Single-crystal Raman and Infrared Study of Aluminium Trichloride Hexahydrate

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Single-crystal Raman spectra obtained at 115 K are reported for $[Al(OH_2)_6]Cl_3$ and its deuteriate. Single-crystal i.r.-reflectance spectra have been recorded at ambient temperature for both materials. All the Raman bands predicted by factor-group analysis (f.g.a.) are observed, as are most of the i.r. bands. On the basis of the f.g.a. an assignment is made of the ' external ' modes (wag, twist, and rock) of co-ordinated water with the order wag > twist > rock, and ν_1 (of AlO_6) is placed at 524 cm^{-1}. An alternative assignment places ν_1 at 701 cm^{-1} but yields less satisfactory force constants. The chief ambiguity remaining is in the location of ν_3 (of AlO_6) which is probably at *ca.* 670 cm^{-1}.

ALTHOUGH much is known about the vibrational motions of water co-ordinated to metal ions, our understanding of these data is still unsatisfactory in many respects. Two reviews [1,2] give the background and summarise data up to 1968. There is relatively little Raman and far-i.r. work on hydrated metal ions in the solid state, the majority of our knowledge being confined to the 250—4 000 cm^{-1} i.r. region. The principal experimental evidence produced in support of assignments is based on changes induced by deuteriation, but very little has been done to establish the symmetries of the modes thus assigned. Despite the faith placed by many workers in normal-co-ordinate analysis (n.c.a.) calculations such as those reported for the i.r.-active modes of $[M(OH_2)_n]^{2+}$ species ($n = 4$ or 6),[3] we find such calculations unconvincing in the absence of prior proof of assignment. A strict examination of the real, substantiated, evidence for assignment of hexahydrated cations, in particular, shows that their spectra are less well understood than the very much more complex spectra of the various phases of ice.

In this paper we report our i.r. and Raman work on $[Al(OH_2)_6]Cl_3$, for which no recent vibrational study has been made. Three Raman single-crystal investigations were made in the mercury-arc era, two [4,5] being confined to the internal modes of water. The third of these reports dealt with the region of shifts up to 1 000 cm^{-1};[6] our work confirms most of their results for the stronger bands but reveals much more detail. The internal modes of water in $[Al(OH_2)_6]Cl_3$ have also been studied

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[1] D. M. Adams, ' Metal–Ligand and Related Vibrations,' Arnold, London, 1967.

[2] G. Brun, *Rev. Chim. minérale*, 1968, **5**, 889.

[3] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, 1964, **20**, 429.

[4] A. Galy, *Compt. rend.*, 1953, **236**, 284.

[5] A. Weil-Marchand, *Compt. rend.*, 1955, **241**, 1456.

[6] G. Champier and A. Galy, *Compt. rend.*, 1954, **B238**, 1708.

by i.r. spectroscopy.[7] Studies of $[Ni(OH_2)_6][SnCl_6]$ [8,9] and $[Ni(OH_2)_6][SO_4]$ [10] have been made recently and now provide a good basis for understanding hexa-aqua-species, and there are partial Raman studies of $[Mg(OH_2)_6][SO_4]\cdot H_2O$ [11] and $[Mg(OH_2)_6][PH_2O_2]$.[12]

When water is co-ordinated to a metal ion the three translational and the three rotational degrees of freedom of water become incorporated into those of the complex in ways that have often been described: see, for example, refs. 2 and 13. For a single co-ordinated water molecule there will be a $\nu(M{-}OH_2)$ mode, two skeletal modes involving deformations of the M–O bond, and three 'external' modes (rock ρ_r, twist ρ_τ, and wag ρ_ω; for details see Figure 1 of ref. 13). The energy order of the three external modes has been the subject of some debate, which has been reviewed,[13] but there is now evidence from monohydrated anions, such as $[FeCl_5(OH_2)]^{2-}$, that the order $\rho_\omega > \rho_r$ is usually obeyed, as is to be expected from the relative values of the moments of inertia associated with the rotational motions of water.[13] This is contrary to the order supported by n.c.a. calculations.[3] Deuteriation evidence supports the order $\rho_\omega > \rho_r > \nu(M{-}OH_2)$.[8,9,13] Much less is known about ρ_τ because it is likely to be weak in i.r. spectra. It originates as a rotation, R(*z*), of symmetry A_2 for the C_{2v} free molecule, and A_2 is not associated with i.r. activity. It may become i.r. active in a complex, but it is the symmetry of the field, subtended by the rest of the complex, that creates the possibility that ρ_τ will be seen. In $[Ni(OH_2)_6][SnCl_6]$ [8] bands at 290(236) cm^{-1} (i.r.) and 357(272) and 365(292) cm^{-1} (Raman) have been attributed to ρ_τ in the complex (deuteriate values in parentheses): in all the cases these bands were only seen clearly at $\leqslant$15 K and the assignment cannot be regarded as well substantiated. Inelastic neutron-scattering [14] studies for several heavily aquated structure types reveals bands attributable to 'external' water modes between 300 and 900 cm^{-1}, a range compatible with results from the many partial (mostly i.r.) studies of aquated complexes. These modes are highly sensitive to metal oxidation state, hydrogen-bonding opportunities, and counter ions, and often show a distinctive thermal dependence. The chief problems in this field are to distinguish the 'external' water modes from $\nu(M{-}OH_2)$, and to find for each system the numbers and symmetry species of the modes predicted theoretically. Some helpful background information is collected in Table 1 for mono- and di-hydrated cations. The work on $Rb_2[NiCl_4(OH_2)_2]$ is of particular value [15] in view of the simplicity of the crystal ($Z = 1$ in the primitive cell) and the very low temperatures at which the data were collected. The fact that only two bands were found in both i.r. and Raman spectra that could be attributed to 'external' modes is important in indicating that ρ_τ is weak and likely to be absent from spectra. Hexa-aqua-cations will show more bands in each region due to coupling of modes of these types.

