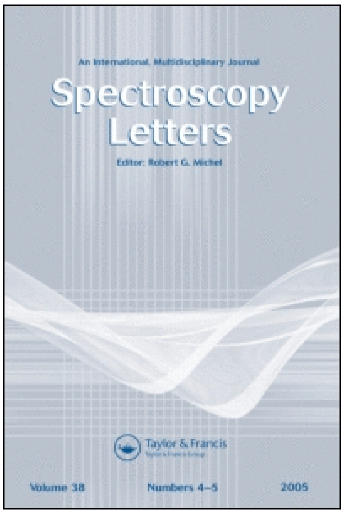

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Vibrational Studies of Different Modifications of the Sodium Hydrogen Sulphate Crystals

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VIBRATIONAL STUDIES OF DIFFERENT MODIFICATIONS OF THE SODIUM HYDROGEN SULPHATE CRYSTALS

Key Words: Infrared Spectra, Raman Spectra, Sodium Hydrogen Sulphate

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ABSTRACT

Three modifications of the sodium hydrogen sulphate ($NaHSO_4 \cdot H_2O$, A-$NaHSO_4$, B-$NaHSO_4$) have been prepared. Their vibrational spectra have been measured. The results are discussed in relation to the structures of crystals. The good agreement between the crystal structure, selection rules and vibrational spectra is observed for $NaHSO_4 \cdot H_2O$ crystal. However, the careful analysis of the infrared spectra of both anhydrous modifications (A-$NaHSO_4$, B-$NaHSO_4$) show that neither of them correspond to β-$NaHSO_4$ form. On the other hand, the infrared spectra of A-$NaHSO_4$ and B-$NaHSO_4$ modifications show that each of them contain some amount of the α-$NaHSO_4$ phase.

INTRODUCTION

The sulphuric acid forms a family of hydrogen bonded crystals with general formula $MHSO_4$ where M=Li^+, Na^+, K^+, Rb^+, Cs^+ and NH_4^+. Some of them exhibit very interesting physical properties, *i.e.* a superionic conductivity [1] (at high temperatures) or ferroelectric properties [2]. Therefore, they were a subject of both Raman and infrared studies [3-10]. However, no vibrational data have been published so far for the $LiHSO_4$ and $NaHSO_4$ crystals. This may be related to the hygroscopic properties of these crystals [11, 12]. In spite of that we have succeeded in preparation of the $NaHSO_4$ crystals. Moreover, we have also noticed that different forms of $NaHSO_4$ crystal were obtained ($NaHSO_4 \cdot H_2O$, A-$NaHSO_4$ and B-$NaHSO_4$) depending on the method of preparation. This conclusion is consistent with an observation made by Sonneveld and Visser [13,14]. Thus, in order to complete the vibrational studies of $MHSO_4$ family, the infrared spectra of all modifications of $NaHSO_4$ crystal have been recorded and are reported in the presented contribution. The vibrational spectra of $NaHSO_4$ crystals are discussed with respect to their crystal structures and in relation to the vibrational spectra of other hydrogen sulphates.

EXPERIMENTAL

The sodium hydrogen monohydrate ($NaHSO_4 \cdot H_2O$) was prepared by mixing Na_2SO_4 and a 96% solution of H_2SO_4 in water. The best $NaHSO_4 \cdot H_2O$ crystals were obtained from aqueous solution containing Na^+ and H_2SO_4 in ratio 1:2.8 to 1:3. Deuterated crystals were obtained by dissolving the Na_2SO_4 in D_2O containing the H_2SO_4 in the amount corresponding to the ratio mentioned above. The good isotopic substitution was reached by fourfold recrystallization from the solution in D_2O.

The $NaDSO_4$ was prepared by dehydration of the monohydrate $NaDSO_4 \cdot D_2O$ crystal. The dehydration was carried out by use of a drying agent (P_2O_5) at *ca.* 110°C. However, the attempts to prepare anhydrous modifications of $NaHSO_4$ crystal by dehydration the $NaHSO_4 \cdot H_2O$ at 110°C (for α-$NaHSO_4$, [14]) and in the region of temperature between 0 -25° C (for β-$NaHSO_4$ [13]) were not successful. Therefore, in order to obtain the α-$NaHSO_4$ crystals, the method described in [16] was used. The appropriate amounts of Na_2SO_4 and H_2SO_4 were mixed and heated up to 150-160° C until the transparent liquid was obtained. Then, the liquid was divided into two parts. One part was poured into paraffin oil. In a few minutes crystals started to grow up. The second part was cooled down and at *ca.* 140°C the crystals appeared. The infrared spectra of α-$NaHSO_4$ obtained by the methods mentioned above are similar in the region below 1400 cm^{-1} and exhibit some differences in the region above 1400 cm^{-1}.

The β-$NaHSO_4$ compound was prepared by mixing Na_2SO_4 and H_2SO_4 in the ratio of 1:1 and heating up to the temperature range of 110-130°C and annealing for few minutes. On cooling down the β-$NaHSO_4$ crystals started to crystallise.

In that procedure the anhydrous modifications of $NaHSO_4$ were obtained by the method different than that described in [13,14], therefore, the other notations for the products were used: A-$NaHSO_4$ (for the form prepared at *ca.* 140°C) and B-$NaHSO_4$ (for the form obtained in the 110-130°C temperature region).

Since all obtained modifications of anhydrous $NaHSO_4$ (*i.e.* $NaDSO_4$, A-$NaHSO_4$, B-$NaHSO_4$) and $NaDSO_4{\cdot}D_2O$ are highly hygroscopic, therefore the crystals were stored under paraffin oil.

The infrared spectra of polycrystalline samples for all obtained crystals have been recorded as an emulsion in nujol at room temperature with a spectrophotometer Perkin-Elmer 180 in the 4000-300 cm^{-1} frequency region. The FT-Raman spectra of $NaHSO_4{\cdot}H_2O$ crystal were recorded by means of FRA-106 attachment to the Bruker IFS-88 spectrometer.

