Vibrational Spectroscopic Studies of Trivalent Hexa-aqua-cations: Single-crystal Raman Spectra of Caesium Aluminium Alums between 300 and 1 200 cm^{-1}

By **Stephen P. Best, Robert S. Armstrong,*** and **James K. Beattie**, School of Chemistry, University of Sydney, New South Wales 2006, Australia

Oriented single-crystal Raman spectra of $CsAl(SO_4)_2{\cdot}12H_2O$, $CsAl(SeO_4)_2{\cdot}12H_2O$, and $CsAl(SO_4)_2{\cdot}12D_2O$ have been recorded at 80 K. A complete assignment of the spectra has been made between 300 and 1 200 cm^{-1} using factor group analysis. All external modes of co-ordinated water for both $[Cs(OH_2)_6]^+$ and $[Al(OH_2)_6]^{3+}$ have been identified. The wavenumbers of the internal modes of $[Al(OH_2)_6]^{3+}$ are ν_1 = 542 cm^{-1} and ν_2 = 473 cm^{-1}, with ν_5 centred at 347 cm^{-1}.

ALTHOUGH there has been a number of single-crystal Raman studies on divalent hexa-aqua-cations [1-4] the trivalent hexa-aqua-cations have attracted little attention. Two studies of the aluminium hexa-aqua-cation have been published; one was on $AlCl_3{\cdot}6H_2O$ [5] and the other was on a series of aluminium alums.[6] Infrared spectroscopy has been used to study a much wider range of trivalent hexa-aqua-cations. The caesium alums in particular [7-10] have been shown to be well suited to vibrational spectroscopy. A recent crystallographic study of a wide range of caesium alums [11] provides the detailed structural information necessary for a comparative study of trivalent hexa-aqua-cations. The object of this paper is to provide a complete and unambiguous assignment of the spectrum in the regions where the internal and external modes of co-ordinated water occur.

We have chosen the series $CsAl(SO_4)_2{\cdot}12H_2O$, $CsAl(SeO_4)_2{\cdot}12H_2O$, $CsAl(SO_4)_2{\cdot}12D_2O$ to make these assignments because the crystals are colourless and very stable, and because there are literature values for the internal modes of the $[Al(OH_2)_6]^{3+}$ species with which we can compare our results. We have chosen the caesium alums because this series is completely ordered [11] and the lattice is able to stabilise some unstable hexa-aqua-cations, notably those of Mn^{3+} and Co^{3+}. Low-temperature studies are necessary since the modes involving co-ordinated water are typically broad at room temperature and their external modes are quite weak. Many of the trivalent hexa-aqua-cations cannot be studied at room temperature owing to their instability, hence any comparative study must be completed at low temperature.

EXPERIMENTAL

Crystals of $CsAl(SO_4)_2{\cdot}12H_2O$ were grown from sulphuric acid (1 mol dm^{-3}). The selenate and deuteriate analogues were grown from selenic acid and $[^2H_2]$sulphuric acid respectively. In each case the alum was prepared by the dissolution under reflux of aluminium turnings in the appropriate mineral acid (1 mol dm^{-3}) followed by the addition of an equimolar quantity of caesium carbonate. The deuteriate was synthesised and handled under a dry atmosphere of argon to eliminate proton exchange with water vapour in the air.

The alums form an isomorphous series of cubic double salts conforming to the space group *Pa*3. Their crystallographic axes could be easily deduced from the crystal morphology which was predominantly octahedral with varying degrees of edge and corner truncation.

Experiments were chosen of the type $X'(\alpha\beta)Z$, where X',Y' are related to X,Y by a rotation about Z of $\pi/4$ radians, since a complete data set could be obtained in this way without reorientation of the crystal. Since the natural faces do not occur normal to the excitation and collection directions chosen for the experiments it was necessary to grind and polish faces in the appropriate directions.

Spectra were obtained using a Spex 1401 double monochromator fitted with a spatial filter in conjunction with an R.C.A. C 31034 GaAs photomultiplier and a P.A.R. photon counter. A Spectra Physics model 164 Ar^+ laser was used to excite the crystals with 514.5 nm radiation. An Oxford Instruments C.F.100 cryostat was used in the low-temperature experiments. Data were stored digitally in a HP 9835 minicomputer. Calibration and temperature measurement of all spectra were accomplished using Stokes and anti-Stokes peaks. The linearity of the frequency scale was checked using plasma emissions of the Ar^+ laser.

RESULTS

The caesium alums are an ideal series of isomorphous salts for the study of many trivalent hexa-aqua-ions. The wide range of trivalent metal cations able to be accommodated in the lattice, a high-symmetry site, and a well ordered structure combine to allow a complete study of the trivalent hexa-aqua-ions. Complications are encountered in analysing spectra as a result of the size of the unit cell. In particular, the complexity added by the internal and external modes of the co-ordination sphere of the monovalent cation requires a detailed study of one complete spectrum before a full investigation of other trivalent hexa-aqua-cations.

Factor group analysis (f.g.a.) links the structural characteristics of the unit cell to the observed vibrational spectrum. The symmetries and numbers of vibrational bands predicted are solely a function of the number of atoms contained in and the symmetry of the unit cell. The labels given to these modes are derived from the molecular model used to describe the unit cell.

As the co-ordination sphere of the monovalent cation is loosely bound, a number of different molecular groupings to describe the structure are possible. Three possibilities are: (*i*) that the caesium is co-ordinated to the six surrounding water molecules, (*ii*) that the sulphate groups are also co-ordinated to the monovalent cation, yielding a co-ordination number of twelve, or (*iii*) that the caesium ion is not co-ordinated and the water molecules are treated as lattice water.

