

IR and Polarized Raman Spectra of $K_2Mg(SO_4)_2 \cdot 6H_2O$

G. SEKAR, V. RAMAKRISHNAN, AND G. ARULDHAS*

*Department of Physics, University of Kerala, Kariavattom,
Trivandrum 695 581, India*

Received February 19, 1986; in revised form May 14, 1986

IR and polarized Raman spectra of $K_2Mg(SO_4)_2 \cdot 6H_2O$ have been recorded and analyzed. From the spectra, the vibrations due to SO_4^{2-} ion, the complex $[Mg(H_2O)_6]^{2+}$ and the water molecules have been identified. The splitting of the nondegenerate ν_1 mode of the SO_4^{2-} ion indicates the presence of a factor group interaction between vibrating ions in the crystal. It has been inferred that the angular distortion of SO_4^{2-} is greater than the bond distortion. Separate bands for the three different water molecules have been observed. © 1987 Academic Press, Inc.

Introduction

Tutton's salts with the general formula $M'_2M''(SO_4)_2 \cdot 6H_2O$ [$M'' = K, NH_4, Rb, Cs, Na, \text{ or } Tl$, and $M' = Mg, Ca, Cu, Mn, Zn, Cd, Co, Fe, \text{ or } Ni$] are one of the best-known series of isomorphous compounds. Different types of investigations have been carried out in various fields, including NMR, X-ray, and neutron diffraction (1-3). Ananthanarayanan (4) and Ananthanarayanan and Danti (5) were the first to investigate the IR and Raman spectra of certain single crystals of Tutton's salts. Later, Brown and Ross (6) analyzed the IR spectra of a number of these hydrated double sulfates and interpreted the spectra in terms of the site group and factor group approximation. Recently, Singh *et al.* (7) made vibrational studies of some of these salts and pointed out the inconsistencies in Ananthanarayanan's assignment of the internal modes of SO_4^{2-} ion. In this paper, the

Raman (polarized) and IR spectra of $K_2Mg(SO_4)_2 \cdot 6H_2O$ are analyzed in order to understand the vibrations of the SO_4^{2-} ion and the complex $[Mg(H_2O)_6]^{2+}$, and the nature of the hydrogen bonding in the crystals.

Experimental

Single crystals of $K_2Mg(SO_4)_2 \cdot 6H_2O$ were grown by slow evaporation of equimolar aqueous solutions of analar grade K_2SO_4 and $MgSO_4 \cdot 7H_2O$ at room temperature (25°C). A parallelepiped with faces perpendicular to the *a*, *b*, and *c* axes was cut from a good single crystal well polished and used for Raman investigation. A SPEX RAMALOG 1401 double monochromator equipped with a Spectra Physics model 165 Ar⁺ laser was used to record the spectra (Figs. 1-3) for the six polarization geometries α_{xx} , α_{yy} , α_{zz} , α_{xy} , α_{xz} , and α_{yz} . The spectra were obtained in the Stokes region using the green line 5145 Å. Laser power ranging from 200 to 300 mW was used for different

* To whom all correspondence should be addressed.

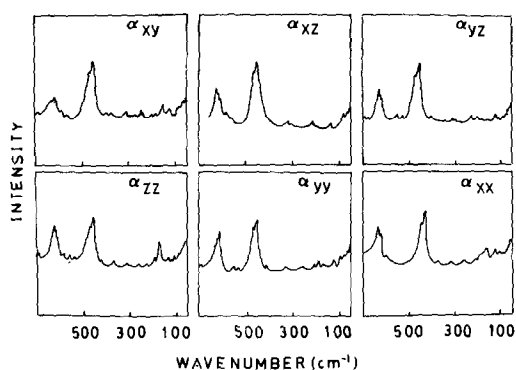


FIG. 1. Raman spectrum of the $K_2Mg(SO_4)_2 \cdot 6H_2O$ single crystal in the 50- to 700- cm^{-1} region.

