

# Infrared and Polarized Raman Spectra of $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

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The IR and polarized Raman spectra of a single crystal  $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  is recorded and analyzed at room temperature. Bands indicate a stronger S–O bond in  $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  than that in a free  $\text{SO}_4^{2-}$  ion. The fraction of reversed sulfate group in the Rb alum is much lower than that in the potassium alum. Broad bands with frequencies considerably shifted from the free state values indicate that water molecules form hydrogen bonds of various strengths. Two crystallographically distinct water molecules are identified in the crystal. © 1996

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## INTRODUCTION

Studies by Larson and co-workers have shown that  $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  belongs to an isomorphous series of hydrated double sulfates, called alums, having the general formula  $M^I M^{II}(\text{XO}_4)_2 \cdot 12\text{H}_2\text{O}$  ( $M^I = \text{NH}_4, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ;  $M^{II} = \text{Al}, \text{Ga}, \text{Cr}, \text{Fe}, \text{V}$ ;  $\text{X} = \text{Se}, \text{S}$ ) (1, 2). There are three types of alums  $\alpha$ ,  $\beta$ , and  $\gamma$  which differ in the arrangement of the six water molecules around the  $M^I$  ion and in the sulfate orientation with respect to the metal ions. The rubidium alum is a good material to use for aligning a single crystal diffractometer (2).

The  $\alpha$  alums are disordered, some of the sulfate groups being in a reversed orientation along the threefold axis (3). These crystals have two occupied nonequivalent crystallographic sites for the sulfate ions. A number of studies has been carried out on potassium alum to understand the temperature dependent occupancy rate (2–4) of these sites. The fraction of reversed sulfate groups apparently increases as the monovalent cation decreases in size (2). In  $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , the Rb ion has a larger size than the K ion in the potassium alum. In this paper, a detailed vibrational analysis of the IR and Raman spectra of  $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  single crystal and its deuterated analog have been carried out in order to understand the nature

of the vibrating ions present and the strength of hydrogen bonding.

## EXPERIMENTAL

Single crystals of  $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  (referred to as RAH) suitable for polarization studies were prepared by the slow evaporation of an aqueous solution containing stoichiometric amounts of rubidium sulfate and aluminum sulfate (1). The polycrystalline deuterated compound (RAD) was prepared by repeated recrystallization in  $\text{D}_2\text{O}$ . The crystal was polished and oriented properly to record the Raman spectra in two different polarization geometries,  $c(aa)b$  and  $c(ac)b$ . The deuterated compound sealed in a capillary tube was used for recording the Raman spectrum. A Spex 1401 double monochromator equipped with a Spectra Physics model 165.08  $\text{Ar}^+$  laser was used to record the Raman spectra in the Stokes region. The spectra were obtained at  $300 \pm 3$  K using 514.5 nm line at a laser power of 100 mW with a resolution better than  $3 \text{ cm}^{-1}$ . IR spectra were recorded on a Perkin–Elmer 577 spectrophotometer with samples taken as KBr pellets.

## FACTOR GROUP ANALYSIS

$\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  crystallizes in the cubic system with the space group  $Pa\bar{3}(T_h^6)$  and having four formula units per unit cell (1). This  $\alpha$  alum was sixfold coordination of oxygen about the central monovalent cation. The trivalent cation is surrounded by six water molecules in a nearly regular octahedron. The octahedron is distorted by compression along the threefold axis. The univalent and trivalent cations occupy sites of  $S_6$  symmetry, while the  $\text{SO}_4^{2-}$  ions occupy sites of  $C_3$  symmetry and the water molecules are in the general site (5). The hydrogen atoms of water (1), which are associated with the monovalent cation, link O(1) of the sulfate group with O(2) of another sulfate group. The hydrogen atoms of water (2), associated with the trivalent cation, form hydrogen bonds with water (1)

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TABLE 1  
Spectral Data and Band Assignments (cm<sup>-1</sup>)