TABLE 1

Selected literature data (wavenumbers/cm^{-1}) for mono- and *trans*-diaqua-complexes (deuteriate data in parentheses)

Complex	ρ_ω	ρ_r	$\nu(M{-}OH_2)$ i.r.	$\nu(M{-}OH_2)$ Raman	Ref.
$K_2[Fe^{III}Cl_5(OH_2)]$	600	460	390		13
$Cs_2[Fe^{III}Cl_5(OH_2)]$	540	460	320		13
	(430)	(340)	(310)		
$Rb_2[Ni^{II}Cl_4(OH_2)_2]$	621	471	353	342	15
$Cs_2[Mn^{II}Cl_4(OH_2)_2]$	570	455	295	290	13
	(430)	(350)	(282)		
$Cs[Mn^{III}F_4(OH_2)_2]$	730 [a]	665	370		*b*
	(525)	(470)	(367)		

[a] The authors preferred not to distinguish between ρ_ω and ρ_r.
[b] P. Bukovec and V. Kavčič, *J.C.S. Dalton*, 1977, 945.

EXPERIMENTAL

Crystals of $[Al(OH_2)_6]Cl_3$ were grown by slow evaporation of aqueous solutions of $AlCl_3$ in HCl–H_2O (1 : 1 v/v). The initially formed precipitate of alumina was filtered off. The composition of the crystals was confirmed by thermogravimetric analysis. The deuteriate was prepared similarly using D_2O, and recrystallised several times from D_2O. The crystals had well developed faces, measured *ca.* 10 × 5 × 2 mm, and were of excellent optical quality. Extinction directions were located using a polarising microscope and are illustrated in Figure 1. The natural face perpendicular to *x* and a face ground and polished normal to *y* were used for the Raman study.

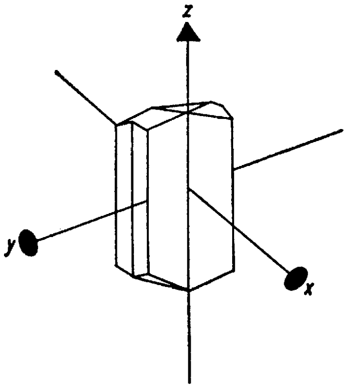

FIGURE 1 Morphology of $[Al(OH_2)_6]Cl_3$ and the indicatrix axis set used in this work

Raman spectra were obtained using a Coderg T800 spectrometer, and excited using 514.5-nm radiation from an argon-ion laser. Crystals were mounted on a copper

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[7] P. J. Lucchesi and W. A. Glasson, *J. Amer. Chem. Soc.*, 1956, **78**, 1347.

[8] J. Jäger and G. Schaack, *Z. Naturforsch.*, 1973, **A28**, 738.

[9] D. M. Adams and W. R. Trumble, *Inorg. Chim. Acta*, 1974, **10**, 235.

[10] Y. S. Jain, H. D. Bist, and A. L. Verma, *J. Raman Spectroscopy*, 1974, **2**, 327.

[11] P. Hillaire, M. Abenoza, and R. Lafont, *Compt. rend.*, 1971, **B273**, 255.

[12] M. Abenoza, P. Hillaire, and R. Lafont, *Comp. rend.*, 1971, **B273**, 297.

[13] D. M. Adams and P. J. Lock, *J. Chem. Soc. (A)*, 1971, 2801.

[14] H. J. Prask and H. Boutin, *J. Chem. Phys.*, 1966, **45**, 3284.

[15] G. E. Shankel and J. B. Bates, *J. Chem. Phys.*, 1976, **64**, 2539.

block with Araldite in a CTI model 20 closed-circuit cryostat and were examined at *ca.* 115 K.

It was impossible to prepare thin enough crystal sections for study by i.r. transmission since the material is deliquescent and mechanically unstable in thin sections. Accordingly these materials were studied in reflectance and the spectra analysed by the Kramers–Krönig procedure to extract the refractive index (n), extinction coefficient (k), and the real (ε') and imaginary (ε'') parts of the complex dielectric constant ε^*. These quantities are related by $\varepsilon^* = \varepsilon' + i\varepsilon'' = |n^*|^2$ and $n^* = n + ik$. Transverse optical (t.o.) mode frequencies are given by ε'' maxima and by n/k crossover points, and longitudinal optical (l.o.) mode frequencies by ε' nodes and the higher n/k crossover points.

