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Infrared Spectra and Lattice Vibrations of $Li_2SO_4 \cdot H_2O$[1]

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Infrared spectra of $Li_2SO_4 \cdot H_2O$ and $Li_2SO_4 \cdot D_2O$ have been measured from 4000 to 30 cm^{-1} at room temperature and liquid-nitrogen temperature. Librational bands of the water of crystallization have been observed and the modes of libration are discussed. The normal coordinate analysis of the crystal as a whole has been performed and the observed bands are interpreted. Translational bands of H_2O and librational bands of SO_4 are also discussed.

The present report deals with a study by infrared spectroscopy and the normal coordinate calculation concerning the vibrations of $Li_2SO_4 \cdot H_2O$ and $Li_2SO_4 \cdot D_2O$ crystals. The investigation was undertaken because of interesting features of the crystals. NMR spectra suggest that the water of crystallization performs a flipping motion around the molecular symmetry axis. There are two different positions for Li ions in a unit cell, one being located close to the water of crystallization and the other tetrahedrally surrounded by the oxygen atoms of the sulfate ions. Some changes in the infrared spectra might take place by variation of temperature on account of this flipping motion of the water of crystallization, and the effect of the environmental difference of the two Li ions might be observed in the infrared spectra.

By the use of X-ray diffraction,[2-4] neutron diffraction[5,6] and NMR spectroscopy,[7-10] several investigators have studied the crystal structure of $Li_2SO_4 \cdot H_2O$ and $Li_2SO_4 \cdot D_2O$, with particular attention to the orientation of the water molecule. Ketudat and Pound concluded from the quadrupole splitting of the deuterium resonance of $Li_2SO_4 \cdot D_2O$ that at room temperature, the water molecule undergoes hindered rotation about the bisector of the D–O–D angle with frequency greater than that of quadrupole interaction.[11] The same conclusion has been reached by other investigators.[12-14] This view is consistent with the large root mean square amplitude of the vibration of the hydrogen atoms observed in the recent neutron diffraction study.[6]

There are only a few works on the infrared[15,16] or Raman spectra[17] of these compounds. The intramolecular vibrations of the SO_4 ion and also the librations of the water molecule have been analyzed to some extent. However, because of the lack of measurements at low temperature the analysis remains still uncertain. There has been no study on the far infrared spectra below 350 cm^{-1}.

Neutron inelastic scattering studies of these compounds have been made by several workers.[18,19] Bajorek *et al.* have observed librational frequencies as well as translational lattice vibrations of the water molecule.[20]

Experimental and Observed Spectra

$Li_2SO_4 \cdot H_2O$ of a special grade (Wako Pure Chemical Industries, Ltd.) was used without further purification.

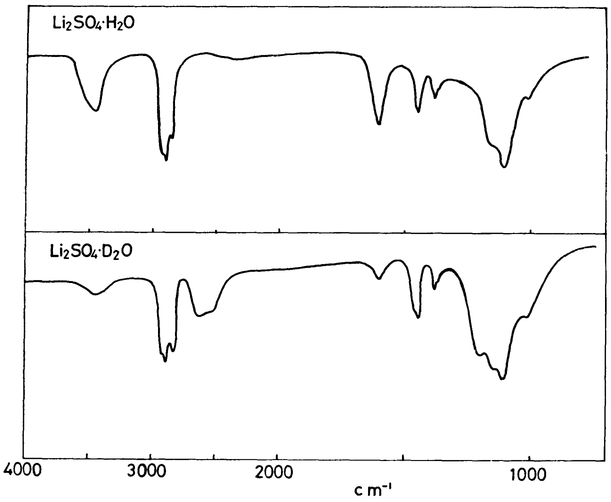

Fig. 1. Infrared spectra of $Li_2SO_4 \cdot H_2O$ and $Li_2SO_4 \cdot D_2O$ in Nujol at room temperature.

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[1] This work was supported partially by a research grant of the Matsunaga Science Foundation and by the Group Project organized by Science and Engineering Research Laboratory, Waseda University 1969—1970.