RbAl(SO <sub>4</sub> ) <sub>2</sub> · 12H <sub>2</sub> O			RbAl(SO <sub>4</sub> ) <sub>2</sub> · 12D <sub>2</sub> O		
Raman					
<i>c(aa)b</i>	<i>c(ac)b</i>	IR	Raman	IR	Assignments
12 m	12 vw				
18 w					
39 m	46 mbr				Lattice modes
58 w	73 w		76 w		
82 w					
118 w	119 m				Translations of SO <sub>4</sub> <sup>2-</sup>
159 s	153 m		147 m		
190 s	191 m		187 m		Rotations of SO <sub>4</sub> <sup>2-</sup>
	228 w	215 m			
238 wbr		275 w			$\nu_{\text{Rb}\cdots\text{O}}$
325 w	328 w		255 w		$\nu_{\text{O}\cdots\text{O}}$
	428 w	430 w	351 w		$\nu_{\text{H}_2\text{O}/\text{D}_2\text{O}}$
441 m	441 m			435 w	
458 m	458 m	450 w	464 mbr		$\nu_2\text{SO}_4^{2-}$
480 vw		480 w			
500 w	500 w				T H <sub>2</sub> O/D <sub>2</sub> O and
535 wbr	530 vw	565 s		520 w	$\nu_{\text{Al}-\text{O}}$
618 s	600 sh	612 m		604 mbr	
632 sh	618 s	635 w	629 mbr	640 w	$\nu_4\text{SO}_4^{2-}$
642 w	655 w	675 m		698 m	
870 w	890 w	884 m		735 w	$\nu_{\text{H}_2\text{O}/\text{D}_2\text{O}}$
975 sh					
990 vs	990 s		1000 vs		$\nu_1\text{SO}_4^{2-}$
1035 w		1030 s	1045 w	1070 s	
1105 wbr	1100 m	1070 vsbr	to	1130 vs	$\nu_3\text{SO}_4^{2-}$
1135 s	1133 s	1110 s	1155 m		
	1328 w				$\delta_{\text{O}-\text{H}\cdots\text{O}}$
1678 vw	1605 w	1600 mbr		1230 m	$\nu_2\text{H}_2\text{O}/\text{D}_2\text{O}$
1735 w	1632 w	1710 wbr		1680 w	
2900–3080 mbr	2985 m		2476 m	2460 m	
3085 m	3120 m	2800–3460 vsbr	2517 w	3000 m	$\nu_1, \nu_3\text{H}_2\text{O}/\text{D}_2\text{O}$
3360 s	3330 s			3300 m	
3412 s	3380 s		3386 m		

and with an O(2) atom. The standard group theoretical analysis (6) gives the distribution of irreducible representation at  $k = 0$ , excluding acoustic modes as

$$\Gamma = 42A_g(\text{R}) + 42E_g(\text{R}) + 50F_g(\text{R}) + 46A_u(\text{IR}) \\ + 46E_u(\text{IR}) + 51F_u(\text{IR}).$$

## RESULTS AND DISCUSSION

The frequencies of the observed bands and their vibrational assignments are given in Table 1. The Raman and IR spectra of RbAl(SO<sub>4</sub>)<sub>2</sub> · 12H<sub>2</sub>O are given in Figs. 1 and 2.

### SO<sub>4</sub><sup>2-</sup> Vibrations

A free tetrahedral SO<sub>4</sub><sup>2-</sup> ion has four normal modes of vibration, distributed as  $\Gamma = A + E + 2F_2$ . The  $\nu_1$  and  $\nu_2$  modes represent the symmetric stretching and deformation vibrations, and  $\nu_3$  and  $\nu_4$  represent the corresponding asymmetric stretching and deformation vibrations (7, 8).

