154	3986	9 789	9

plates, and as KBr discs. The cryostat used was of conventional design and fitted with KBr windows. Spectra in the region 400—50 cm⁻¹ were run on a Beckman-RIIC IR-720 far-infrared spectrophotometer. Samples were examined as Nujol mulls between polythene plates mounted in a Beckman-RIIC VLT-2 variable-temperature unit. As a check on possible phase changes on cooling to liquid nitrogen temperature, the i.r. and Raman spectra of K_3 [CH-(SO)₃)₃]·H₂O and K_3 [CH(SO₃)₃] were also recorded at ambient temperature. Apart from the general sharpening of bands and improved resolution at 77 K, there were no significant differences between the spectra.

Raman Spectra.—Raman spectra were recorded on a Cary model 82 laser spectrophotometer. An argon-krypton laser (Coherent Radiation, model 52 HD) was used to produce the exciting radiation (514.5 nm). Spectra were calibrated by reference to non-coherent discharge lines of the argon-krypton laser. Samples were held in a glass tube (4-mm diameter) mounted vertically to receive the laser beam through the optically flat base. The laser power at the sample was *ca.* 400 mW. The cryostat used was supplied by The Oxford Instrument Co. Ltd. (model CF100). The observed i.r. and Raman frequencies are estimated to be accurate to $\pm 2 \text{ cm}^{-1}$ below 2 000 cm⁻¹ and $\pm 4 \text{ cm}^{-1}$ above 2 000 cm⁻¹.

RESULTS AND DISCUSSION

Crystal Structure.—The CS₃ skeleton of the [CH- $(SO_3)_3$]³⁻ ion (Figure 1) is distorted with all S-C-S angles greater than the tetrahedral angle [Table 2(*a*)]. All S-O bond lengths (mean 1.459 Å) and O-S-O angles (mean 112.7°) are similar to those found in the related compounds K₂[CH₂(SO₃)₂] (1.461 Å, 113.3°),¹¹ Ca[CH₃-SO₃]₂ (1.445 Å, 112.5°),¹² and Cs[CH₃SO₃] (1.47 Å, 112°).¹³ An unusual feature of the structure is that one C-S bond length [1.851(13) Å] is significantly greater than the other two [1.795(13) and 1.807(12) Å].

A comparison of the C-S bond length in $K_3[CH(SO_3)_3]$. H₂O (mean 1.813 Å) with those of $K_2[CH_2(SO_3)_2]$ (1.770 Å) and Ca[CH₃SO₃]₂ (1.754 Å) shows a tendency towards longer C-S bonds with the successive replacement of hydrogen atoms by SO₃ groups, presumably due to repulsion between the latter. This effect is also observed in the case of tris(methylsulphonyl)methane, $CH(CH_3-SO_2)_3$ ¹⁴ and tris(ethylsulphonyl)methane, $CH(C_2H_5-SO_2)_3$,¹⁵ where the lengths of the C-S bonds which involve the methane carbon atoms (1.83 and 1.834 Å, respectively) are considerably greater than those which involve the methyl (1.73 Å) and ethyl (1.785 Å) carbon atoms.



FIGURE 1 Atomic numbering system and structure of an individual $[CH(SO_3)_3]^{3-}$ ion viewed perpendicular to the plane of S(3), C(1), and S(2)

The C-S bond length in $[Cu(CH_3SO_3)_2(H_2O)_4]$ (1.754 Å) ¹⁶ is consistent with this scheme but in Cs $[CH_3SO_3]$ (1.80 Å) it is slightly larger for the uncorrected distance. The

TABLE 2

(a) Interatomic distances (Å) and angles (°) for $[CH(SO_3)_3]^{3-1}$ with estimated standard deviations given in parentheses

