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Raman Spectra of KCl-$AlCl_3$ Melts and Normal Coordinate Analysis of $Al_2Cl_7^-$

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The Raman spectrum of molten mixtures of KCl-$AlCl_3$ was studied between 170 and 300°C in the concentration range 50–100 mol% $AlCl_3$. An illumination system allowing heating of the sample and multiple reflections of the Raman exciting beam up to 20 times has been constructed. Four absorption bands, verifying T_d symmetry, were observed for $AlCl_4^-$, and six bands were assigned to $Al_2Cl_7^-$. A normal coordinate analysis showed that $Al_2Cl_7^-$ probably has D_{3d} symmetry, but that D_{3h} or internal rotation is possible. The Al_2Cl_6 spectra verified former investigations. The force constants for $AlCl_4^-$ and $Al_2Cl_7^-$ were calculated using a modified valence force field. The spectral studies allowed a semiquantitative determination of the dissociation equilibrium

$$2\ Al_2Cl_7^- = Al_2Cl_6 + 2\ AlCl_4^-$$

for which $K = (4 \pm 2) \times 10^{-3}$ in the temperature range 170–240°C.

The alkali chloride–aluminium chloride molten systems [1–3] are well suited for setting melt structure models in perspective.[1] By varying the composition, the properties change from the ones of a purely covalent Al_2Cl_6 melt in pure aluminium chloride to structures with postulated Al-Cl complex ions, and over to the simple ionic melt of KCl.

Between 66 and 50 mol % $AlCl_3$, indirect evidence of the species $Al_2Cl_7^-$, has been obtained from the spectral work of Morrey, Moore and Voiland,[4,5]

and of Øye and Gruen,[6] and from the vapour pressure data of Dewing.[7,8] The possible existence of this species is stated in recent papers [9–11] but no direct evidence for its existence has come forth. Having access to a Cary Raman spectrophotometer, suited for use with heated systems, it was considered of great interest to perform a Raman spectroscopic study of the $KCl-AlCl_3$ system.

The main purpose of this work was to look for possible evidence for $Al_2Cl_7^-$ but it was also desired to probe into the present disagreement as to the structure of $AlCl_4^-$ in $KAlCl_4$ [12,13] and the spectra of Al_2Cl_6 in pure $AlCl_3$.[14–20] A preliminary communication of the present work has been published.[21]

EXPERIMENTAL

Apparatus. Fig. 1 gives the principles for the experimental set-up. The molten salt was contained in an optical fluorescence cell (A) $10 \times 10 \times 25$ mm, made of quartz, with all sides and base polished (Thermal Syndicate Ltd., Wallsend, England). The cell was joined to a quartz tube with a liquid trap (B) to prevent gas bubbles entering the cell. A porous vitreous silica filtering disk (C), with maximum pore size 15 μ, and a side tube (D) enabled repeated filtering if solid particles were formed in the melt.