Reflectance spectra were obtained from 40 to 1 000 cm^{-1} at ambient temperature using a Beckman-RIIC FS-720 Fourier spectrometer equipped with a RS-7F reflectance module and Perkin-Elmer wire-grid polarisers. Crystals were mounted on copper discs using epoxy-resin. Many attempts were made to obtain reflectance spectra at low temperatures but these experiments were frustrated by loss of reflectivity at the sample. Attempts to obtain reflectance spectra at >1 000 cm^{-1} using a dispersive instrument also failed due to partial dehydration of the crystals by the heat of the beam.

THEORY

The compound $AlCl_3 \cdot 6H_2O$ crystallises with the symmetry of space group $R\bar{3}c$ (D_{3d}^6) in a bimolecular primitive cell.[16,17] A factor-group analysis (f.g.a.) is given in Table 2(*a*). The correlation scheme of Table 2(*b*) is helpful in indicating that for the AlO_6 skeletal modes *A*- and *E*-symmetry bands should be in close proximity because they would be degenerate if the complex ion were of O_h symmetry. The overall symmetry of $[Al(OH_2)_6]^{3+}$ is S_6 thereby requiring both components of the O_h-inactive ν_6 mode to be i.r. active.

TABLE 2

Factor-group analysis and correlation for crystalline $[Al(OH_2)_6]Cl_3$

(*a*) F.g.a.[a]

D_{3d}^6	N_T	T_A	T	R	N_S	$\rho\omega$	ρ_τ	ρ_r	δ	ν	Activities
A_{1g}	10		1	1	2	1	1	1	1	2	$x^2 + y^2, z^2$
A_{2g}	11		2	1	2	1	1	1	1	2	
E_g	21		3	2	4	2	2	2	2	4	$(x^2 - y^2, xy), (xz,yz)$
A_{1u}	11		2		3	1	1	1	1	2	
A_{2u}	12	1	2		3	1	1	1	1	2	z
E_u	23	1	4		6	2	2	2	2	4	(x,y)

(*b*) Correlation for skeletal modes of AlO_6

O_h		Site, S_6 $\xrightarrow{\times 2}$	Crystal,[b] D_{3d}^6
ν_1	a_{1g}	A_g	$A_{1g} + A_{2g}$
ν_2	e_g	E_g	$2E_g$
ν_5	t_{2g}	$A_g + E_g$	$A_{1g} + A_{2g} + 2E_g$
ν_3	t_{1u}	$A_u + E_u$	$A_{1u} + A_{2u} + 2E_u$
ν_4	t_{1u}	$A_u + E_u$	$A_{1u} + A_{2u} + 2E_u$
ν_6	t_{2u}	$A_u + E_u$	$A_{1u} + A_{2u} + 2E_u$

[a] N_T = Total number of modes = $3N$, T_A = number of acoustic modes, T = number of optic branch translatory modes, R = number of libratory modes, N_S = number of internal vibrations of AlO_6, $\rho\omega$, ρ_τ, and ρ_r = numbers of wag, twist, and rock modes of co-ordinated water, $\delta = \nu_2$ bending modes of water, and $\nu = \nu$(O–H) modes of water. [b] This column sums to N_S.

The order of the skeletal modes of a regular octahedral species follows from the dynamical equations and is $\nu_1(a_{1g}) > \nu_2(e_g) > \nu_5(t_{2g})$, $\nu_3 > \nu_4$ (both t_{1u}), and $\nu_5 \approx 2^{\frac{1}{2}}\nu_6(t_{2u})$. The position of ν_3 relative to ν_1 and ν_2 (the other two skeletal stretching modes) depends on the magnitude of the *GF* matrix elements[18] and may be greater or less than ν_1, but greater than ν_2.

