

INFRARED SPECTROSCOPIC STUDY OF SITE SYMMETRY EFFECTS  
FOR SULPHITE AND SULPHATE ANIONS  
IN SOLID SODIUM SULPHITE OXIDIZED BY AIR OXYGEN

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The mutual replacement of  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$  anions was studied in  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$  crystals where sulphite is slowly oxidized to sulphate by air oxygen. In a series of  $\text{Na}_2(\text{SO}_3, \text{SO}_4) \cdot 7\text{H}_2\text{O}$  samples, the  $C_1$  or  $C_s$  site symmetry appears for the  $\text{SO}_3^{2-}$  anion and the site symmetry of the  $\text{SO}_4^{2-}$  anion is lowered gradually from  $T_d$  through  $D_{2d}$  or  $C_{3v}$  to  $C_1$ . The replacement was also studied for anhydrous sodium sulphite obtained by dehydration or by evaporation from aqueous solution. Despite the different structures of  $\text{Na}_2\text{SO}_3$  and  $\text{Na}_2\text{SO}_4$  crystals ( $C_{3i}^1$  and  $D_{2h}^{24}$ , respectively), the favourable dimensions of the sterically different anions allow the  $\text{SO}_4^{2-}$  ions, with their own symmetry  $T_d$ , to be located in the  $C_3$  sites of the  $\text{SO}_3^{2-}$  ions in  $\text{Na}_2\text{SO}_3$ .

The space group of  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$  was determined by Dunsmore and Speakman<sup>1</sup> to be  $C_{2h}^3 - B2_1/a$  or  $C_{2h}^2 - P2_1/m$  in the monoclinic system, with elementary cell parameters for  $Z = 8$  or  $Z = 4$ .

The structure of anhydrous  $\text{Na}_2\text{SO}_3$  was determined by Zachariasen and Buckley<sup>2</sup> as long ago as 1931 and refined later by other authors<sup>3-5</sup>.  $\text{Na}_2\text{SO}_3$  crystallizes in the trigonal space group  $C_{3i}^1 - P3$  with  $Z = 2$ ; the S—O distances in the anion are 150.4 pm, the nonbonding O—O distances<sup>9</sup> are 239.7 pm, the trigonal pyramid height is 58.9 pm.

The  $\text{Na}_2\text{SO}_4 - V$  modification, stable at room temperature<sup>6-9</sup>, crystallizes in the space group  $D_{2h}^{24} - Fddd$ ,  $Z = 8$ ; the S—O distances<sup>9</sup> in the regular tetrahedron are 149.3 pm, the O—O distances, 243.5 pm.

Vibrational spectra of  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$  have not been so far published. The published spectra of anhydrous  $\text{Na}_2\text{SO}_3$  do not show crystal symmetry effects<sup>10,11</sup>. The  $\nu_1$  and  $\nu_3$  vibrations are not always resolved<sup>12</sup>. Static crystal field manifests itself in the infrared spectrum of  $\text{Na}_2\text{SO}_4 - V$ , where the spectral patterns of the anion correspond to site symmetry<sup>13</sup>  $D_2$ .

## EXPERIMENTAL

Samples of  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$  of different sulphate content were obtained by spontaneous oxidation of the heptahydrate at room temperature. Thin layers of powdered samples were allowed to rest

in air for 70–90 h. Reagent grade chemicals of Lachema, Brno (approximately 50 mol.%  $\text{Na}_2\text{SO}_4$ ) and Mallinckrodt, USA (approximately 99 mol.% content) were used.

Anhydrous samples were prepared either directly, by dehydration of heptahydrate in a vacuum desiccator over  $\text{P}_2\text{O}_5$ , or by evaporation of aqueous solutions of sodium sulphite. Six anhydrous samples with increasing concentrations of sulphate, up to pure  $\text{Na}_2\text{SO}_4$ , were obtained in this manner.

Sulphite and sulphate were determined titrimetrically by combined indirect iodometric titration of sulphite and indirect chelometric determination of the sum of sulphite and sulphate as their barium salts using thymolphthalein as the indicator.

The infrared spectra were measured in KBr disks ( $4\,000\text{--}200\text{ cm}^{-1}$ ) and in Nujol mulls ( $4\,000\text{--}450\text{ cm}^{-1}$ ) on a Perkin-Elmer 325 spectrophotometer.