Crystal Structure and Selection Rules

The $NaHSO_4{\cdot}H_2O$ crystal belongs to the $Cc = C_s^4$ space group of the monoclinic system with Z=2 formal molecules in the primitive unit cell [15]. The hydrogen sulphate anions are linked by hydrogen bonds (with the O···O distances equal to 2.658Å) into infinite zigzag chains spreading along the [101] direction. The water molecules are tied to the HSO_4^- chain by two weak hydrogen bonds with the O···O distances equal to 2.839 and 2.898Å (Fig. 1).

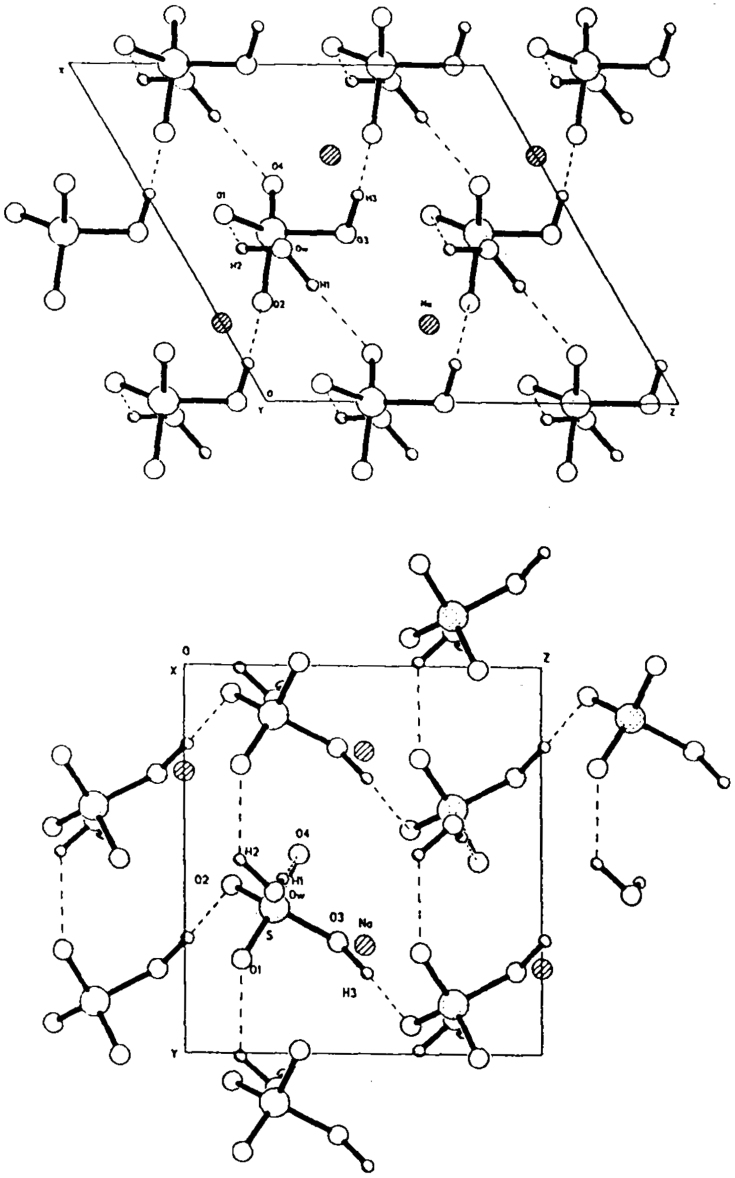

FIG. 1 Projections of the Crystal Structure of the $NaHSO_4 \cdot H_2O$ onto ac (upper) and bc (lower) Planes.

The β-$NaHSO_4$ crystal belongs to the $P2_1/n$ space group of the monoclinic system with Z=4 molecules in the primitive unit cell [13]. The HSO_4^- anions are linked into cyclic dimers (Fig. 2) by medium strong hydrogen bonds with the O···O distances equal to 2.67Å.

The α-$NaHSO_4$ form crystallises in the $P\bar{1}$ space group of the triclinic system [14]. It contains two types of the HSO_4^- anions ($HS(1)O_4^-$ and $HS(2)O_4^-$) which are linked by means of hydrogen bonding between O(1) and O(5) with O···O distance equal to 2.690(8)Å (Fig. 3). The disorder of the H atoms in the $HS(2)O_4^-$ anion was found in the α-$NaHSO_4$ phases. As the H atom is distributed between the O(7) and O(8) atoms, therefore, the hydrogen bonding may exist between the O(6) and O(8') atoms (R_{oo}=2.692Å) as well as between the O(7) and O(7') atoms (R_{oo}=2.497Å). Due to this the $HS(2)O_4^-$ anions form infinite chains in the [110] direction.

As mentioned above the hydrogen sulphate anions form dimers (β-$NaHSO_4$, α-$NaHSO_4$) or chains ($NaHSO_4{\cdot}H_2O$, α-$NaHSO_4$) in the studied crystals. The symmetry of dimers is C_i. The adjacent hydrogen sulphate anions in the chains are related by the glide plane which is approximated by the C_s group. The correlation diagrams between the symmetry of free SO_4^{-2} anion (T_d), the symmetry of free HSO_4^- anion (C_{3v}), the site symmetry (C_1) (Table 1) and the symmetry of dimer or chain (Table 2) are very helpful in the discussion of the internal vibrations of the hydrogen sulphate anion. The correlation diagram (Table 2) shows that for the dimer each mode splits into two components; one allowed only in the IR spectrum (A_u) and the second one allowed only in the Raman spectrum (A_g). For the chain type structure each mode also splits into two components (A' + A''), however, both simultaneously allowed in the IR and Raman spectra. Thus, taking this into account one should expect in the 1100-1000 cm^{-1} region of IR spectra either one band or two bands for dimer or for chain, respectively (Table 2). Moreover, taking into account the geometry of the HSO_4^- anions in the studied crystal [6,13,15] one can suggest that the internal vibrations of the HSO_4^- anion might be considered according to one of three models described in [3]. In these models the structure of HSO_4^- ion is approximated by the formula $HOSO_3^-$ and the vibrations of the longest S-O_H bonds are treated