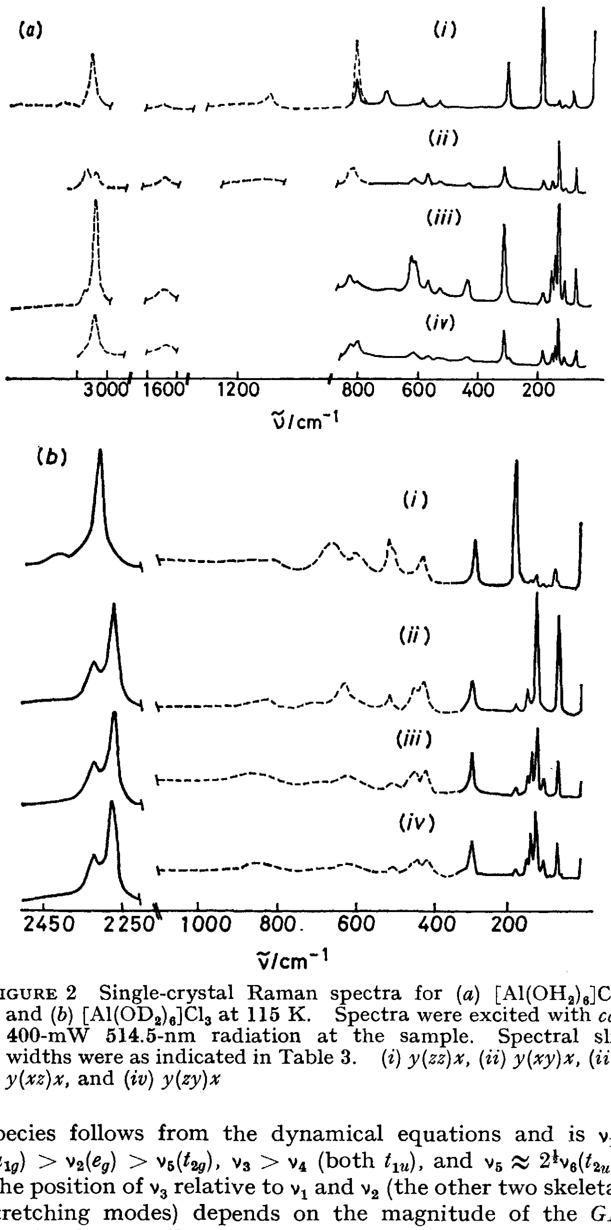

FIGURE 2 Single-crystal Raman spectra for (*a*) $[Al(OH_2)_6]Cl_3$ and (*b*) $[Al(OD_2)_6]Cl_3$ at 115 K. Spectra were excited with *ca.* 400-mW 514.5-nm radiation at the sample. Spectral slit widths were as indicated in Table 3. (*i*) $y(zz)x$, (*ii*) $y(xy)x$, (*iii*) $y(xz)x$, and (*iv*) $y(zy)x$

RESULTS AND DISCUSSION

Raman and i.r. data are in Tables 3 and 4, and are illustrated by Figures 2—4. The extinctions between the spectra obtained with different polarising directions are good.

Assignment.—The <350 *cm*$^{-1}$ *region.* In this low-frequency region the only 'external' mode of water that might appear is ρ_τ, judging by values quoted for it. All the other bands will be due to internal vibrations of

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[16] K. R. Andress and C. Carpenter, *Z. Krist.*, 1934, **87**, 446.

[17] D. R. Buchanan and P. M. Harris, *Acta Cryst.*, 1968, **B24**, 953.

[18] K. Nakamoto, 'Infrared Spectra of Inorganic and Co-ordination Compounds,' Wiley, New York, 1963, p. 267.

the AlO_6 group, or to lattice modes. In fact, none of the bands in this region shows a large deuteriation shift: therefore we may confidently attribute them as follows.

The region below 200 cm^{-1} shows exactly the numbers of lattice modes predicted by f.g.a. for all the species other than E_u, for which one is missing or is accidentally degenerate. All the i.r.-active lattice modes are translatory in type (Table 2). The two lowest-energy Raman-active lattice modes [71 (E_g) and 78 cm^{-1} (A_g)] are considered to be the two expected libratory modes, the others being translatory in type. In accord with these assignments, all modes <200 cm^{-1} show very little or no sensitivity to deteriation, exept for the highest A_g mode (183 cm^{-1}) which is reduced in energy by the amount calculated for a simple translation of the $[Al(OH_2)_6]^{3+}$ ion.

The remaining bands at <350 cm^{-1} are assigned as components of the AlO_6 ν_6, ν_5, and ν_4 modes. Of these only ν_5 is allowed to have an A_g component: the only reasonable assignment for it is at 295 cm^{-1}, and it is accompanied at 310 cm^{-1} by the required E_g component. Taking their degeneracy-weighted average, $\nu_6 = 2^{-\frac{1}{2}}\nu_5$ is calculated to be at 216 cm^{-1}, in near coincidence with the average of the i.r. bands at 229(A_u) and 209 and 218 cm^{-1} (E_u) which are accordingly ascribed to ν_6. ν_4 is present at 309 cm^{-1} (A_{2u}), but no E_u component was seen at ambient temperature in either the hydrate or the deuteriate. However, a weak band was found at 327 cm^{-1} in a mull of the hydrate at liquid-nitrogen temperature. All these modes show a deuteriation shift as is required by forms of their G-matrix elements, but these shifts are very much smaller than those of the 'external' water modes. Thus $\nu_5' = \nu_5[m(H_2O)/m(D_2O)]^{\frac{1}{2}}$; taking masses of 18 and 20 respectively we have the following assignments (cm^{-1}):

$$\nu_5 \begin{cases} 310 \\ 295 \end{cases} \qquad \nu_5' \text{ (calc.)} \begin{cases} 294 \\ 278 \end{cases} \qquad \nu_5' \text{ (obs.)} \begin{cases} 291 \\ 284 \end{cases}$$

These are in good agreement in view of the crudity of the model.

