SPECTROSCOPIC STUDIES OF
FERROELECTRIC METHYL AMMONIUM ALUMS
(MASD, MASeD and MCrSD)

By G. M. VENKATESH AND P. S. NARAYANAN

(Deparment of Physics, Indian Institute of Science, Bangalore-12, India)

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ABSTRACT

The Raman spectra of $CH_3NH_3Al(SO_4)_2$ $12H_2O$ (MASD), CH_3NH_3Al $(SeO_4)_2$ $12H_2O$ (MASeD) *and deuterated* MASD *and the iufrared spectra of* MASD, MASeD, MCrSD $[CH_3NH_3Cr(SO_4)_2 \cdot 12H_2O]$ *and deuterated* MASD *at different temperatures have shown that the sulphate or the selenate ion does not undergo any appreciable distortion by the ferroelectric phase transition. A comparison of the Raman spectra of* MASD *at* 300°, 200° *and* 100°K *has shown that the* $\nu_2(SO_4)$, CH_3 *stretching and* H_2O *stretching vibrations at* 988, 2991 *and* 3380 cm^{-1} *respectively appear with enhanced intensity in the spectrum of the ferroelectric phase. The observation of new infrared bands in the region* 2750- 000 cm^{-1} *and at about* 500 cm^{-1} *respectively due to the stretching and torsional vibrations of the* $CH_3NH_3^+$ *ion suggests that a rearrangement of the* CH_3NH_3 *ion is probably the triggering mechanism as suggested by O'Reilly and Tsang from magnetic resonance studies of* MASD.

1. INTRODUCTION

In recent years, the spectroscopic methods have been increasingly employed to the study of hydrogen bonded crystals, particularly the ferro-electrics. Methylammonium aluminium sulphate dodecahydrate (*MASD*) undergoes a first-order ferroelectric phase transition from the cubic phase to the orthorhombic phase at the Curie point −96°C[1]. The structure of *MASD* has been determined in the ferroelectric phase by Fletcher and Steeple[2] and in the cubic phase by Okaya *et al*[3]. $CH_3NH_3Al(SeO_4)_2 \cdot 12H_2O$ (*MASeD*) and $CH_3NH_3Cr(SO_4)_2 \cdot 12H_2O$ (*MCrSD*) are also ferroelectric below −57° and −109°C[1], respectively. Hence an investigation of the Raman spectra of *MASD, MASeD, MCrSD,* and deuterated *MASD* at different temperatures was undertaken to follow the changes in the symmetry of the sulphate and the

selenate ions and also to follow the changes in the hydrogen bond scheme on phase transition and thus to throw some light on the mechanism of phase transition. The Raman spectrum of *MASD* only has been studied by the Russian workers[4].

2. EXPERIMENTAL DETAILS

Single crystals of *MASD* or *MCrSD* were obtained by a slow evaporation of an aqueous solution of CH_3NH_3Cl, H_2SO_4 and $Al_2(SO_4)_3 \cdot 12H_2O$ or $Cr_2(SO_4)_3 \cdot 15H_2O$ in molar proportions. To prepare crystals of deuterated *MASD*, *MASD* was repeatedly recrystallized from D_2O. The Raman spectra of single crystals of *MASD*, *MASeD* and of small crystals of deuterated *MASD* were recorded on zenith plates with a Hilger medium quartz spectrograph having a dispersion of 140 cm^{-1} at $\lambda 2537$ Å. A comparative study of the Raman spectra of *MASD* at 300°K (room temperature), 200°K (temperature of solid carbon dioxide and acetone mixture) and 100°K (liquid oxygen temperature) was also made. The infrared spectra of *MASD*, *MASeD*, *MCrSD* and deuterated *MASD* were obtained at 100° and 300°K with a Cart-Zeiss, UR-10 spectrometer by the KBr pellet technique. The microphotometer records and the corresponding Raman spectra and the infrared absorption curves of these alums are reproduced in Fig. 1-6. The Raman and infrared spectral data are given in Tables 1-3.