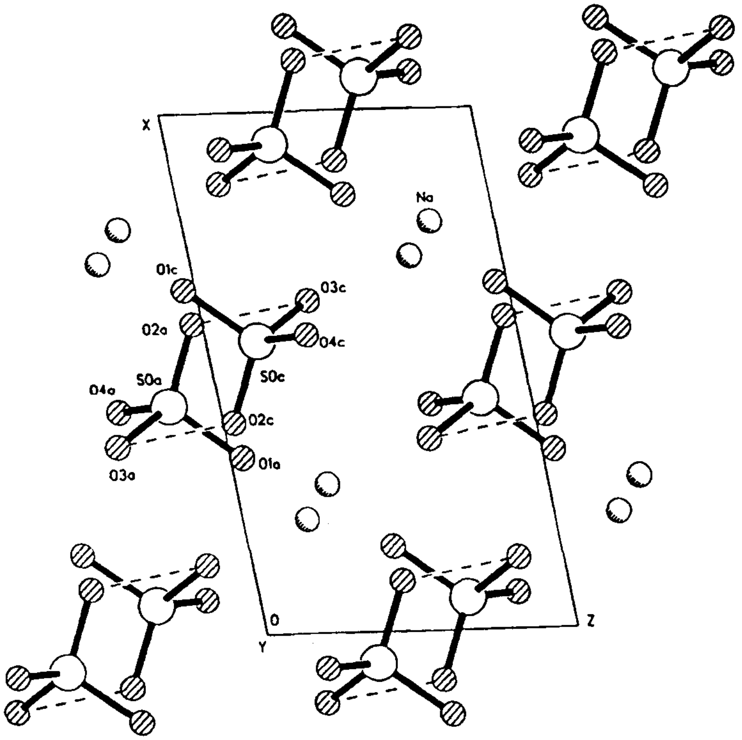

FIG. 2 Projection of the Crystal Structure of the β-$NaHSO_4$ onto ac Plane.

independently from the vibrations of the SO_3 group, which has two similar S-O bonds and one slightly longer S-O bond.

RESULTS AND DISCUSSION

The vibrational spectra of polycrystalline samples of hydrated and anhydrous modifications of the $NaHSO_4$ crystal are shown in Figs. 4 and 5, respectively. The wavenumbers of the bands observed in the spectra are listed in Table 3. The bands observed in the 4000-300 cm^{-1} frequency region are derived from internal vibrations of sulphate anion, water molecule and hydrogen bonds.

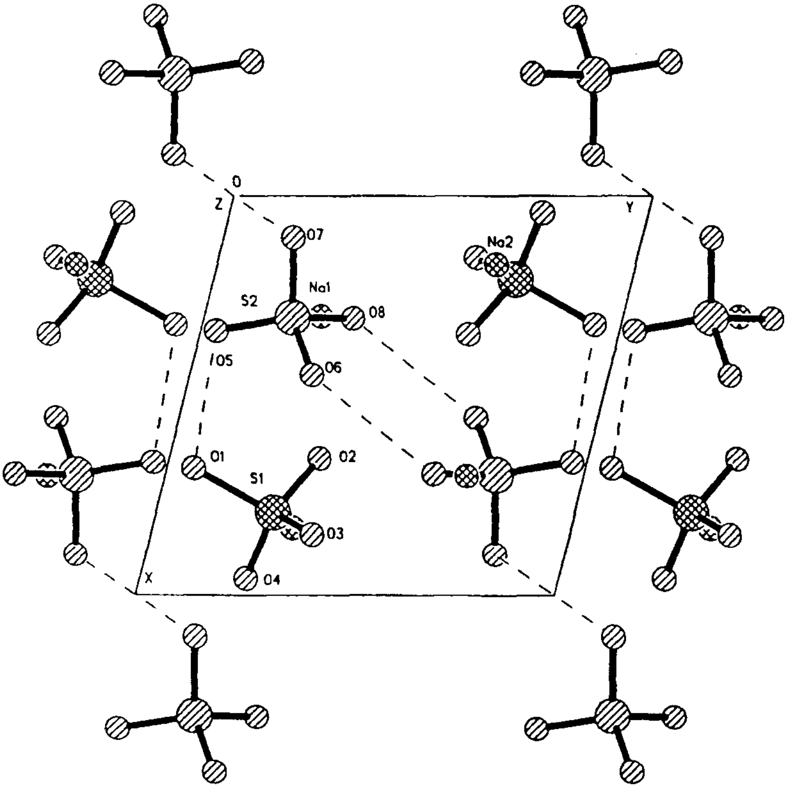

FIG. 3 Projection down c axis of the Crystal Structure of the α-$NaHSO_4$ onto ab Plane.

The Vibrational Spectra of $NaHSO_4.H_2O$

Internal vibrations of the sulphate anion

Two strong bands observed at 1078 and 1040 cm^{-1} in the IR spectrum of $NaHSO_4{\cdot}H_2O$ and at 1078 and at 1048 cm^{-1} in the IR spectrum of deuterated species have been assigned to the $\nu_s SO_3$ vibration which corresponds to the ν_1 (981 cm^{-1}) mode of the „free" SO_4^{-2} anion. Note that this observation as well as an assignment are consistent with the prediction of selection rules (Table 2). Unexpectedly, in the

TABLE 1
Correlation Diagram for the Internal Vibrations of the Sulphate Ions in the $NaHSO_4 \cdot H_2O$, α-$NaHSO_4$ and β-$NaHSO_4$.