TABLE 1

Factor group analysis of the alums

(*i*) Internal modes *

(*a*) $[Al(OH_2)_6]^{3+}$ and $[Al(OD_2)_6]^{3+}$

Free ion (O_h)	Site (S_6) .. × 4	Factor group (T_h)
ν_1 A_{1g}	A_g	$A_g + F_g$
ν_2 E_g	E_g	$E_g + 2F_g$
ν_3 F_{1u}	A_u E_u	$A_u + F_u$ $E_u + 2F_u$
ν_4 F_{1u}	A_u E_u	$A_u + F_u$ $E_u + 2F_u$
ν_5 F_{2g}	A_g E_g	$A_g + F_g$ $E_g + 2F_g$
ν_6 F_{2u}	A_u E_u	$A_u + F_u$ $E_u + 2F_u$

(*b*) SO_4^{2-} and SeO_4^{2-}

Free ion (T_d)	Site (C_3) .. × 8	Factor group (T_h)
ν_1 A_1	A	$A_g + F_g + A_u + F_u$
ν_2 E	E	$E_g + 2F_g + E_u + 2F_u$
ν_3 F_1	A E	$A_g + F_g + A_u + F_u$ $E_g + 2F_g + E_u + 2F_u$
ν_4 F_2	A E	$A_g + F_g + A_u + F_u$ $E_g + 2F_g + E_u + 2F_u$

(*ii*) External modes of co-ordinated water

$[Al(OH_2)_6]^{3+}$, $[Al(OD_2)_6]^{3+}$, $[Cs(OH_2)_6]^+$, and $[Cs(OD_2)_6]^+$

Water (C_{2v})	Site (C_1) .. × 6	(S_6) .. × 4	Factor group (T_h)
Rock B_1	A	A_g, A_u E_g, E_u	$A_g + F_g$, $A_u + F_u$ $E_g + 2F_g$, $E_u + 2F_u$
Wag B_2	A	A_g, A_u E_g, E_u	$A_g + F_g$, $A_u + F_u$ $E_g + 2F_g$, $E_u + 2F_u$
Twist A_2	A	A_g, A_u E_g, E_u	$A_g + F_g$, $A_u + F_u$ $E_g + 2F_g$, $E_u + 2F_u$

(*iii*) Lattice modes

	Translations		
Ion	$[Al(OH_2)_6]^{3+}$	$[Cs(OH_2)_6]^+$	SO_4^{2-}
A_g	0	0	1
E_g	0	0	1
F_g	0	0	3
A_u	1	1	1
E_u	1	1	1
F_u	3	3	3

	Rotations		
Ion	$[Al(OH_2)_6]^{3+}$	$[Cs(OH_2)_6]^+$	SO_4^{2-}
A_g	1	1	1
E_g	1	1	1
F_g	3	3	3
A_u	0	0	1
E_u	0	0	1
F_u	0	0	3

* Excluding the internal modes of water since these modes are expected above 1 200 cm^{-1}. Values × 4 *etc.* indicate the number of molecules on the site required for factor group symmetry T_h.

The results of each of the above approaches leads to equivalent f.g.a. predictions with only a difference in the labelling scheme. We have chosen to use the first alternative because it leads to a clearer discussion of the spectra and is equally applicable to α-alums and β-alums. The f.g.a. presented in Table 1 follows from the symmetry of the unit cell ($Pa3-T_h^6$), and the site symmetries of the constituent ions {S_6 for $[Al(OH_2)_6]^{3+}$ and $[Cs(OH_2)_6]^+$, and C_3 for SO_4^{2-}}.

Schematic representations of the six internal modes of the octahedral MX_6 species and the four internal modes of the tetrahedral AB_4 species may be found in many vibrational texts; for example, see ref. 12. The representations of the external or librational modes of water may be found in the literature.[13,14] The activities of the Raman bands for these modes in each of the scattering experiments are given in Table 2.

TABLE 2

Raman activities for the different scattering experiments *

Tensor component	Activity
$(X'X')$, $(Y'Y')$	$A_g + F_g + E_g/4$
(ZZ)	$A_g + E_g$
$(X'Y')$	E_g
$(X'Z)$, $(Y'Z)$	F_g

* X', Y' are related to X, Y by a rotation of $\pi/4$ radians about Z.

Spectra were obtained both at room temperature and at liquid-nitrogen temperature. No evidence of any phase changes was observed on cooling. Room temperature spectra are not shown since the broadness of many of the bands, particularly those involving water modes, obscures many features and may lead to ambiguous or incorrect conclusions. The narrower widths at half-height of bands found in the low-temperature spectra also allow more precise determination of the vibrational frequencies. The spectra obtained are shown in Figures 1—3, and Table 3 contains their vibrational frequencies and assignments.

Spectra of the deuteriate also have been recorded in the region 1 200—4 000 cm^{-1}. An estimate of the isotopic purity can be made by comparison between the intensity of the OD stretches and the OH stretches. The isotopic purity of the deuteriate is at least 99% based upon these measurements. Because of this high level of isotopic purity the occurrence of bands due to isotopic impurity can be neglected.

Strong modes of F_g symmetry are observed only in very low intensity in the E_g spectra of both the sulphate alums (Figures 1 and 3). This indicates that the crystals are well oriented. For the spectrum of the selenate alum (Figure 2) we found approximately 10% leakage of the F_g modes into the E_g spectrum and *vice versa*. This leakage arises from a small misorientation of the crystal. The degree to which these unwanted polarisations are formally allowed depends on the crystal orientation. All of the bands of the unwanted polarisation will be observed with the same relative intensities as in the pure spectrum. With the appropriate scaling of experimentally obtained spectra it is possible to subtract the unwanted polarisations and so separate the mixed spectra. Appropriate scaling factors have been obtained so that any obvious leakage has been eliminated and no negative peaks occur. We have used this technique for the E_g and F_g components of the selenate spectra shown in Figure 2 to simplify the description and discussion of the spectra. The original spectra are available as Supplementary Publication No. SUP 23298 (2 pp.).* Similar techniques have been used to locate weak A_g components. This is particularly useful since there is no other way of obtaining the A_g components separately.

