

Review Article

Polarized Raman Spectra of $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

M. Boujelbene and T. Mhiri

Laboratoire de l'État Solide, Faculté des Sciences de Sfax, B.P. 1171.3000, Sfax, Tunisia

Correspondence should be addressed to M. Boujelbene, m_boujelbene2010@yahoo.fr

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The study by spectroscopic Raman relate to compound $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was interpreted and attributed one being based Theory of group and by comparison with others composed. The current studies of the polarised Raman spectra of $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ give evidence that the disorder is indeed present in the ammonium alum. This is best manifested through the appearance of surplus bands in the spectral regions of vibrations of the sulphate anion.

1. Experimental

1.1. Preparation. Alum $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ crystals were prepared by the slow evaporation of an aqueous solutions containing stoichiometric amounts of $(\text{NH}_4)_2\text{SO}_4$ and $\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ salts.

1.2. Polarised Raman Spectra of $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

1.2.1. Factor Group Analysis. The ammonium alum, $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, belongs to a family of compounds with general formula $\text{AM}(\text{XO}_4)_2 \cdot 12\text{H}_2\text{O}$ (A is a univalent metal such as Na, K, Rb, and Cs; M is a trivalent metal: Al, Ce, In, Fe, Cr, Ir etc.; X is S or Se).

According to the crystallographic data [1], the ammonium alum crystallizes in the cubic structure Pa-3 (T_h^6), $Z = 4$. The site symmetry of sulfate is C_3 , the trivalent cations occupy S_6 sites, and the site symmetry of the two crystallographically distinct types of water molecules is C_1 . In the model the site symmetry of NH_4^+ is S_6 . However, X-ray diffraction studies of ammonium alum by with C_3 symmetry. Abdeen et al. [2] indicated the unusual situation of two possible orientations of the sulfate ion, and the site symmetry of NH_4^+ is C_3 . Similar suggestions were deduced from neutron diffraction data by Abdeen et al. [3]. Factor group analysis using standard correlation method [4] has been carried out to determine the symmetries of the vibrations and to predict the IR and Raman active modes.

Excluding the acoustic modes, 227 normal modes are predicted.

These are distributed as follows:

$$\Gamma_{\text{optic}} = 42A_g(\text{R}) + 42E_g(\text{R}) + 50F_g(\text{R}) + 46A_u(\text{I}) + 46E_u(\text{I}) + 51F_u(\text{IR}). \quad (1)$$

The A_g , E_g , and F_g modes are Raman active, and F_u mode is infrared active.

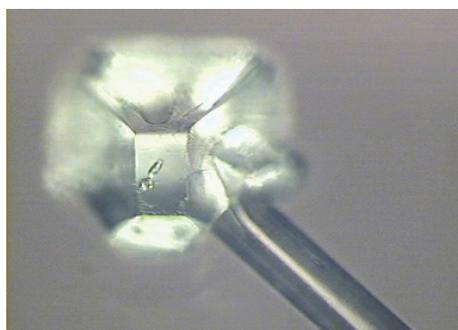
The A_u and E_u modes exposed by Suresh et al. [5] as being IR active are really inactive.

The contribution of the different groupments (SO_4 , NH_4 , and H_2O) and the Al^{3+} ion to the Raman active vibrations are given in Table 2.

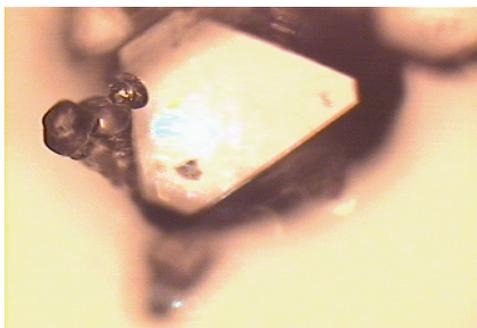
Our polarized measurements were conducted on the (001) and (111) faces of the single crystal (Figure 1).