Symmetry of the "free" SO_4^{-2} T_d		Symmetry of the "free" HSO_4^- C_{3v}	Site symmetry C_1		Wavenumbers (cm^{-1}) expected for the internal vibrations of HSO_4^- anion
A_1	$\nu_1=981$	A_1	A	$\nu_s SO_3$*	*ca.* 1000-1100
E	$\nu_2=451$	E	A	δS-O_H	*ca.* 420-440
			A	γS-O_H	
F_2	$\nu_3=1104$	A_1	A	νSOH	*ca.* 860 ± 20
		E	A	$\nu_a {}^\circ SO_3$	*ca.* 1170
			A	$\nu_s {}^\circ SO_3$	*ca.* 1200
F_2	$\nu_4=613$	A_1	A	$\delta_s SO_3$	*ca.* 570±10
		E	A	$\delta_a {}^\circ SO_3$	*ca.* 600
			A	$\delta_s {}^\circ SO_3$	*ca.* 580-590

*the notation was taken from [3].

TABLE 2
The Correlation Diagram Between the Site Symmetry and Symmetry of Dimer/Chain for Internal Vibration of HSO_4^- anions in $NaHSO_4 \cdot H_2O$, α-$NaHSO_4$ and β-$NaHSO_4$.

Site Symmetry C_1	Symmetry of Dimer C_i	Activity	Wavenumbers (cm^{-1}) Expected for the Internal Vibrations of the HSO_4^- Anion
A	A_u	IR	*ca.* 1070
	A_g	R	
Site Symmetry C_1	Symmetry of Chain C_s	Activity	Wavenumbers (cm^{-1}) Expected for the Internal Vibrations of the HSO_4^- Anion
A	A'	IR, R	*ca.* 1000
	A"	IR, R	*ca.* 1060

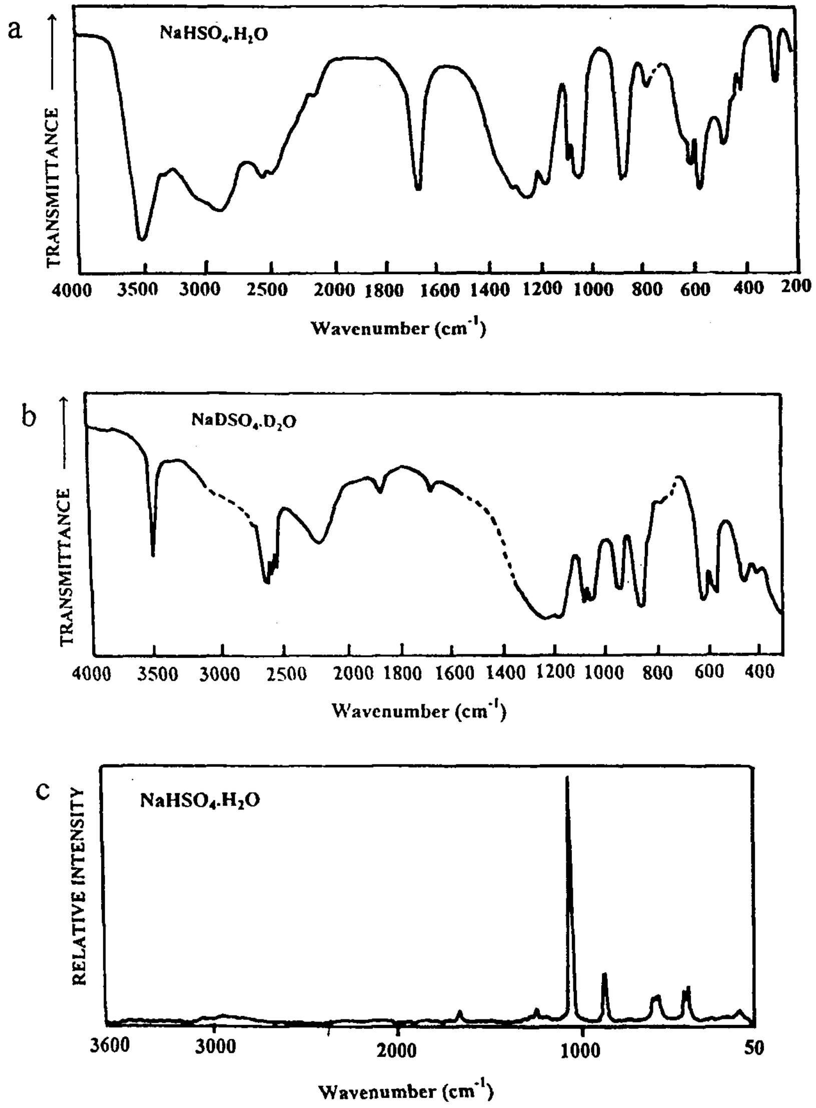

FIG. 4 Vibrational Spectra of Polycrystalline Samples:

a) Infrared Spectrum of $NaHSO_4 \cdot H_2O$ Crystal Recorded as an Emulsion in Nujol and Fluorolube

b) Infrared Spectrum of $NaDSO_4 \cdot D_2O$ Crystal Recorded as an Emulsion in Nujol.

c) Raman Spectrum of $NaHSO_4 \cdot H_2O$ Crystal.

