

AN INFRA-RED STUDY OF CRYSTALLO-HYDRATES

BY J. M. JANIK, G. PYTASZ AND T. STANEK

Laboratory of Chemical Physics of the Jagellonian University, Cracow*

(Received January 10, 1969)

An infra-red study of the crystallohydrates: $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ is presented, special attention being paid to the region $400\text{--}1000\text{ cm}^{-1}$. The results are compared with the neutron inelastic scattering study of the same substances. On the basis of this comparison it was possible to interpret certain peaks appearing in the region 400 cm^{-1} to 800 cm^{-1} as arising from vibrational motions of the H_2O molecules. Some qualitative statements concerning the seventh water in $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ are also given.

1. Introduction

The molecular dynamics of water molecules in crystalline hydrates has been the subject of several investigations in which various experimental methods were used. This paper presents the infra-red study (IR) of the following hydrates: $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, and their deuterized analogues. The same substances had been investigated by the neutron inelastic incoherent scattering method (INS) [1], so it was natural to perform the infra-red study for the same samples. It was especially important to confirm which bands in the INS spectrum arise from other molecular motions than those of H_2O -groups. Owing to the selective sensitivity of neutron incoherent scattering cross-section for hydrogen all such nonhydrogenous bands appear in the neutron spectrum as weak ones, which leads to very uncertain interpretation. The infra-red method, on the other hand, giving no special preference to hydrogen, makes it possible to observe the nonhydrogenous bands with much greater accuracy, thus giving a complementary picture to that obtained by the INS method.

We decided to confirm the interpretation of H_2O librational peaks obtained in [1] by performing the infra-red measurement for ordinary hydrates and their deuterized analogues. Our interpretation could in this way be based on approximate $1/\sqrt{2}$ shifts of corresponding vibrational frequencies. Some auxiliary information concerning motions of H_2O groups could be obtained from measurements for water-free substances.

* Address: Zakład Fizyki Chemicznej UJ, Kraków, Krupnicza 41, Polska.

It should be pointed out that the crystallographic situation of H_2O molecules in the $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ crystal is different from that in other hydrates subjected to the present study. The H_2O molecules in $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ crystal are linked together by an open hydrogen bond, *i.e.* they form a zigzag chain like in ice. (An important difference between these chains in the $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ crystal and in ice is that it is one-dimensional in the former and three-dimensional in the latter substance.) In the other hydrates hydrogen bonds are closed, *i.e.* they occur only between the H_2O molecules and the corresponding anions. It could be expected that these differences between the two types of hydrogen bonds would lead to some differences in crystal dynamics, and hence to differences in infra-red spectra. It should be pointed out, however, that on the basis of the results presented in paper [1] these differences in dynamics appear at very low wave numbers ($70\text{--}100\text{ cm}^{-1}$), not detectable by the IR technique applied in this paper (which allows spectra starting from 400 cm^{-1} to be obtained).

Another problem arises in connection with the $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ crystal where the situation of the seventh water molecule is not certain. It was expected that a comparison of infra-red spectra of the $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ crystals and also of the totally or partly deuterized substances will give some new information concerning this problem.

The structure of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ was studied by X-ray diffraction [2] [3], [4] and by neutron diffraction [5], [6]. It was proved that water molecules are connected by hydrogen bonds forming a one-dimensional zigzag chain of bonds $\dots\text{O}\text{--}\text{H}\dots\text{O}\text{--}\text{H}$. The remaining hydrogen bonds connect this chain to SO_4^- tetraheders (Fig. 1). This configuration of water