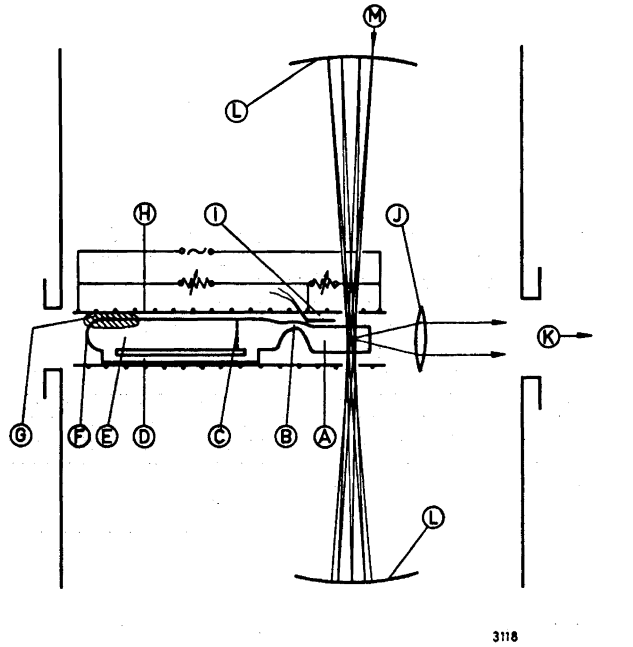

Fig. 1. Cell arrangement and illumination system for obtaining Raman spectra of molten salts. 16 reflections of the Raman beam through the sample is depicted. A, optical cell compartment. B, liquid trap. C, vitreous silica filtering disk. D, side tube. E, secondary cell compartment. F, sealed off end. G, quartz wool. H, nichrome wound quartz furnace. I, Pt-Pt 10 % Rh thermocouple. J, collecting lens. K, monochromator of spectrophotometer. L, aluminized spherical mirrors. M, laser beam.

The cell was placed in a nichrome wound uninsulated quartz furnace (H) 21 mm ID, with holes for the laser beam to pass through. To obtain a suitable temperature distribution in the cell, the current in the resistance wires around the cell could be varied independently of the current in the rest of the furnace. The temperature near the cell was determined by a Pt – Pt 10 % Rh thermocouple (I).

A Cary 81 Raman Spectrophotometer with a Spectra Physics Model 125 He – Ne laser, having an exciting line at 6328.17 Å, was used for obtaining the spectra. The ordinary illumination system was modified to allow perpendicular illumination with multiple reflections of the laser beam through the sample. The advantage of this illumination system is that the furnace and the hot sample could be kept at a distance from the optical parts. In the experimental work so far, the temperature has not exceeded 350°C, but there are no principle objections against raising the temperature to 1200°C with this system. The principle was first suggested to us by Hendra,[23] but it is related to Clarke and Hester's [23] assembly for the Perkin-Elmer Raman Spectrophotometer LR-1.

The illumination system consisted of the laser beam (M), two aluminized spherical mirrors (L), of which a 2 mm hole was bored through the upper one, and a collecting lens (J) with focal length 20 mm. The mirrors, the lens and the furnace could be adjusted by means of separate screws to optimize the illumination of the cell and to focus the emitted Raman light before entering the monochromator (K) of the Raman spectrophotometer. The available lenses for making the mirrors (L) had somewhat different radii of curvature; the one with the smallest radius was placed at the bottom.

The standard unit which supports the half wave plate and the focusing lens for the laser beam was left in the instrument, but was raised to its highest position. We found it convenient to remove the whole front of the instrument sample compartment and to record the spectra in a darkened laboratory.

Chemicals. $AlCl_3$ was prepared as described by Øye and Gruen [8] by letting dry HCl from a HCl generator flow over an Al wire, purity 99.99 % (Vigeland bruk, Vigeland, Norway). The Al metal was heated to about 450°C, at which temperature the reaction with HCl gas to form $AlCl_3$ proceeded at a convenient rate without melting of the metal. KCl, p.a. (Merck, Darmstadt, West Germany) was dried, melted under vacuum, and purified by crystallization. Only clear, well formed crystals were used.

Procedure. Proper amounts of $AlCl_3$ and KCl were weighed in a dry-box and transferred to the prolongation of the quartz tube from (F) (Fig. 1). The cell arrangement was sealed off under vacuum, and the mixture was kept molten for several days. After flocculation of some of the remaining organic material, the melt was filtered through an additional filtering disk down into part (E) of the cell, and sealed off at (F). Filtering through (C) was performed, and the cell was then placed in the quartz furnace (H), plugging the left part of the furnace tube with quartz wool (G).

As mentioned above, the lower mirror (L) had a smaller radius of curvature than the upper one. The important point in getting good multiple reflections is, however, to have the center of curvature of the two mirrors close to each other, both being within the sample, and then to direct the laser beam a little to the side of these curvature centers. One is then able to get the reflected laser beam to rotate approximately on the surface of a double cone (see Fig. 1). By proper adjustments 20 reflections were obtained. After maximizing the number of reflections, the lens (J) was moved to the position of maximum intensity of light going into the spectrophotometer.