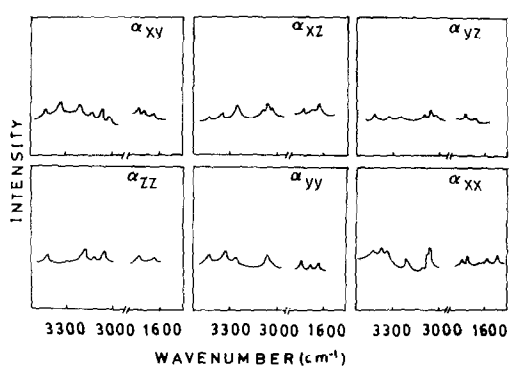


FIG. 3. Raman spectra of the $K_2Mg(SO_4)_2 \cdot 6H_2O$ single crystal in the 1500- to 3400- cm^{-1} region.

regions of the spectrum. The IR spectrum (Fig. 4) of microcrystalline sample was recorded on a Perkin-Elmer 283 spectrophotometer using the KBr pellet technique.

Results and Discussion

Factor Group Analysis

$K_2Mg(SO_4)_2 \cdot 6H_2O$ crystallizes in a monoclinic system with the space group $P2_1/a(C_{2h}^2)$ and has two molecules in the unit cell (3). All of the atoms except Mg are at general positions. The three water molecules occupy crystallographically non-equivalent C_1 sites. The magnesium atom

has an octahedral coordination of six water oxygens with a mean metal-oxygen distance of 2.092 Å. The sulfur-oxygen coordination is tetrahedral with a mean S-O bond length of 1.4745 Å. Each of the six water oxygens is hydrogen bonded to two sulfate oxygens. One water and five sulfate oxygen atoms form the nearest neighbors of potassium atom with a mean distance ~ 2.9 Å (3).

The standard group theoretical analysis (8) has been carried out to find the active modes for each symmetry species of the crystal's factor group at $k = 0$. The expected 186 fundamentals including three acoustic modes split into

$$\Gamma_{186} = 45 A_g + 45 B_g + 48 A_u + 48 B_u.$$

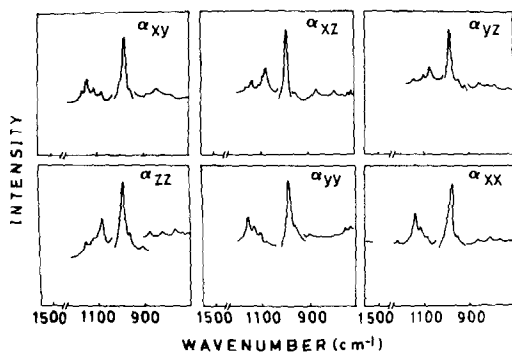


FIG. 2. Raman spectra of the $K_2Mg(SO_4)_2 \cdot 6H_2O$ single crystal in the 700- to 1500- cm^{-1} region.

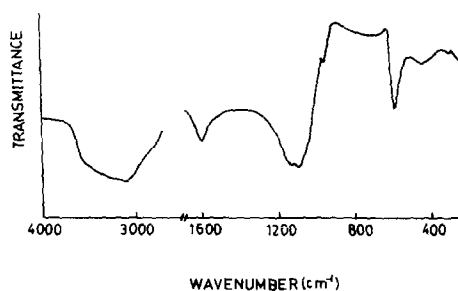


FIG. 4. IR spectrum of $K_2Mg(SO_4)_2 \cdot 6H_2O$ in the 200- to 4000- cm^{-1} region.

The species with subscripts g and u are Raman and IR active, respectively.

The correlation scheme for different normal modes of SO_4^{2-} , $[Mg(H_2O)_6]^{2+}$, and the water molecule to the crystal's factor group through their site symmetry is shown in Table I. The form of the Raman scattering tensors for a monoclinic system with C_{2h} point group is given by Loudon (9).

Internal Modes of the SO_4^{2-} Ion

Under free ion symmetry (T_d), the SO_4^{2-} ion has four normal modes of vibration: $\nu_1(A_1)$ symmetric stretching, $\nu_2(E)$ symmetric bending, $\nu_3(F_2)$ asymmetric stretching, and $\nu_4(F_2)$ asymmetric bending. ν_3 and ν_4 are active in both IR and Raman, whereas

ν_1 and ν_2 are active only in Raman. Since the SO_4^{2-} ion occupies the general position, the IR inactive modes are likely to appear with weak intensity. The stretching and bending frequencies of the SO_4^{2-} ion usually occur in the 950–1200 cm^{-1} and 400–650 cm^{-1} regions (10). Though the librational modes of water (500–900 cm^{-1}) fall within the ranges of the bending modes of the SO_4^{2-} ion, one can easily distinguish the sharp well-defined bands due to the SO_4^{2-} ion.