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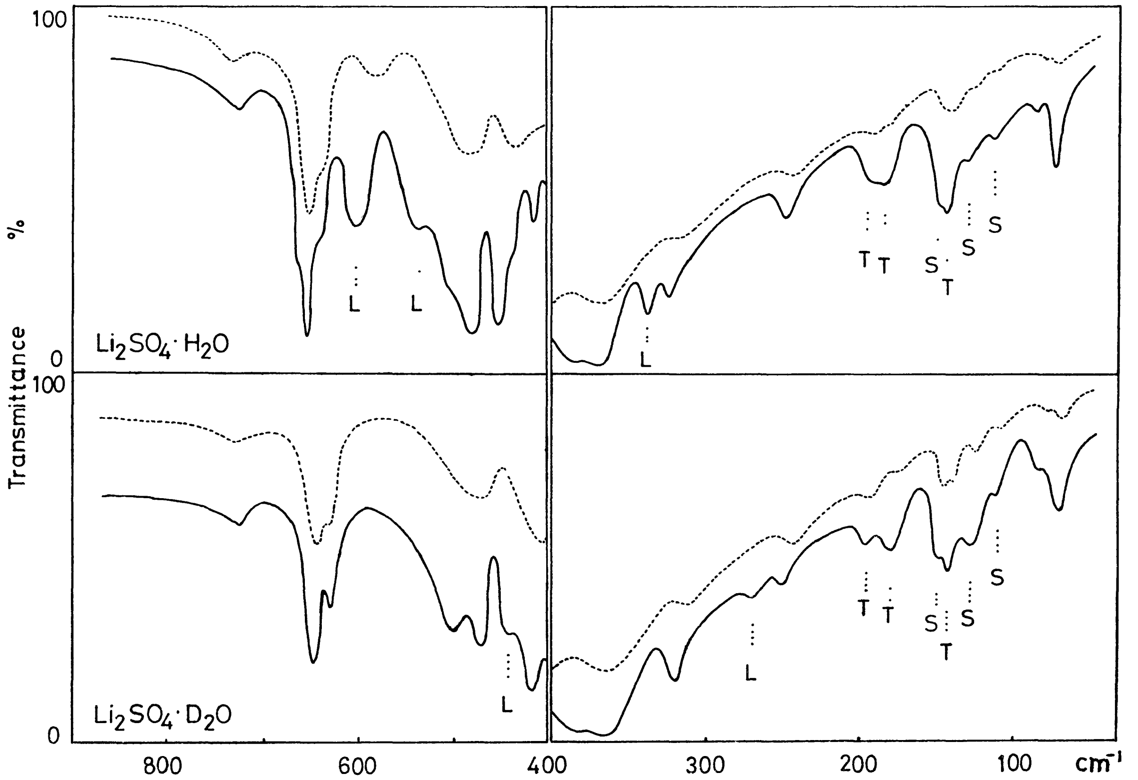

Fig. 2. Infrared spectra of $Li_2SO_4 \cdot H_2O$ and $Li_2SO_4 \cdot D_2O$ in Nujol, ······ 300°K, —— 110°K. L, T, and S denote a librational band of H_2O, a translational band of H_2O and a librational band of SO_4 respectively.

An infrared spectrophotometer Hitachi EPI-G3 (4000—400 cm^{-1}) and a far infrared spectrophotometer Hitachi FIS-3 (400—30 cm^{-1}) were used. Each measurement was carried out at room temperature and also at liquid nitrogen temperature. The deuterated samples were prepared by gradual recrystallization from a heavy water solution of the anhydrous compound. Although a small amount of light water still remained in the deuterated sample, the heavy water content was sufficiently large for the assignment of infrared bands of $Li_2SO_4 \cdot D_2O$. The observed infrared spectra are shown in Figs. 1-3. By lowering the temperature, all the bands become sharp and intense. At the same time, the bands except for those due to intra-molecular vibrations shift to higher frequencies.