We had a limited supply of optical cells of somewhat uneven quality with respect to the ability to withstand pressure and temperature. It was therefore decided to heat samples with $AlCl_3$ content greater than 60 mol % with the utmost care to prevent bursting of the cell. These samples were not heated more than 10 – 20°C over their melting points. A disadvantage of this is that the spectra could not be compared isothermally, but this is not considered to change the semiquantitative results for the dissociation equilibrium, as no detectable changes in the spectra were observed for melts with 58 mol % $AlCl_3$ in the temperature range 240° – 300°C.

The spectra were recorded in the range 40 – 1600 cm^{-1}. The incident laser light (y-axis) was polarized in the x and z directions, respectively, by turning the half wave plate. In the directon of observation (x-axis), a polaroid sheet, transmitting only in the z direction, was inserted. For depolarized bands, this gives a maximum depolarization ratio of 3/4.

To avoid the formation of gas bubbles scattering the laser beam, it was found necessary to keep the temperature of the optical cell proper 10 – 20°C lower than the rest of the cell arrangement. This was accomplished by individual current regulation of the two branches of the furnace windings. The temperature during a run was kept constant within ± 3°C.

The spectra were disturbed by strong, slow and nonperiodic intensity variations which made it necessary to use the highest period control, 60, and slow speed, 0.2 cm^{-1} sec^{-1}. The disturbance problem was due to micro particles in the melts which were very hard to filter out. The problem was overcome by repeated filtering and successive runs of spectra to eliminate statistical errors. An attempt to investigate mixtures with 75 mol % $AlCl_3$ has not yet met with success because of the formation of micro particles.

The strong bands were recorded with a slit width of 8 cm^{-1} and gain 400 (dynode 4), while it was necessary to increase the slit width to 14 cm^{-1} and gain to 3000 for recording some of the weak bands.

RESULTS

Fig. 2 shows the Raman spectra and polarization information for the 4 different compositions investigated.

Spurious peaks due to noise have been removed. Also peaks due to emission lines from the He – Ne – laser[24] other than the 6328.17 Å line have been removed. These lines were, however, used for calibration of the wave number scale. Good spectra of these peaks were obtained by scattering the laser beam by a piece of paper. The correction was determined to be – 2.6 cm^{-1} independent of the spectral range.

The results are summarized in Table 1, where the different frequencies have been assigned to the species $AlCl_4^-$, $Al_2Cl_7^-$, and Al_2Cl_6.

Table 1. Raman spectral frequencies (cm^{-1}) of the $AlCl_3$ rich part of the system $KCl - AlCl_3$.[a]

50 % $AlCl_3$ Temp.: 300°C No. of spectra: 8			58 % $AlCl_3$ Temp.: 300 and 240°C No. of spectra: 13			66 % $AlCl_3$ Temp.: 170°C No. of spectra: 7			100 % $AlCl_3$ Temp.: 200°C No. of spectra: 2		
σ	I		σ	I		σ	I		σ	I	
			102	3	dp	**99**	5	dp	106	6	dp?
122	4	dp	*(121)*	3	dp	*(118)*	2	dp	118	6	dp?
			(167)	2	dp	**164**	3	dp	165	1	dp
182	4	dp	*182*	4	dp	*(178)*	2	dp	219	3	p
									240	< 1	
			312	4	p	**312**	10	p	280	< 1	dp
									(324)	2	p
350	10	p	*350*	10	p	*350*	5	p	339	10	p
						394	1	dp?			
			(425)	< 1	p?	**(425)**	1	p?			
			435	1	dp	**435**	2	dp	511	1	p
487	< 1	dp							606	< 1	dp

[a] Frequencies assigned to $AlCl_4^-$ in italics, to $Al_2Cl_7^-$ in boldface, and to Al_2Cl_6 in Roman. Frequencies for shoulders given in parentheses.