(1) Distances			
C(1) - S(1)	1.795(13)	S(2) - O(21)	1.440(11)
C(1) - S(2)	1.851(13)	S(2) - O(22)	1.465(11)
C(1) - S(3)	1.807(12)	S(2) - O(23)	1.444(12)
S(1) - O(11)	1.465(9)	S(3) - O(31)	1.462(9)
S(1) - O(12)	1.484(9)	S(3) - O(32)	1.461(10)
S(1) - O(13)	1.450(10)	S(3)O(33)	1.460(10)
(ii) Angles			
S(1) - C(1) - S(2)	112.2(5)	C(1)-S(3)-O(3	3) 106.9(2)
S(1) - C(1) - S(3)	115.3(5)	O(11) - S(1) - O(1)	(12) 111.9 (2)
S(2) - C(1) - S(3)	111.8(5)	O(11) - S(1) - O(1)	(13) 112.1 (3)
C(1) - S(1) - O(11)	103.9(2)	O(12) - S(1) - O(12)	(13) 112.9 (3)
C(1) - S(1) - O(12)	108.1(3)	O(21) - S(2) - O(21)	(22) 113.2(3)
C(1) - S(1) - O(13)	107.4(3)	O(21) - S(2) - O(2)	(23) 115.1 (3)
C(1) - S(2) - O(21)	106.3(2)	O(22)-S(2)-O	(23) 111.7(3)
C(1) - S(2) - O(22)	103.9(2)	O(31) - S(3) - O(3)	(32) 113.4 (2)
C(1) - S(2) - O(23)	105.5(3)	O(31) - S(3) - O(3)	(33) 112.2 (3)
C(1) - S(3) - O(31)	107.6(2)	O(32)-S(3)-O((33) 112.2(3)
C(1) - S(3) - O(32)	103.8(2)		

(b) Interatomic K–O distances (Å) less than 3.4 Å. Means include only those distances less than 3.1 Å.

	O(11)	O(12)	O(13)	O(21)	O(22)	O(23)
K(1)	2.994	2.791	2.756	2.884	2.713	. ,
$\mathbf{K}(2)$	2.718		2.831	2.771		2.765
$\mathbf{K}(3)$	2.799	2.843	3.070		3.341	
	O(31)	O(32)	O(33)	O(H)	Mean	
$\mathbf{K}(\mathbf{l})$	2.676	2.719		3.010	2.818	
$\mathbf{K}(2)$	2.977	2.662	3.015	2.898	2.830	
$\mathbf{K}(3)$	2.731		2.821		2.853	
			Gra	nd Mean	2.834	



FIGURE 2 Stereoscopic view of the packing of $K_2[CH(SO_3)_3] \cdot H_2O$ in the cell viewed down the c axis

corrected distance is 1.85 Å. The packing of molecules in the unit cell is illustrated in Figure 2. The potassium ions are surrounded by five to eight oxygen atoms from the sulphonate groups or water molecule [Table 2(b)] at distances ranging from 2.662 to 3.070 Å. Intraionic and other short O–O contacts less than 3.2 Å are O(11)– O(33), 3.092; O(12)–O(21), 3.045; O(12)–O(22), 3.019; O(12)–O(H), 2.887; O(13)–O(33), 3.150; O(22)–O(H), 2.886; and O(23)–O(32), 2.906 Å.

Vibrational Investigation.—For an isolated [CH- $(SO_3)_3$]³⁻ ion of C_{3v} symmetry, the 36 normal modes of vibration are distributed among the symmetry species as follows, $8A_1 + 4A_2 + 12E$. The A_1 and E modes are i.r. and Raman active, whereas the A_2 modes are i.r. and Raman inactive. Approximate descriptions of these modes in terms of internal co-ordinate contributions are given in Table 3. Considerable mixing of these motions

is expected in the actual normal modes. In the crystal, all atoms of the $K_3[CH(SO_3)_3]$ · H_2O unit occupy general positions and hence factor-group analysis yields the vibrational representation shown in Table 4 (acoustic modes omitted). The *A* modes are Raman active only, whereas the B_1 , B_2 , and B_3 modes are i.r. and Raman active. The correlation between point, site, and unitcell symmetry species is given in Table 5. The i.r. and Raman spectra of $K_3[CH(SO_3)_3]$ · H_2O at 77 K are shown in Figure 3. The observed frequencies {including those for $K_3[CD(SO_3)_3]$ · D_2O and aqueous (H_2O or D_2O) solutions of $Li_3[CH(SO_3)_3]$ · $4H_2O$ and $Li_3[CD(SO_3)_3]$ · $4D_2O$ } and their assignments are given in Table 6.