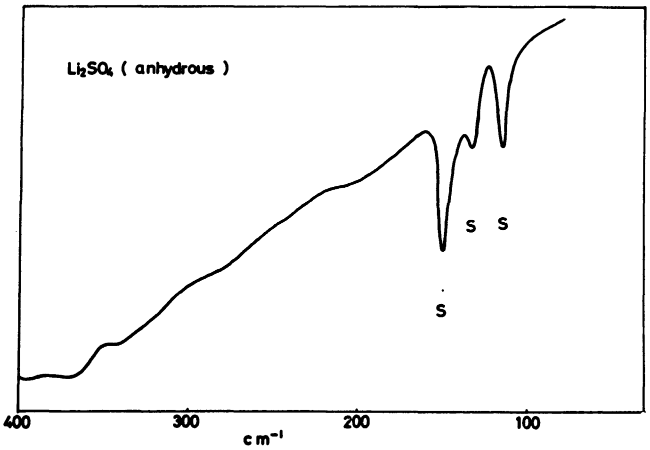

Fig. 3. Infrared spectrum of anhydrous Li_2SO_4 in Nujol at room temperature.
S denotes a librational band of SO_4.

Normal Coordinate Analysis

The crystal structure of $Li_2SO_4 \cdot H_2O$ is $P2_1$–C_2^2 and the crystal parameters are a=5.4537 Å, b=4.8570 Å, c=8.1734 Å, and β=107°22′.[6] A Bravais unit cell contains two $Li_2SO_4 \cdot H_2O$ unit. The optically active lattice vibrations as well as the intra-molecular vibrations were calculated according to the method developed by Shimanouchi *et al.*[21]

A Urey-Bradley type force field was applied to the H_2O molecule and SO_4 ion, and a valence force type potential was used for the interactions within a distance of 3.0 Å between H_2O molecule and SO_4 and Li ions. The bound state of the crystalline water in $Li_2SO_4 \cdot H_2O$ has some characteristic features. The hydrogen atoms of H_2O molecule make hydrogen bondings: one with another water and the other with the oxygen atom of the sulfate ion. One of the lone pairs of the oxygen atom of the water molecule directs toward the Li ion. The other is in the direction toward a hydrogen atom of another H_2O molecule to make a hydrogen bonding. Thus the H_2O molecules constitute a zigzag chain in the crystal by hydrogen bondings.

The potential around the H_2O molecule was assumed to be as shown in Fig. 5 by analogy with the H_2O molecule in ice.[22] In the course of the calculation the interaction coordinates around the H_2O

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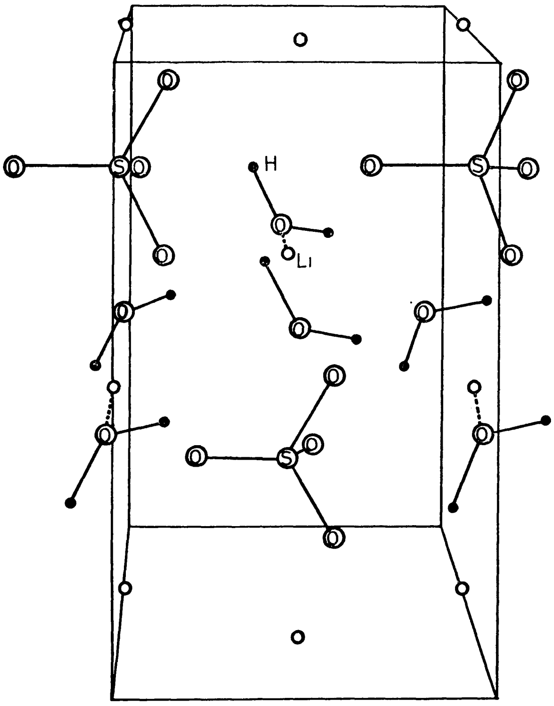

Fig. 4. Crystal structure of $Li_2SO_4 \cdot H_2O$.