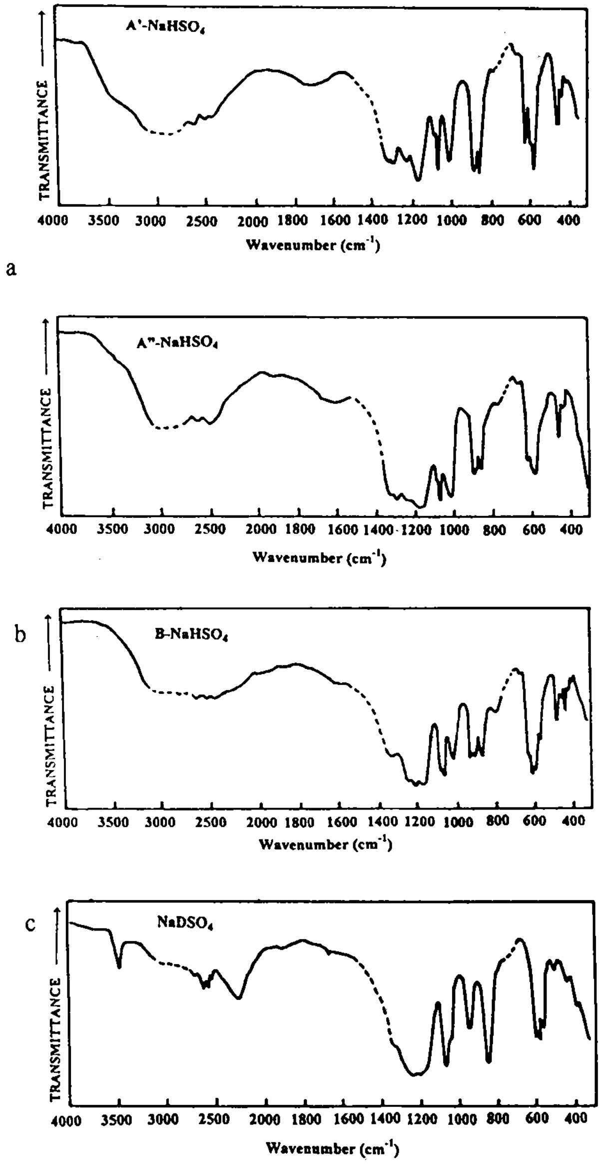

FIG. 5 Infrared Spectra of Polycrystalline Sample of
a) A'-NaHSO$_4$ and A"-NaHSO$_4$; b) B-NaHSO$_4$ and c) NaDSO$_4$ Recorded as an Emulsion in Nujol.

Raman spectrum only one band is observed in this region. It appears at 1060 cm^{-1} and exhibits the highest intensity in the spectrum. The bands which appear in the 1078-1069 cm^{-1} region may also arise from stretching vibration of S-O bond with medium S-O distance (*ca.* 1.47Å).

The bands due to the stretching vibrations derived from the ν_3 mode of the „free" SO_4^{-2} anion occur in two regions (900-800 and 1243-1170 cm^{-1}) in the case of hydrogen sulphate anion. The $\nu S\text{-}O_H$ vibration gives rise to the bands observed at 873 cm^{-1} in the spectrum of $NaHSO_4 \cdot H_2O$ and at 856 cm^{-1} in the spectrum of the deuterated analogue. The Raman counterpart of $\nu S\text{-}O_H$ mode appears at 874 cm^{-1}. The bands which appear in the latter region (1243-1170cm^{-1}) one can attribute in two different ways. A similar problem occurs in the infrared spectra of $KHSO_4$ [6] and $KHSeO_4$ [17]. Thus, the bands at 1170 and 1175 cm^{-1} may arise from $\nu_s^cSO_3$ mode. The bands observed at 1243 cm^{-1} in the $NaHSO_4 \cdot H_2O$ and at 1240 and 1206 cm^{-1} in the spectra of $NaDSO_4 \cdot D_2O$ have been attributed to the $\nu_a^cSO_3$ vibration. However, the bands observed in the 1243-1170 cm^{-1} region might be also ascribed to the ν_aSO_2 and ν_sSO_2 vibrations (*e.g.* out-of-phase and in-phase coupling between the stretching vibrations of the two shortest S-O bonds; 1.44-1.45Å). Note that both those assignments seem to be reasonable. The bands of the $\nu_s^cSO_3$, $\nu_a^cSO_3/\nu_aSO_2$ and ν_sSO_2 in the Raman spectra show very low intensity and appear at 1241 and 1191 cm^{1}.

The assignment of the bands due to deformation vibrations of the hydrogen sulphate anions presented here is similar to that proposed for other hydrogen sulphates [3, 6]. The absorption arising from bending modes is observed in the 650-400 cm^{-1} region. The strong bands at 603 and at 574 cm^{-1} observed in the infrared spectrum and weak doublet at 612 and 577 cm^{-1} observed in Raman spectrum are assigned to the $\delta_a^cSO_3$ and δ_sSO_3 modes, respectively. Deuteration leads to the noticeable change in the shape and number of bands. They become narrower and each of them splits into two well defined components (Fig. 4b).

The bands observed at 454 and 395 cm^{-1} in the infrared spectrum of $NaDSO_4 \cdot D_2O$ and at 476, 437 and 411 cm^{-1} in the infrared spectrum and at 435 and

TABLE 3
The Wavenumbers (cm^{-1}) Observed in the Vibrational Spectra of Polycrystalline Sample of $NaHSO_4 \cdot H_2O$, $NaDSO_4 \cdot D_2O$, A-$NaHSO_4$, B-$NaHSO_4$, $NaDSO_4$ Crystals*.