The assignment of the polarized Raman bands at 2 952 and 2 210 cm⁻¹ to the C-H and C-D stretches (A_1) , respectively, is straightforward. Correlation field splitting of both modes is observed in the solid-state Raman



FIGURE 3 Vibrational spectra of $K_3[CH(SO_3)_3]$ ·H₂O at 77 K; (a) i.r., 4 000—400 cm⁻¹; (b) Raman, 4 000—20 cm⁻¹; and (c) i.r., 400—50 cm⁻¹ (peaks marked * are due to Nujol)

TABLE 3

Approximate internal co-ordinate contributions to the vibrational modes of $[CH(SO_3)_3]^{3-}(C_{3v})$

C–H stretch	A_1
HCS deformations	E
C–S stretches	$A_1 + E$
CS ₃ deformations	$A_1 + E$
S–O stretches	$2A_1 + A_2 + 3E$
SO ₃ deformations	$2A_1 + A_2 + 3E$
SO ₃ rocks	$A_1 + A_2 + 2E$
SO ₃ torsions	$A_2 + E$

TABLE 4

Vibrational representation	for	\mathbf{K}	3[C	CH	SC) ₃) ₃]•ŀ	₹₂O	
internal [CII/CO] 3=madea)	96 /			D		D		D \	

[{internal [CH(SO ₃) ₃] ³⁻ modes}]	$36 (A + B_1 + B_2 + B_3)$
Γ (internal H ₂ O modes)	$3(A + B_1 + B_2 + B_3)$
Γ(rotatory modes)	$6(A + B_1 + B_2 + B_3)$
r(translatory modes)	$15A + 14B_1 + 14B_2 + 14B_3$



Correlation scheme for K₃[CH(SO₃)₃]·H₂O



spectra where, in both cases, a weak shoulder appears on the low-frequency side of a relatively intense component.

The assignment of the weak, depolarized Raman band at 1 155 cm⁻¹ to antisymmetric (*E*) modes which are mainly HCS bending in character is made on the basis of its observed isotopic frequency ratio, $v_{\rm H}/v_{\rm D}$ (1.22), and by comparison with the frequency of the CH₃ rocking modes of [CH₃SO₃]⁻ (967 cm⁻¹).² These modes appear as doublets in both the i.r. and Raman spectra of the solid, presumably through loss of degeneracy under the influence of the static crystal field. No other features ascribable to the anion above 820 cm⁻¹, apart from the C-H stretching bands, show major isotopic frequency shifts.

In the Raman solution spectrum, five other bands are observed in the region normally ascribed to S-O stretching (1 000—1 300 cm⁻¹), in accordance with predictions. The strong, polarized line at 1 092 cm⁻¹ is attributed to symmetric S-O stretching (cf.² 1 049 cm⁻¹ in [CH₃SO₃]⁻). The weak band of uncertain polarization at 1 030 cm⁻¹ is assigned to antisymmetric (E) S-O stretches since it appears as a doublet in both the i.r. and Raman spectra of the solid. The other band of uncertain polarization (1 240 cm⁻¹) is assigned to an A_1 mode since the correct number of depolarized bands corresponding to the remaining antisymmetric modes (2E) is observed (at 1 202 and 1 258 cm⁻¹). Collectively, the modes in the 1 200—1 300 cm⁻¹ region ($A_1 + 2E$) are split into at least ten components in the solid-state spectrum. No assignment is made for the S-O stretch of A_2 species which obtains activity only through solid-state effects.