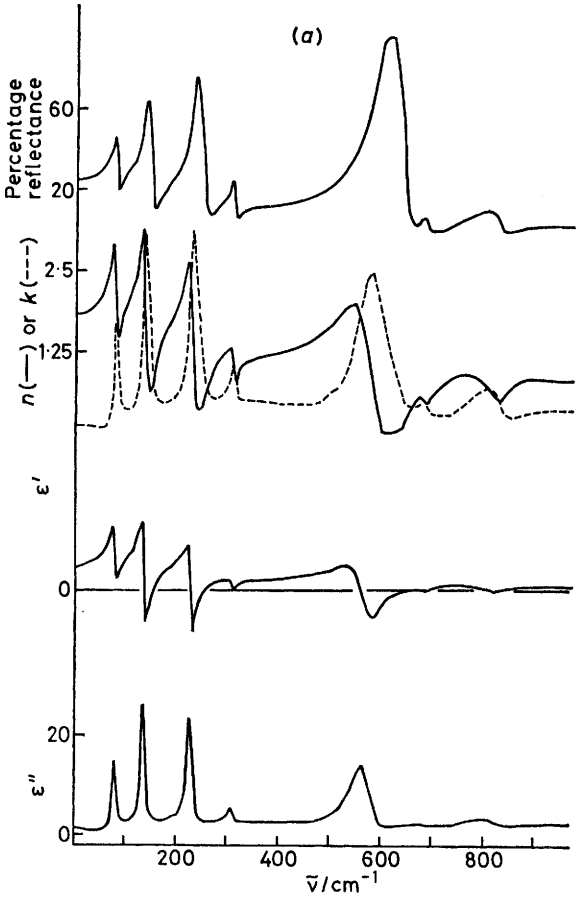

FIGURE 3

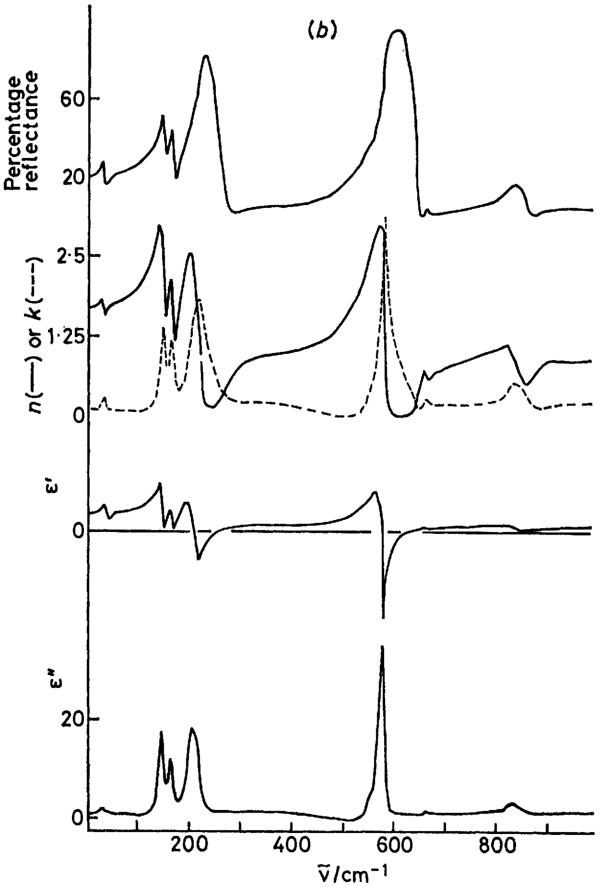

FIGURE 3 Single-crystal i.r. reflectance spectra and derived parameters for $[Al(OH_2)_6]Cl_3$ at ambient temperature: (*a*) A_{2u} modes, (*b*) E_u modes

The 350—1 000 cm^{-1} *region*. This region contains all the 'external' modes of water (since ρ_τ is shown to be absent at <350 cm^{-1}) together with the AlO_6 vibrations ν_1, ν_2, and ν_3. It is here that the real assignment problems arise. The A_g spectrum should show four bands in this range due to ν_1, ρ_ω, ρ_τ, and ρ_r (Table 2): four were observed. Similarly, the E_g spectrum shows exactly the number of bands predicted for the 'external' mode region of co-ordinated water. Of itself this is of significance because these bands must include the elusive ρ_τ and, moreover, place a lower limit at 524 cm^{-1} on it.

All the four A_g bands in this region (524, 584, 701, and 800 cm^{-1}) are substantially shifted by deuteriation, but it is not immediately obvious which band shifts to where when relating the two spectra. The shift in ν_1 on deuteriation is given by $\nu_1' = \nu_1[m(H_2O)/m(D_2O)]^{\frac{1}{2}}$.

TABLE 3

Raman wavenumbers (cm^{-1}) and relative intensities [a] for single-crystal $[Al(OH_2)_6]Cl_3$ and its deuteriate

ν/cm^{-1}		$y(zz)x$	$y(xy)x$	$y(xz)x$	$y(zy)x$	Assignment
(*a*) $[Al(OH_2)_6]Cl_3$						
71	E_g		20	40	15	ν_R
78	A_{1g}	15				
110	E_g		15	22	10	ν_T
128	E_g		74	100	35	
138	E_g		37	50	20	
150	E_g		18	30	14	
183	A_{1g}	100	8	10	13	
295	A_{1g}	42				ν_5
310	E_g		50	80	33	
432	E_g		5	14	5	ν_2
524	A_{1g}	5				ν_1
534	E_g		5	8	3	$\rho\omega$, $\rho\tau$, ρr (' external ' H_2O modes)
566	E_g		10	10	5	
584	A_{1g}	10				
610	E_g		8	30	7	
622	E_g		6	35	8	
701	A_{1g}	15				
800	A_{1g}	30		5	10	
825	E_g		15 [b]	12	12	
1 094	A_{1g}	15				
1 645	$A_{1g} + E_g$	3	8	10	6	$\delta(OH_2)$
3 045	E_g		13	80	30	$\nu_1(H_2O)$
3 053	A_{1g}	45				
3 076	E_g		18	11		
3 162	A_{1g}	3				$\nu_3(H_2O)$
3 289	A_{1g}	2				$2 \times \delta(OH_2)$
(*b*) $[Al(OD_2)_6]Cl_3$						
71	E_g		70	25	25	ν_R
78	A_{1g}	20				
109	E_g			12	13	ν_T
128	E_g		80	48	50	
139	E_g			30	30	
149	E_g		15	15	14	
180	A_{1g}	90				
284	A_{1g}	30				ν_5
291	E_g		20	30	25	
418	$A_{1g} + E_g$	10	15	10	8	ν_2 + ' external ' (D_2O)
443	E_g		(10)	10	8	ν_1 (504 cm^{-1}) and $\rho\omega$, $\rho\tau$, ρr (' external ' D_2O modes)
497	A_{1g}	10				
504	$A_{1g} + E_g$	15	7	6	4	
593	A_{1g}	8				
617	E_g		15	8	5	
650	A_{1g}	12				
820	E_g		5	6	5	
(1 208) [b]	E_g					$\delta(OD_2)$
2 272	E_g		60	60	60	$\nu_1(D_2O)$ [c]
2 309	A_{1g}	85				$\nu_3(D_2O)$ [c]
2 320	E_g		28	25	25	
2 416	A_{1g}	18				$2 \times \delta(OD_2)$