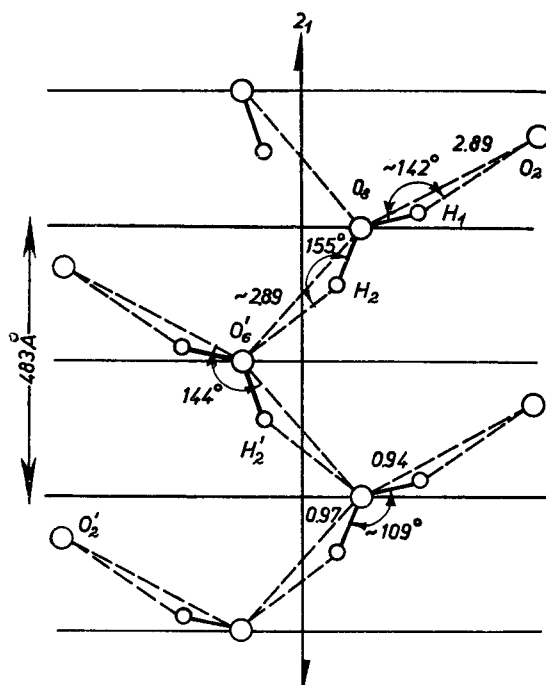


Fig. 1. Hydrogen bonds in the $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ structure. O_3 — oxygen atoms of water molecules, O_2 — oxygen atoms of SO_4^- tetraheders

molecules is rather exceptional for hydrates. All H_2O molecules in the $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ crystal are equivalent. There are two such molecules in the unit cell.

The neutron diffraction data [7] concerning the structure of the $\text{LiClO}_4 \cdot 3 \text{H}_2\text{O}$ crystal lead to the conclusion that the hydrogen bonds are closed in this crystal and they connect the $\text{Li}(\text{OH}_2)_6$ octaheders with ClO_4 tetraheders ($\text{Li}-\text{O}-\text{H}\dots\text{O}-\text{Cl}$). All water molecules lie in positions corresponding to a sixfold symmetry axis and they are structurally equivalent (Fig. 2).

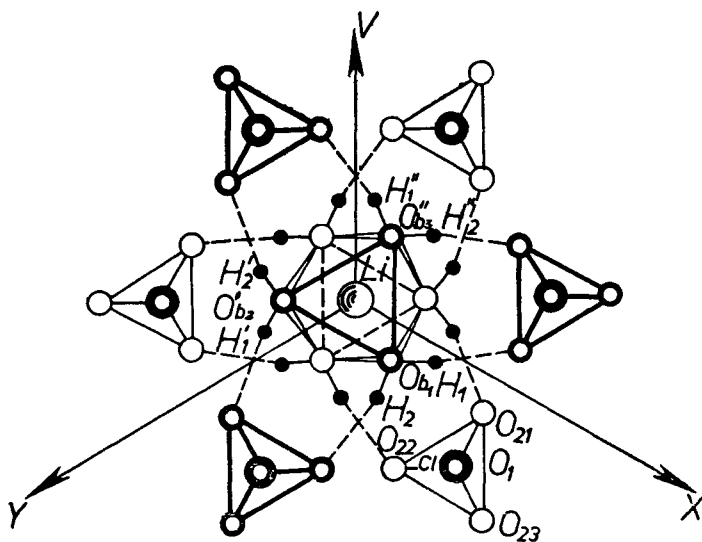


Fig. 2. The crystal structure of the $\text{LiClO}_4 \cdot 3 \text{H}_2\text{O}$

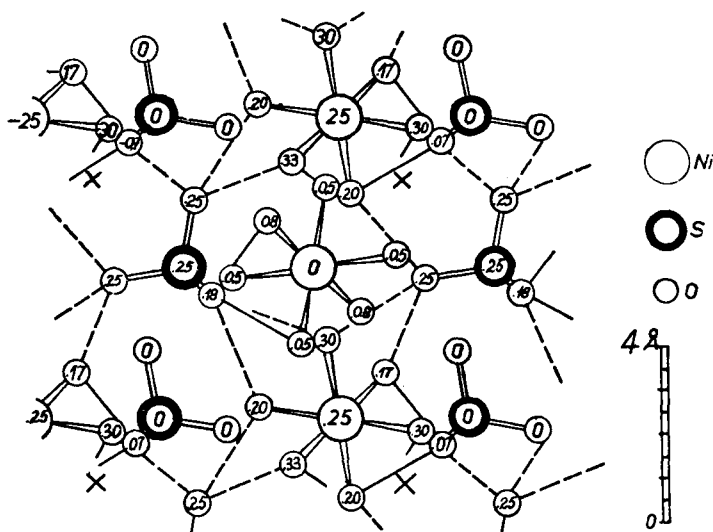


Fig. 3. The crystal structure of the $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$