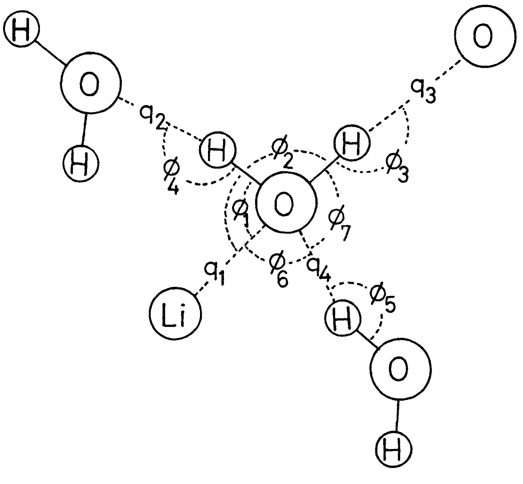

Fig. 5. Coordinates around a H_2O molecule.

molecule are simplified, and $\Delta q(\mathrm{Li \cdots O})$, $\Delta q(\mathrm{O \cdots H})$, $\Delta\phi(\mathrm{Li \cdots O\text{-}H})$, $\Delta\phi(\mathrm{O\text{-}H \cdots O})$, and $\Delta\phi(\mathrm{O \cdots Li \cdots O})$ are used from the following consideration. The coordinate $\Delta\phi(\mathrm{H\text{-}O \cdots H})$, which is the interaction between the two H_2O molecules in a unit cell, serves to enlarge the frequency splittings between A and B symmetry species. The A and B species, however, are not observed separately so this coordinate is excluded. Further, the coordinate $\Delta\phi(\mathrm{Li \cdots O \cdots H})$ is omitted, because this has little effect on the librational frequencies and on the other lattice vibrations. Consequently the potential function in the crystal is expressed as

$$
\begin{aligned}
V = V_{intra} &+ \tfrac{1}{2}\sum_{ij} K_i^1(\Delta q_{ij}(\mathrm{Li \cdots O}))^2 \\
&+ \tfrac{1}{2}\sum_{ij} K_i^2(\Delta q_{ij}(\mathrm{O \cdots H}))^2 \\
&+ \tfrac{1}{2}\sum_{ij} H_i^1(\Delta\phi_{ij}(\mathrm{Li \cdots O\text{-}H}))^2 \\
&+ \tfrac{1}{2}\sum_{ij} H_i^2(\Delta\phi_{ij}(\mathrm{O\text{-}H \cdots O}))^2 \\
&+ \tfrac{1}{2}\sum_{ij} H_i^3(\Delta\phi_{ij}(\mathrm{O \cdots Li \cdots O}))^2
\end{aligned}
$$

where V_{intra} denotes the intra-molecular potentials of SO_4 ion and H_2O molecule. K_i^1, K_i^2, H_i^1, H_i^2, and H_i^3 represent the force constants corresponding to the coordinates $\Delta q(\mathrm{Li \cdots O})$, $\Delta q(\mathrm{O \cdots H})$, $\Delta\phi \cdots (\mathrm{Li \cdots O\text{-}H})$, $\Delta\phi(\mathrm{O\text{-}H \cdots O})$ and $\Delta\phi(\mathrm{O \cdots Li \cdots O})$, respectively. The sum was taken over all kinds of internal coordinates i, and all the internal coordinates j for each kind of i in a Bravais unit cell.

TABLE 1. FORCE CONSTANTS

	Distance (Å)	f. c. (mdyn/Å)
K(O-H)	0.95	6.52
K(S=O)	1.48	6.10
H(H-O-H)		0.57
F(H···H)		0.10
H(O=S=O)		0.59
F(O···O)		0.81
$\kappa(SO_4)$		0.25[a]
$K(\mathrm{Li \cdots OH_2})$	1.91	0.40
K(Li···O)	1.92	0.34
K(Li···O)	1.95	0.22
K(Li···O)	1.99	0.12
K(O···H)	2.00	0.20
K(O···H)	2.78	0.17
K(O···H)	2.97	0.09
H(Li···O-H)		0.15
H(O···Li···O)		0.03
H(O-H···O)		0.01