$NaHSO_4 \cdot H_2O$		$NaDSO_4$ $\cdot D_2O$	$NaDSO_4$	B-$NaHSO_4$	A'-$NaHSO_4$	A''-$NaHSO_4$	Assignments
IR	Raman**	IR	IR	IR	IR	IR	
3494vs							
		3482s					$\nu_3 H_2O$
3470vssh			3475w				
					3330wsh		
3284m							$\nu_1 H_2O$
3040ssh							
2900s	2940(2.8)		~2900s	~2900s	2905s	~2900s	νOH(A)
				2640w			νOH(B)
					2605m	2600m	νOH(B)
		2606s	2605w				$\nu_3 D_2O$
		2570s	2569w				$\nu_3 D_2O$
		2540s	2539w				$\nu_3 D_2O$
2555m				2520w	2497m	2490m	νOH(B)
2452m				2430w	2420m	2400msh	νOH(B)
		2390msh					νOD
				2300w			νOH(B)
			2260m				νOD(A)
					2200wsh		νOH(B)
		2197m					νOD(A)
2125w							νOH(B)
				1995vw		1945vwb	
		1860w	1900vw				νOD(B)
				1850vw			
					1730wb	1750vwsh	νOH(C)
1660s	1656(4.7)	1661w	1663vw				$\nu_2 H_2O$
					1620wsh	1615wb	νOH(C)
				1575vwb			νOH(C)
	1549(1.7)						
1355ssh			1333s	1335s	1320vs	1325vs	δOH
1299vs	1308(2.2)				1290vs	1290vs	δOH
	1268(3.1)						
1243vs	1241(6.0)	1240vs	1240vs	1243vs	1234vs	1230vs	$\nu_a^e SO_3$ or $\nu_a SO_2$
		1206vs	1200vs	1207vs			$\updownarrow (\nu_3 SO_4^{-2})$
1170vs	1191(3.0)	1175vs	1180vs	1170vs	1173vs	1173vs	$\nu_s^e SO_3$ or $\nu_s SO_2$
				1080vs	1085msh	1085ssh	$(\nu_1 SO_4^{-2})$
1078vs	1060(100)	1078vs	1070vs		1069vs	1069vs	$\nu_s SO_3$
				1061vs			$\updownarrow (\nu_1 SO_4^{-2})$
1040vs		1048vs	1045ssh				$\nu_s SO_3$
				1011s	1008s	1008vs	$(\nu_1 SO_4^{-2})$

TABLE 3 (continued)

The Wavenumbers (cm^{-1}) Observed in the Vibrational Spectra of Polycrystalline Sample of $NaHSO_4 \cdot H_2O$, $NaDSO_4 \cdot D_2O$, A-$NaHSO_4$, B-$NaHSO_4$, $NaDSO_4$ Crystals*.

$NaHSO_4 \cdot H_2O$		$NaDSO_4$ $\cdot D_2O$	$NaDSO_4$	B-$NaHSO_4$	A'-$NaHSO_4$	A''-$NaHSO_4$	Assignments
IR	Raman**						
		939s	945s				δOD
		934ssh					δOD
				919s			
				899s	886vs	890vs	νSO_H
873vs	874(20.5)			869s	875s	875vs	$\updownarrow (\nu_3 SO_4^{-2})$
860vssh		856vs	848s		853vs	851vs	νSO_H
773m		772w		790m	773w	770w	γOH
				664w	660w	660w	γOH
	655(3.1)						
625ssh							τH_2O
		610vs		614s	613s	613s	$\delta_a^{\circ}SO_3$
603vs	612(11.5)	599vssh	603s	600vs	593s	593s	$\updownarrow (\nu_4 SO_4^{-2})$
			589vs	589vs	580ssh	589ssh	$\delta_s^{\circ}SO_3$
574vs	577(12.2)	575ssh			576vs	575vs	$\updownarrow (\nu_4 SO_4^{-2})$
		565vs	563s	565s			$\delta_s SO_3$
			509w				γOD
476s				473m			$\delta S\text{-}O_H$, $(\nu_2 SO_4^{-2})$
		454s		452m	454m	450m	$\nu_2 SO_4^{-2}$
437ssh	435(14.0)		437w	437m	433m	430w	$\delta S\text{-}O_H$, $(\nu_2 SO_4^{-2})$
				425w			$\nu_2 SO_4^{-2}$
411m	411(15.9)	395s	390m		416w		$\delta S\text{-}O_H$, $(\nu_2 SO_4^{-2})$
		3445vs		405w	407w		$\nu_2 SO_4^{-2}$
263w	278(2.8)						
	224(3.4)						
	188(3.4)						
	140(5.7)						
	87(2.9)						

*Abbreviations: vs-very strong; s-strong; m-medium; w-weak; sh-shoulder; ν-stretching vibration; δ-deformation vibration; τ-twisting vibration.

**Relative intensities of the bands (in brackets) are given in relation to the strongest band (at 1060 cm^{-1};intensity=100) in the spectrum.

411 cm^{-1} in the Raman spectrum of $NaHSO_4 \cdot H_2O$ are due to deformation modes of the S-O_H bond. It should be noticed that unambiguous attribution of the bands arising from deformation vibrations of hydrogen sulphate anion is not easy. They may couple with deformation vibration (γOH/γOD) of hydrogen bond. Moreover, in the infrared spectrum of the $NaHSO_4 \cdot H_2O$ the bands due to the libration modes of water molecule also appear in the 650–400 cm^{-1} region.

Hydrogen bond and water molecule vibrations.

The $NaHSO_4 \cdot H_2O$ crystal contains two types of hydrogen bonds [15]. The weak hydrogen bonds with the O···O distances in the range of 2.83-2.89Å are formed between the oxygen atom of water molecule and the oxygen atoms of the hydrogen sulphate anions. Since these hydrogen bonds are rather weak, therefore one can expect quite small changes in the water molecule vibrations. The doublet of bands observed in the infrared spectrum at 3494 cm^{-1} (very strong) and at 3284 cm^{-1} (medium) has been attributed to the stretching vibrations of water molecules (ν_3 and ν_1, respectively). Bands due to stretching vibrations of water molecule have not been observed in the FT-Raman spectrum as they are outside of the detector sensitivity. The band of δH_2O vibration has been identified at 1660 cm^{-1}. It appears to be strong and relatively sharp. Its Raman counterpart is observed at 1656 cm^{-1} and exhibits low intensity. However, the absorption arising from the libration mode of the water molecule appears as a diffused broad band in the 650-400 cm^{-1} region of the infrared spectra. The detailed determination of its position is very difficult because in this region the bands of the bending vibrations of hydrogen sulphate anion also appear. Any bands due to the libration mode of water molecule have not been identified in the Raman spectrum. On deuteration the bands due to stretching vibration of the water molecule become narrow and shift to lower frequency (2605, 2569 and 2539 cm^{-1}). The bands derived from the δD_2O and libration modes in the spectra of deuterated species have not been identified. Note that absorption pattern due to internal vibrations of water molecule as well as the assignment is consistent with that proposed for $CsHSu \cdot H_2O$ [18] and $K_2HPO_4 \cdot 3H_2O$ [19] crystals.