σ, frequency. I, relative intensity (strongest peak = 10). dp, depolarized. p, polarized.

Between 2 and 13 spectra were used for determination of the average location of the bands in the $KCl-AlCl_3$ mixtures, and standard deviations were determined to 2 cm^{-1} for most of the shoulders, and otherwise to 1 cm^{-1}. Only two spectra of pure $AlCl_3$ were recorded; hence no standard deviation calculations were possible in that case.

The intensities of the bands are given as the height of the spectral curve relative to the strongest band for each experiment; the latter is set equal to 10. For overlapping bands, lorentzian curves were constructed and fitted to match the experimental results.

Special care was taken in determining the intensities of the two strongest peaks for 58 and 66 mol% $AlCl_3$, as these were used for a semiquantitative determination of the dissociation equilibrium for the $Al_2Cl_7^-$ species. In these cases the integral intensities were determined and the intensity ratios were calculated to:

$$58 \text{ mol\% } AlCl_3\text{: } I_{58}{}^{D}/I_{58}{}^{\beta} = 0.60 \pm 0.02$$
$$66 \text{ mol\% } AlCl_3\text{: } I_{66}{}^{D}/I_{66}{}^{\beta} = 3.0 \pm 0.1$$

Here, I^D and I^β denote the bands at 312 and 350 cm^{-1}, respectively. The uncertainties are the estimated standard deviations.

The values for the composition are based on weighed-in amounts. The change in composition of the liquid because of enrichment of $AlCl_3$ in the vapour phase was estimated to 0.1 mol% $AlCl_3$, using the density data of Morrey and Carter,[25] and assuming a vapour pressure of 0.5 atm. The filtering procedure may, however, also have changed the composition slightly, so that the uncertainty of composition is estimated to ± 0.5 mol%.

The observed frequencies can be grouped in three classes:

(1) The four frequencies observed for 50 mol% $AlCl_3$ and decreasing in relative intensities upon addition of $AlCl_3$. These are assigned to $AlCl_4^-$ and marked with Greek letters on Fig. 2 and italics in Table 1.

(2) The new bands increasing in relative size upon addition of $AlCl_3$ to a mixture with 50 mol% $AlCl_3$. These are assigned to $Al_2Cl_7^-$ and marked with capital Roman letters on Fig. 2 and boldface numerals in Table 1.

(3) The bands for pure $AlCl_3$ assigned to Al_2Cl_6; small Roman letters on Fig. 2 and Arabic numerals in Table 1.

Neither of the band classes could be attributed to the species $AlCl_3$[26] found in the gas phase. The spectra of the mixture containing 58 mol% $AlCl_3$ were recorded at 240°C and 300°C, and no change in either the position or the intensity of the peaks could be detected.

DISCUSSION AND ASSIGNMENT OF FREQUENCIES

Aluminium tetrachloride ion ($AlCl_4^-$). The observed spectrum for molten $KAlCl_4$ agrees well with previous studies of similar compounds assuming the presence of tetrahedral $AlCl_4^-$.[27,28] Table 2 gives a comparison with previous results.

Good agreements with previous investigations are found for the "breathing" mode $\sigma_1(A_1)$ and the mixed mode $\sigma_4(F_2)$. For the pure bending mode $\sigma_2(E)$ and the mode $\sigma_3(F_2)$, the present investigation gives frequencies about