In the Raman spectrum, the band due to the $\nu_1(A_1)$ mode is expected to be the most intense. The strong band at 984 cm^{-1} with a shoulder at 960 cm^{-1} in all six polarization settings is assigned to this mode. The split-

TABLE I
CORRELATION SCHEME FOR THE VIBRATIONAL MODES OF SO_4^{2-} , $[Mg(H_2O)_6]^{2+}$,
AND H_2O

Molecular symmetry	Site symmetry	Factor group symmetry
SO_4^{2-} T_d	C_1	C_{2h}^s
A_1 E F_2	A	A_g B_g A_u B_u
Molecular symmetry	Site symmetry	Factor group symmetry
$[Mg(H_2O)_6]^{2+}$ O_h	C_1	C_{2h}^s
A_{1g} E_g F_{2g} F_{1u} F_{2u}	A_g A_u	A_g B_g A_u B_u
Molecular symmetry	Site symmetry	Factor group symmetry
H_2O C_{2v}	C_1	C_{2h}^s
A_1 B_1	A	A_g B_g A_u B_u

TABLE II
VIBRATIONAL SPECTRAL DATA AND BAND ASSIGNMENTS (CM⁻¹) OF K₂Mg(SO₄)₂ · 6H₂O

Raman							IR	Assignments
A _g			B _g					
xx	yy	zz	xy	xz	yz			
3385	3380	3380	3385	3385	3380			ν_3^w H ₂ O I
3328	3320		3326	3326	3320			ν_3^w H ₂ O II
3240	3270	3220	3240	3270	3280			ν_3^w H ₂ O III
3140		3145	3180				3000-3500	ν_1^w H ₂ O I
3110				3120	3120		br	ν_1^w H ₂ O II
3087	3080	3080	3088	3088	3080			ν_1^w H ₂ O III
			3040	3040	3040			
1696	1690	1690	1690	1690	1690			ν_2^w H ₂ O III
1675	1655	1620	1670	1650	1650		1610	ν_2^w H ₂ O II
1620	1625	1617	1630	1620				ν_2^w H ₂ O I
1580								$\nu_1^s + \nu_4^s$
1532								$\nu_3^s + \nu_2^s$
1209								2 ν_4^s
1140	1156	1150	1156	1156				ν_3^s
1135	1135	1120	1140	1135	1140		1135	
1114	1101	1114	1104	1105	1099		1100	
1088	1077	1077	1088	1088				$\nu_2^s + \nu_4^s$
			1077	1077	1075			
984	984	984	984	984	984		981	ν_1^s
960	960	960	960	960	960			
	896	910			920			2 ν_2^s
862		880	880	861	850			ν_1^w H ₂ O III
810		824	840	821	821			ν_1^w H ₂ O II
770		771	790	781	784		650-900	ν_1^w H ₂ O I
							br	
730	740	734		750				ν_1^w H ₂ O III

721	720	718	725	725	725	$\nu_1^w H_2O$ II
	692	698	684	702	696	$\nu_1^t H_2O$ I
626	626	626	626	626	670	
621	620	621	621	620	626	ν_4^s
613	614	614	613	613	620	
589	592	580	583	582	613	$\nu_6^w H_2O$ III
	550	555	562	562	550	$\nu_6^w H_2O$ II
458	537	536			526	$\nu_6^w H_2O$ I
454	461	461	461	461	461	ν_2^t
402	454	454	454	454	454	ν_1^f
367	406	418	395	407	407	$2 \nu_5^s$
310		367	375			ν_3^f
	326	314	305	314	310	$\nu K^+ \dots O$
			298	294	298	
			285			ν_4^c
254	254	253	274			ν_2^s
		224	247	224	224	
			236	224	224	
204	204	204	200	216	199	
194	188	187	186	202	186	
161	167	164	156	186	160	
126	124	126	124	126	126	
117		117		126		
102		106	103		109	External modes of SO_4^{2-} ion
86	92	80	92	82	88	$\nu OH \dots O$
73	74	76	83	76		
			71	73	73	
70			69	70		Lattice modes
66	62		64	64	66	
57	55	58	57	56	55	