In the Raman spectra, the strongest band is obtained at 990 cm<sup>-1</sup> in both *c(aa)b* and *c(ac)b* orientations. A less intense band at 975 cm<sup>-1</sup> is also obtained in this region. The intensity of these bands are considerably reduced in the *c(ac)b* orientation. Factor group analysis predicts two bands for the symmetric nondegenerate stretching region, one with  $A_g$  symmetry and the other with  $F_g$  symmetry. As the 975 cm<sup>-1</sup> band is sufficiently shifted from the  $A_g$

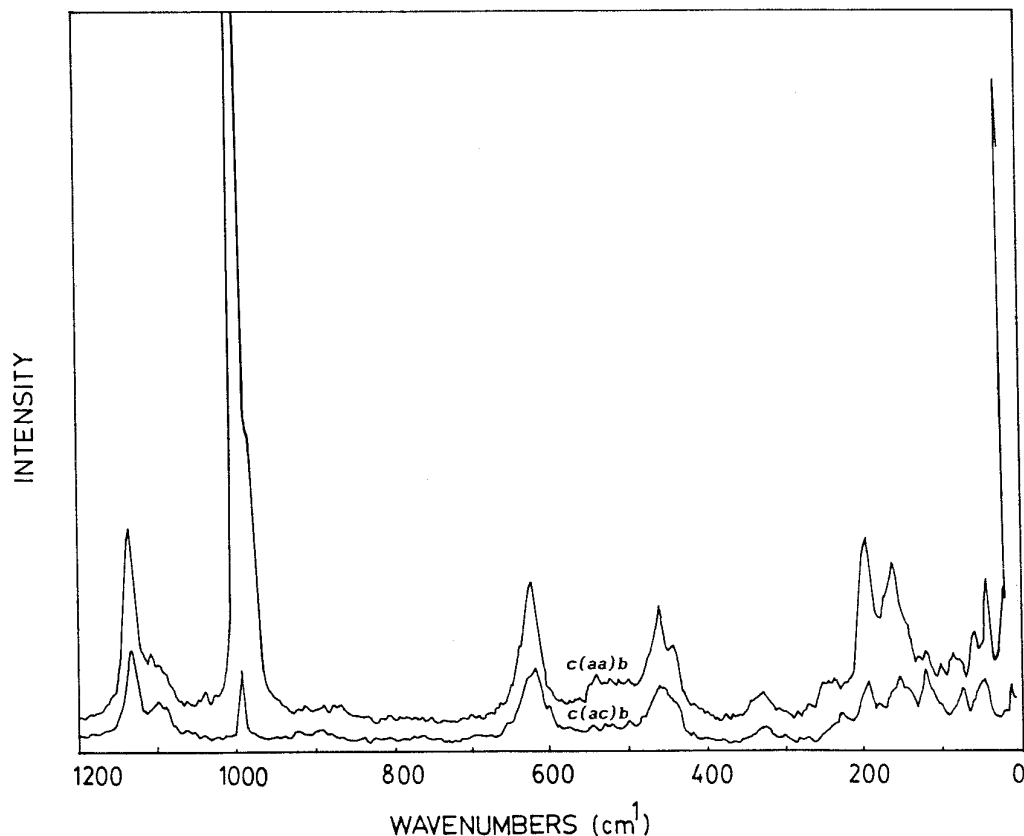


FIG. 1. Raman spectra of  $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  in the 30–1200  $\text{cm}^{-1}$  region for the  $c(aa)b$  and  $c(ac)b$  orientation.

component, it cannot be treated as the  $F_g$  component (9, 10). Therefore, the two bands at 990 and 975  $\text{cm}^{-1}$  are assigned to  $A_g$  components of the nondegenerate  $\nu_1$  mode corresponding to sulfates in site 1 and site 2, respectively, as observed in  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  (3, 4, 9). In the deuterated compound, this band is observed at 1001  $\text{cm}^{-1}$  in the Raman

spectrum. A shoulder is also observed at the lower wavenumber side even for repeated recording of Raman spectra in this region.