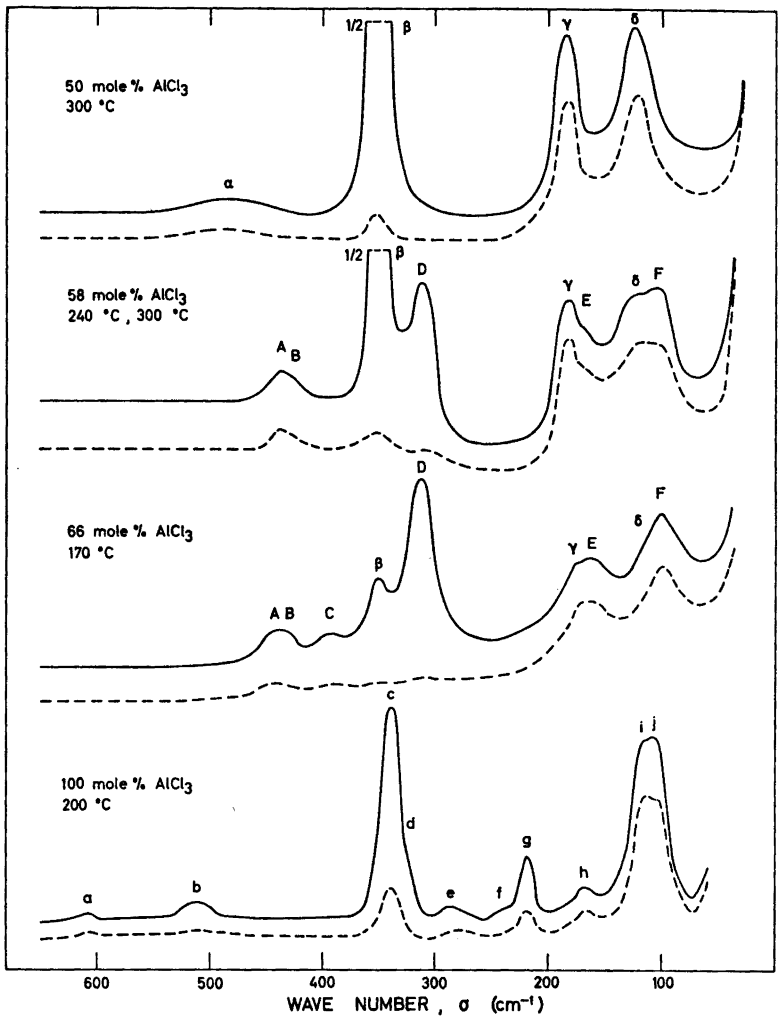

Fig. 2. Polarized Raman spectra of $AlCl_3$-KCl melts. ————, the intensity I (||) (obs. (⊥)). – – –, the intensity I (⊥) (obs. (||)). The absolute intensity scale for each composition is arbitrary. Frequencies assigned to $AlCl_4^-$: α, β, γ, δ. $Al_2Cl_7^-$: A, B, C, D, E, F. Al_2Cl_6: a, b, c, d, e, f, g, h, i, j.

20 % lower than those of $NaAlCl_4$ showing the influence of the cations on the $AlCl_4^-$ modes.

It is planned at a later stage to investigate further the influence of cations on simple vibrational entities such as $AlCl_4^-$; *i.e.* to study the vibrational interaction with the bulk melt. At present, there is no justification for a further elaboration of these effects, especially since it has been found that $NOCl \cdot AlCl_3$,

Table 2. Fundamental frequencies (cm^{-1}) of $AlCl_4^-$.

Substances	$NaCl \cdot AlCl_3$ *a*	$NOCl \cdot AlCl_3$ *b*	$PCl_5 \cdot AlCl_3$ *c*	$PCl_5 \cdot AlCl_3$ *d*	$NaCl \cdot AlCl_3$ *e*	$KCl \cdot AlCl_3$ *f*
$\sigma_1(A_1)$	349	349	352	347	349	350
$\sigma_2(E)$	146	136	147		145	122
$\sigma_3(F_2)$	575	495	495	490	580	487
$\sigma_4(F_2)$	180	182		180	183	182