3. POLARIZATION STUDIES

In the notation of Couture and Mathieu[5] the observed Raman lines in cubic crystals can be classified into *Ag*, *Eg* and *Fg* species by studying cases 2*a* and 3*a*. In case 2*a* the light is incident normally on the (100) face and the scattered radiation is gathered in the ⌊011⌋ direction. In case 3*a*, the light incident in the [111] direction is scattered in the plane normal to [111]. Accordingly two polarization pictures of *MASD* were obtained on zenith astronomical plates. From the calibration curves obtained by the varying slit width method, the intensities of the horizontal and vertical components were estimated and the observed Raman lines were classified as shown in Table 1.

4. DISCUSSION

MASD, *MASeD* and *MCrSD* are all cubic in the room temperature phase the speca group being $Pa3$ (T_h^6). There are four molecules in the unit cell. The lattice constants of *MASD*, *MASeD* and *MCrSD* are respectively 12.502, 12.694, and 12.538 Å. In the cubic phase of these alums the trivalent ions are situated at the centres of symmetry on the three fold axes. To achieve this centrosymmetric structure, the CH_3NH_3 ions must be either freely rotating or statistically distributed about the three axis.
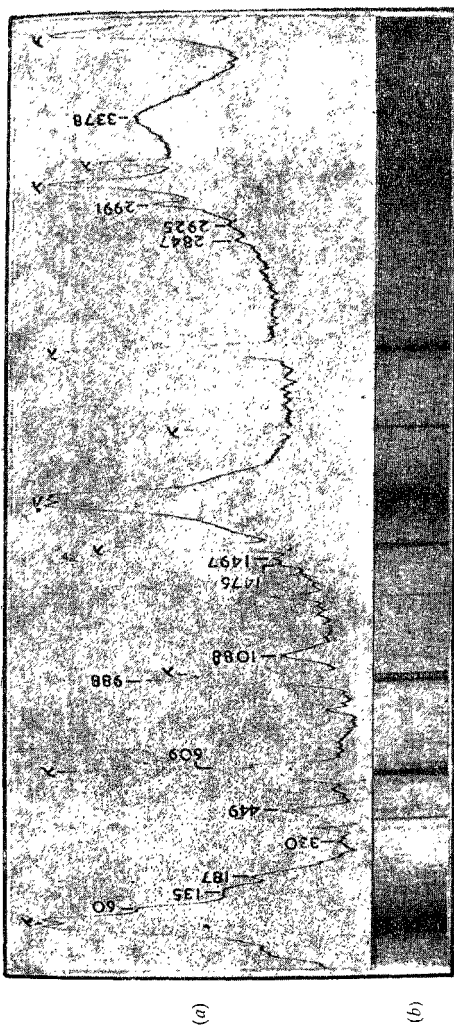
FIG. 1

(a) Microphotometer Record of the Raman Spectrum of MASD
(b) Photograph of the spectrum

* Peaks marked λ in microphotometer record are due to the Hg arc source
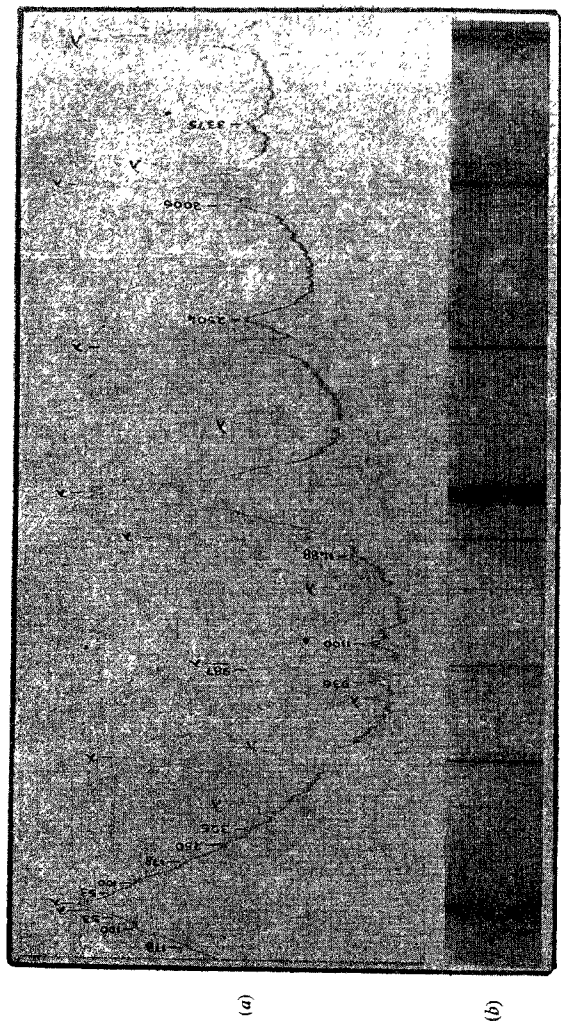
FIG. 2