The weak, depolarized band at 820 cm⁻¹ and the polarized band at 762 cm⁻¹ in the Raman spectrum of [CH- $(SO_3)_3]^{3-}$ are assigned to the antisymmetric (E) and symmetric (A_1) C-S stretching modes respectively by analogy with the C-S stretch of $[CH_3SO_3]^-$ (784 cm⁻¹).² In the solid, the degeneracy of the antisymmetric modes is lifted by the lower site symmetry to give doublets * in both the i.r. and Raman, with one component of the i.r. doublet being further split by the correlation field. Correlation coupling between symmetric C-S stretching modes is apparent in the Raman spectrum where two features are observed. These assignments are supported by isotropic (deuterium) frequency shifts, ca. 90 (E) and 12 cm⁻¹ (A_1) , respectively. In the Raman solution spectrum of $[CD(SO_3)_3]^{3-}$, the band ascribable to the E modes is masked by the more intense band at 750 cm^{-1} . However, unmasked bands ascribable to the former are apparent in the i.r. (738 cm⁻¹) and Raman spectra (739 cm^{-1}) of the solid.

The SO₃ and CS₃ bending and the SO₃ rocking vibrations are crowded together in the region below 700 cm⁻¹ and hence considerable vibrational coupling between these vibrations is expected. However, it is a reasonable assumption that modes having predominantly SO₃ bending character will generally occur at higher frequencies than those which are predominantly SO₃ rocking. This is consistent with the assignments ² made for the SO₃ bending (528 and 557 cm⁻¹) and rocking modes (347 cm⁻¹) of [CH₃SO₃]⁻. Also, modes having appreciable contributions from bending vibrations of the CS₃ skeleton are expected to occur below those associated mainly with the SO₃ groups, as in the case of their respective stretching frequencies.

On this basis, the three polarized bands observed in this region are assigned to the symmetric (A_1) , SO₃ bending (680 and 522 cm⁻¹), and rocking modes (290 cm⁻¹), and the three depolarized bands to the antisymmetric (E) SO₃ bending modes. The latter show both site and factor-group splitting in the solid-state spectrum. Doublets in the 310-320 and 280-290 cm⁻¹ regions respectively of the solid-state spectrum are assigned to the antisymmetric (E) rocking modes. The weak shoulder at 583 cm^{-1} in the i.r. spectrum of the solid may be due to factor-group splitting of the Emodes which give rise to the group of bands in the 605---620 cm⁻¹ region. However, we prefer to assign this feature to the A_2 SO₃ bending mode because of its relatively large displacement (22 cm⁻¹) from the latter. Also, the very weak band at 465 cm⁻¹ in the ambienttemperature i.r. spectrum of K₃[CH(SO₃)₃]·H₂O is assigned to the A_2 SO₃ rocking mode. Masking by the strong absorption of the KBr windows of the cryostat prevented the detection of this band in the low-temper-

^{*} That these doublets are due to site effects and not to correlation field splitting is indicated by the presence of residual doublet bands of the isotopically dilute $[CH(SO_3)_3]^{3-}$ species in the i.r. spectrum of $K_3[CD(SO_3)_3] \cdot D_2O$.

TABLE 6

Observed frequencies and assignments for $[CH(SO_3)_3]^{3-}$ and $[CD(SO_3)_3]^{3-}$ ions, $K_3[CH(SO_3)_3] \cdot H_2O$ and $K_3[CD(SO_3)_3] \cdot D_2O$