In this compound, the intensity difference between 990 and 975  $\text{cm}^{-1}$  bands is considerably larger than those observed in potassium alum (3, 9). This shows that the fraction

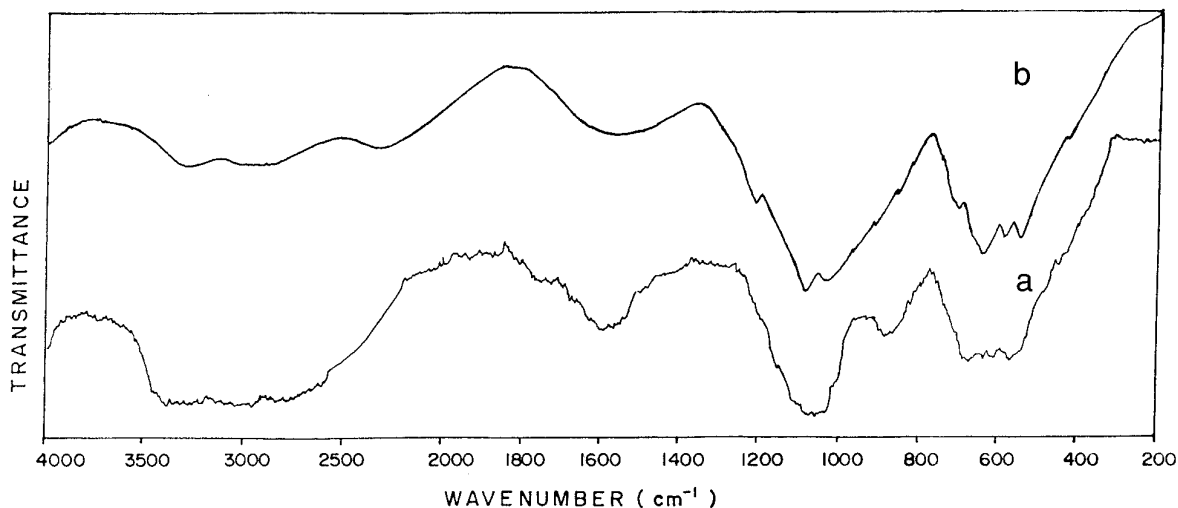


FIG. 2. Infrared spectra of (a)  $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  and (b)  $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{D}_2\text{O}$  in the 200–4000  $\text{cm}^{-1}$  region.

of reversed sulfate group is much lower than that in potassium alum, in agreement with the fact that Rb has a larger size than K. Deuteration causes the  $\nu_1$  mode to appear at marginally higher wavenumbers indicating changes in the hydrogen bonding between  $\text{SO}_4^{2-}$  ions and water molecules. The  $\nu_1$  mode is IR inactive. Even if this band became active it is observed in the IR as intercalated with the broad band profile of the triply degenerate asymmetric stretching ( $\nu_3$ ) mode.

In the Raman spectra, two medium intense bands at 441 and 458  $\text{cm}^{-1}$ , and a very weak band at 480  $\text{cm}^{-1}$ , are observed in the region of the symmetric bending ( $\nu_2$ ) mode. In the IR spectrum, two weak bands at 450 and 480  $\text{cm}^{-1}$  are observed for this mode (Table 1). The observed bands are attributed to the  $E_g$  species of the doubly degenerate symmetric bending mode of the  $\text{SO}_4^{2-}$  ion. In the deuterated compound only one broad band at 464  $\text{cm}^{-1}$  is observed in the Raman spectrum.

For the triply degenerate asymmetric stretching and bending vibrations, factor group analysis predicts  $A_g$ ,  $E_g$ , and  $F_g$  species for the anion. In the IR spectrum, an intense broad band covering the 1000–1160  $\text{cm}^{-1}$  region with peaks at 1030, 1070, and 1110  $\text{cm}^{-1}$  are observed for the  $\nu_3$  mode. Three bands at 1035, 1105, and 1135  $\text{cm}^{-1}$  are observed for this mode in the  $c(aa)b$  orientation of the Raman spectrum. In the  $c(ac)b$  orientation, intensity is considerably reduced and only two bands at 1100 and 1113  $\text{cm}^{-1}$  are visible in the spectra. In the Raman and IR spectra, three bands each are observed for the asymmetric bending ( $\nu_4$ ) mode. In the deuterated compound, the  $\nu_3$  mode is observed as a broad band in the 1045–1155  $\text{cm}^{-1}$  region with a peak at 1145  $\text{cm}^{-1}$ .