(a) Microphotometer Record of the Raman Spectrum of Deuterated MASD
(b) Photograph of the Spectrum.
• Peaks marked λ in the microphotometer record are due to the Hg are source
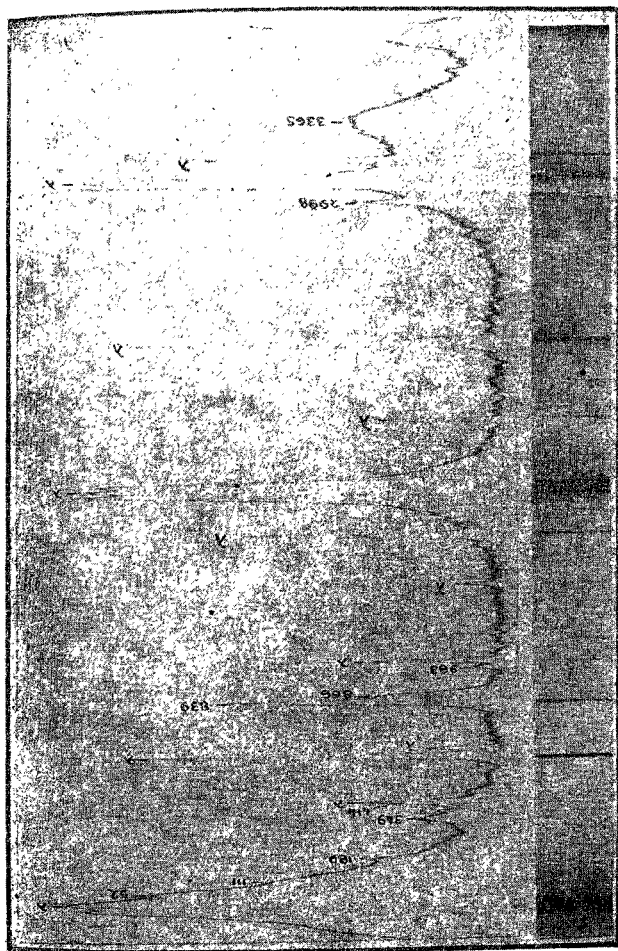
FIG. 3