Note. The superscripts w, s, and c refer to the modes of water, sulfate ion, and the complex $[Mg(H_2O)_6]^{2+}$, respectively, whereas the subscripts r, w, and t refer to the rocking, wagging, and twisting modes of the water, respectively.

ting of this nondegenerate mode indicates the presence of a factor group interaction between vibrating SO_4^{2-} ions. In the IR spectrum, a weak band at 981 cm^{-1} is observed for this mode. For the doubly degenerate ν_2 mode, a strong band at 454 cm^{-1} and a relatively weak one at 461 cm^{-1} are observed in all polarizations. The splitting of this doubly degenerate mode is due to static field effect. A very weak band observed around 460 cm^{-1} in the IR spectrum corresponds to this mode. Three bands in the $1090\text{--}1160\text{ cm}^{-1}$ region (Raman) and two at 1100 and 1135 cm^{-1} (IR) have been assigned to the triply degenerate $\nu_3(F_2)$ mode. In the $\nu_4(F_2)$ mode region, three bands with mean frequencies of 613 , 620 , and 626 cm^{-1} in the Raman spectrum and only one at 610 cm^{-1} in the IR spectrum have been observed.

From the complete lifting of degeneracies of the bending modes and the slight shifting of the stretching modes from the free ion values, it can be inferred that the angular distortion of the SO_4^{2-} ion is greater than the bond distortion (10). This result is consistent with the crystal structure data, as the mean S–O bond length (1.4745 \AA) is only slightly deviated from its free state value (1.4768 \AA).

Internal Modes of the Complex

$[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$

The divalent metal cation Mg occupying the center of symmetry forms an octahedron with the six water molecules. A free octahedral molecule will have the six normal modes of vibration: $\nu_1(A_{1g})$, $\nu_2(E_g)$, $\nu_3(F_{2g})$ —Raman active; $\nu_3(F_{1u})$, $\nu_4(F_{1u})$ —IR active; and $\nu_6(F_{2u})$ —IR inactive. A strong line around 405 cm^{-1} corresponding to the symmetric stretching $\nu_1(A_{1g})$ has been observed in all polarizations except α_{xz} . The Raman active $\nu_2(E_g)$ is observed as a single line in α_{xx} , α_{yy} , α_{xz} , and α_{yz} in the $220\text{--}260\text{ cm}^{-1}$ region (two lines appeared in α_{zz} and α_{xy} settings). The appearance of three bands

with mean frequencies of 204 , 188 , and 167 cm^{-1} in all polarizations reveals that the degeneracy of the $\nu_5(F_{2g})$ mode is completely lifted.

The identification of the internal modes of the complex has become difficult as the external modes of the SO_4^{2-} ion overlap with this. In the IR spectrum, the triply degenerate $\nu_3(F_{1u})$ mode appeared as a weak band at 340 cm^{-1} . The band at 270 cm^{-1} (IR) is assigned to the $\nu_4(F_{1u})$ mode. Observation of the IR active $\nu_3(F_{1u})$ mode in the Raman spectrum (α_{xy} , α_{xx} , and α_{yz}) is due to the strain induced by the crystalline field. This feature has also been noticed in certain molybdate and sulfate tellurate crystals (11, 12).

Internal Modes of Water

The unit cell contains four sets of three different water molecules. The coordination of water oxygen with metal cation is expected to distort the structure of the water molecules. The O–H \cdots O distances (the hydrogen bonds made by the three different water molecules are 2.746 \AA ($\text{H}_2\text{O I}$), 2.672 \AA ($\text{H}_2\text{O II}$), and 2.646 \AA ($\text{H}_2\text{O III}$). The longest distance (2.746 \AA), corresponding to the weakest hydrogen bond strength, will give rise to the highest stretching frequency whereas the one with distance 2.646 \AA will give the lowest. The reverse will be the case for the bending mode. Broad bands with frequencies shifted considerably from the free ion values have been observed in most of the polarization settings. This is indicative of the effect of hydrogen bonding.