[a] In part (*a*) spectral slit widths for $y(zz)x$ experiments were 1.5 cm^{-1} for bands at <800 cm^{-1}, 3.3 cm^{-1} for bands at >800 cm^{-1}. Equivalent settings for all the other orientations were 2.4 and 4.7 cm^{-1} respectively. In part (*b*), for all the crystal orientations, modes in the 0—300 and 1 000—3 100 cm^{-1} intervals were recorded at a spectral slit width of 1 cm^{-1}, those from 300 to 1 000 cm^{-1} at 2.9 cm^{-1}. [b] Calculated from predicted isotope shift: [23] $\delta(D_2O) = \delta(H_2O) \times 0.732$. [c] Assignment based on deuteriation shift relations: [23] $\nu_1'(D_2O) = \nu_1(H_2O) \times 0.723$; and $\nu_3'(D_2O) = \nu_3(H_2O) \times 0.732$.

Applied to each of the four A_g modes we have the assignments (cm^{-1}):

A_g mode (H_2O)	ν_1' (calc.)	A_g mode (D_2O) obs.
524	497	418
584	554	504
701	665	593
800	759	650

Since the highest A_g mode in the deuteriate is at 650 cm^{-1} it is plain that ν_1 cannot be at 800 cm^{-1}, and the

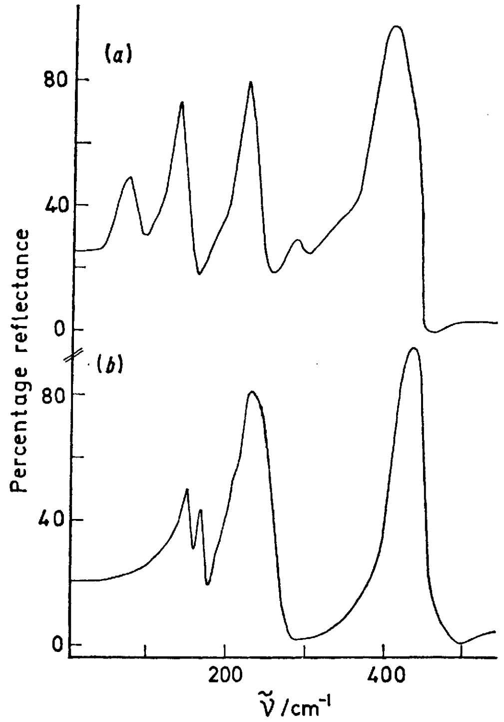

FIGURE 4 Single-crystal i.r. reflectance spectra for $[Al(OD_2)_6]Cl_3$ at ambient temperature: (*a*) A_{2u} modes, (*b*) E_u modes

TABLE 4

Infrared wavenumbers (cm^{-1}) for (*a*) single-crystal $[Al(OH_2)_6]Cl_3$ and its deuteriate (in parentheses) at ambient temperature, and (*b*) a mull of the hydrate at liquid-nitrogen temperature

(*a*)

A_{2u}	E_u	Assignment
	55	ν_T
82 (80)	151 (151)	
138 (138)	167 (167)	
229 (215)	209 218 [a] (208)	ν_6
309 (282)		ν_4
560 (400)	580 (420)	ρr
678	664	ν_3
790 [588] [b]	836 [623]	$\rho\omega$

(*b*)

57m	E_u	ν_T	205s	E_u	ν_6
92m	A_{2u}		224s	E_u	
145(sh)	A_{2u}		250s	A_{2u}	
154s	E_u		316m	A_{2u}	ν_4
174s	E_u		327w	E_u	

[a] The shape of the reflectance band and Kramers–Krönig analysis both indicate the presence of two bands, and mull spectra at low temperature show an additional peak in this region. [b] Calculated position for deuteriate taking $\rho = 0.745$ [*i.e.* $(I_a/I_a')^{\frac{1}{2}}$].

shift required for the band at 584 cm^{-1} also eliminates it as a possible ν_1. However, the bands could be paired either as 800(593), 701(650), 584(504), and 524(418) cm^{-1} for ν_1 at 701, or as 800(650), 701(593), 584(418), and 524(504) cm^{-1} for ν_1 at 524 cm^{-1}.