(a) Microphotometer Record of the Raman Spectrum of MASeD
(b) Photograph of the Spectrum
* Peaks marked λ in the microphotometer record are due the Hg arc source
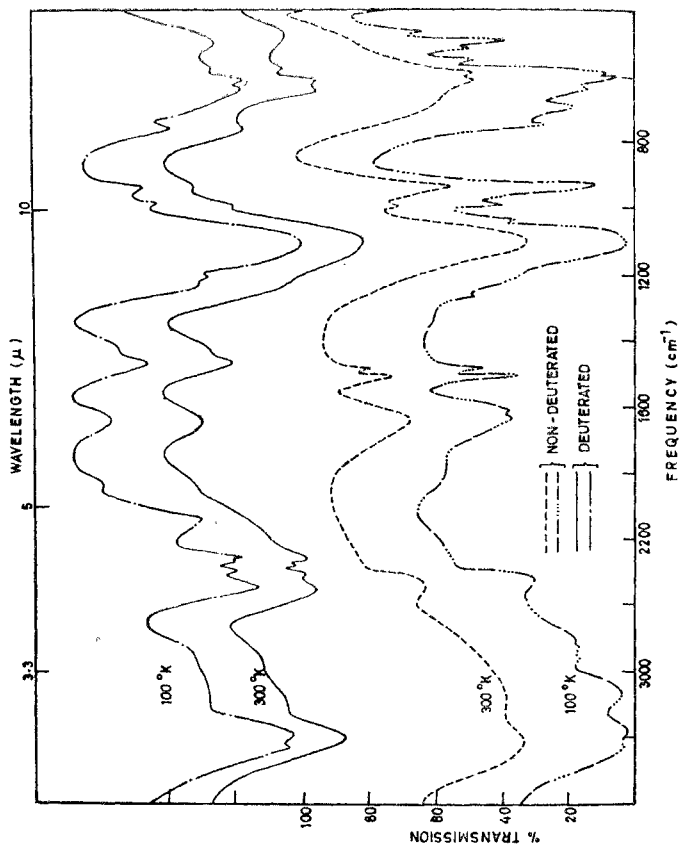
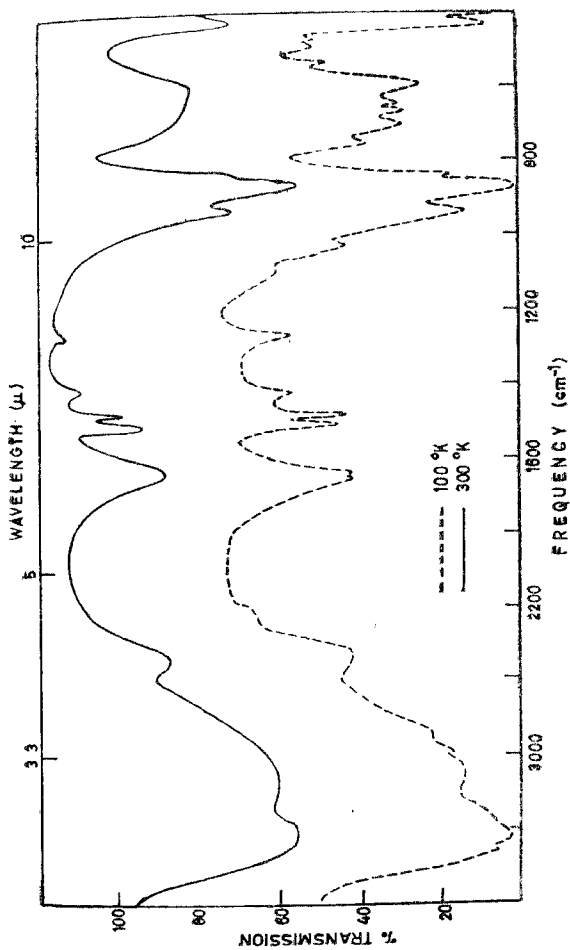Fig. 4

IR Spectrum of MASD in KBr pellet
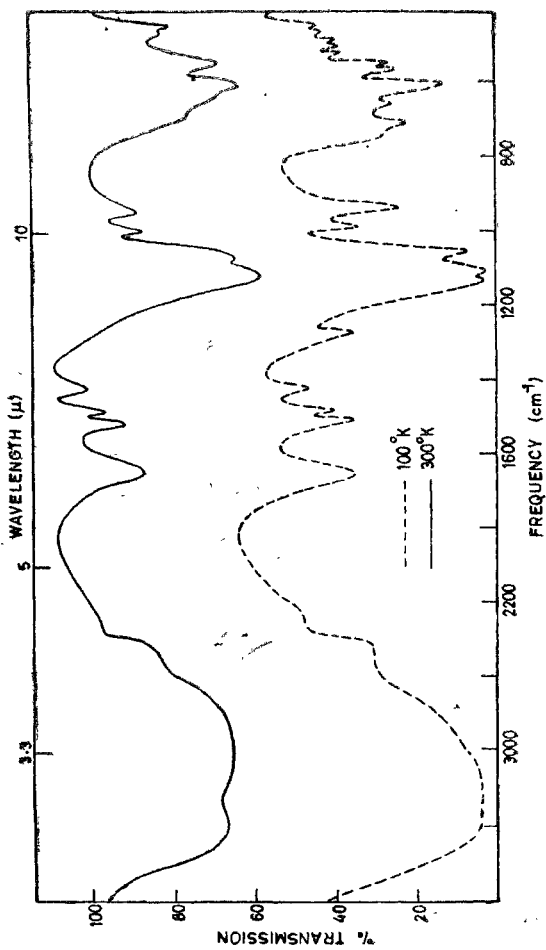
Fig. 5