DISCUSSION

General Considerations.—The Raman spectra may be conveniently divided into three regions: (*a*) 1 200—4 000

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

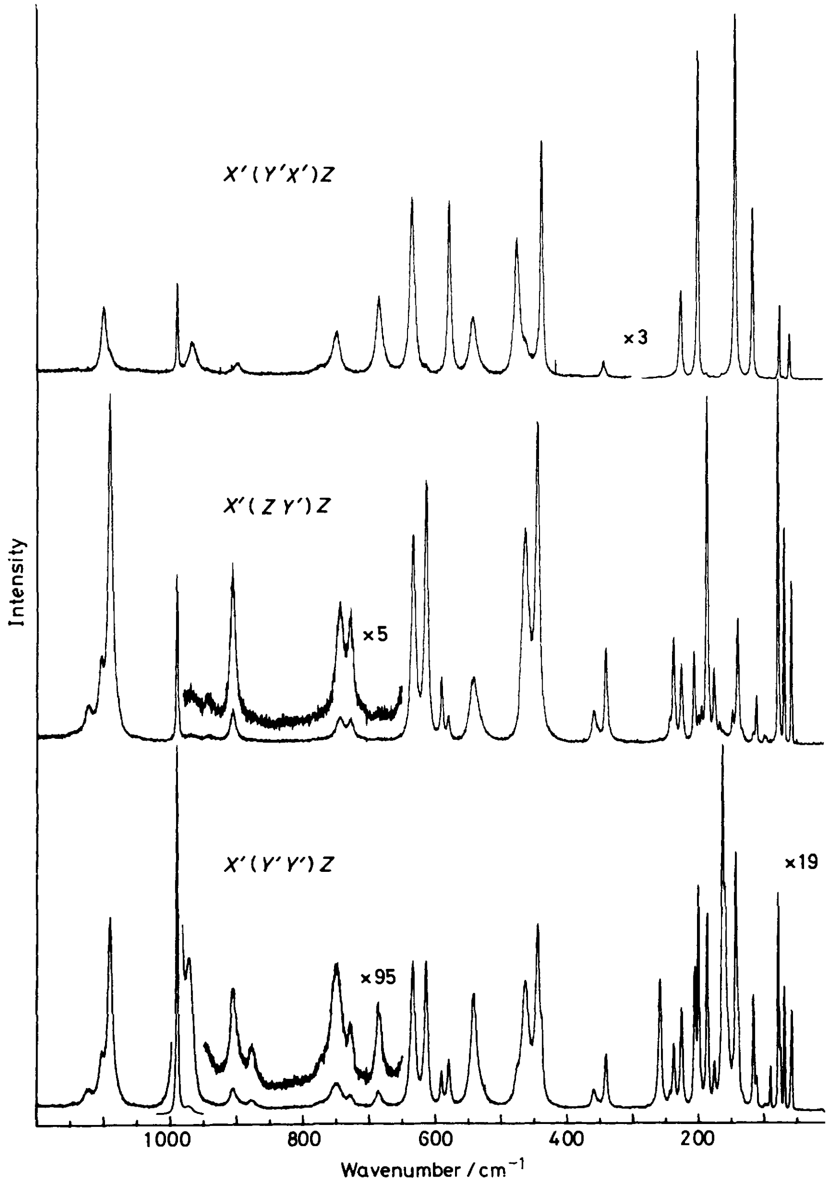

FIGURE 1 Single-crystal Raman spectra of $CsAl(SO_4)_2·12H_2O$ at 80 K (spectral bandwidth 1.6 cm^{-1} at 600 cm^{-1}; 514.5 nm radiation, 80 mW at the sample)

cm^{-1}, the O–H stretching and bending regions; (*b*) 300—1 200 cm^{-1}, the internal modes of sulphate and the hexa-aqua-aluminium ions and the librational modes of water co-ordinated to both the monovalent and trivalent cations; (*c*) below 300 cm^{-1}, the lattice modes and the internal modes of the caesium hexa-aqua-ion.

In order to study the trivalent hexa-aqua-cation it is necessary to make a complete assignment of the spectra in the range 300—1 200 cm^{-1}. We have chosen to defer assignment of the other two regions. In both of these regions the spectra are complicated by extensive coupling. For this reason the unambiguous assignment of these regions requires additional results. Work involving a wider range of trivalent cations and partial deuteriation is being pursued to resolve the assignments.

The spectra in Figures 1—3 include data recorded in the range 8—300 cm^{-1}. Although this region is not assigned, the numbers of bands of each symmetry species may be compared with the f.g.a. predictions. This provides a check on the validity of our description of the spectra.

According to our analysis there should be $6A_g + 6E_g + 18F_g$ modes in this frequency region. We find $5A_g + 6E_g + 17F_g$ bands for $CsAl(SO_4)_2·12H_2O$, $6A_g + 6E_g + 14F_g$ bands for $CsAl(SeO_4)_2·12H_2O$, and $5A_g + 6E_g + 17F_g$ bands for $CsAl(SO_4)_2·12D_2O$. The results are in good agreement with our expectations, and in exact agreement with respect to the numbers of E_g modes observed.