0.1 mol dm ⁻³	0.1 mol dm ⁻³	K ₃ [CH(SO ₃) ₃]·H ₂ O (77 K)		K ₃ [CD(SO ₃)		
Raman (and i.r.)	Raman (and i.r.)	Raman	Lr.	Raman	Lr.	Assignment
and find they	raman (ana m.)	47	£9	46	40	lattica madea
		47VW	52VW	40VW	49VW	lattice modes
		12W	09VW 76vw	12W	70VW 76xxxx	
		81w	20VW 84vw	80.00	20VW 83VW	
		01W	03sh	30 W	03sh	
		98w	100w	100w	97w	
		0011	112w	1000	109vw	
		117vw	119w	118vw	119w	
			132w		131w	
		141vw	140w	140vw	140w	
			148w			
		160vw		160vw		
		185w	189w	187vw,br	186w	
		010.1	170w,br		165w,br	$\delta(CS_3) (A_1)$
		213sh	210w	010	207w	$\delta(CS_3)(E)$
		219W	000	219W	077	(CO)(E)
		285111 200m	282VW 202ch	28110 208cb	277W 287ch	$\rho(SO_3)(E)$
900m n	202m n	290w 301e	2325H 980yw	270511	$\frac{20751}{2020}$ a	(SO)(4)
20011,1	202m,p	311m	210vw	311e	300sh	$\rho(SO_3) (H_1)$
		320m	319vw	3185	308vw	$P(3O_3)$ (E)
		020111	01011	0105	ca. 325vw.br	HDO rock (A')
		390w.br	380w.br		380vw.br	H ₀ O rock (B_0)
		ca. 450w.vbr	,.		····,	H _o O twist (A_{o})
			465vw ^b			$\rho(SO_3) (A_2)$
					480w	D_2O wag (B_1)
$522 \mathrm{sh,p}$	519sh,p	510w	508m	509w	507m	$\delta(SO_3)$ (A_1)
535w,dp	5 3 9w,dp	523sh	523m	524sh	528m	$\delta(SO_3)$ (E)
		$528 \mathrm{sh}$	529m			
		532w	533m	533 sh		
5 4 5sh,dp		538w		538m		$\delta(SO_3)(E)$
		543w	F 40	543sh	541m	
		947sn	540m		F00-1	
61 Ave do	Blow do		0835n 605ab	609ab	582SN	$\delta(SU_3) (A_2)$
014w,up	010w,up	610,000	6089	008511	0085	$o(SO_3)(E)$
		616w	0085	619vw		
		620sh	6185	621sh	6175	
		020011	657w	0.21011	0115	$H_{\bullet}O$ wag (B_{\bullet})
			668w		666vw	
680w,p	678w,p	684w	681w	678w	676sh	$\delta(SO_3)(A_1)$
	750m,p			739w	738s	$\nu(C-S)$ (A_1) and
				751s	749sh	ν (C-S) (E)
					753s	
762m,p		752sh				ν (C–S) (A ₁)
000 1		763s	761w		000	
820w,ap		827w	824m		828vw	ν (C-S) (E)
		839W	829sh		0.49	
	945w dr		83911	050m	843VW	(DCS)(E)
	arow, up			950W 961w	940VW 969vw	$\delta(DCS)(E)$
(1.027s)	(1.043s)	1 027w	1.026s	1 039w	1 044s	$\nu(S-0)(F)$
1 030w.dp?	1 045w.dp?	1 040w	1 0205	1 048sh	1 051sh	V(0,0)(L)
1 092s,p	1 092s,p	1 096vs	1 094w	1 096vs	1 098w	$\nu(S-O)(A_{1})$
1 155w dp	1	1 164w	1 161w			$\delta(HCS)(E)$
•		1 181w	1 180w			
				1 182vw,br	1 179m	$\delta(\text{DOD})(A_1)$
1 202sh,dp		1 206w	1 197sh	1 210sh	1 192sh	ν (S–O) (\dot{E})
		1 228sh	1 204m	1 220w	1.204sh	
1 240 3		1.235w	1 222s	1 230sh	1 222s	
1 240w,p?	С	1 250w	1 238s	1 237w	$1\ 235s$	ν (S-O) (A_1)
(1 250s, br)		1 257w	1 263s	1 246sh	1 251s	
1 958ch Ju		1.970	1.079	1 248W	1 260s	
i 200sn.ap		1 270W	1 273m 1 940ab	1 268W	1 272sh	$\nu(S-O)(E)$
		1 280VW	1 249SN	1 289VW	1 294SN	
					1 442SN 1 447	8(HOD) (A)
		1 644yw br	1.639w		1 649	8(HOH) (4)
	2 210sh.p		2 000m	2 189sh	I JIGYW	$\nu(C-D) (A_1)$
	····/r			2 199m	2 199w	. () (**1/
					2 280vw	1044 + 1235
						(=2279)
			2 280vw			1039 + 1238