IR Spectrum of MASeD in KBr pellet

FIG. 6

IR Spectrum of MCrSD in KBr pellet

There are two crystallographically non-equivalent sets of water molecules, six water molecules octrahedrally surrounding the trivalent ion (Al-0 $\sim$ 1.9 Å) and the remaining six water molecules being associated with the CH_3NH_3 ion. These alums possess the β structure. The differences among the α, β and τ structures in the alums have been discussed elsewhere. The most conspicuous difference that distinguishes a β alum from the α and τ alum is the number of nearest neighbours around the monovalent ion. There are twelve oxygen atoms in the coordination shell of the monovalent ion with six sulphate oxygens and six water oxygens at respective distances of 3.55 and 3.58 Å. The sulphate group possess C_{3v} symmetry in the lattice with one of the sulpaate oxygens and the sulphur atom being situated on the three fold axis and the remaining oxygens in the general positions. All the water molecules in the lattice are H-bonded to neighbouring sulphate oxygens or to water oxygens. In the ferroelectric phase, *MASD* belongs to the orthorhombic system with the space group $Pca2$1[2]. The site symmetry of the sulphate group is reduced to c_1. Details of the structure of *MASeD* and *MCrSd* are not yet available in literature.

TABLE 1

Raman Spectral Data on *MASD* and *MASed* in cm^{-1}

MASD*	Sym. species	MASD-d	MASeD	Assignments
55(6)	Ag +	55(6)	52(6)	
135(5b)	Eg +	100(5)	111(3)	Lattice vibrations
187(5)	Eg +	178(4b)	189(5)	
330(1)	....	325(2b)		$\nu_2(AlO_6)$
449(4)	Eg	447(1)	349(4b)	$\nu_2(SO_4)/\nu_2(SeO_4)$
609	....	609	414(2)	$\nu_4(SO_4)/\nu_4(SeO_4)$
988	Ag	987(10)	839(10)	$\nu_1(SO_4)/\nu_1(SeO_4)$
		936(3)	983(2)	C-N stretching
1088	Fg	1100(4)	866(3)	$\nu_3(SO_4)/\nu_3(SeO_4)$
1476(1)	Ag	1480(1)		$CH_3NH_3^+$ bending
1497(1)	Ag			
2847(3)	Ag			CH$_3$ stretching
2927(1)				
2991(7)	Ag	3000(6)	2998(4)	
3378(7b)	Ag + Fg	2504(6b)	3365(6b)	
		3375(2)		OH stretching

* Visually estimated intensities are given in brackets, b —broad, d—denotes deuterated.

TABLE 2

Infrared Spectral Data on *MASD* (cm⁻¹)

MASD* 300°K	MASD-d 300°K	MASD 100°K	MASD-d 100°K	Assignments
460(w)		460(w)		$\nu_2(SO_4)$
		460(s)		H_2O libration
		512(m)	500(s)	$CH_3NH_3^+$ torsion
612(s)	612(s)	588(vs)	615(s)	$\nu_4(SO_4)$
	636(s)	608(vs)	645(s)	
		640(s)		
	480(mb)	695(s)	500(s)	$H_2O(A1)/D_2O$ rocking
	575(w)	750(s)	575(w)	
935(s)	758(m)	933(vs)	757(s)	$H_2O(A1)/D_2O$ wagging + CH_3 rocking
	938(w)	945(sh)	941(w)	
988(w)	988(w)	990(m)	988(w)	$\nu_1(SO_4)$
	938(w)	1028(w)	941(w)	C-N streching
1110(vs)	1105(vs)	1080(vs)	1105(vs,b)	$\nu_3(SO_4)$
		1100(vs)		
		1116(vs)		
		1267(w)		NH_3^+ recking
1480(w)	1225(sh)	1480(m)	1217(w)	CH_3NH_3 bending
1504(m)	1470(m)	1504(s)	1435(m)	
			1470(m)	
1640(m)	1225(sh)	1635(s)	1230(m)	H_2O/D_2O bending
	1470(m)		1640(m)	
2480(m)	1880(w)	2450(m)	1880'w)	Combination
		2860(s)	2090(s)	H_2O/D_2O stretching + $CH_3NH_3^+$ stretching
	2380(s)	2923(s)	2310(s)	
3120(vs,b)	2350(s)	3145(vs)	2350(s)	
	2390(s)		2390(s)	
3410(vs)	2510(s)	3380(vs)	2425(s)	
	3395(s)	3460(vs)	3380(s)	
			3460(s)	

* Symbols : s—strong, m—medium, w—weak, sh—shoulder, b—broad. v—very.