The hydrates $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ were studied only by X-ray diffraction [8], [9], [10], [11]. It was deduced that in the $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ crystal the $\text{Bi}(\text{OH}_2)$ octaheders are connected with SO_4 tetraheders by closed hydrogen bonds $\text{Ni}-\text{O}-\text{H}\dots\text{O}-\text{S}$. It is suggested that the seventh water molecule in $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ crystal comes in between, forming the bonding $\text{Ni}-\text{O}-\text{H}\dots\text{O}-\text{H}\dots\text{O}-\text{S}$.

In $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ (Fig.3) all water molecules have the same situations in the crystal lattice; each oxygen of the H_2O molecules has three bonds, one directed towards the Ni atom two towards oxygen atoms of two SO_4 groups (through hydrogen bonds).

In $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ the seventh water molecule is responsible for the fact that now different water molecules have different situations in the crystal lattice [12]. There are four water molecules having three bonds, which, however, are not equivalent among themselves;

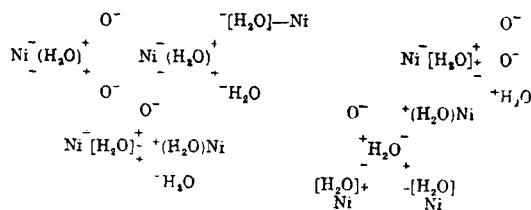


Fig. 4. The situation of water molecules in the $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$. Explanations in text

there are two water molecules which have four bonds, though in slightly different situations; there is the seventh water molecule clearly distinguished from all the others, which also has four tetrahedric bonds.

All possible environments of water molecules in $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ are presented in Fig. 4. In this figure the three bonded water molecules are denoted by (H_2O) , the four bonded water molecules by $[\text{H}_2\text{O}]$, and the four bonded, seventh water molecule by H_2O .

2. Experimental method

The measurements were made by applying a Zeiss UR 10 infra-red spectrophotometer in the region from 400 cm^{-1} — 4000 cm^{-1} , special attention being paid to the region of 400 cm^{-1} — 1000 cm^{-1} . In using this low wave number region the KBr prism was applied for wave numbers 400 cm^{-1} — 700 cm^{-1} and an NaCl prism was used for wave numbers above 700 cm^{-1} . For higher wave numbers the LiF prism was used.

All measurements were performed at room temperature. The samples were prepared by applying the usual nujol technique. The application of the KBr pellets technique was proved to be incorrect on account of an ion exchange, a similar phenomenon having been observed by other authors [13], [14], [15].

The deuterized samples were prepared by solving the water-free substances in 95% heavy water; then the liquid phase was slowly evaporated till crystals fell out. Special care was taken to keep the temperature of crystallization proper for each hydrate.

The heavy water content was checked by weighing, though the IR spectra themselves provide good evidence of the presence of heavy water in the samples.

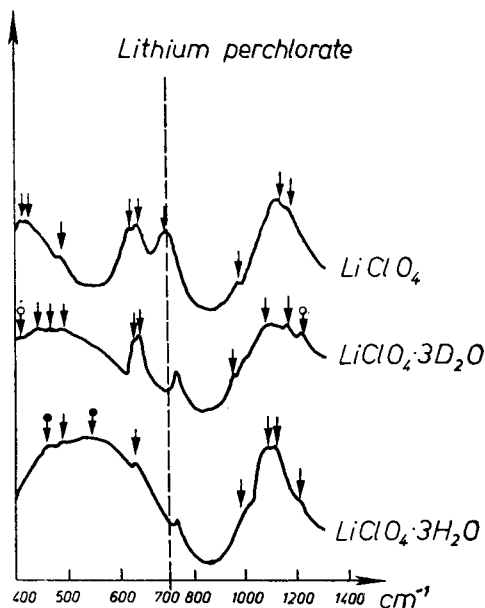


Fig. 5. Infra-red absorption spectrum of lithium sulphate. Wave number region 400–1400 cm^{-1} . ● — denote the positions of peaks ascribed to H_2O groups, ○ — denote the positions of peaks ascribed to D_2O groups, ↓ — denote the positions of all other peaks