 $(=2\ 277)$

0.1mol dm ⁻³ [CH(SO ₂) ₂] ³⁻	0.1mol dm^{-3}	K3[CH(SO3)]	H ₂ O (77 K)	K ₃ [CD(SO ₃) ₃		
Raman (and i.r.)	Raman (and i.r.)	Raman	I.r.	Raman 2 567w	I.r. 2 569m 2 590vw 2 627sh	Assignment $\nu(O-D)(D_2O) (A_1)$ $\nu(O-D)(HDO) (A')$ $\nu(O-D)(HDO) (A')$
2 952,mp		2 935sh	2.041	2 660w,br	2 651m	ν (O-D)(D ₂ O) (\dot{B}_2) ν (C-H) (A_1)
		2 9428 3 492w	2 941w 3 490m 3 520vw		$\begin{array}{c} 2 9480 \\ 3 499 \\ 3 503 \\ sh \\ d \end{array}$	ν (O-H)(H ₂ O (A_1)
« Interference	from D.O. rock (B)	3 565w	3 563m	t-temperature spe	3 570w)	$\nu(O-H)(H_2O)(B_2)$ masked by $\delta(DOD)$ of
interierence	$\frac{1000}{1000} D_2 O 100K (D_2)$	j. Observed on	ily in the ambien	te temperature spe	culum. Region	masked by b(DOD) of

TABLE 6 (Continued)

^a Interference from D_2O rock (B_2) . ^b Observed only in solvent. ^d Contains contribution from $\nu(O-H)(HDO)$ (A'). ambient-temperature spectrum.

ature spectrum. The corresponding feature in the $K_3[CD(SO_3)_3] \cdot D_2O$ spectrum is not observed. However, a band of similar intensity is observed in the i.r. spectrum of the anhydrous salt, $K_3[CH(SO_3)_3]$, at 461 cm⁻¹, thus precluding its assignment to a water librational mode.

Having accounted for the SO3 bending and rocking modes, bands in the 200-220 cm⁻¹ region and at 170 cm⁻¹ in the spectrum of the solid are assigned to the antisymmetric (E) and symmetric (A_1) CS₃ bending modes, respectively. The latter, which has a counterpart in the K₃[CH(SO₃)₃] spectrum, shifts by 5 cm⁻¹ on deuteriation. No assignment is made for the SO₃ torsional modes, which are expected to occur at very low frequency ($< 50 \text{ cm}^{-1}$).

Bands corresponding to the internal modes of H₂O are assigned on the basis of their isotopic frequency shifts and by their absence from the spectra of the anhydrous compound. Correlation field splitting of one O-H stretch, presumably the A_1 mode, is apparent in the i.r. spectrum. The frequencies of the O-H stretches and HOH deformation suggest that the water molecule is involved in hydrogen bonding. The minimum distance between water-oxygen atoms in the lattice (5.1 Å)precludes their involvement in hydrogen bonding with each other. Therefore, hydrogen bonding must be of the type $O(SO_3) \cdots H - O(H_2O)$.

For $K_3[CD(SO_3)_3] \cdot D_2O$ however, the assignment of i.r. bands in the O-D stretching region is based also on a study of the changes which occur in this region for samples having varying degrees of deuteriation. Due to incomplete deuteriation of $K_3[CD(SO_3)_3] \cdot D_2O$, this region also contains contributions from the HDO species. This study provides further evidence that the water molecule is involved in hydrogen bonding. The conclusion is supported by the accompanying changes in the HOD deformation region.