We now consider three lines of argument aimed at resolving this problem. First, we note that there have been several Raman studies [19-21] of aqueous solutions of $AlCl_3$ which agree in showing bands at [20] 525(polarised) (ν_1), 447(depolarised) (ν_2), and 340 cm^{-1} (ν_5), with deuteriate values of 503, 433, and 313 cm^{-1} respectively. These are very close to bands observed in solid $[Al(OH_2)_6]Cl_3$ and its deuteriate and support the lower value for ν_1. We assign ν_2 to the E_g band at 432 cm^{-1} which is in a reasonable position relative to ν_5.

Secondly, having now assigned ν_1 (two possibilities), ν_2, and ν_5 we may use them to determine the three force constants necessary to describe an octahedral complex on the basis of the Urey–Bradley force field, and hence to calculate the positions of ν_3 and ν_4. The results were:

	ν_3(calc.)	ν_4(calc.)	ν_4(obs.)	K	F	H
$\nu_1 = 701$	591	209	309	1.22	0.92	-0.28
$\nu_1 = 524$	653	319	321	1 79	0.26	0.09

Here K is the Al–O bond-stretching force constant, F is the stretch–stretch interaction, and H the angle-bending force constant (in 10^{-5} mdyn Å^{-1}).* The Al–O distance was taken as 1.88 Å.[17,22]

These results strongly support the lower choice for ν_1. The calculated value of ν_4 is very close to that observed, and K and F have reasonable magnitudes. In contrast F is too big relative to K for ν_1 at 701 cm^{-1}. A similar calculation for the deuteriate, with ν_1 at 504 cm^{-1}, gave ν_3 at 644 and ν_4 at 302 cm^{-1} [*cf.* ν_4 (obs.) at 282 cm^{-1}]. We defer further consideration of ν_3.

The third line of reasoning by which the ν_1 assignment may be illuminated begins by noting that for each ρ_r, ρ_ω, and ρ_τ mode there should be a group of three bands bearing the symmetry labels A_g, E_g, and E_g (Table 2). How much splitting there might be between the members of a group may be guessed at from the behaviour of ν(OH) and δ(HOH). The latter shows no detectable splitting between the A_g and E_g components. The ν(OH) bands are all low compared with situations in which little or no hydrogen bonding is possible {*e.g.* 3 300 and 3 400 cm^{-1} in the Raman spectrum [15] of *trans*-$[NiCl_4(OH_2)_2]^{2-}$}. The two predicted A_g components are due to ν_1 and ν_3 of H_2O respectively, but two of the E_g modes are missing. The most probable assignment is to regard the two observed E_g bands as components, of ν_1, which then shows a total Davydov splitting of 31 cm^{-1}. It is evident that the water molecules vibrating around Al^{3+} are coupled but not very strongly. From this we deduce that there should be equally modest splittings between the components of ρ_ω, ρ_τ, and ρ_r. Armed with this insight we consider two alternative groupings, depending on the choice of ν_1. Thus:

	ρ_τ	ρ_ω	ρ_r	
$\nu_1 = 524$	825 E_g	701 A_{1g}	584 A_{1g}	Raman
	800 $A_{1g} + E_g$	622 E_g	566 E_g	
		610 E_g	534 E_g	
	836wm E_u	(678w A_{2u})	580vs A_{2u}	i.r.
	790wm A_{2u}	(664w E_u)	560vs E_u	
$\Delta\nu$/cm^{-1}	46	91	50	
or				
$\nu_1 = 701$	825 E_g	622 E_g	566 E_g	Raman
	800 $A_{1g} + E_g$	610 E_g	534 E_g	
		584 A_{1g}	524 A_{1g}	
$\Delta\nu$/cm^{-1}	46	94	56	

Here the i.r. assignment is the same in each case and the values in parentheses will be commented on later. The total Davydov splitting, $\Delta\nu$, is relatively large for the middle group of bands whichever choice of ν_1 is made.

In this region both A_{2u} and E_u i.r. spectra show reflectance bands at similar positions (Figure 3) and of comparable intensities. The A_{2u} spectrum has three of the four bands predicted but the E_u spectrum shows only three of the theoretical eight. The reason for this deficiency is simply that the coupling between the two complex ions in the primitive unit cell is weak. This is no surprise in that, physically, coupling must be *via* the weakly hydrogen-bonded chlorides which separate the complex ions. In this situation the appropriate selection rules are those of the site group (S_6) which describes the symmetry of the field acting on one complex ion [Table 2(*b*)]. This correctly accounts for the observation that ν_2 and ν_5 show only one E_g component each. Since the A_{2g} modes are inactive no further test of the strength of the correlation field can be made for these modes. The exception to this behaviour is ν_6 for which both E_u components were seen in mull spectra at low temperature, and for which the shape of the ε'' function, calculated from room-temperature data, indicates that two components are present *ca.* 210 cm^{-1}.