a) mdyn·Å

Results and Discussion

Intra-molecular Vibrations. Since the site symmetry of sulfate ion in the crystal is C_1, ν_1 becomes infrared active, ν_2 splits into two bands, and ν_3 and ν_4 both split into three bands.[23] The observed spectra are in good agreement with the predictions: ν_1 (1010 cm^{-1}), ν_2 (513 and 478 cm^{-1}), ν_3 (1170, 1155, and 1110 cm^{-1}) and ν_4 (656, 647, and 637 cm^{-1}) at a low temperature. This assignment is also in line with the fact that the frequencies show no frequency shifts on deuteration and little temperature dependence. It is interesting that the splittings of ν_2 and ν_4 become greater on deuteration. The bands at around 1170, 1155, and 1110 cm^{-1} are as strong as other sulfates, and so broad that the positions of the peaks are difficult to determine. Although these bands are considered to be due to the splitting of the stretching mode of the sulfate ion belonging to the F_2 symmetry species, such large splittings have not been obtained by the normal coordinate calculation.

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[23] nomenclature after G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand (1945)

TABLE 2. FREQUENCIES AND ASSIGNMENT OF $Li_2SO_4 \cdot H_2O$

Obsd (cm^{-1})		Calcd (cm^{-1})		Assignment
300°K	110°K	A	B	
3520 3500 3475	3600 3495 3455	3499 3464	3498 3461	O-H str.
1612	1600	1601	1606	H-O-H bend.
1170 1155 1110	1170 1155 1110	1125 1117 1114	1126 1117 1115	SO_4 ν_3
1010	1010	1006	1008	SO_4 ν_1
— 645 634	656 647 637	658 641 635	654 642 639	SO_4 ν_4
580	600	602	604	H_2O lib.
—	533	541	542	H_2O lib.
— 475	513 478	505 472	505 474	SO_4 ν_2
432	447	437	437	Li···OH_2 str.
380	387	392	392	Li···O str.
	372	370	369	Li···O str.
—	—	346	346	Li···O str.
—	338	330	337	H_2O lib.
318	325	310	305	O···Li···O bend.
245	249	270	277	O···Li···O bend.
194	196	223	214	H_2O trans.
175	180	174	209	H_2O trans.
145	147	150	161	SO_4 lib.
137	143	130	149	H_2O trans.
123	128	110	100	SO_4 lib.
109	113	96	94	SO_4 lib.
83	84	74	—	
71	72	50	52	

TABLE 3. FREQUENCIES AND ASSIGNMENT OF $Li_2SO_4 \cdot D_2O$

Obsd (cm^{-1})		Calcd (cm^{-1})		Assignment
300°K	110°K	A	B	
2600 2550	2610 2560 2540	2565 2497	2564 2493	O-D str.
1195	1195	1165	1172	D-O-D bend.
1150 1130 1110	1150 1130 1110	1125 1117 1114	1125 1117 1115	SO_4 ν_3
1010	1010	1006	1008	SO_4 ν_1
— 643 629	— 647 631	651 639 634	649 640 636	SO_4 ν_4
490 465	512 473	518 506	521 509	SO_4 ν_2
423	440	440	437	D_2O lib.
405	420	432	432	Li···OD_2 str.
370	380	394	399	Li···O str.
360	370	367	366	Li···O str.
—	—	363	353	D_2O lib.
—	—	341	342	Li···O str.
315	322	310	305	O···Li···O bend.
—	269	271	277	D_2O lib.
242	249	241	269	O···Li···O bend.
190	194	214	208	D_2O trans.
170	176	172	187	D_2O trans.
142	147	149	161	SO_4 lib.
137	141	129	145	D_2O trans.
122	126	109	98	SO_4 lib.
104	110	96	93	SO_4 lib.
80	82	72	—	
68	66	49	52	

H_2O Librational Modes. The behavior of the water in the crystalline lattice is observed directly by the librational bands which have three characteristic features.

1) The bands are observed in the region between 1100 and 200 cm^{-1}.

2) These frequencies become approximately $1/\sqrt{2}$ on deuteration.

3) The intensities of the bands are very sensitive to temperature change.