[a] Gerding and Houtgraaf,[27] $NaCl \cdot AlCl_3$, Raman (l) 160–170°C.
[b] Gerding and Houtgraaf,[27] $NOCl \cdot AlCl_3$, Raman (l) 190–200°C.
[c] Carlson,[28] $PCl_5 \cdot AlCl_3$, Raman (s).
[d] Carlson,[28] $PCl_5 \cdot AlCl_3$, IR(s).
[e] Balasubrahmanyam and Nanis [12] $NaCl \cdot AlCl_3$, Raman (l) 200°C.
[f] Present, $KCl \cdot AlCl_3$, Raman(l) 300°C.

and also probably $PCl_5 \cdot AlCl_3$, is best considered as being intermediate between an ionic compound containing $AlCl_4^-$ and a pure molecular compound.[27]

Our results are at variance with the investigation of Balasubrahmanyam and Nanis [12] where they claim the observation of nine vibrational frequencies concluding the presence of a distorted $AlCl_4^-$ tetrahedron having C_{2v} symmetry. But as pointed out by Bredig [13] the narrowness of the observed lines and the poor reproducibility reported by Balasubrahmanyam and Nanis [12] strongly suggest several of the additional lines to be electronic noise, and that a sounder interpretation should be based on vibrations of an undistorted tetrahedral $AlCl_4^-$ also in this case.

Force constants were calculated by Wilson's **FG**-matrix method [29] as solutions of the secular determinant

$$|\mathbf{GF} - \lambda \mathbf{E}| = 0$$

using a modified valence force field with the following **F**-matrix pertaining to the symmetry T_d.

$$F_{11}(A_1) = f_r + 3f_{rr}$$
$$F_{22}(E) = f_\alpha - 2f_{\alpha\alpha}$$
$$F_{33}(F_2) = f_r - f_{rr}$$
$$F_{44}(F_2) = f_\alpha$$
$$F_{34}(F_2) = 0$$

The force constants calculated from the present wave numbers, together with those found by Müller and Krebs [30] using the vibrational frequencies 352, 147, 490, and 176 cm^{-1}, are given in Table 3. The differences are small, and the correspondence is satisfying.

Dialuminium heptachloride ion ($Al_2Cl_7^-$). The Raman spectra give clear indication of a new formation on adding $AlCl_3$ to $KAlCl_4$. In view of the previous indirect evidence [4–8] only the $Al_2Cl_7^-$ model was considered for this formation, having the structure of two possibly distorted $AlCl_4^-$ tetrahedra sharing one bridging Cl^-.

Table 3. Force constants (mdyne/Å) of a modified valence force field for $AlCl_4^-$ with symmetry T_d.

	Müller and Krebs[30]	Present
f_r	1.76	1.704
f_{rr}	0.28	0.285
f_α	0.17	0.193
$f_{\alpha\alpha}$	0.02	0.020

The symmetry of this model with a linear Al – Cl – Al bridge may be D_3, D_{3h}, or D_{3d} giving rise to 11, 10, and 6 Raman-active fundamentals, respectively. A bent Al – Cl – Al bridge, symmetry C_{2v}, C_s, C_2, or C_1, giving rise to 21 Raman-active fundamentals, is considered as improbable, and the high number of predicted frequencies are not observed.

Assuming a linear Al – Cl – Al bridge, *i.e.* an ethane-like configuration, one is then left with the models D_{3d}, D_{3h}, and D_3. These models differ in the rotational angles between the two end groups; whether the chloride ions are staggered, eclipsed or randomly oriented. The activation energy for rotation around the bridge Al – Cl – Al is expected to be low, so that the energetic difference between these models are small.