TABLE 3

Infrared Spectral Data on MASeD and MCrSD (cm^{-1})

MASeD		MCrSD		Assignment
300°K	100°K	300°K	100°K	
		447(w)	447(w) 458(w)	} $\nu_2(SO_4)$
		465(w)	476(w)	$\nu_3(CrO_6)$
	473(w) 488(w)		498(w) 514(w)	} $CH_3NH_3^+$ torsion
595(m)	595(s)	545(m)	545(s) 514(w)	} H_2O libration
427(s)	430(s)	601(s)	603(s)	$\nu_4(RO_4)$
	649(m) 668(m)	650(sh)	655(w)	} H_2O libration
670(s)	700(s) 752(m)	690(w)	708(m) 745(w)	} H_2O (M^{3+}) reckoning
933(s)	935(s)	938(s)	936(s)	H_2O (M^{3+}) wagging $+ CH_3$ rocking
	1025(m)			C-N stretching
835(sh	835(sh)	985(m)	988(m)	$\nu_1(RO_4)$
868(vs)	870(vs)	1065(s) 1118(vs)	1064(s) 1104(vs) 1124(vs)	} $\nu_3(RO_4)$
1262(w)	1265(m)		1270(m)	NH_3^+ rocking
1410(w) 1478(w) 1508(m)	1415(w) 1478( ) 1506(m)	1423(w) 1478(w) 1506(m)	1425(m) 1478(m) 1503(m)	} $CH_3NH_3^+$ bending
1640(m)	1640(m)	1640(m)	1640(m)	H_2O bending
2430(m)	2460(m)	2480(m)	2460(m)	Combination
3100(vs,b)	2880(vs) 2980(vs) 3100(vs) 3440(vs) 3506(vs)	2800— 3200(vs) 3400(vs)	2800— 3200(vs) 3400(vs)	} H_2O stretching $+ CH_3NH_3^+$ stretching
3440(vs)				

From the group theoretical considerations[6], 5 translatory and 5 rotatory type of lattice vibrations are expected for the sulphate group alone. However, the Raman spectra of *MASD*, *MASeD* and deuterated *MASD* show only three Raman lines each in the low frequency region (0-200 cm^{-1}). Even when the Raman spectrum of *MASD* was recorded with a large Littrow quartz spectrograph having higher dispersion (40 cm^{-1}/mm at λ 2537 Å), the rich Raman spectrum of *MASD* reported to have been observed by Korshunov et al.[4] could not be observed. It was found possible to analyse the observed spectroscopic data by considering only the vibrations of the sulphate and the selenate groups, the $CH_3NH_3^+$ ions and the H-bond water molecules with the p appropriate site symmetry (Halford[7]) and hence the correlation coupling effects were not pronounced.

5. VIBRATIONS OF SO$_4$ OR SeO$_4$ GROUP

All the four fundamental vibrations $\nu_1(a_1)$, $\nu_2(e)$, $\nu_3(f_2)$ and $\nu_4(f_2)$ of the XO_4^- (where X is S or Se) ion with T_d symmetry in the free state[8] are expected to be both Raman and infrared active in the case of *MASD*, *MASeD* and *MCrSD*, since the sulphate or the selenate ion possesses only C_{3v} symmetry in the lattice. Further, one would expect the F_2 modes to split into A_1 and E modes, the separation between the split components depending on the crystal field strength. However, in the Raman spectrum of MASD, only four Raman lines are observed at 449 cm^{-1} due to $\nu_2(SO_4)$, at 988 cm^{-1} due to $\nu_1(SO_4)$ and at 1088 and at about 610 cm^{-1} respectively due to ν_3 and ν_4 vibrations, with the polarization characteristics corresponding to the Eg, Ag and Fg species respectively. On the other hand, Korshunov et al[4]. have reported the presence of 4 Raman lines in the S-O stretching region alone *i.e.*, at 995, 1107, 1117, and 1132 cm^{-1}. However, the present observation on *MASD* is in agreement with the observation of four Raman lines approximately with the same frequency shifts (451, 990, 1097 and ~ 610 cm^{-1}) in the spectrum of $CsAl(SO_4)_2$ 12H$_2$O, a typical representative of the β alums[9]. Because of the presence of two mercury lines at 608.6 (λ 2576.3 Å) and 640.9 (λ 2578.4 Å) cm^{-1}, the presence of the Raman line due to ν_4 (SO$_4$) has to be inferred by a comparison of the relative intensities of the mercury lines. In the infrared spectrum of *MASD* also, four bands are observed at 460, 612, 988 and 1110 cm^{-1} respectively due to ν_2, ν_4, ν_1 and ν_3 modes of the sulphate ion. In the case of *MASeD*, 4 Raman lines at 349, 414, 8.9 and 866 cm^{-1} respectively due to ν_2, ν_4, ν_1 and ν_3 vibrations and three infrared bands at 430, 835 and 875 cm^{-1} due to ν_4, ν_1 and ν_3 modes of the selenate group are observed. The infrared band due to ν_2 (SeO$_4$) lies below 400 cm^{-1}.