## RESULTS AND DISCUSSION

$\text{Na}_2\text{SO}_3 \cdot 7\text{ H}_2\text{O}$  crystallizes in the monoclinic system in the space group  $C_{2h}^3 - B2_1/a$ :  $C_1(8)$ ,  $4C_{2h}(2)$ ,  $2C_i(4)$ ,  $2C_2(4)$ ,  $C_s(4)$ ,  $Z_p = 4$ ; or in the space group  $C_{2h}^2 - P2_1/m$ :  $C_1(4)$ ,  $4C_i(2)$ ,  $C_s(2)$ ,  $Z_p = 4$ . From the multiplicity and subgroups aspect, the  $\text{SO}_3^{2-}$  anion (trigonal pyramid) possesses the  $C_1$  or  $C_s$  site symmetry and the fundamental crystal symmetry correlation is  $C_{3v} \rightarrow C_1$  or  $2C_s \rightarrow C_{2h}$  (Table I).

The infrared spectra reveal that all the samples of hydrated  $\text{Na}_2\text{SO}_3$ , including the starting commercial preparation, contain  $\text{SO}_4^{2-}$  anions. The samples were arranged in a series with increasing sulphate content (Fig. 1). The spectra of all of them display  $\nu_s(\text{H}_2\text{O})$  and  $\nu_{as}(\text{H}_2\text{O})$  vibrations at  $3\,450\text{ cm}^{-1}$  and  $\delta(\text{H}_2\text{O})$  vibrations at  $1\,640\text{ cm}^{-1}$ . The  $\nu_1(\text{SO}_3^{2-})$ ,  $\nu_3(\text{SO}_3^{2-})$ , and  $\nu_1(\text{SO}_4^{2-})$  vibrations overlap within the  $980\text{--}950\text{ cm}^{-1}$  range, as do the  $\nu_2(\text{SO}_3^{2-})$  and  $\nu_4(\text{SO}_4^{2-})$  vibrations within the  $635\text{--}620\text{ cm}^{-1}$  range. The band of the  $\nu_4(E)$  ( $\text{SO}_3^{2-}$ ) vibration shows splitting into

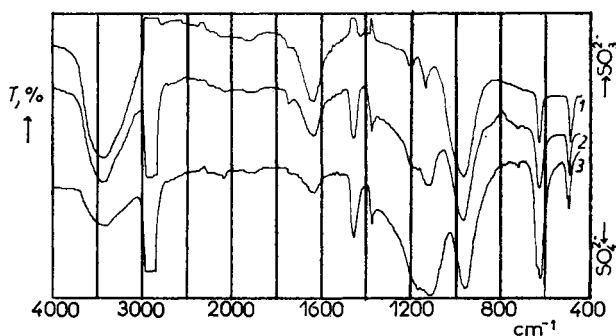


FIG. 1

Infrared spectra of  $\text{Na}_2(\text{SO}_3, \text{SO}_4) \cdot 7\text{ H}_2\text{O}$  powder in Nujol mulls for samples with the  $\text{SO}_4^{2-}$  content increasing in the series 1–3

TABLE I  
Crystal symmetry correlation table for the  $\text{SO}_3^{2-}$  anion in  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$

Vibration	$C_{3v}$ $\longrightarrow$ $C_1$ $\longrightarrow$ $C_{2h}$		$C_{3v}$ $\longrightarrow$ $C_s$ $\longrightarrow$ $C_{2h}$			
	$\nu_1$	$A_1(\text{IR}, \text{RA})$	$A(\text{IR}, \text{RA})$	$A_g(\text{R,A}) + B_g(\text{R,A}) + A_u(\text{IR}) + B_u(\text{IR})$	$A_1(\text{IR}, \text{RA})$	$A'(\text{IR}, \text{RA})$
$\nu_2$	$A_1(\text{IR}, \text{RA})$	$A(\text{IR}, \text{RA})$	$A_g(\text{R,A}) + B_g(\text{R,A}) + A_u(\text{IR}) + B_u(\text{IR})$	$A_1(\text{IR}, \text{RA})$	$A'(\text{IR}, \text{RA})$	$2A_g(\text{RA}) + 2B_u(\text{IR})$
$\nu_3, \nu_4$	$E(\text{IR}, \text{RA})$	$2A(\text{IR}, \text{RA})$	$2A_g(\text{R,A}) + 2B_g(\text{R,A}) + 2A_u(\text{IR}) + 2B_u(\text{IR})$	$E(\text{IR}, \text{RA})$	$A'(\text{IR}, \text{RA}) + A''(\text{IR}, \text{RA})$	$2A_g(\text{RA}) + 2B_g(\text{R,A}) + 2A_u(\text{IR}) + 2B_u(\text{IR})$