The second hydrogen bond with the O···O distances equal to 2.65(8)Å links the hydrogen sulphate anions into infinitive chains. The absorption due to the νOH mode of this hydrogen bond should appear as a characteristic broad triplet (so-called A,B,C bands [20]) and it should be similar to those observed in other hydrogen sulphates [3,6] and hydrogen selenates [17]. Since the hydrogen bond in $NaHSO_4 \cdot H_2O$ crystal is a little weaker than in other hydrogen sulphates and selenates [3,6,17], the ABC bands should appear at higher wavenumbers. Contrary to expectation, a careful examination of the infrared spectrum above 1600 cm^{-1} shows that the absorption due to νOH vibration exhibits only AB structure. The A band is observed at 2900 cm^{-1} with the shoulder at 3040 cm^{-1}. The B band has maximum at about 2500 cm^{-1} and exhibits additional structure with maxima at 2555, 2452 and 2125 cm^{-1}. This observation can be easily explained. The ABC structure of the νOH absorption arise from a Fermi resonance of the νOH mode with the overtones of the δOH (B) and γOH (C) bending modes [21-23]. In our case only the overtone of the δOH mode fulfils the conditions for the Fermi resonance, whereas the overtone of the γOH mode (2×773 cm^{-1}) is far from the νOH band. Therefore, the overtone of the γOH may appear as a very weak band. However, in the 1600-1400 cm^{-1} region no bands are observed. A similar observation was made for the νOH absorption of the dimer hydrogen bond in $KHSO_4$ [6] crystal. In the Raman spectrum only A band is observed. It appears as a very broad and weak band with maximum at 2940 cm^{-1}. In the spectrum of $NaDSO_4 \cdot D_2O$ crystal the νOD absorption appears in the 2500-1800 cm^{-1} region and exhibits simpler shape then that of the νOH. The broad and intense band at 2197 cm^{-1} is assigned to the A component of νOD absorption, the weak and sharp band at 1860 cm^{-1} is analogue of the B component. The bands due to bending in-plane (δOH) and out-of-plane (γOH) vibrations of hydrogen bond are identified at 1355, 1299 and 773 cm^{-1}, respectively. However, the deuterated counterparts have only been observed for δOD mode at 939 and 934 cm^{-1}.

The IR Spectra of the Anhydrous Modifications of the Sodium Hydrogen Sulphate (B-$NaHSO_4$, A-$NaHSO_4$ and $NaDSO_4$).

Internal vibrations of sulphate anions

Taking into account the crystal structure of β-$NaHSO_4$ compound [13] one expects only one band arising from the ν_sSO_3 vibration (Table 2) in the 1100-1000cm^{-1} region of the infrared spectrum. Contrary to expectation, three strong bands are observed (strong doublet at 1080 and 1061 cm^{-1} and broad band at 1011 cm^{-1}) in the that region (Fig.5b). This observation allows to suggest that the anhydrous modification of sodium hydrogen sulphate obtained by us and called as B-$NaHSO_4$

very likely does not correspond to the β-$NaHSO_4$ form. However, in the IR spectrum of $NaDSO_4$ crystal only one very strong band at 1070 cm^{-1} is observed in the 1100-1000 cm^{-1} region. The shoulder at 1045 cm^{-1} is probably caused by an internal vibration of the D_2O molecule. Moreover, in the spectrum of $NaDSO_4$ the band due to γOD vibration is observed at 509 cm^{-1}. Its counterpart in the spectrum of β-$NaHSO_4$ should appear at *ca.* 712 cm^{-1} (509 cm^{-1} ×1.4=712 cm^{-1}). However, in the infrared spectrum of B-$NaHSO_4$ near this wavenumber no band is observed. So, these two observations allow us to suppose that the deuterated counterpart of β-$NaHSO_4$ phase was obtained. The comparison of the infrared spectra of $NaDSO_4{\cdot}D_2O$ and $NaDSO_4$ shows that $NaDSO_4$ sample obtained by us includes a small amount of the $NaDSO_4{\cdot}D_2O$.

Detailed examination of the infrared spectra of A-$NaHSO_4$ and B-$NaHSO_4$ crystals reveals that some frequency regions are similar (*e.g.* in the 1100-1000cm^{-1} region, compare Fig. 5a and Fig. 5b) and the others exhibit differences (1350-1100 cm^{-1}, 950-800 cm^{-1} region and below 700 cm^{-1}). This observation leads to the following question: Which modification of the anhydrous sodium hydrogen sulphate (A-$NaHSO_4$ or B-$NaHSO_4$) crystals was obtained by us? The crystal structure of α-$NaHSO_4$ modification should be considered in order to answer this question. As follows from the X-ray data [14] for the α-$NaHSO_4$ crystal, the hydrogen atom of the $HS(2)O_4^-$ anion is disordered and can occupy two positions. If we assume that it is localised between O(6) and O(8') atoms and O(8) and O(6') atoms, the $HS(2)O_4^-$ anions will form only dimers and $HS(1)O_4^-$ anions are linked to these dimers by means of the O(1)···O(5) hydrogen bond (Fig. 3). In such a case one can expect two bands in the 1100-1000 cm^{-1} region; one band arising from the dimer and the second one related to the $HS(1)O_4^-$ anion. In the infrared spectrum of the A-$NaHSO_4$ (Fig. 5a, Table 3), the strong band at 1069 cm^{-1} and strong and broad band at 1008 cm^{-1} is observed. The former may arise from the ν_sSO_3 ($\nu_1SO_4^{-2}$) vibration of dimer, the latter may be related to symmetrical stretching vibration of $HS(1)O_4^-$ anion. The shoulder observed at 1085 cm^{-1} may be assigned to a combination mode [24]. The assumption presented above is also supported by the bands at 790 and 664 cm^{-1} (B-