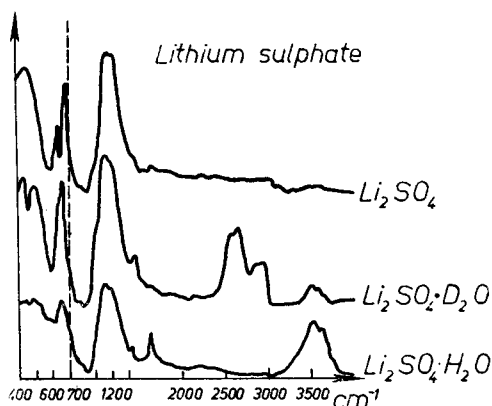


Fig. 6. Infra-red absorption spectrum of lithium sulphate. Wave number region 400–4000 cm^{-1}

3. Results and discussion

The IR results obtained from measurements are presented in Figs 5–8 and wave numbers assigned to the peaks in Tables I–III. For comparison the IR data obtained by other authors and the INS data given in the paper [1] are also included in these Tables. In the discussion given below all these data are used special attention being paid to the results of the present study and to those of the paper [1].

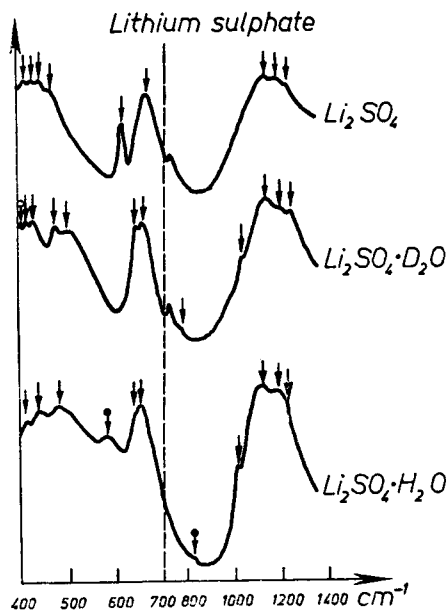


Fig. 7. Infra-red absorption spectrum of lithium perchlorate. Wave number region 400–1400 cm^{-1} . \bullet — denote the position of peaks ascribed to H_2O groups, \circ — denote the positions of peaks ascribed to D_2O groups, \blacktriangledown — denote the positions of all other peaks

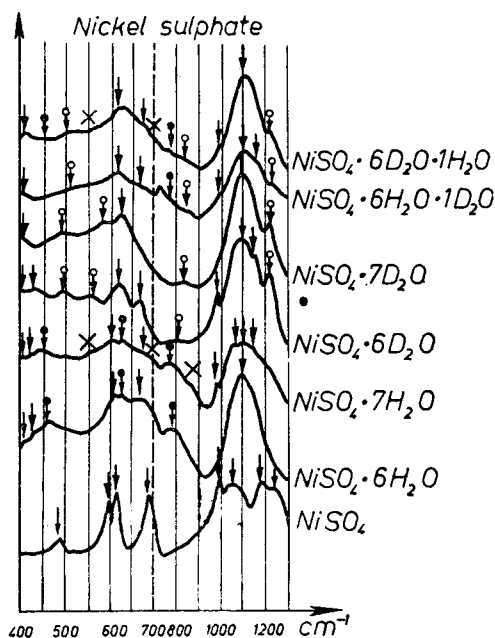


Fig. 8. Infra-red absorption spectrum of nickel sulphate. Wave number region 400–1300 cm^{-1} . \bullet — denote the positions of peaks ascribed to H_2O groups, \circ — denote the positions of peaks ascribed to D_2O groups, \blacktriangledown — denote the positions of all other peaks

3.1. $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$

It was pointed out in [1] that the bands obtained for this substance may be divided into groups:

Group 1 contains low frequencies of vibration ($76, 103 \text{ cm}^{-1}$) which appear in solid $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ as a strong band, unlike in other hydrates but like in ice. It is believed that this band arises from out of plane deformation vibration of hydrogen bonds. This group was detected only by the INS technique, not being approachable by our IR apparatus.