TABLE II  
Correlation table for the symmetry lowering of the  $\text{SO}_4^{2-}$  anion in  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$

Vibration	$T_d$	$\longrightarrow C_1$ or $C_s$	
$\nu_1$	$A_1(\text{RA})$	$A(\text{IR, RA})$	$A'(\text{IR, RA})$
$\nu_2$	$E(\text{RA})$	$2A(\text{IR, RA})$	$A'(\text{IR, RA}) + A''(\text{IR, RA})$
$\nu_3, \nu_4$	$F_2(\text{IR, RA})$	$3A(\text{IR, RA})$	$2A'(\text{IR, RA}) + A''(\text{IR, RA})$

TABLE III  
Crystal symmetry correlation table for the  $\text{SO}_3^{2-}$  anion in  $\text{Na}_2\text{SO}_3$

Vibration	$C_{3v} \longrightarrow C_3 \longrightarrow C_{3i} \equiv S_6$			$C_3 \longrightarrow C_1$	
$\nu_1$	$A_1(\text{IR, RA})$	$A(\text{IR, RA})$	$A_u(\text{IR}) + A_g(\text{RA})$	$A(\text{IR, RA})$	$A(\text{IR, RA})$
$\nu_2$	$A_1(\text{IR, RA})$	$A(\text{IR, RA})$	$A_u(\text{IR}) + A_g(\text{RA})$	$A(\text{IR, RA})$	$A(\text{IR, RA})$
$\nu_3, \nu_4$	$E(\text{IR, RA})$	$E(\text{IR, RA})$	$E_u(\text{IR}) + E_g(\text{RA})$	$E(\text{IR, RA})$	$2A(\text{IR, RA})$

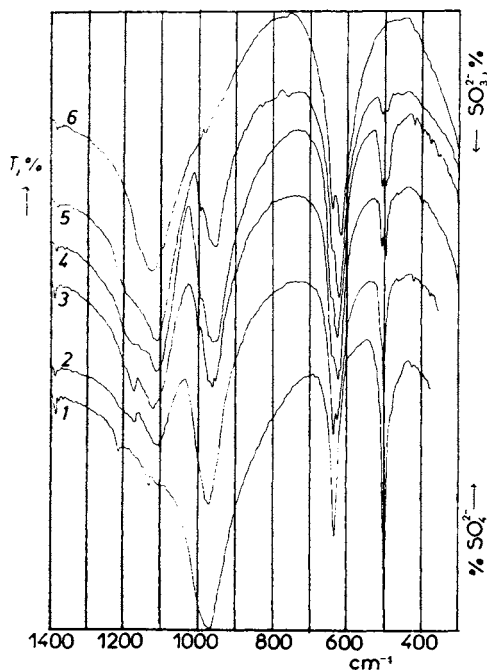


FIG. 2

Infrared spectra of  $\text{Na}_2(\text{SO}_3, \text{SO}_4)$  powder in KBr disks for samples with the  $\text{SO}_4^{2-}$  content increasing in the series 1–5; 6 pure  $\text{Na}_2\text{SO}_4$

TABLE IV  
Crystal symmetry correlation table for the  $\text{SO}_4^{2-}$  anion in  $\text{Na}_2\text{SO}_3$

Vibration	$T_d$ → $D_2$ → $D_{2h}$	$T_d$ → $C_3$
$\nu_1$	$A_1(\text{RA})$	$A_1(\text{RA})$
$\nu_2$	$E(\text{RA})$	$E(\text{RA})$
$\nu_3, \nu_4$	$F_2(\text{IR}, \text{RA})$	$F_2(\text{IR}, \text{RA})$
	$A(\text{RA})$	$A(\text{IR}, \text{RA})$
	$2A(\text{RA})$	$E(\text{IR}, \text{RA})$
	$B_1(\text{IR}, \text{RA}) + B_2(\text{IR}, \text{RA})$ + $B_3(\text{IR}, \text{RA})$	$A(\text{IR}, \text{RA}) + E(\text{IR}, \text{RA})$
	$A_g(\text{RA}) + A_u(\text{ia})$	
	$2A_g(\text{RA}) + 2A_u(\text{ia})$	
	$B_{1g}(\text{RA}) + B_{1u}(\text{IR}) + B_{2g}(\text{RA}) +$ $B_{2u}(\text{IR}) + B_{3g}(\text{RA}) + B_{3u}(\text{IR})$	