Thus the three bands at 600, 533, and 338 cm^{-1} at low temperature are assigned to the librational bands of the water of crystallization in $Li_2SO_4 \cdot H_2O$ crystal. The bands at 600 and 338 cm^{-1} shift respectively to 440 and 269 cm^{-1} on deuteration. The deuterated band corresponding to 533 cm^{-1}, however, seems to be buried under the strong and broad bands at 387 and 372 cm^{-1} of the Li ion. The frequency ratios are 1.35 and 1.26 respectively. Janik *et al.* have observed a band at 835 cm^{-1} and assigned it to a libration of the water molecule.[16] However, we have observed no bands near that frequency.

The librational bands of water of crystallization have been observed in many compounds, but it is difficult to determine the modes of the librational motions experimentally. A normal coordinate analysis is useful for elucidating the behavior of the water molecule in a crystalline lattice.[24–26] The eigen vector (***Lx***) matrix set up by the Cartesian coordinate method shows the displacements of the atoms which correspond to each normal mode. It is seen from this ***Lx*** matrix that the band at 600 cm^{-1} is the rocking mode and the other two bands are mixtures of the wagging and twisting modes. As the values of ***Lx*** depend on the potential field around the water molecule, the interaction coordinates around the water molecule are chosen as thoroughly as possible. The bands at 533 and 338 cm^{-1} can not be observed distinctly until the sample is cooled to liquid nitrogen temperature. This suggests that the bands corresponding to the wagging and twisting motions become diffuse at ordinary temperature as a result of the 180° flipping motion of the water molecule.

H_2O Translational Modes. As the intensities of the bands at 196, 180, and 143 cm^{-1} are very sensitive to temperature change and the frequency shifts are small on deuteration, the bands are assigned to translational lattice vibrations in which water mole-

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Table 4. Lattice vibrations of water in $Li_2SO_4 \cdot H_2O$ (low temp.) (cm^{-1})

	IR		Neutron I. S.
	H_2O	D_2O	H_2O
Libration			
rock	600	440	769
wagg + twist	533	—	556
twist + wagg	338	269	343
Translation			
	196	194	235
	180	176	186
	143	141	164

cule moves dominantly. Corresponding to these bands, 235, 186, and 164 cm^{-1} were observed by neutron inelastic scattering.[20)]

Bands due to Li Ion. The nature of the metal $\cdots OH_2$ bonds in aquo-complexes has been studied by Nakagawa, and it is proposed that both ionic and covalent characters are involved in the bonds.[24)] In this study the band at 432 cm^{-1} is assigned to the $Li \cdots OH_2$ stretching because the frequency shift is small on deuteration and is as sensitive as other lattice vibrations to temperature change. The $Li \cdots OH_2$ stretching force constant (0.40 mdyn/Å) together with the distance (1.91 Å) indicates that this bond may have a considerable covalent character.

The broad and intense bands at 387 and 372 cm^{-1} and the weak bands at 325 and 249 cm^{-1} were assigned to bands due to the Li ion for the following reasons. These bands do not change on deuteration and are less dependent upon temperature than those due to H_2O lattice vibrations. It is strange that the bands at 325 and 249 cm^{-1} are much weaker than those at 387 and 372 cm^{-1}. However, they cannot be explained by combination bands or difference bands. Thus they are assumed to be $O \cdots Li \cdots O$ bending.

SO_4 Librational Modes. The spectrum of the anhydrous sample shows that the bands at 150, 133, and 105 cm^{-1} are markedly sharp and the frequencies correspond to 147, 138, and 113 cm^{-1} respectively in the spectrum of the hydrate. The bands have therefore been assigned to the librational modes of the sulfate ion. It is worthy of notice that the librational frequencies of the sulfate ion have little dependence on the existence of the water of crystallization. The same phenomena have been observed in other compounds in our laboratory. From these considerations the assignment of the vibrations of $Li_2SO_4 \cdot H_2O$ and $Li_2SO_4 \cdot D_2O$ crystals were made as shown in Tables 2 and 3.

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