The α_{xx} , α_{xy} , α_{xz} , and α_{yz} spectra contain as many as six bands due to the three different water molecules for the ν_1 and ν_3 modes. The bands in the region $3200\text{--}3400\text{ cm}^{-1}$ and $3000\text{--}3180\text{ cm}^{-1}$ are assigned to the ν_3 and ν_1 modes of the three different water molecules, respectively (Table II). Separate bands have been observed (in α_{xx} , α_{yy} , α_{zz} , and α_{xz}) for the ν_2 mode of the three different water molecules in the $1610\text{--}1700$

cm^{-1} region (Table II). In the IR spectrum, only a broad band covering the 3000–3500 cm^{-1} region and a weak band at 1610 cm^{-1} have been observed for the stretching and bending modes, respectively.

Librational Modes of Water

The librational modes of water fall in the range of 500–900 cm^{-1} (13). These modes are more sensitive to interactions involving hydrogen bonds and less sensitive to those involving metal–oxygen coordination. The low polarizability of water molecules makes these bands appear weak. The frequency assignments can be made by considering the hydrogen bond strengths and the fact that the rocking mode will have a greater frequency than the wagging mode. Hence the Raman bands in the 780–880 cm^{-1} and 690–750 cm^{-1} regions have been assigned to the rocking and twisting modes, respectively (Table II). The wagging modes have been observed in the 520–580 cm^{-1} region (Table II). In the IR spectrum, only a broad band covering the 650–900 cm^{-1} region could be observed for these modes.

External Modes

Assignments of external modes of the SO_4^{2-} ion and $\nu K^+ \cdots O$ are given in Table II. As hydrogen bond vibrations $\nu O-H \cdots O$ and $\delta O-H \cdots O$ occur below 200 cm^{-1} (14), the band around 100 cm^{-1} in Raman may be due to $\nu O-H \cdots O$.

Conclusions

(i) The splitting of the nondegenerate ν_1 mode of the SO_4^{2-} ion into two components indicates the presence of factor group inter-

action between the vibrating ions in the crystal.

(ii) Angular distortions of the SO_4^{2-} ion are greater than the bond distortions.

(iii) Separate bands for the three different water molecules have been observed.

Acknowledgments

One of the authors (G.S.) is grateful to the University of Kerala for the award of a fellowship. Thanks are due to the Council of Scientific and Industrial Research, New Delhi, for financial support (to V.R.K.).

References

1. R. CHIDAMBARAM AND C. R. RAO, *J. Chem. Phys.* **38**, 210 (1963).
2. N. W. GRIMES, H. F. KAY, AND M. W. WEBB, *Acta Crystallogr.* **16**, 823 (1963).
3. K. K. KANNAN AND M. W. VISWAMITRA, *Z. Kristallogr.* **122**, 161 (1965).
4. V. ANANTHANARAYANAN, *Z. Phys.* **163**, 144 (1961).
5. V. ANANTHANARAYANAN AND A. DANTI, *J. Mol. Spectrosc.* **20**, 88 (1966).
6. R. G. BROWN AND S. D. ROSS, *Spectrochim. Acta Part A* **26**, 945 (1970).
7. B. SINGH, S. P. GUPTA, AND B. N. KHANNA, *Pramana* **14**, 509 (1980).
8. W. G. FATELY, F. R. DOLLISH, N. T. McDEVITT, AND F. F. BENTLEY, "Infrared and Raman Selection Rules for Molecular and Lattice Vibrations: The Correlation Method," Wiley (1972).
9. R. LOUDON, *Adv. Phys.* **13**, 423 (1964).
10. V. RAMAKRISHNAN, V. U. NAYAR, AND G. ARULDHAS, *Infrared Phys.* **25**, 607 (1985).
11. R. K. KHANNA, E. R. LIPPINCOTT, AND P. J. MILLER, *J. Phys. Chem. Solids* **34**, 533 (1973).
12. K. VISWANATHAN, V. U. NAYAR, AND G. ARULDHAS, *Infrared Phys.* **26**, 89 (1986).
13. I. NAKAGAWA AND T. SHIMANOUCI, *Spectrochim. Acta* **20**, 429 (1964).
14. A. NOVAK, *Croat. Chem. Acta* **55**, 147 (1982).