two components at 495 and 505  $\text{cm}^{-1}$  with increasing sulphate concentration. This splitting, appearing for sample where the sulphate concentration exceeds the sulphite concentration, hence, for  $\text{Na}_2(\text{SO}_3, \text{SO}_4) \cdot 7 \text{H}_2\text{O}$  mixed crystal, indicates the occurrence of static crystal field effect, with the  $C_1$  or  $C_s$  site symmetry of the sulphite anion (Table I). Multiplication of vibrations according to the  $C_{2b}$  factor symmetry does not appear in the sample with the lowest sulphate content (nearly pure sulphite); however, the site symmetry of  $\text{SO}_4^{2-}$  manifests itself, the  $\nu_3(F_2)(\text{SO}_4^{2-})$  vibration being markedly split into two bands at 1 210–1 190 and 1 140  $\text{cm}^{-1}$ . Two bands seem to overlap in the former, broad band. This splitting indicates that the site symmetry of the sulphate anion lowers from  $T_d$  through  $D_{2d}$  or  $C_{3v}$  as far as  $C_1$  (Table II); the splitting vanishes with increasing sulphate content of samples.

Anhydrous crystalline  $\text{Na}_2\text{SO}_3$  is oxidized slowly by air oxygen to  $\text{Na}_2\text{SO}_4$ . Absorption bands of sulphate are therefore always present in the spectra of sodium sulphite. This system can again be discussed in terms of mixed crystals.

$\text{Na}_2\text{SO}_3$  crystallizes in the trigonal space group  $C_{3i}^1 - P3$ :  $C_1(6)$ ,  $2C_{3i}$ ,  $2C_3(2)$ ,  $2C_2(3)$ ,  $Z = Z_p = 2$ . The own symmetry of the trigonal pyramid of the anion is  $C_{3v}$ , its site symmetry is unambiguously  $C_3$ . The basic correlation scheme  $C_{3v} \rightarrow C_3 \rightarrow C_{3i}$  applies to the vibrational spectra patterns of the anion (Table III).

At room temperature,  $\text{Na}_2\text{SO}_4$  (modification V) crystallizes in the orthorhombic space group  $D_{2h}^{24} - Fddd$ :  $C_1(32)$ ,  $2D_2(8)$ ,  $2C_2(16)$ ,  $3C_2(16)$ ,  $Z = 8$ ,  $Z_p = 2$ . The site symmetry of the anion is unambiguously  $D_2$ . From the point of view of the crystal symmetry theory, an  $\text{SO}_3^{2-}(C_{3v})$  particle cannot be located in a site with  $D_2$  symmetry ( $\text{SO}_4^{2-}$ ), while an  $\text{SO}_4^{2-}(T_d)$  particle can be located in a site with  $C_3$  symmetry ( $\text{SO}_3^{2-}$ ). And indeed, the  $\nu_3$  vibration of  $\text{SO}_4^{2-}$  is split ( $F_2 \rightarrow A + E$ ) into components at 1 215 and 1 135  $\text{cm}^{-1}$  (Table IV). This "replacement" of  $\text{SO}_3^{2-}$  by  $\text{SO}_4^{2-}$  ions is consistent with the slow oxidation of sulphite to sulphate. When the concentration of sulphite is below 50 mol.%, the degeneracy of the  $\nu_4(E)(\text{SO}_3^{2-})$  vibration in the initial  $C_3$  site is removed (Fig. 2, spectra No 3, 4, 5) which indicates that in agreement with the theory<sup>14,15</sup>, the  $C_3(E)$  site symmetry is lowered to the effective  $C_1(2A)$  site symmetry.

Irrespective of whether the mixed crystal has been obtained from a homogeneous phase (solution) (sample No 5) or by mere surface oxidation of the starting  $\text{Na}_2\text{SO}_3$  (sample No 4), it can be inferred from the splitting of the degenerate  $\nu_4(E)(\text{SO}_3^{2-})$  vibration (505 and 495  $\text{cm}^{-1}$ ) that mixed crystals have formed where the site symmetry manifests itself markedly for the species present in the lower concentration. Hence, a product which has the character of a mixed crystal, rather than a thin oxidized layer not affecting the crystal symmetry of the  $\text{Na}_2\text{SO}_3$  bulk, is formed even during the gradual oxidation of sulphite crystals by air oxygen.

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