In the region 300—1 200 cm^{-1} it can be shown with the

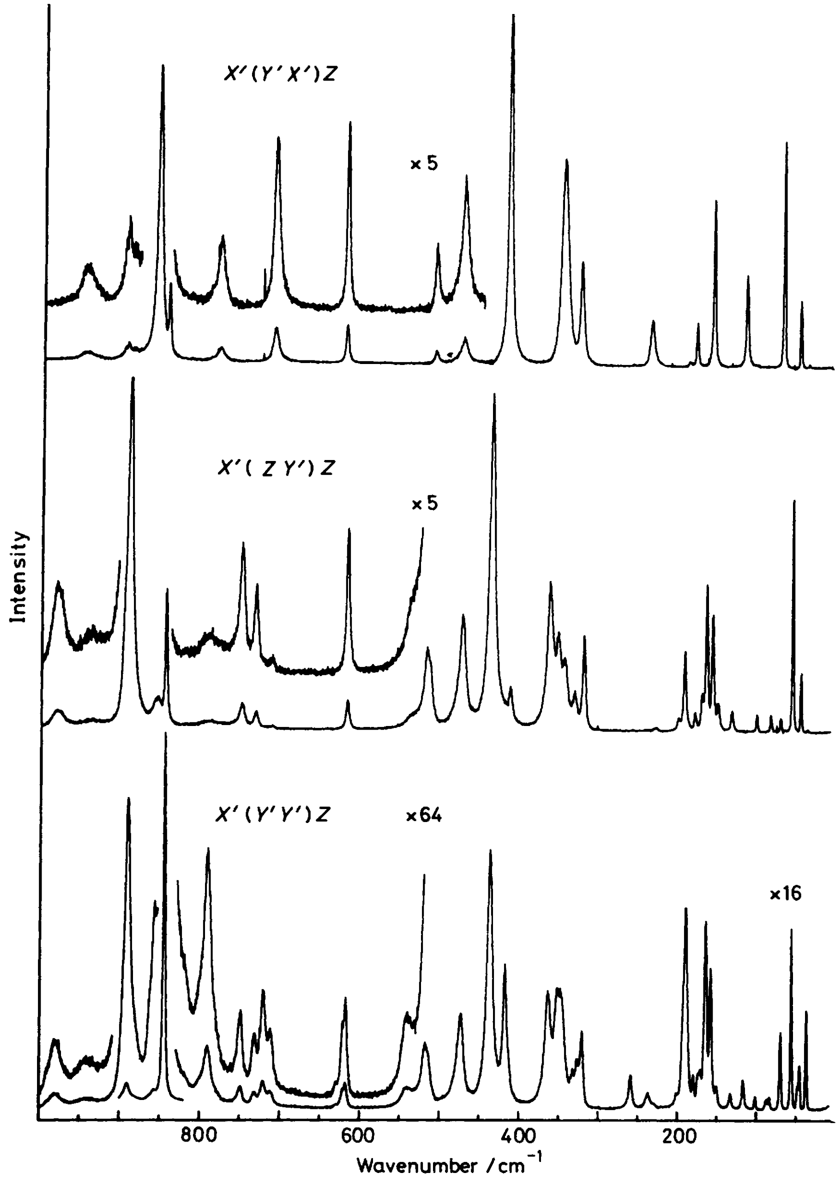

FIGURE 2 Single-crystal Raman spectra of $CsAl(SeO_4)_2 \cdot 12H_2O$ at 80 K (conditions as for Figure 1). $X'(Y'X')Z$ and $X'(ZY')Z$ spectra have had unwanted polarisations subtracted for clarity (see text)

aid of the f.g.a. given in Table 3 that $11A_g + 11E_g + 33F_g$ modes are expected. For $CsAl(SO_4)_2 \cdot 12H_2O$, $6A_g + 11E_g + 17F_g$ bands are observed, for the selenate $8A_g + 11E_g + 21F_g$, and for the deuteriate $10A_g + 11E_g + 23F_g$ bands. The differences between the number of predicted and observed bands are likely to be a consequence of vanishingly weak intensities in the case of the A_g and some of the F_g modes. The remainder of the F_g modes may be accidentally degenerate where the expected splitting between pairs of F_g modes is too small to be observed. Once again exact agreement between theory and results is found for the numbers of E_g modes in each spectrum. This agreement enables assignment of the external modes, since each of these modes has an E_g component.

Comparisons among the spectra of the three compounds are straightforward because no gross structural changes perturb the spectra even on substitution of selenate for sulphate. The spectra are markedly similar, particularly in the low-wavenumber region.

For compounds in which a large number of modes of the same symmetry are allowed coupling between different modes is probable. Frequency shifts and intensity borrowing are characteristic of the process. The extent of coupling is dependent on the energy separation of the modes involved.

All of the bands assigned to fundamentals display consistent behaviour in the spectra of the three compounds; two bands alone do not conform. These occur in $CsAl(SO_4)_2 \cdot 12D_2O$ at 525 cm^{-1} (F_g) and 830 cm^{-1} (E_g)

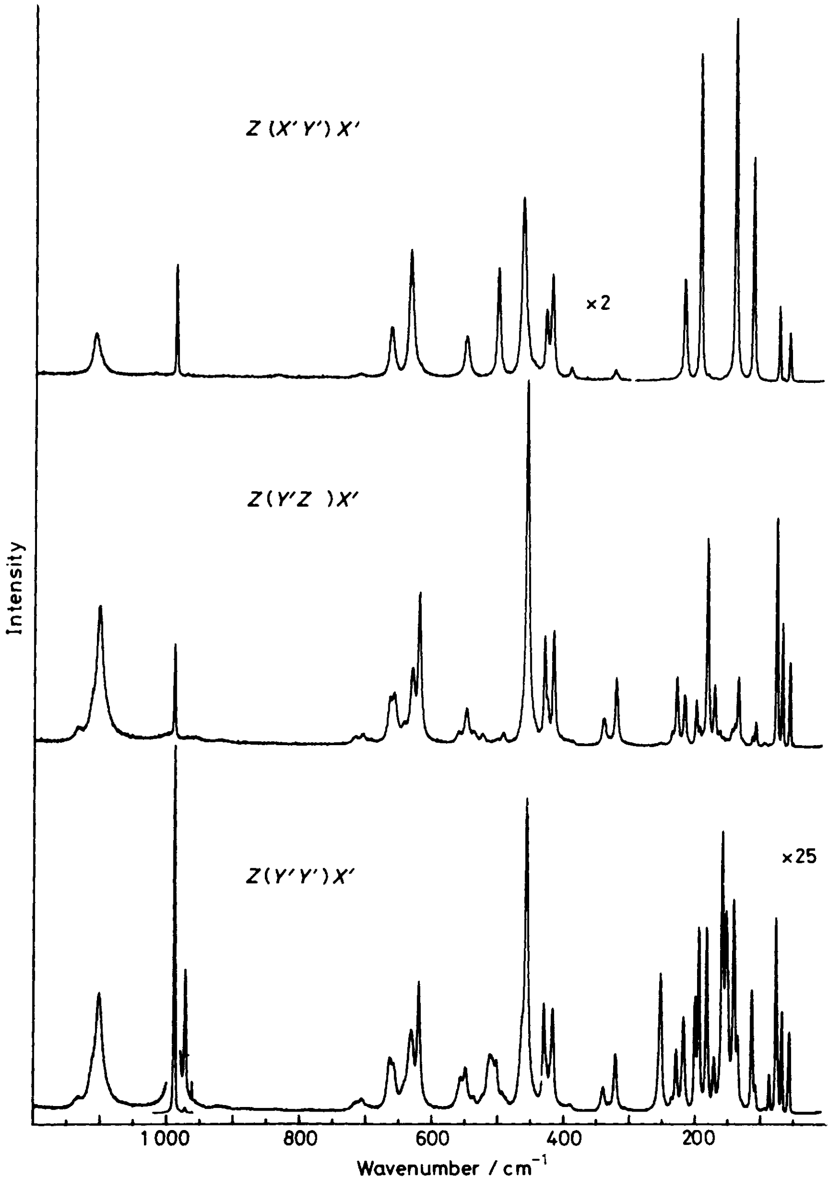

FIGURE 3 Single-crystal Raman spectra of $CsAl(SO_4)_2\cdot12D_2O$ at 80 K (conditions as for Figure 1)

and may arise from combinations of strong fundamentals.