Analysis of the tensor components shows that, on (001) face, the F_g modes were obtained in the $z(xy)\bar{z}$ geometry, the $z(xx)\bar{z}$ geometry gives both the A_g and the E_g modes. E_g mode can be observed when the crystal is oriented as in (111) face and incident and scattered beams are perpendicular $-Z(X'Y')\bar{Z}$, and in polarizations parallel $-Z(X'X')\bar{Z}$ geometry the A_g , E_g , and F_g modes can be observed.

The polarized Raman spectra recorded for these different geometries are shown in Figure 2, and the frequencies of the observed bands and their vibrational assignments are given in Tables 1 and 2 (the spectra were collected from 5 to 4000 cm^{-1}).



(a)



(b)

FIGURE 1: Photograph showing (a) face (001) and (b) face (111) things of $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

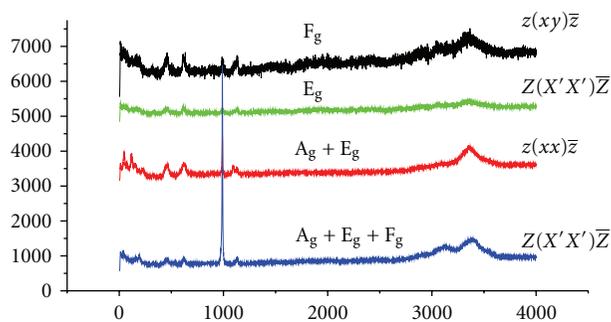


FIGURE 2: Raman spectra of $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. The geometries and the corresponding mode symmetries are given in each diagram.

1.2.2. Results and Discussions

NH_4^+ Vibrations. The internal modes of vibration of free NH_4^+ ion with T_d symmetry have average frequencies at 3033, 1685, 3134, and 1397 cm^{-1} for $\nu_1(A_1)$, $\nu_2(E)$, $\nu_3(F_2)$, and $\nu_4(F_2)$ modes, respectively, [6].

The stretching vibrations NH_4^+ ion and the water molecule were observed in the 2900 to 3500 cm^{-1} . It was possible to separate the absorption bands observed in the Raman spectra of $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ by comparison with the $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ sample. The differences observed between the two spectra are most likely due to the NH_4^+ vibrations. Indeed, the bands observed in the second at 1444 cm^{-1} in the $Z(XX)\bar{Z}$ polarisation and at 1453 in the

$Z(X'Y')\bar{Z}$ polarisation, and not observed in $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, are most likely assignable to the asymmetric bending (ν_4) mode of NH_4^+ . By similar reasoning we can deduce that the band observed in $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ at 2442/2482 and at 2210/2473 cm^{-1} in the $-z(xx)\bar{z}$ and $-Z(X'X')\bar{Z}$ polarisation, respectively, corresponds to the combinations of bending modes ν_2 with the internal rotation mode ν_6 . Appearance of these bands indicates that the NH_4^+ ion does not rotate freely in the crystalline lattice, thus the ammonium ions form hydrogen bonds in the crystals [7–10]. The bands observed in the $z(xx)z$ polarisation at 3134 cm^{-1} can be assigned to the asymmetric stretching $\nu_3(A_g)$ vibrations.

H_2O Vibration. The vibrational frequencies of a free water molecule are at 3756 (ν_3), 3652 (ν_1), and 1595 cm^{-1} (ν_2) [11]. By comparison with $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{D}_2\text{O}$, and $(\text{CH}_3)_2\text{NH}_2\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, it was possible to identify the vibrational frequencies of water molecule in $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

From group theoretical predictions, 18 lines ($6A_g + 6F_g + 6E_g$) are expected in all orientation (Table 1).