The appelations ρ_ω, ρ_τ, and ρ_r applied to the bands grouped above are supported by the following considerations, neglecting for the moment the fact that we have yet to locate ν_3 in our spectra. For a free water molecule the rotational motions that in a co-ordination complex become ρ_ω, ρ_τ, and ρ_r have moments of inertia in the ratios 1 : 1.9 : 2.9. When water is co-ordinated to a metal ion these moments of inertia are altered since the Al–O axis probably lies at *ca.* 110° to the HOH plane and the mass of the rest of the complex must be considered. Nevertheless, the largest displacements will still be associated with the hydrogen atoms. Therefore we take, as a working hypothesis, the order $\rho_\omega > \rho_\tau > \rho_r$ for the 'external' modes of co-ordinated water. There is good evidence that, at least in mono- and di-aquated complexes, $\rho_\omega > \rho_r$ but the place of ρ_τ is unsettled. We propose that it lies between the other two, at least in hexa-aqua-complexes. Secondly, the feebleness of the i.r.

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* Throughout this paper: 1 dyn = 10^{-5} N.

[19] J. P. Mathieu, *Compt. rend.*, 1950, **231**, 896.

[20] A. da Silveira, M. A. Marques, and N. M. Marques, *Compt. rend.*, 1961, **252**, 3983.

[21] A. da Silveira, M. A. Marques, and N. M. Marques, *Mol. Phys.*, 1965, **9**, 271.

[22] T. E. Hopkins, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, 1969, **8**, 2421.

bands tentatively attributed to ρ_τ is consistent with this assignment because ρ_τ arises from a motion inactive in C_{2v}, made active only by the field subtended by the surroundings.

We return to the problem of the location of ν_3. Since the evidence now strongly favours ν_1 at 524 cm^{-1} we must look for ν_3 near the calculated position of 653 cm^{-1}, shifting to 644 cm^{-1} in the deuteriate. These values do not exactly coincide with any observed i.r. bands. Two possible assignments may be advanced. First, ν_3 is roughly coincident with the intense bands at 560 (A_{2u}) and 580 cm^{-1} (E_u) or, more probably, near their high-frequency edges. However, the assignment of these intense bands to ρ_r modes cannot be disturbed since they both suffer very large deuteriation shifts to 400 (ρ 0.71) and 420 cm^{-1} (ρ 0.72) respectively, which are very close to the expected $\rho = 0.72$ for rocking modes as calculated either by taking $(I_c/I_c')^{\frac{1}{2}}$ (where I_c is the moment of inertia of water about the c axis) or by Krimm's method.[23] Unfortunately the i.r.-reflectance spectra for the deuteriate in the >500 cm^{-1} region were of much lower quality than those of the hydrate. It was not possible to be certain whether or not there were weak bands at *ca.* 644 cm^{-1} that might be attributed to ν_4. Alternatively, we might assign ν_3 to the weak bands at 664 and 678 cm^{-1} which were considered above as candidates for ρ_τ. Suppressing our natural feeling that ν_3 should be intense, this second alternative makes sense because the missing A_{2u} band is now ρ_τ and not ν_3, which is more probable than the reverse. Removal of these two bands from the groupings above does not reduce the Davydov splitting attributed to ρ_τ for ν_1 at 524 cm^{-1}, although it would for ν_1 at 701 cm^{-1}, at the expense of much greater ambiguities.

In the E_g spectrum of the deuteriate it appears that some of the observed bands must be ascribed to more than one mode since fewer bands were found than in the hydrate and the span of the spectrum will be reduced by the shifts. We note that all these E_g bands are due to 'external' modes of co-ordinated water since we have previously located ν_2 at 432 (418) cm^{-1}. On the basis of relative intensities, equivalents are proposed as follows [$\rho = \nu(D)/\nu(H)$]:

Protiate	Deuteriate	ρ
534	418	0.78
566	443	0.78
610	504	0.83
825	617	0.75

The deuteriate assignments are not entirely satisfactory. For their definitive and final assignment much more detailed experimental evidence must be obtained over a range of temperature for both i.r. and Raman spectra in the 350—1 000 cm^{-1} region.

Comparison of our assignment with those for MO_6 skeletal modes of $[M(OH_2)_6]^{2+}$ ions (M = Mg or Ni) (Table 5) shows that all the frequencies are considerably raised by the greater charge on aluminium. Since the masses of Al and Mg are similar, the differences between their hexa-aqua-complex vibrational frequencies are almost entirely due to this charge difference. For M = Ni there is a further reduction in ν_2, ν_3, and ν_5 due to the increased mass of the metal. Equivalent reductions are seen for the 'external' water modes for which the highest values are 660 (Raman) and 662 (i.r.) for M = Ni, and 825 (Raman) and 836 cm^{-1} (i.r.) for M = Al.

TABLE 5

Comparison of skeletal modes (wavenumbers/cm^{-1}) for $[Mg(OH_2)_6][H_2PO_2]$,[12] $[Ni(OH_2)_6][SnCl_6]$,[8] and $[Al(OH_2)_6]Cl_3$

$[Mg(OH_2)_6]^{2+}$	$[Ni(OH_2)_6]^{2+}$	$[Al(OH_2)_6]^{3+}$	Assignment
	142, 146	209, 208, 229	ν_6
268—285 [a]	209, 191	295, 310	ν_5
200—215 [b]	209, 207	309, 327	ν_4
421	333, 381	664, 678	ν_3
310	301	432	ν_2
363	382	524	ν_1

[a] Five bands. [b] Four bands.

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[23] S. Krimm, *J. Chem. Phys.*, 1960, **32**, 1780; values for water calculated by R. W. Berg (personal communication).