Assignments.—The lowest energy set of bands for $CsAl(SO_4)_2\cdot12H_2O$ occur at 363 cm^{-1} (A_g), 343 cm^{-1} (E_g), and 340 and 359 cm^{-1} (F_g). Each of the bands exhibits sensitivity to deuteriation. The average ratio for ν_D/ν_H is found to be 0.95 ± 0.01. Assignment of this set of bands to the $\nu_5(AlO_6)$ mode follows since the observed shift on deuteriation is in very good agreement with the calculated ratio of 0.943, and the numbers of bands of each symmetry species closely follow the f.g.a. description. Only one of the two F_g components arising from the factor group coupling of the E_g mode in the isolated molecule is found. It is likely that the factor group splitting of the F_g modes is too small to be observed. The site splitting of 20 cm^{-1} is obtained from the frequency difference between the A_g and E_g components. The separation of the F_g components of 19 cm^{-1} is in good agreement with this value.

Assignment of the spectrum of $CsAl(SO_4)_2\cdot12D_2O$ follows directly from that of $CsAl(SO_4)_2\cdot12H_2O$. It can be seen in Figure 3 that there are no other bands in this region. The relative intensities and relative positions are similar to the hydrate illustrated in Figure 1. The environment about the hexa-aqua-aluminium ion in the hydrate and deuteriate must be remarkably similar since the band shapes, site splitting, and factor group coupling are nearly identical.

The complicated spectrum observed in this region for the selenate alum results from the presence of another mode lying close in energy to the $\nu_5(AlO_6)$ mode. Both the pattern of bands and their relative intensities are sub-

TABLE 3

Vibrational frequencies and assignments

ν [a]/cm^{-1}	$X'(Y'Y')Z$	$X'(ZY')Z$	$X'(Y'X')Z$	Assignment
(*a*) $CsAl(SO_4)_2 \cdot 12H_2O$				
340 F_g	15	25		$\nu_5(AlO_6)$
343 E_g			2	
359 F_g	6	9		
ca. 363 A_g	0.5			
438 E_g	*ca.* 2		22	$\nu_2(SO_4^{2-})$ + $\nu_2(AlO_6)$
444 F_g	51	88		
468 E_g	36	56	1	
475 E_g	*ca.* 1		12	
542 $A_g + F_g + E_g$	32	18	6	$\nu_1(AlO_6)$ (A_g) + ρ_6
578 E_g			16	ρ_5
580 F_g	14	8		
590 F_g	11	18		
613 F_g	41	70		
633 F_g	41	57		$\nu_4(SO_4^{2-})$
634 E_g			16	
685 $E_g + A_g$ (?)	6		8	ρ_4
728 F_g	4	7		ρ_3
743 F_g	8	8		
747 E_g			5	
753 A_g	2			
878 A_g	1			ρ_2
897 E_g			1	
905 F_g	7	10		
966 E_g			3	ρ_1
973 A_g [b]	41.5			
989 A_g	1 914	46	9	$\nu_1(SO_4^{2-})$
1 090 F_g	53	96		$\nu_3(SO_4^{2-})$
1 099 E_g			6	
1 103 F_g	6	12		
1 124 F_g	4	7		
(*b*) $CsAl(SeO_4)_2 \cdot 12H_2O$				
321 F_g	24	27		$\nu_5(AlO_6)$ + $\nu_2(SeO_4^{2-})$
327 E_g	7		29	
332 F_g	6	11		
346 F_g	6	8		
348 E_g	15		59	
353 F_g	20	24		
356 A_g	*ca.* 1			
364 F_g	38	40		
418 $F_g + E_g$	44	15	99	$\nu_4(SeO_4^{2-})$
437 $F_g + A_g$ (?)	84	93	8	
473 $F_g + E_g$	30	31	10	$\nu_2(AlO_6)$
510 E_g			4	ρ_6
513 F_g		*ca.* 2		
518 F_g	21	23	1	
538 F_g		2		$\nu_1(AlO_6)$
545 A_g	8			
618 F_g	8	8		ρ_5
621 E_g	2		10	
628 A_g	1			
712 $F_g + E_g$	4	1	10	ρ_4
720 A_g	8			
732 F_g	5	5		
750 F_g	7	8		
779 E_g			4	ρ_3
787 F_g	*ca.* 1	*ca.* 1		
791 A_g	20			
845 A_g	2 019	39	25	$\nu_1(SeO_4^{2-})$
857 $F_g + E_g$	*ca.* 20	15	82	$\nu_3(SeO_4^{2-})$ + ρ_2
891 $F_g + E_g + A_g$ (?)	100	100	12	
898 A_g	*ca.* 5			
941 E_g			2	ρ_1
981 F_g	5	6		

TABLE 3 (*continued*)

(*c*) $CsAl(SO_4)_2 \cdot 12D_2O$

ν [a]/cm^{-1}	$Z(Y'Y')X'$	$Z(Y'Z)X'$	$Z(X'Y')X'$	Assignment
321 F_g	19	19		$\nu_5(AlO_6)$
325 E_g			2	
340 F_g	8	8		
392 $F_g + E_g$	2	2	2	ρ_6
417 F_g	32	31		ρ_5
421 E_g			14	
430 $F_g + E_g$	35	30	10	$\nu_2(AlO_6)$
457 F_g	100	98		$\nu_2(SO_4{}^{2-})$
465 E_g			25	
488 A_g	*ca.* 3			ρ_4
496 F_g	4	3		
503 E_g	5		15	
513 A_g	*ca.* 10			$\nu_1(AlO_6)$
525 F_g	3	3		[457 (F_g) + 69 (F_g)] (?)
536 F_g	3	3		ρ_3
550 $F_g + E_g$	15	10	6	
556 A_g	*ca.* 8			
561 F_g	*ca.* 3	3		
620 F_g	42	41		$\nu_4(SO_4{}^{2-})$
632 F_g	26	20		
635 E_g			18	
642 F_g	*ca.* 4	3		ρ_2
659 F_g	15	14		
664 $F_g + E_g$	16	13	7	
704 F_g	2	3		ρ_1
708 A_g	*ca.* 6			
710 E_g	*ca.* 1		1	
717 F_g	2	3		
830 E_g			*ca.* 1	[635 (E_g) + 195 (E_g)] (?)
973 A_g	45			$\nu_1(SO_4{}^{2-})$
989 A_g	2 913	36	15	
1 102 F_g	38	38		$\nu_3(SO_4{}^{2-})$
1 110 $F_g + E_g$	*ca.* 5	4	6	
1 133 F_g	*ca.* 5	4		