In the $z(xx)\bar{z}$ orientation six bands are observed at 1620, 1726, 2856, 3103, 3356, and 3400 and are close to those (1678, 1735, 2900, 3085, 3360, and 3412 cm^{-1}) reported by Abdeen et al. [3], $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ for $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. In the $z(xy)\bar{z}$ geometrics (F_g symmetry) five bands are observed at 1617, 1738, 2936, 3365, and 3376 cm^{-1} . Their analogues in $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ appear at 1605, 1632, 2985, 3120, 3330, and 3380 cm^{-1} . In the $Z(X'Y')\bar{Z}$ geometry (E_g symmetry) only three bands (from six predicted) are observed at 2908, 3072, and 3338 cm^{-1} . The bands observed in each orientation at $\sim 1700 \text{ cm}^{-1}$ can be assigned to the HOH bending vibration $\nu_2(\text{H}_2\text{O})$. The bands observed in the 2800–3500 cm^{-1} region are assigned to the symmetric and asymmetric stretching modes of water molecules. The observed bands in the stretching and bending regions show the presence of two distinct water molecules in $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. The significant decrease in the frequencies of the stretching modes and the increase in frequencies of the bending modes from the free state values show that water molecules form hydrogen bonds of medium and strong strength [12, 13].

The librational modes of water are characteristic of coordinated water and fall in the 500–900 cm^{-1} region [14, 15]. This region is complicated by presence of strong absorptions of $\nu_4(\text{SO}_4)$ and $\nu_1(\text{Al}(\text{H}_2\text{O})_6)$, and the $\nu_3(\text{Al}(\text{H}_2\text{O})_6)$ is Raman inactive Table 2. The low polarizability of water molecules makes these bands appear weak. Librational modes of water are assigned by comparison with $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ [5], $\text{CsAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ [15], and its partly deuterated analogues. There is no doublet that the bands observed in the 700–900 cm^{-1} region should be attributed to librations of water molecules, as done in all previous assignments [5–17].

$\text{Al}(\text{H}_2\text{O})_6$ Vibrations. The metal cation Al^{3+} forms an octahedron with surrounding six water molecules. Under O_h symmetry, the ion has six modes of vibration $\nu_1(A_{1g})$, $\nu_2(E_g)$, $\nu_3(F_{1u})$, $\nu_4(F_{1u})$, $\nu_5(F_{2g})$, and $\nu_6(F_{2u})$. Out of these ν_1 , ν_2 , and

TABLE 1: Active modes of $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

	External modes								Internal modes									Activity	
	$L_{\text{SO}_4}, T_{\text{SO}_4}, T_{\text{Al}}, L_{\text{H}_2\text{O}}, T_{\text{H}_2\text{O}}, L_{\text{NH}_4}, T_{\text{NH}_4}$								SO ₄			NH ₄				H ₂ O			Raman
	ν_1	ν_2	ν_3	ν_4	ν_1	ν_2	ν_3	ν_4	ν_1	ν_2	ν_3	ν_1	ν_2	ν_3					
A _g	1	1	0	3	3	1	1	1	0	1	1	1	0	1	1	2	2	2	($\alpha_{xx} + \alpha_{yy} + \alpha_{zz}$)
E _g	1	1	0	3	3	1	1	0	1	1	1	0	1	1	1	2	2	2	($2\alpha_{zz}\alpha_{xx} - \alpha_{yy}, \alpha_{xx}\alpha_{yy}$)
F _g	3	3	0	9	9	3	3	1	2	3	3	1	2	3	3	2	2	2	($\alpha_{xy}, \alpha_{yz}, \alpha_{xz}$)

TABLE 2: Correlation table of the $\text{Al}(\text{H}_2\text{O})_6^{3+}$ octahedral.

Free $\text{Al}(\text{H}_2\text{O})_6^{3+}$ O _h symmetry	Site groups S ₆ symmetry	Factor groups T _h ⁶
A _g (ν_1) (541)	A _g	A _g ($\nu_1 + \nu_5$)
E _g (ν_2) (400)	E _g	E _g ($\nu_2 + \nu_5$)
F _{2g} (ν_5) (322)	F _{2g}	F _g ($\nu_1 + 2\nu_2 + 2\nu_5$)
F _{1u} (ν_3) (568)	A _u	A _u ($\nu_3 + \nu_4 + \nu_6$)
F _{1u} (ν_4) (387)	E _u	E _u ($\nu_3 + \nu_4 + \nu_6$)
F _{2u} (ν_6) (228)	F _{2u}	F _u ($3\nu_3 + 3\nu_4 + 3\nu_6$)

ν_5 are Raman active, ν_3 and ν_4 IR active, and ν_6 inactive in both IR and Raman. Table 2 shows the correlation diagram between the free $\text{Al}(\text{H}_2\text{O})_6$ group vibrations in O_h symmetry and the $\text{Al}(\text{H}_2\text{O})_6$ internal vibrations in T_h factor group symmetry through the S₆ one in the crystal.