Group 2 contains only three peaks ($104, 186, 235 \text{ cm}^{-1}$) which are interpreted as arising from translatory vibrations of the H_2O group in the crystal lattice. These frequencies were also detected by the INS technique only.

Group 3 gives a possibility of comparison of the INS results with the IR ones. In this group are numbered the following frequencies: $414, 438, 633, 650, 1019$ and 1120 cm^{-1} , which we believe arise from internal vibrations of the SO_4 group; we think that the following arguments support this suggestion:

a) similar peaks at frequencies close to those given in Table [1] appear in anhydrous Li_2SO_4 and in aqueous solutions of this salt.

b) these peaks appear also in the INS spectrum but with much lower intensities, suggesting that they do not arise from vibrations of hydrogen atoms.

The appearance of six peaks corresponding to internal vibration of SO_4 groups instead of only four, as expected for molecules of XY_4 symmetry, may be explained by the fact that the degeneration is partly cancelled by the crystal field.

Besides these internal frequencies characteristic for SO_4 groups there remain four peaks: at 343 cm^{-1} (observed in INS), at 480 cm^{-1} (observed in IR) at 580 cm^{-1} (observed in both INS and IR) and at 835 cm^{-1} (observed also in both INS and IR).

We believe that the peak corresponding to 480 cm^{-1} is caused by Li—O stretching vibrations. The peak at 343 cm^{-1} is caused by librational motion of H_2O molecules (twisting), in agreement with the frequency value for twisting (365 cm^{-1}) measured by the NMR technique [16]. We may tentatively accept that the peaks at 580 cm^{-1} and 835 cm^{-1} arise from the two remaining librational motions of H_2O molecules (wagging and rocking). Our infra-red measurements for deuterized substance support this suggestion. We observe in Fig. 5. a shift of the corresponding librational bond (580 and 835 cm^{-1}) towards lower frequencies ($410, 590$). As the result of this shift, the SO_4 vibration peak at about 640 cm^{-1} relatively increases its intensity in the case of the $\text{Li}_2\text{SO}_4 \cdot \text{D}_2\text{O}$ crystal as compared with the same peak for $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. Also the valley between this peak and the lower frequency band at about 480 cm^{-1} become much deeper for a deuterized substance, as a result of disappearance of the 580 cm^{-1} peak, which was shifted towards lower frequencies.

The internal vibrations of the H_2O molecule appearing at 1620 cm^{-1} and at the band $3400\text{--}3600 \text{ cm}^{-1}$ form the fourth group (see Table I). They are clearly visible in IR and not attainable in INS. They are all shifted after deuteration by approximately $1/\sqrt{2}$. This shift is observed in Fig. 5. In this region there are also weak bands corresponding to light water molecules. This follows from the fact that the heavy water used for recrystallization contained *ca* 5% of light water. Hence the $\text{Li}_2\text{SO}_4 \cdot \text{D}_2\text{O}$ must also contain $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.

Peak frequencies in crystalline lithium sulphate obtained in various experiments (in cm^{-1})