$NaHSO_4$) and at 773 and 660 cm^{-1} (A-$NaHSO_4$) in the spectra of both anhydrous modifications. They are derived from the deformation modes γOH of the chain hydrogen bond (bands at higher frequencies) and dimer hydrogen bond (bands at lower frequencies). At similar wavenumbers the bands due to γOH mode of chain and dimer hydrogen bond were observed in the spectra of $KHSO_4$ crystal [6].

However, if we assume that the hydrogen atom of the $HS(2)O_4^-$ anion in α-$NaHSO_4$ crystal is distributed between O(7') and O(8) atoms the excess of the bands observed in the 1100-1000 cm^{-1} region (doublet at 1080 and 1061 cm^{-1} and band at 1011 cm^{-1}) of the B-$NaHSO_4$ spectrum may be easily explained. Thus, in this case the $HS(2)O_4^-$ anions may be joined into infinitive chains in the [110] direction to which the $HS(1)O_2^-$ anions are linked by means of the O(1)···O(5) hydrogen bond. If so, the doublet observed at 1080 and 1061 cm^{-1} may arise from the $\nu_sSO_3(\nu_1SO_4)$ vibration of chain, however the band which appears at 1011 cm^{-1} may be related to the $\nu_sSO_3(\nu_1SO_4)$ vibration of the $HS(1)O_4^-$ anion.

Detailed analysis of the infrared spectra of A-$NaHSO_4$ and B-$NaHSO_4$ crystal in the 1100-1000 cm^{-1} frequency region reveals that both infrared spectra exhibit some absorption features expected for the α-$NaHSO_4$ modification. However, it is quite difficult to decide which structure of the anhydrous modification of sodium hydrogen sulphate proposed by us is closer to that followed from the X-ray methods and denoted as α-$NaHSO_4$ [14].

The bands due to other internal vibrations of hydrogen sulphate anions observed in both A-$NaHSO_4$ and B-$NaHSO_4$ crystals are listed in Table 3. The proposed assignments are also given there. Note that in most cases the positions and shape of the bands due to internal vibrations of hydrogen sulphate anions observed in the infrared spectra of monohydrous and anhydrous modifications of $NaHSO_4$ crystal are different.

Hydrogen bond vibrations

In the infrared spectra of both A-$NaHSO_4$ and B-$NaHSO_4$ crystals above 1500 cm^{-1} region an absorption with characteristic ABC structure is observed. The A band appears at *ca.* 2900 cm^{-1}, the B band occurs at *ca.* 2500 cm^{-1} and exhibits additional structure with maxima at 2640, 2520 and 2300 cm^{-1} in the spectrum of B-$NaHSO_4$ and at *ca.* 2605, *ca.* 2497 and *ca.* 2420 cm^{-1} in the spectrum of A-$NaHSO_4$. The C band appears to be less intense than the A and B bands in both spectra and it is located at 1575 cm^{-1} in the spectrum of B-$NaHSO_4$ and at 1730 and 1615 cm^{-1} in the spectra of A'-$NaHSO_4$ and A''-$NaHSO_4$, respectively. The presence of the ABC bands in infrared spectra are consistent with their origin from the νOH vibration of the medium hydrogen bonds [20, 21] with an $O\cdots O$ distance equal *ca.* 2.65Å. The bands due to the in-plane deformation vibration of hydrogen bond (δOH) appear at 1335 cm^{-1} in the spectrum of B-$NaHSO_4$ and at 1320 and 1290 cm^{-1} in the spectrum of A-$NaHSO_4$. The bands due to the out-of-plane γOH mode are identified at 790 and 664 cm^{-1} and at 773 and 660 cm^{-1} in the spectra of B-$NaHSO_4$ and A-$NaHSO_4$, respectively.

CONCLUSION

The good agreement is observed between the vibrational spectra of $NaHSO_4 \cdot H_2O$ crystal and its crystal structure. Two bands at 1078 and 1040 cm^{-1} are observed in the 1100-1000 cm^{-1} region of infrared spectrum. This region is very important for distinction of the hydrogen sulphate anions linked either into dimers or chains(by the hydrogen bonds). This observation shows that the hydrogen sulphate anions are linked into infinitive chains by hydrogen bonds that is consistent with the reported X-ray data. The infrared spectra in the region above 1800 cm^{-1} is dominated by the absorption with a characteristic AB structure arising from the stretching vibration νOH of the medium strong hydrogen bond linking the HSO_4^- anions into infinitive chain.

The lack of correlation between the infrared spectra of the anhydrous modification (B-$NaHSO_4$) of $NaHSO_4$ obtained by us and the crystal structure of β-$NaHSO_4$ phase shows that the obtained compounds (B-$NaHSO_4$) do not correspond to the β-$NaHSO_4$ phase. However the dehydration of $NaDSO_4 \cdot D_2O$ gives the β-$NaDSO_4$ crystals with only a small contamination of the $NaDSO_4 \cdot D_2O$.

The infrared spectra of A-$NaHSO_4$ and B-$NaHSO_4$ crystal reveal that both anhydrous modifications of the sodium hydrogen sulphate obtained by us show features expected for the α-$NaHSO_4$ phase. But it is very difficult to decide which anhydrous modification exhibits the structure much closer to that of the α-phase.

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