Unambiguous assignments of these modes are difficult as they fall in the region of the anion bending modes, librational modes of water molecules, and external modes. However, a few of these modes are assigned by comparison with the bands observed for the $\text{Al}(\text{H}_2\text{O})_6^{3+}$ complex in $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ [5] and in similar compounds in $(\text{CH}_3)_2\text{NH}_2\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ [13]. The medium bands around 530 cm^{-1} are due to the ν_1 mode of the ion. ν_2 modes are observed as very weak bands around 400 cm^{-1} . The triply degenerate symmetric bending mode (ν_5) is observed with medium intensity in the Raman spectra, around 330 cm^{-1} , being observed at similar frequencies ($517, 416$ and 386 cm^{-1}) in the spectrum of potassium alum [18].

SO₄²⁻ Vibration. The four internal modes of a free SO₄²⁻ ion with tetrahedral, T_d symmetry are at $\nu_1(\text{A}_1)$ 981 cm^{-1} , $\nu_2(\text{E})$ 451 cm^{-1} , $\nu_3(\text{F}_2)$ 1104 cm^{-1} , and $\nu_4(\text{F}_2)$ 613 cm^{-1} [19]. Table 2 shows resultant of correlation diagram between the free SO₄ group vibrations in T_d symmetry and the SO₄ internal vibrations in T_h factor group symmetry through the C₃ one in the crystal. In an ordered structure 15 Raman lines are predicted:

- (i) 7 stretching modes: $2\nu_1(1\text{A}_g, 1\text{F}_g); 5\nu_3(1\text{A}_g, 1\text{E}_g, 3\text{F}_g);$
- (ii) 8 deformation modes: $3\nu_2(1\text{E}_g, 2\text{F}_g); 5\nu_4(1\text{A}_g, 1\text{E}_g, 3\text{F}_g).$

In the ordered lattice, group theory analysis (Table 1) predicts two bands arising from the symmetric stretching

mode $\nu_1(\text{A}_g$ and F_g modes). This vibration that involves large changes in polarizability is observed as very intense bands at 990 cm^{-1} and medium bands at 975 cm^{-1} : in the $z(xx)\bar{z}$ geometry (A_g and F_g symmetry), in the $z(xy)\bar{z}$ geometry (E_g symmetry), and in $Z(X'X')\bar{Z}$ geometry (A_g, E_g, and F_g symmetry). The two bands should be attributed to A_g component to two types of sulfate anion, as done in all previous assignments (see [5–17]). The two bands with different intensity are also observed in the single crystal Raman spectrum of potassium alum for $x(zz)y$ and $x(xy)x$ orientations at 973 and 989 cm^{-1} [20]. These last authors assert that the two bands have some A_g symmetry, and there is no indication of a band with F_g symmetry. Although in the studied Raman spectrum of polycrystalline K-alum only one very strong band is observed below 1000 cm^{-1} originating from the SO₄ symmetry stretching mode $\nu_1(991\text{ cm}^{-1})$, the weak intensity in the $z(xy)\bar{z}$ orientation was attributed to spillover of the A_g intensity because the peak positions were identical in both orientations. Intensity ratio of the bands due to the two sites gave a higher value ($p_1/p_2 \sim 9.9$) than ($p_1/p_2 \sim 5$) calculated from X-Ray studies [20]. In the $Z(X'Y')\bar{Z}$ orientation where only the E_g modes are expected, two very weak bands, with equal intensity, are observed at 986 and 993 cm^{-1} . The presence of two bands for the symmetric stretching mode $\nu_1(\text{F}_g)$ confirms the hypothesis of a disordered structure. The two F_g modes are observed at 985 and 968 cm^{-1} in the single crystal Raman spectrum of K-Alum [21]. For the symmetric bending mode ν_2 , three Raman components ($1\text{E}_g + 2\text{F}_g$) are predicted in all polarization geometries. In the $z(xx)\bar{z}$ and $Z(X'Y')\bar{Z}$ orientations where only the F_g modes are expected, three bands are observed at $440, 460,$ and at 471 cm^{-1} . Their analogues in $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