INS		IR					Interpretation	
J. A. Janik <i>et al.</i> [1] $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (77°K)	H. J. Prask <i>et al.</i> [18] $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (293°K)	This paper			F. A. Miller <i>et al.</i> [19] $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (293°K)	S. A. Shukarev <i>et al.</i> [20] $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (293°K)		
		$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (293°K)	Li_2SO_4 (293°K)	$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (293°K)				
76 103	107						Deformation acoustic vibrations of hydrogen bonds	Group I
164 186 235	203 260						H_2O transl.	Group II
343				405	367		H_2O rot. $580/\sqrt{2}$	Group III
448		414	413	416			$\nu_2 - \text{SO}_4$	
		438	442	430	437	435	Li-O str.	
		480	467	476	480	480		
				495				
556	524	580		639	577	570	H_2O rot.	
617	672	638	616	639	646	632	$\nu_4 - \text{SO}_4$	
		650	666	651		642		
769 1014	832	835		780			H_2O rot.	
		1019		1019		980	$\nu_1 - \text{SO}_4$	
		1120	1113	1106		1110	$\nu_3 - \text{SO}_4$	
		1178	1160	1175				
		1210	1210	1210				
		1622		1620			Internal H_2O vibrations	Group IV
				2560			Internal D_2O vibrations	
				2670				
		3485		3493			Internal H_2O vibrations	
		3590		3580				
		3603		3600				
		3620		3625				

3.2. $\text{LiClO}_4 \cdot 3 \text{H}_2\text{O}$

Following the paper [1] we again make use of the division of the bands into three groups (Table II).

The band at 90 cm^{-1} (group 1) appears only in INS, and is very weak, unlike what was observed in the $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ crystal and in ice. As suggested in [1], this fact may be connected with a difference in hydrogen bonding in the two substances.

TABLE II

Peak frequencies in crystalline lithium perchlorate obtained in various experiments (in cm^{-1})

INS	IR				Interpretation	
	This paper			S. A. Shukarev <i>et al.</i> [20] $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ (293°K)		
	$\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ (293°K)	LiClO_4 (293°K)	$\text{LiClO}_4 \cdot 3\text{D}_2\text{O}$ (293°K)			
90						Group I
128					Three of these frequencies are H_2O transl. Li — O str.	Group II
157						
209						
277						
304						
380			410		H_2O rot. (T) $550/\sqrt{2}$	Group III
		418 425				
456	460 490	485	445 470 497		H_2O rot. $\nu_2 - \text{ClO}_4$	
515	~550			~550	H_2O rot.	
617	635 645	635 641 680	633 643	624 630	} $\nu_4 - \text{ClO}_4$	
866	960 1090 1110	970	945 1073 1160	938 1080		

The maxima belonging to the group 2 (observed only in INS) were interpreted as arising from translatory vibrations of water molecules.

Group 3 again belongs to the region where a comparison of the infra-red and neutron methods is possible. The lowest frequency of this group (observed only in INS) at 380 cm^{-1} was interpreted in [1], in agreement with NMR measurements [17], as arising from twisting vibrations of the H_2O molecules. We think that IR peaks at 635 cm^{-1} and 1090 cm^{-1} are connected with internal vibrations of the ClO_4 -ions. This interpretation is based on the fact that such peaks appear for anhydrous LiClO_4 as well as for solutions containing the ClO_4 -ions.

The H_2O librational peaks are not resolved distinctly in IR; they appear as such in the neutron spectrum at 456 cm^{-1} and 515 cm^{-1} . Instead of this, we observed in the IR spectrum a broad band with a maximum at *ca* 550 cm^{-1} . This broad band shifts toward lower frequencies after deuteration, indicating that it contains librational peaks of H_2O groups. We believe that this band is so broad because it covers the remaining internal frequencies of ClO_4 -ions, which, due to a selective sensitivity of neutrons for hydrogen, do not contribute

Peak frequencies in crystalline nickel sulphate obtained in various experiments (in cm^{-1})