[a] Frequencies of sharp peaks are correct ± cm^{-1}. [b] Also includes the $\nu_1(S^{16}O_3{}^{18}O)$ mode.

stantially different from the spectra of the sulphates (see Figures 1—3). Spectra of alkaline-earth selenates identify the $\nu_2(SeO_4{}^{2-})$ mode in the region 330—340 cm^{-1}, with active modes of E_g and F_g symmetries (Table 2). Hence the total number of bands expected in this region is $A_g + 2E_g + 5F_g$. This pattern is observed with bands at 356 cm^{-1} (A_g), 327 and 348 cm^{-1} (E_g), and 321, 332, 346, 353, and 364 cm^{-1} (F_g). Other vibrations can be eliminated since only the external modes are likely to occur in this frequency region. All the external modes contain a component with E_g intensity and all of the E_g modes have been observed. The next lowest E_g mode is at 418 cm^{-1} which is both too high in energy and too intense to be assigned to the $\nu_5(AlO_6)$ mode. It follows that no other modes are expected in this region.

Neither of the E_g components is sufficiently weak to be assigned to a pure component of the $\nu_5(AlO_6)$ mode. Strong coupling between the internal selenate mode and the hexa-aqua-aluminium mode accounts for the dramatic intensity change. Considerable coupling between the F_g components also results. Since the $\nu_2(SeO_4{}^{2-})$ mode does not contain any components of A_g intensity the A_g component of the $\nu_5(AlO_6)$ mode cannot be involved in any coupling with the selenate vibration. Consistent with this analysis, the A_g mode found in the selenate alum is of intensity comparable with that of the sulphate alum and is found close in energy to it. This means that the $\nu_5(AlO_6)$ mode is consistently assigned and that the difference in intensity of the E_g and F_g modes is due to coupling with the selenate. The strong coupling makes any assignment of the E_g and F_g bands to an uncoupled mode unrealistic.

In the range 400—500 cm^{-1}, bands are found at 438 and 475 cm^{-1} (E_g) and 444 and 468 cm^{-1} (F_g). No bands of A_g symmetry were found (Figure 1). Published results of the alkaline-earth sulphates [15,16] indicate that the $\nu_2(SO_4{}^{2-})$ mode will occupy this region of the spectrum. We assign the lower energy pair of E_g and F_g components to this mode by comparison with these alkaline-earth sulphates and the spectra of the deuteriate and selenate alums.

Of the remaining modes only $\nu_2(AlO_6)$ and external modes of co-ordinated water can occur in the region 400—500 cm^{-1}. The vastly different shifts expected on deuteriation provide the easiest means of distinguishing between the internal and the external modes. The internal modes are expected to shift with the ratio ν_D/ν_H of 0.95 while the corresponding ratio for the external modes is 0.73. Assignment of either of the E_g bands to an external mode is inconsistent with the spectrum of the deuteriate where a band of E_g symmetry is required close to 350 cm^{-1} or 320 cm^{-1}. Only the E_g component of the $\nu_5(AlO_6)$ mode already assigned (325 cm^{-1}) is found below 390 cm^{-1} in this spectrum. The coincidence of two E_g bands at 325 cm^{-1} is excluded since all the E_g bands predicted to lie below 1 200 cm^{-1} have been found. We assign the higher energy E_g and F_g bands to the $\nu_2(AlO_6)$ mode where the other F_g component expected is either vanishingly weak or is accidentally coincident with the F_g component found.

This assignment is substantiated by the spectra of the selenate and the deuteriate alums. In the spectra of the selenate alum, bands are found at 418 and 473 cm^{-1} (E_g) and at 418, 437, and 473 cm^{-1} (F_g). The $\nu_4(SeO_4^{2-})$ mode has been shown [17] to lie in the region 404—430 cm^{-1} for the alkaline-earth selenates. The bands at 418 and 437 cm^{-1} (F_g) and 418 cm^{-1} (E_g) are assigned to the $\nu_4(SeO_4^{2-})$ mode. The expected A_g component is too weak to be found and the third F_g component is either weak or is coincident with one of the F_g components found. The remaining bands at 473 cm^{-1} ($E_g + F_g$) are assigned to the $\nu_2(AlO_6)$ mode where once again the other expected F_g component is either too weak or is accidentally coincident with the observed F_g component. Since the frequencies of these internal modes are not expected to vary greatly on substitution of sulphate for selenate the observation of this mode at 473 cm^{-1} is consistent with our assignment of the higher energy E_g and F_g components (475 and 468 cm^{-1}) to the $\nu_2(AlO_6)$ mode.

The factor group splitting for the $\nu_2(AlO_6)$ mode, which can be estimated by the energy difference of the E_g and F_g components, is much greater for the sulphate alum (7 ± 2 cm^{-1}) than for the selenate alum (0 ± 2 cm^{-1}). The observed pattern of bands in the sulphate spectrum is that of two bands of E_g symmetry encompassing the two bands of F_g symmetry (Figure 1). Different coupling between the pair of E_g components and the pair of F_g components of the modes may result in such a pattern of bands and may also account for the large factor group splitting.

In the spectrum of the deuteriate alum we find the $\nu_2(SO_4^{2-})$ mode at 457 cm^{-1} (F_g) and 465 cm^{-1} (E_g). Some shifts of the sulphate modes are expected on deuteriation since there may be some changes in the strength of the hydrogen bonding. It is interesting to note that the intensity of the $\nu_2(SO_4^{2-})$ mode relative to the intensities of the other bands is different in the hydrate and the deuteriate spectra (Figures 1 and 3). This change in the relative intensity of the sulphate mode confirms the presence of coupling involving the $\nu_2(SO_4^{2-})$ mode in $CsAl(SO_4)_2 \cdot 12H_2O$. Based on the bands found in the hydrate, the $\nu_2(AlO_6)$ mode in the deuteriate is calculated to lie at 444 cm^{-1}. Bands are found at 430 and 421 cm^{-1} (E_g), and 430 and 417 cm^{-1} (F_g). The pair at 430 cm^{-1} are obvious candidates for the assignment. The uncertainty of the position of the $\nu_2(AlO_6)$ mode resulting from coupling with the $\nu_2(SO_4^{2-})$ mode accounts for most of the discrepancy between the calculated and observed positions. The assignment of the pair of lower energy bands to the $\nu_2(AlO_6)$ mode is excluded because it is in substantially poorer agreement with the calculated shift and because an external mode of co-ordinated water is expected to occur at 420 cm^{-1}, coincident with the position of these bands.