The bands observed for  $\nu_2$ ,  $\nu_3$ , and  $\nu_4$  modes show the lifting of degeneracy in agreement with intermolecular coupling as observed by Eysel and Eckert (10, 11). The separate modes due to site 2 sulfates cannot be identified from these bands.

The symmetric and asymmetric stretching frequencies of the  $\text{SO}_4^{2-}$  ion are observed at slightly higher wavenumbers than those of the free ion values (7). This indicates the presence of fairly strong S–O bonds in this crystal in agreement with the structural data (2) showing that the average S–O bond length (1.438 Å) is less than that of the free ion value (1.4768 Å).

### Water Vibrations

A free water molecule has three normal modes of vibration corresponding to the  $2A_1 + B_1$  species of the  $C_{2v}$  point group. The wavenumbers observed in the spectra can be explained using the Novak's criteria relating O...O distance to the  $\nu(\text{OH})$  frequency of hydrogen bonds in crystals (12). The longest O...O distance of 2.864 Å corresponding to the weakest hydrogen bond strength will give rise

to the highest stretching frequency of 3412  $\text{cm}^{-1}$  in the Raman spectrum. The value of 3085  $\text{cm}^{-1}$  corresponds to an O...O distance of 2.73 Å in water–sulfate hydrogen bond. Broad bands from 3080  $\text{cm}^{-1}$  to values lower than 2900  $\text{cm}^{-1}$  indicate O...O distances up to 2.53 Å (2).

A strong broad band from 2800–3460  $\text{cm}^{-1}$  is obtained in the IR in this region. Deuteration of the compound is only partial as seen from the observed spectra. In the Raman spectrum, stretching bands of water are retained with less intensity while two bands at 2517 and 2476  $\text{cm}^{-1}$  are obtained corresponding to  $\text{D}_2\text{O}$  stretching modes. The medium intense broad IR band at 1600  $\text{cm}^{-1}$  and a weak band at 1710  $\text{cm}^{-1}$  are assigned to the HOH bending mode.

Broad bands with frequencies considerably shifted from the free state values (13) have been observed in RAH indicating the presence of hydrogen bonds of various strengths. This agrees with the structural data showing the different O...O distances involving water molecules. The two bands in the bending region and the broad band (with four peaks) in the stretching region correspond to two crystallographically distinct water molecules existing in this crystal.

The librational modes of water are characteristic of coordinated water and fall in the 500–900  $\text{cm}^{-1}$  region (14). 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. Librational modes are assigned in the sequence  $\nu_{\text{rocking}} > \nu_{\text{twisting}} > \nu_{\text{wagging}}$  on the basis of the criteria of Eriksson and Lindgren (15).

### External Modes

Each external mode may contain contributions from all cations. However, in certain frequency ranges the external modes may be dominated by the contribution from one kind of cation. The external modes of the trivalent cation will lie at higher energy than those of the monovalent cation since the aluminum–water bond is much stronger than the rubidium–water bond (11). The translational frequencies of the alkali metal atoms are expected to occur below 300  $\text{cm}^{-1}$  (16). This region is complicated by the presence of translation and rotation modes of the  $\text{SO}_4^{2-}$  ion. However, a weak intense band at 238  $\text{cm}^{-1}$  in the Raman spectrum is assigned to the Rb–O stretching mode (17). In the Raman spectra, the rotational modes are stronger than the translational modes. Thus, the bands in the 90–150  $\text{cm}^{-1}$  region are assigned to translational modes, and those in the 150–250  $\text{cm}^{-1}$  region to rotational modes (8, 17) of  $\text{SO}_4^{2-}$  ions.

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