INS	IR						I. Gamo [21] $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (293°K)	Interpretation	
	This paper								
	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (293°K)	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (293°K)	$\text{NiSO}_4 \cdot 6\text{D}_2\text{O}$ (293°K)	$\text{NiSO}_4 \cdot 7\text{D}_2\text{O}$ (293°K)	$\text{NiSO}_4 \cdot 6\text{D}_2\text{O} \cdot \text{H}_2\text{O}$ (293°K)	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O} \cdot \text{D}_2\text{O}$ (293°K)			
215									Group II
244							H_2O transl.		
358									
456	412	414	411	406	410	410	760	} $\nu_2 - \text{SO}_4$ H_2O rot. (T)	Group III
	430	422	438						
471	467		507	500	507	515		D_2O $790/\sqrt{2}$	
617	620	618	625	625	625	623		$\nu_4 - \text{SO}_4$	
	633	632						H_2O rot. (W)	
770	676	673	675	668	675	675		$\nu_4 - \text{SO}_4$	
	790	790						H_2O rot. (R)	
			820	840	848	850		D_2O (T+TW)	
		990	993		995	990		$\nu_1 - \text{SO}_4$	
	1110	1096	1095	1098	1100	1110		$\nu_3 - \text{SO}_4$	
		1158	1160			1155			
	1650	1655	1645	1640	1658	1655	D_2O $1650/\sqrt{2}$ Internal H_2O vibrations	Group IV	

to neutron scattering. This allows the appearance of distinct librational peaks in the neutron spectrum.

It may be seen in Fig. 7 that, as a result of a shift of the librational after deuterization, the band containing the ClO_4 vibrations at 635 and 645 cm^{-1} becomes more distinct and the valley between this band and the librational one becomes deeper.

3.3 $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$

The interpretation of INS experiments [1] was limited to the $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ only and to the statement that the $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ spectrum was practically the same as that of $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$, thus giving evidence of a rather weak bonding of the seventh water in comparison with the other six. It is worth while to mention that further support of this statement is connected with the fact the $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ loses the seventh water at a much lower temperature (31.5°C) than the remaining six water molecules (103°C).

From the three groups of peaks discussed in [1] for the two other hydrates mentioned above and for ice, there is almost no evidence of peaks of group I in $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ neutron

spectra. The three frequencies observed in group 2 were interpreted as arising from translational vibrations of water molecules (with a possible alternative explanation for one of them as Ni-O stretching). This group was accessible to the INS experiments only.

As regards group 3, we believe that the peak at 469 cm^{-1} arises from H_2O twisting, in view of this similarity to the corresponding peaks in neutron spectra in the two other substances and also in view of this shift in IR for deuterized substance. (It cannot be observed after deuterization because it shifts outside the range of our instrument.)

The two other peaks at 615 cm^{-1} and 790 cm^{-1} we also describe to librational H_2O motions on the grounds of their shifts in IR after deuterization.

The peaks at *ca* 420 cm^{-1} , 620 cm^{-1} , 620 cm^{-1} , 670 cm^{-1} , 990 cm^{-1} , and 1100 cm^{-1} we interpret as arising from the internal vibrations of SO_4^- on the basis of arguments similar to those given for $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.

A comparison of the IR spectra of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{D}_2\text{O}$, $\text{NiSO}_4 \cdot 7\text{D}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{D}_2\text{O} \cdot 1\text{H}_2\text{O}$, and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O} \cdot 1\text{D}_2\text{O}$ does not give any conclusive statements concerning the behaviour of the seventh water. Weak and not clearly distinct bands which appear when the seventh water is present are marked by asterisks in Fig. 8. In view of their uncertainty they are not included in the Table. It should be pointed out, however, that their appearance was reproduced in several repeated measurements.

We may draw the general conclusion that the IR spectra of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ are diffuse then those with six water molecules. This fact supports the opinion of the paper [1] that the seventh water possesses a relatively large degree of freedom for rotational motions, giving a fairly continuous spectrum. If this is true, the additional maxima obtained with seventh water molecules in our IR investigations should reflect a distortion of crystallographic equivalency of H_2O groups if we pass from six to seven H_2O groups.

4. Conclusion

A comparison of the results of the present IR investigation with those of the INS study [1] shows that these experiments together allow the peaks to be interpreted with much greater certainty than does one experiment alone. This is especially true for hydrogen atom motions. The elimination of peaks corresponding to internal vibrations of anions leads to the interpretation of some peaks as H_2O libration, which in some cases (for instance for twisting) is very difficult to achieve by purely optical methods. Thus it was demonstrated that the two methods could be treated as complementary and that in some cases also the NMR experiments should be taken into consideration.