The i.r. spectra of partially deuteriated samples of K₃[CH(SO₃)₃]·H₂O at 77 K in the O-D stretching and HOD deformation regions are shown in Figure 4. In the spectrum of the least deuteriated sample (a) there are two bands in both the O-D stretching (2 622 and 2 590 cm^{-1}) and HOD deformation (1 449 and 1 445 cm^{-1}) regions. The D_2O concentration (0.1 mol %) in this sample is negligible and hence the former are also ascribed to the HDO species. Furthermore, the HDO concentration (7.7 mole %) is low enough to prevent significant correlation coupling from occurring, and hence the presence of two bands in each region is indicative of two types of HDO molecules in the crystal. This is consistent with the space group requirement that the hydrogen atoms of the water molecule are nonequivalent.



FIGURE 4 I.r. spectra of partially deuteriated K₃[CH(SO₃)₃]. H₂O in the O-D stretching and HOD deformation regions

On increased deuteriation [(b) and (c)], the growth of two new bands is observed in the O-D stretching region. These bands increase in intensity relative to those of HDO and are therefore assigned to the A_1 (2 569 cm⁻¹) and B_2 (2.651 cm⁻¹) modes of D_2O . Spectrum (c) represents the highest deuteriation achieved. No correlation field splitting of the D₂O modes is apparent, possibly because of masking by HDO bands. In the HOD deformation region there is no apparent change at higher deuteriations and hence the bands at 1 442 and 1447 cm^{-1} in spectrum (c) are assigned to the deformations (A') of non-equivalent molecules.

In the region below 200 cm⁻¹, at least 14 lattice vibrations are observed. Above 200 cm⁻¹, i.r. bands ascribable to the H₂O wagging (B_1) (657 and 668 cm⁻¹) and rocking (B_2) (380 cm⁻¹) modes appear. The rocking mode is also observed in the Raman spectrum. The isotopic frequency ratio of the 380 cm⁻¹ band is uncertain, due to overlapping of the D₂O band by bands assigned to the SO3 rocking modes. However, it is estimated to be ca. 1.36 on the basis of the intensity changes which occur in the SO₃ rocking region at about 280 cm⁻¹ on deuteriation, thus precluding its assignment to a translatory mode. The wagging mode, which splits into two components under the influence of the correlation field, has an isotopic frequency ratio of 1.38. No correlation field splitting of the D_2O wag is apparent. The assignment of the band at $ca. 325 \text{ cm}^{-1}$ in the i.r. spectrum of the deuteriated compound to the HDO rock (A') is based on the expectation that the frequency of oscillation of the HDO molecule within the molecular (HDO) plane will be approximately mid-way between that of H_2O (380 cm⁻¹) and D_2O (estimated *ca*. 280 cm⁻¹).

The assignment of the weak Raman band at ca. 450 cm^{-1} to the H₂O twisting mode (A₂) is supported by its absence from the i.r. spectrum since it gains i.r. activity through solid-state effects only. The D₂O twist is not observed, probably because of masking by the relatively intense bands ascribed to SO3 rocking modes. All bands assigned to the rotatory modes of water are absent from the spectrum of the anhydrous compound.

The isotope (D) effect on the vibrational frequencies of $[CH(SO_3)_3]^{3-}$ is in accordance with the predictions of the Teller-Redlich product rule. The observed (and calculated) products of the isotopic frequency ratios $\{[CD(SO_3)_3]^3 / [CH(SO_3)_3]^3 \}$ for the A_1 and E species are 0.714 (0.709) and 0.735 (0.709) respectively. The agree-

* The calculated products were determined by the method of Herzberg ¹⁷ for an XYZ₃ molecule of C_{3v} symmetry. Each SO₃ group was regarded as a single entity (Z) of 80 atomic mass units with its centre of mass at the point of half-height (0.2 Å) of the SO₃ pyramid. All CSO angles were assumed to be equal and hence the C-(SO₃) distance was taken to be 2.0 Å (1.8 + 0.2 Å). The C-H distance was taken to be 1.0 Å. The S-O stretches in The C-H distance was taken to be 1.0 Å. The S-O stretches in the 1 200–1 300 cm⁻¹ region, and the SO₃ torsions, were neglected

ment between observed and calculated values is considered satisfactory in view of the approximations made in the calculations * and the use of fundamental rather than zero-order frequencies.

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