Although the assignments of the $\nu_2(AlO_6)$ and the $\nu_2(SO_4^{2-})$ are consistent with the results and analysis of the selenate and deuteriate alums there has been shown to be substantial coupling between these modes. The frequency of the uncoupled $\nu_2(AlO_6)$ mode may be obtained from the spectrum of the selenate alum.

We have yet to assign the ν_1, ν_3, and ν_4 internal sulphate modes, the $\nu_1(AlO_6)$ mode, and the external modes. These assignments will be considered in order of ease of assignment rather than on a sequence based on their energies.

The assignments of the internal sulphate modes are straightforward because there are well documented literature values available [12] and they are found to be strong bands. Assignment of the selenate modes is similarly straightforward and provides a check of the assignments of the spectra of the sulphates.

Spectra of the alkali-metal sulphates [15,16] indicate that the $\nu_1(SO_4^{2-})$ mode should be very intense and lie in the region 970—990 cm^{-1}. For both the sulphate alums a band of A_g symmetry was found at 989 cm^{-1} with intensity at least one order of magnitude greater than any other mode in the spectrum. The expected F_g components are weak and could in neither case be observed under the leakage of the intense A_g component into the F_g spectrum. A band of A_g symmetry is expected for the $(S^{16}O_3{}^{18}O)^{2-}$ species 15 cm^{-1} to lower energy with a natural abundance of 0.75%. In the deuteriate a sharp band of A_g symmetry is found at 973 cm^{-1} with a relative intensity of 0.8 ± 0.2% in good agreement with the natural abundance and with a shift of 16 cm^{-1} from the parent peak. For the sulphate alum we find a broad band of A_g symmetry centred at 973 cm^{-1}. The broadness of this band is explained by the presence of an external mode of co-ordinated water coincident with this sulphate mode.

The assignment of the $\nu_1(SeO_4^{2-})$ mode is similarly straightforward with an extremely strong band of A_g symmetry found at 845 cm^{-1}. This frequency is consistent with values of the $\nu_1(SeO_4^{2-})$ mode found in the literature.[17] As with the sulphates the expected F_g component is weak and could not be separated unambiguously from the leakage of the strong A_g component.

Previous vibrational studies indicate that the $\nu_3(SO_4^{2-})$ mode will be in the region close to 1 100 cm^{-1}. Bands are found at 1 110 cm^{-1} (E_g) and 1 090, 1 103, and 1 124 cm^{-1} (F_g). The expected A_g component is vanishingly weak and was not found. The spectrum of the deuteriate is similar with bands found at 1 109 cm^{-1} (E_g) and 1 102, 1 110, and 1 133 cm^{-1} (F_g). Once again the A_g component is vanishingly weak.

The selenate spectrum is more complicated because the $\nu_3(SeO_4^{2-})$ mode falls in the region 850—900 cm^{-1}, close to external modes of the trivalent hexa-aqua-cation. Bands of E_g symmetry are found at 891 and 857 cm^{-1}, F_g modes at 890 and 856 cm^{-1}, and A_g modes at 890 and 898 cm^{-1}. Since the $\nu_3(SeO_4^{2-})$ mode is expected to be strong the assignments can be made by considering relative intensities. The strong E_g mode at 857 cm^{-1} has only a weak F_g component at 856 cm^{-1}. The A_g component at 890 cm^{-1} has a very strong F_g component at the same frequency. The other bands are assigned to an external mode of the $[Al(OH_2)_6]^{3+}$ cation. It is clear that some coupling exists between the external mode and the selenate mode; however, the uncertainty of the intensity of the uncoupled external mode makes the calculation of uncoupled frequencies a doubtful exercise. The uncertainties introduced by this coupling could be overcome by the study of $CsAl(SeO_4)_2 \cdot 12D_2O$. However, the correctness of the assignments for $CsAl(SO_4)_2 \cdot 12H_2O$ is unaffected by these problems.

The $\nu_4(SO_4^{2-})$ vibration is found at 634 cm^{-1} (E_g) and at 613 and 633 cm^{-1} (F_g). The expected A_g component is too weak to observe. The assignment of these bands to the sulphate vibration is most clearly seen by comparison of the sulphate spectra with those of the selenate alum in which these bands are absent. The deuteriate spectra show a similar pattern with bands appearing at 635 cm^{-1} (E_g), 632 and 620 cm^{-1} (F_g). Although external modes lie close to the sulphate modes there appears to be no significant coupling. The analysis of the $\nu_4(SeO_4^{2-})$ mode has already been discussed.

The assignment of the $\nu_1(AlO_6)$ mode is complicated by the close proximity of external modes. Distinction between the external modes and this internal mode may be made on the basis of the different f.g.a. predictions, invariance to selenate substitution, and the differing shifts on deuteriation predicted for these modes. The f.g.a. predicts an A_g and an F_g component. In the sulphate alum, bands of A_g symmetry occur at 973, 878, 753, and 542 cm^{-1}. The remaining bands predicted are either vanishingly weak or accidentally coincident. The bands above 800 cm^{-1} are unacceptably high for the $\nu_1(AlO_6)$ mode. Either the A_g component of this mode is not found or it is at 753 or 542 cm^{-1}. We can distinguish between these alternatives by considering the spectra of the selenate and the deuteriate. In the selenate, bands of A_g symmetry are found at 791, 720, 628, and 545 cm^{-1}. Since we expect the frequency of $\nu_1(AlO_6)$ to shift only by a small amount on substitution of selenate for sulphate we can exclude the band at 753 cm^{-1}. The band at 542 cm^{-1} in the sulphate has a corresponding band at 545 cm^{-1} in the selenate and may be considered further. For the $\nu_1(AlO_6)$ mode the ratio ν_D/ν_H should equal 0.974. A band of A_g symmetry is found in the deuteriate at 513 cm^{-1}, in excellent agreement with the value calculated for $\nu_1(AlO_6)$ of 514 cm^{-1} from the position of this mode in the hydrate (542 cm^{-1}).