The following extension of the present study in the near future would appear to be natural:

1) The low temperature measurement should be made in IR in view of the fact that the present IR data are obtained at room temperature, whereas the neutron data are obtained at a much lower temperature. As lattice vibrations are temperature dependent this effect should facilitate the interpretation.

2) It is also clear that the IR study of our substances should be performed in the range of lower wave numbers *i. e.* at far infra-red, thus making it possible to obtain peaks which

were hitherto accessible only with neutron methods. It is to be expected that at these wave numbers a characteristic difference will appear between the $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ on the one hand and the remaining hydrates of the other.

Our thanks are due to the authors of paper [1] for enabling us to use the INS results prior to publication, and especially to Professor J. A. Janik for stimulating discussions. We thank Professor A. Bielański and Dr M. Dyrek for putting at our disposal the IR spectrometer of the Chemistry Institute of the Jagellonian University and for their instructive help. We also thank Professor Baličeva for interesting discussions and Miss A. Pałczyńska and A. Migdał for technical assistance.

REFERENCES

- [1] A. Bajorek, J. A. Janik, J. M. Janik, I. Natkaniec, K. Parliński, J. N. Pokotilovskij, M. Sudnik-Hrynkievicz, V. E. Komarov, R. P. Ozerov, S. P. Solevev, *Proc. of IAEA Symposium on Neutron Inelastic Scattering*, Vol. II., p. 143, Vienna 1968.
- [2] G. E. Ziegler, *Z. Kristall.*, **89**, 456 (1934).
- [3] A. C. Larson, L. Helmholtz, *J. Chem. Phys. (USA)*, **22**, 2049 (1954).
- [4] A. C. Larson, *Acta Cryst. (Internat.)*, **18**, 717 (1965).
- [5] N. B. Rannev, I. D. Datt, A. B. Tovbis, R. P. Ozerov, *Kristallografiya (USSR)*, **10**, 914 (1966).
- [6] H. G. Smith, S. V. Peterson, H. A. Levy, *Meeting of the Amer. Cryst. Association* 1961.
- [7] I. D. Datt, N. B. Rannev, R. P. Ozerov, *Kristallografiya (USSR)*, **13**, 2 (1968).
- [8] C. A. Beevers, H. Lipson, *Z. Kristall.*, **83**, 123 (1932).
- [9] C. A. Beevers, C. M. Schwartz, *Z. Kristall.*, **91**, 157 (1935).
- [10] A. Zalkin, H. Ruben, D. H. Templeton, *Acta Cryst. (Internat.)*, **17**, 235 (1964).
- [11] W. H. Baur, *Acta Cryst. (Internat.)*, **17**, 1167 (1964).
- [12] A. F. Wells, *Structural Inorganic Chemistry*, Oxford of the Clarendon Press 1962.
- [13] V. W. Melocke, G. E. Kalbus, *J. Inorg. Nuclear Chem. (GB)*, **6**, 104 (1958).
- [14] L. H. Jones, M. M. Chamberlain, *J. Chem. Phys. (USA)*, **25**, 365 (1956).
- [15] R. A. Durie, J. Szewczyk, *Spectrochim. Acta (GB)*, **15**, 593 (1959).
- [16] D. F. Holcomb, B. Pederson, *J. Chem. Phys.*, **36**, 3720 (1962).
- [17] J. Pietrzak, *Thesis*, Poznań 1966.
- [18] R. J. Prask, H. Boutin, *J. Chem. Phys. (USA)*, **45**, 699, 3284 (1966).
- [19] F. A. Miller, G. L. Carlson, F. F. Bentley, W. H. Jones, *Spectrochim. Acta*, **16**, 135 (1960).
- [20] C. A. Shukarev, T. G. Baličeva, B. B. Lavrov, *Vestnik Leningrad Univ.* (in press).
- [21] I. Gamo, *Bull. Chem. Soc. (Japan)*, **34**, 760 (1961).