TABLE 3: Raman band positions and assignments of $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

$z(xx)\bar{z}$		$z(xy)\bar{z}$		$Z(X'Y')\bar{Z}$		$Z(X'X')\bar{Z}$		Assignment
$A_g + E_g$		F_g		E_g		$A_g + E_g + F_g$		
11	m	11	m	—		11	m	Lattice modes
14	w	—		14	w	14	w	
16	m	—		—		16	m	
39	w	—		—		39	w	
44	w	47	w	48	w	44	w	
—		53	w	—		59	w	
61	w	59	m	60	m	61	m	
—		73	w	—		73	w	
80	w	—		—		—		
120	w	120	m	—		—		Trans of SO_4^{2-}
159	s	153	m	—		159	m	
—		186	m	167	m	—		
193	s	—		196		193	m	Rota of SO_4^{2-}
—		195	m	—		—		
245	wbr	228	w	—		246	w	$\nu_{\text{NH}_4\text{-O}}$
326	w	329	w	320	w	327	w	
440	m	440	w	434	w	440	w	$\nu_2\text{SO}_4^{2-}$
460	m	460	m	459	m	458	m	
539	wbr	471	w	—		—		
—		581	sh	—		—		
615	s	610	s	614	s	614	s	$\nu_4\text{SO}_4^{2-}$
—		621	s	634	s	—		
—		632	m	—		—		
902	w	—		913	w	905	w	$\nu_1\text{SO}_4^{2-}$
—		915	s	986	s	990	s	
990	vs	990	m	993	m	1099	m	
1094	wbr	1034	m	—		1101	m	
1104	s	1091	m	1102	m	—		
1112	s	1102	s	1123	s	1131	m	
1131	m	1130	m	1132	m	1134	m	$\nu_3\text{SO}_4^{2-}$
-1190	m	—		—		1191	m	
—		—		—		—		
—		—		—		1444	s	$\nu_4\text{NH}_4^+$
1444	s	—		1453	s	—		
—		—		—		1540	s	$\nu_2\text{H}_2\text{O}$
—		—		—		1621	s	$\nu_2\text{NH}_4^+$
—		—		—		1750	s	
1620	m	1617	mbr	—		—		
1726	m	1738	wbr	—		2210	m	
—		—		—		2473	m	
2442	w	—		—		—		$\nu_1\text{H}_2\text{O}$
2482	w	—		2908	m	2920	m	
—		—		3072	m	—		
2856	m	2936	m	—		3132	m	
3103	m	—		—		—		
3134	s	—		3338	m	3350	m	
3356	mbr	3365	s	—		—		$\nu_3\text{H}_2\text{O}$
—		—		—		3400	wbr	
3400	mbr	3376	s	—		—		

s: strong; w: weak; m: medium; sh: shoulder; v: very; br: broad.

appear at (441, 458 and 480 cm^{-1}) and (441, 458, and 475 cm^{-1}), respectively. Two E_g modes ($z(xy)z$ geometry) are observed at 439 and 460 cm^{-1} . Thus the number of deformation mode ν_2 of SO_4 shows very clearly the two different orientations of SO_4^{2-} groupments in this structure.