In the main part of this work, only the model D_{3d} is considered, since this is the most favourable model in view of chlorine-chlorine repulsions and also predicts a number of Raman-active frequencies consistent with experiments. In subsequent sections, however, it is shown that the data may also possibly be interpreted in terms of free rotation around the bridging single bond. The D_{3d} model predicts just six Raman-active fundamental frequencies: three depolarized (E_g) and three polarized (A_{1g}), of which one of the A_{1g} fundamentals probably is too low to be observed. The two polarized bands could be 312 and 394 or 425 cm^{-1}. In a recently published short communication[21] the band at 394 cm^{-1} was reported as uncertain, and 425 cm^{-1} was used in the calculations, but further investigations have confirmed the 394 cm^{-1} band. One of these bands then presumably results from combinations, overtones, or one vibrational mode of a small amount of a higher associated complex, *e.g.* $Al_3Cl_{10}^-$. The bands 99, 164, and 435 cm^{-1} are assigned to E_g.

Dialuminium hexachloride (Al_2Cl_6). The present Raman bands of Al_2Cl_6, compared with earlier investigations, are given in Table 4.

The only significant deviation from the work of Pershina and Raskin[17] is the observed band at 240 cm^{-1} in this work. In the present work, the three bands below 80 cm^{-1} were not detected. Depolarization characteristics fit exactly those found by Gerding and Smit,[14] and the band positions are compatible. We did, however, find that the 112 cm^{-1} band could be resolved into 106 and 118 cm^{-1} bands, and also the presence of additional bands at 240 and 324 cm^{-1}. Unfortunately, a weak laser excitation band made it impossible to confirm the 438 cm^{-1} band.

The bridged ethylene-like structure of Al_2Cl_6 is now well established by several electron-diffraction works,[31–33] and several normal coordinate analyses

Table 4. Raman-active frequencies (cm^{-1}) of $Al_2Cl_6(l)$.[a]

Gerding and Smit[14] Temp.: 215°C			Pershina and Raskin[17]		Present Temp.: 200°C		
σ	I		σ	I	σ	I	
			19[b]	2			
			36[b]	10			
			75[b]	½			
			104	10	106	6	dp?
112	6	dp?					
			119	9½	118	6	dp?
164	3	dp	164	2	165	1	dp
217	5	p	219	4	219	3	p
					240	<1	
284	2	dp	282	1	280	<1	dp
			330	1	(324)	2	p
340	10	p	339	8½	339	10	p
438	0–1	dp?					
506	3	p	510	1	511	1	p
606	2–3	dp	605	<1	606	<1	dp

[a] See footnote to Table 1.
[b] Obtained only by photographic detection.

have been performed,[15, 16, 18, 19] all of them using an assignment from the Raman-bands of Gerding and Smit[14] and the IR-bands of Klemperer.[15] Comparing the spectra of Al_2Cl_6 and Al_2Br_6, Adams[20] proposed the following assignment, using the Pershina and Raskin[17] results (in cm^{-1} units):

$$\sigma_1(A_g) = 510 \quad \sigma_2(A_g) = 339 \quad \sigma_3(A_g) = 219$$
$$\sigma_4(A_g) = 119 \quad \sigma_6(B_{1g}) = 330 \quad \sigma_7(B_{1g}) = 282$$
$$\sigma_{11}(B_{2g}) = 605 \quad \sigma_{12}(B_{2g}) = 164 \quad \sigma_{15}(B_{3g}) = 104$$

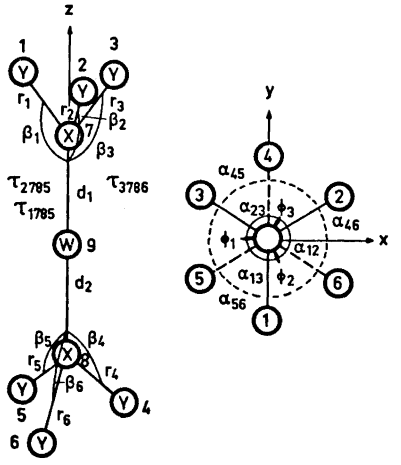

Fig. 3. Numbering of atoms and the cartesian and valence coordinates of the WX_2Y_6 D_{3d} molecular model.