In the ferroelectric phase of *MASD*, the site symmetry of the sulphate group is only C_1. Then all the degenerate vibrations of the sulphate group are expected to split into non-degenerate components, the separation between the split components depending on the strength of the perturbing crystalline

field. However, the distortion of the sulpnate group is not very appreciable, as the infrared spectrum of *MASD* exhibits three closely spaced absorption bands at 1080, 1100 and 1116 cm^{-1} all due to $\nu_3(SO_4)$. Also, the infrared bands due to $\nu_1(SO_4)$ and $\nu_2(SO_4)$ are weak, suggesting that the crystalline field effect is not appreciable. In the case of *MASeD*, the $\nu_3(SeO_4)$ band broadens out with no splitting in the ferroelectric phase. On the other hand *MCrSD* behaves differently (Fig. 6). In the room temperature spectrum two absorption bands are present at 1065 and 1113 cm^{-1} due to $\nu_3(SO_4)$. In the spectrum of the ferroelectric phase, three well resolved absorption bands at 1064, 1106 and 1127 cm^{-1} are observed. The presence of three components in the region 1050-1150 cm^{-1} in the spectrum of the ferroelectric phase of *MCrSD* can, however, be due to the lower site symmetry of the sulphate group, namely C$_1$ as in the case of *MASD*. On the other hand, the splitting of the $\nu_3(SO_4)$ mode in the room temperature spectrum and the greater separation of the split components of $\nu_3(SO_4)$ in the low temperature spectrum suggest that the perturbing crystalline field is comparatively of greater magnitude in the case of *MCrSD*.

6. VIBRATIONS OF CH$_3$NH$_3^+$ ION

The assignment of the fundamental vibrations of the methyl-ammonium ion with C$_{3\nu}$ symmetry has been made by Theoret and Sandorfy[10] from a study of the infrared spectra of methylammonium halides. From a comparison, the frequencies observed in the alums are assigned as shown in Tables 1−3. However, the infrared band and the Raman line due to NH$_3^+$ degenerate bending observed at about 1580 cm^{-1} in the case of methylammonium halides, have not been observed in the spectra of the alums. The presence of four Ramen lines in the region 2830-3050 cm^{-1}, which have been shown to arise from the methyl group vibrations, has been explained in terms of a resonance effect involving the CH$_3$ deformation and CH$_3$ stretching vibrations[11]. In the present case, three Raman lines at 2991, 2927 and 2847 cm^{-1}, all belonging to the same symmetry species Ag are observed. Theoret and Sandorfy[10], from an infrared study of ordinary and C-x and N-deuterated methylammonium halides have concluded that the CH$_3$ and NH$_3^+$ rocking modes observed at 954 and 1275 cm^{-1} respectively, are strongly coupled. In the case of *MASD*, the ND$_3^+$ rocking mode at 1265 cm^{-1} shifts to lower frequency on deuteration. However, the CH$_3$ rocking mode at about 940 cm^{-1} does not appear to shift on deuteration unlike in the case of methylammonium halides. The C-N stretching vibration falls on the $\nu_1(SO_4)$ Raman line in the case of *MASD* and is observed at 983 cm^{-1} in the Raman spectrum of *MASeD*. In the infrared spectrum, it appears at about 1030 cm^{-1}. In the case of deuterated *MASD*, the Raman line at 936 cm^{-1} and the infrared band at about 941 cm^{-1} are assigned to C-N stretching mode. This observation indicates a strong coupling between the C-N stretching and NH$_3^+$ rocking vibrations.