From group theoretical predictions, five lines ($1A_g + 1E_g + 3F_g$) are expected in all orientation for the asymmetric bending mode ν_4 . In the $Z(X'Y')\bar{Z}$ geometry (E_g symmetry) two bands are observed at 614 and 634 cm^{-1} . In the $z(xx)\bar{z}$ geometry ($A_g + E_g$ symmetry) three bands are observed at 615, 634, and 648 cm^{-1} . The two bands appearing at 615 and 648 cm^{-1} are assigned to the A_g symmetry. The splitting of the A_g and E_g modes confirms the existence of two types of tetrahedral. In the $z(xy)\bar{z}$ geometry (F_g symmetry) three bands are observed at 610, 621, and 632 cm^{-1} .

The asymmetric stretching mode ν_3 is found in the 1000–1160 cm^{-1} region. Group theory analysis predicts five bands for this mode ($1A_g + 1E_g + 3F_g$). In the $x(zz)x$ geometry ($A_g + E_g$ symmetry) as in the $x(z)y$ geometry (F_g symmetry) and in the $Z(X'Y')\bar{Z}$ geometry (E_g symmetry), three (1107, 1131, and 1189 cm^{-1}), four (1034, 1092, 1102, and 1131 cm^{-1}), and two (1134 and 1189 cm^{-1}) bands are obtained, respectively. The bands observed at 1107 and 1131 cm^{-1} , for the first orientation, can be associated to the A_g mode, and those at 1134 and 1189 cm^{-1} are attributed to the E_g mode. The four peaks observed in the second orientation are attributed to the F_g mode. In the $Z(X'X')\bar{Z}$ geometry ($A_g + E_g + F_g$) symmetry five bands are observed at 1099, 1101, 1131, 1134, and 1191 cm^{-1} . In the polycrystalline spectrum of Raman are observed in the region of the $\nu_3(\text{SO}_4)$ modes, in the IR spectra of various alums [21], where $3\nu_3(\text{SO}_4)$ modes predict [19] two intense doublet at ≈ 1100 – 1090 cm^{-1} and two less intense bands at ≈ 1070 – 1200 cm^{-1} . These last were assigned to $\nu_3(\text{SO}_4)$ modes of the mirror sulfates [22]. Thus the number of $\nu_3(\text{SO}_4)$ modes observed in spectra gives evidence that the disorder is indeed in NH_4 -alum.

In conclusion, X-Ray diffraction studies indicated that the sulphate groups in NH_4^+ alum is orientationally disordered. The current studies of the polarised Raman spectra give evidence that the disorder is indeed present in the ammonium alum. This is best manifested through the appearance of surplus bands in the spectral regions of vibrations of the sulphate anion.

External Modes. 10 A_g , 10 E_g , and 21 F_g lines can be expected in the Raman low-frequency range, corresponding to external modes. Experimentally, 11 lines in the $z(xx)z$ geometry ($A_g + E_g$ symmetry), 5 lines in the $Z(X'Y')Z$ geometry (E_g symmetry), and 10 lines in the $x(z)y$ geometry (F_g symmetry) indeed exist (Table 3). Each external mode may be dominated by the contributions from all cations. However, in certain frequency ranges the external modes may be dominated by contribution from one kind of cation (translations) or groups of atoms (rotation). The external modes are assigned by comparison with attribution proposed in $\text{RbAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and by considering the fact that the translator and libratory modes of NH_4^+ ion occur at higher wave numbers than those of the SO_4^{2-} ions.

The librations of both NH_4^+ and SO_4^{2-} ions are found to be stronger in intensity than the corresponding translational modes. By relative data comparison to the ammonium and rubidium alum, the bands observed in the 53–61 cm^{-1} region, at 167, 186, and at ~ 245 cm^{-1} , can be attributed to the translations and librations of NH_4^+ ion, since these bands are not observed in the rubidium alum. By similar reasoning we can confirm the attribution of the band observed at 238 cm^{-1} in rubidium alum to the Rb–O stretching mode [5–18]. Thus, the other bands observed in the 90–150 cm^{-1} region can be assigned to translational modes and those in the 150–200 cm^{-1} region to rotational modes of SO_4^{2-} [5–21].

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