Coincident with this band of A_g symmetry in the sulphate alum are bands of E_g and F_g symmetry. The presence of any E_g component must arise from another mode coincident with the $\nu_1(AlO_6)$ mode. This interpretation is confirmed by consideration of the selenate alum. The A_g band arising from the $\nu_1(AlO_6)$ mode is observed on the high-energy side of two bands, one of E_g and the other of F_g intensity. These bands are assigned to an external mode of co-ordinated water and as expected exhibit sensitivity to sulphate/selenate substitution. Further confirmation of this analysis can be obtained from the deuteriate spectrum where the A_g component of the $\nu_1(AlO_6)$ mode is not coincident with any bands of E_g intensity. The E_g component of the external mode found at 540 cm^{-1} in the hydrate should shift to 394 cm^{-1} on deuteriation. Weak bands are found at 392 cm^{-1} consistent with this assignment.

Although the A_g intensity of the band at 542 cm^{-1} in the sulphate alum arises predominantly from the $\nu_1(AlO_6)$ mode and the E_g intensity is derived totally from the external mode it is difficult to partition the F_g intensity into internal and external mode contributions. Consideration of the spectra of $CsAl(SeO_4)_2 \cdot 12H_2O$ and $CsAl(SO_4)_2 \cdot 12D_2O$ indicates that the total intensity results from components from each of these modes. The close agreement of the frequencies found in the sulphate and selenate alums and the closeness of the observed shift to the calculated shift on deuteriation show that the extent of coupling between the $\nu_1(AlO_6)$ mode and the external mode is small.

The external modes of water, the rocks, wags, and twists, arise from rotations of the co-ordinated water molecule. A thorough analysis of these modes has been hampered because they are typically weak and broad in the Raman spectrum. Although the rocks and wags are usually found in vibrational studies the twists have proved to be more difficult to locate. The relative weakness of the twisting mode in the i.r. spectrum is explained because it is derived from a rotation about the z axis of the water molecule, which is inactive under C_{2v} symmetry. It is not clear why the mode is apparently so weak in the Raman spectrum since that rotation is Raman active.

For a free water molecule in an isotropic environment all three rotations occur at the same energy. As the environment becomes more anisotropic, by co-ordination to the metal cation and by the formation of hydrogen bonds, the relative energies of the external modes will change according to the directional nature of the field about it. From consideration of the equations for the frequencies of these modes derived from harmonic potentials [18] the energies of the external modes have been shown to be sensitive to the hydrogen bonding but insensitive to metal–oxygen co-ordination. Further, the relative ordering of the rocking and wagging modes were shown to depend on the nature of the hydrogen bonding. Previous workers have mostly relied on an early study by Nakagawa and Shimanouchi [19] where the ordering $\rho_r > \rho_w$ was found and a study by Adams and Lock [13] who found that $\rho_w > \rho_r$ for a series of aquated complexes. Irrespective of the correctness of these particular assignments, it can be seen from the preceding discussion that it is likely that the relative ordering of the rocks and wags will change with changes in the hydrogen bonding in the crystal.

It is then more appropriate to label the external modes as ρ_1, ρ_2, and ρ_3 based purely on their relative energies and only where an unambiguous assignment to the specific external mode is possible the more familiar ρ_t, ρ_r, ρ_w can be used.

In the case of the alums there are external modes associated with both the monovalent and the trivalent hexa-aqua-cations. It is expected that the external modes of the trivalent cation will lie to higher energy than those of the monovalent cation since the aluminium–water bond is much stronger than the caesium–water bond and crystallographic data indicate that the strongest hydrogen bonds involve the co-ordination sphere of the trivalent cation. Directional effects of the hydrogen bonding may allow an overlap between the lowest energy external modes of the trivalent hexa-aqua-ion and the highest energy external modes of the monovalent hexa-aqua-ion. For these reasons the six external modes expected in the alums are labelled ρ_1—ρ_6 and in order of decreasing frequency, where ρ_1—ρ_3 are most likely associated with $[Al(OH_2)_6]^{3+}$ and ρ_4—ρ_6 with $[Cs(OH_2)_6]^+$.

Each of the spectra contain six modes of E_g symmetry yet to be assigned. Each external mode has one component of E_g symmetry so the assignment of these modes to the external modes is simply one-to-one. The A_g components are found close to E_g modes and their assignment is similarly straightforward. The F_g components are treated in the same way. All of the external modes are expected to shift on deuteriation with a ratio $\nu_D/\nu_H = 0.73$. In each case the shift on deuteriation is close to the calculated value. It is significant that within this set of six external modes we have necessarily found the elusive twisting modes for both the monovalent and the trivalent cation. Although the individual modes are not assigned it is clear that the relative intensity of the twists compared to the rocks or wags is not significantly different, contrary to most reports but consistent with the activities of these modes in the Raman spectrum.

Finally, the assignments can be compared with the literature values. The assignments of the internal sulphate and aluminium hexa-aqua-ion modes are essentially in agreement with those of Eysel and Eckert.[6] The major differences with this previous work are with respect to the external modes which left the previous assignments incomplete. The Raman-active internal modes of the aluminium hexa-aqua-ion in $AlCl_3 \cdot 6H_2O$ [5] lie some 10—15 cm^{-1} to lower energy than those found in the alums. The difference can be attributed to the large difference in the strength of hydrogen bonding within the two crystals. Consistent with this, the external modes of water co-ordinated to the aluminium ion are about 100 cm^{-1} to higher energy in the alums.

The results can also be compared with values for the aluminium hexa-aqua-cation obtained from aqueous solution. Frequencies for the ν_1, ν_2, and ν_5 modes in solution are 525, 447, and 340 cm^{-1} respectively.[20,21] These values are 5—17 cm^{-1} to lower energy than in the alum crystal. The solution data must be treated with caution, however, since problems may arise with ion pairing and inner-sphere co-ordination of the counter ion.

By using low-temperature spectra of the sulphate, selenate, and deuteriate caesium aluminium alums we have been able to make complete and self-consistent assignments of the spectra in the range 300—1 200 cm^{-1}. This provides the groundwork for a comparative study of other trivalent hexa-aqua-cations.

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