7. Vibrations of H_2O

The fundamental vibrations of the bound water are considerably affected by H-bond formation and also by the coordination of the water oxygen to the metal ion. Also, the restricted rotation of the water molecules about the principal axes of inertia gives rise to librations which can be clasified as H_2O rocking, wagging and twisting modes. If the coordinating bonding is also prominent, the metal-oxygen stretching mode is observed. Both the effect of H-bonding and that of metal oxygen bonding result in a decrease of the frequencies of O-H stretching vibrations and in an increase of the frequencies of D_2O librations and that of metal-oxygen stretching. From these considerations, the Raman lines and the infrared bands observed at about 3400 cm^{-1} and in the region 2800-3200 cm^{-1} are assigned to the stretching vibrations of the water molecules associated with the monovalent and the trivalent ions respectiuely. The assignments of the observed frequeneies to the librations of these water molecules are shown in Tables 2 and 3. On deuteration, frequencies of vibrations of H_2O show an isotope shift by a ratio of about 1.3. The appearance of two infrared bands at 2090 and at about 2310 cm^{-1} indicates that all the six water molecules around the aluminium are not equivalent.

In these alums the centrosymmetric structure is achieved by a free rotation of the CH_3NH_3 ions or by a statistical distribution of these ions about the three fold axis. In the latter case, the individual unit cells are not centrosymmetric and hence the (g, u) selection rule need not apply. The infrared frequencies can coincide with those found in Raman effect ; but because of the limited dispersion of the instruments employed, it is difficult to conclude from the spectroscopic data whether the unit cell is centro-symmetric or not.

8. Vibration Spectrum and Ferroelectricity

In the paraelectric phase the $CH_3NH_3^+$ ion is either rotating or statisti-cally arranged about the three fold axis. Both the X-ray and the spectros-copic methods are. not able to distinguish between the two possibilities. However, in the ferroelectric phase, the $CH_3NH_3^+$ ion has a fixed orientation in the orthorhombic lattice[2]. Also, the six water molecules no longer form six of the nearest neighbours of the $CH_3NH_3^+$ ion with a mean contact distance of 3.55 Å ; but instead form two groups of three which are at respective distances of 2.98 and 4.21 Å from the NH_3^+ ion. Also, the six water molecules associated with the trivalent ion are not equivalent in the ferroelectric phase. Considerable changes in the hydrogen bond scheme occur on phase transition. Though all the contacts between atoms are unaltered, the individual O-H $\cdots$ O distances vary from 2.4 to 2.9 Å.

A comparative study of the Raman spectra of *MASD* at 300°, 200° and 100°K has shown that as the Curie point is approached from the paraelectric phase, the $\nu_1(SO_4)$ vibration at 988 cm^{-1}, the CH_3 stretching mode at 2991 cm^{-1} and the H_2O stretching vibration at 3378 cm^{-1} gain intensity and that in the spectrum of the ferroelectric phase, these vibrations appear with enhanced intensity. In the infrared spectra of *MASD*, *MASeD* and *MCrSD*, the CH_3 rocking mode at about 935 cm^{-1} gains in intensity in the low temperature phase. New vibrations are observed in the region 2750-3000 cm^{-1}. These bands are most probably due to the stretching vibrtions of the $CH_3NH_3^+$ ion. The other possibility is that these bands together with those in the region 3000-3200 cm^{-1} may correspond to the stretching vibrations of the non-equivalent water molecules around the trivalent ion, as indicated earlier. The band at 3400 cm^{-1} also shows some structure. The broad band at about 3400 cm^{-1} and the sharp band at about 3460 cm^{-1} are due to the stretching vibrations of the non-equivalent water molecules associated with the $CH_3NH_3^+$ ion. The observation of the infrared bands due to $CH_3NH_3^+$ torsional vibrations at about 500 cm^{-1} only in the spectra of the ferroelectric phase suggests that the $CH_3NH_3^+$ ion possesses at least C_{3v} symmetry in the cubic phase and only the lowest possible symmetry in the ferroelectric phase. These observations suggest that the rearrangement of the $CH_3NH_3^+$ ion is most probably responsible for the onset of ferroelectric transition as suggested by O'Reily and Tsang[12] from *NMR* and *EPR* studies of *MASD*. From the infrared spectra reproduced in Figs. 4-6, it is seen, as indicated earlier, that no striking distortion of the sulphate or the selenate groups takes place at the Curie point.

9. Acknowledgement

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