Calculations on this basis are in progress.

After this work was completed, we became aware of a new investigation [34] of Al_2Cl_6 gas at 450°C. These experimental results agree well with the present ones.

NORMAL COORDINATE ANALYSIS FOR $Al_2Cl_7^-$

Molecular model. Fig. 3 shows the D_{3d} molecular model with cartesian coordinate axes, the numbering of the atoms and the notation of valence coordinates.

Symmetry coordinates. A suitable set of symmetry coordinates in terms of the valence coordinates [29] is given in the following.

$$
\begin{aligned}
S_1(A_{1g}) &= 6^{-\frac{1}{2}}(r_1+r_2+r_3+r_4+r_5+r_6)\\
S_2(A_{1g}) &= 2^{-\frac{1}{2}}(d_1+d_2)\\
S_3(A_{1g}) &= -[R/(6K^2R+6D)]^{\frac{1}{2}}[KR(\alpha_{23}+\alpha_{13}+\alpha_{12}+\alpha_{56}+\alpha_{46}+\alpha_{45})\\
&\quad +D(\beta_1+\beta_2+\beta_3+\beta_4+\beta_5+\beta_6)]\\
S_{1a}(E_g) &= 12^{-\frac{1}{2}}(2r_1-r_2-r_3+2r_4-r_5-r_6)\\
S_{2a}(E_g) &= 12^{-\frac{1}{2}}R(2\alpha_{23}-\alpha_{13}-\alpha_{12}+2\alpha_{56}-\alpha_{46}-\alpha_{45})\\
S_{3a}(E_g) &= 12^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(2\beta_1-\beta_2-\beta_3+2\beta_4-\beta_5-\beta_6)\\
S_{1b}(E_g) &= \tfrac{1}{2}(r_2-r_3+r_5-r_6)\\
S_{2b}(E_g) &= \tfrac{1}{2}R(\alpha_{13}-\alpha_{12}+\alpha_{46}-\alpha_{45})\\
S_{3b}(E_g) &= \tfrac{1}{2}(RD)^{\frac{1}{2}}(\beta_2-\beta_3+\beta_5-\beta_6)\\
S(A_{1u}) &= -3^{-\frac{1}{2}}R(\tau_{1784}+\tau_{2785}+\tau_{3786})\\
S_1(A_{2u}) &= 6^{-\frac{1}{2}}(r_1+r_2+r_3-r_4-r_5-r_6)\\
S_2(A_{2u}) &= 2^{-\frac{1}{2}}(d_1-d_2)\\
S_3(A_{2u}) &= -[R/(6K^2R+D)]^{\frac{1}{2}}[KR(\alpha_{23}+\alpha_{13}+\alpha_{12}-\alpha_{56}-\alpha_{46}-\alpha_{45})\\
&\quad +D(\beta_1+\beta_2+\beta_3-\beta_4-\beta_5-\beta_6)]\\
S_{1a}(E_u) &= \tfrac{1}{2}(r_2-r_3-r_5+r_6)\\
S_{2a}(E_u) &= \tfrac{1}{2}R(\alpha_{13}-\alpha_{12}-\alpha_{46}+\alpha_{45})\\
S_{3a}(E_u) &= \tfrac{1}{2}(RD)^{\frac{1}{2}}(\beta_2-\beta_3-\beta_5+\beta_6)\\
S_{4a}(E_u) &= 6^{-\frac{1}{2}}D(2\phi_1-\phi_2-\phi_3)\\
S_{1b}(E_u) &= -12^{-\frac{1}{2}}(2r_1-r_2-r_3-2r_4+r_5+r_6)\\
S_{2b}(E_u) &= -12^{-\frac{1}{2}}R(2\alpha_{23}-\alpha_{13}-\alpha_{12}-2\alpha_{56}+\alpha_{46}+\alpha_{45})\\
S_{3b}(E_u) &= -12^{-\frac{1}{2}}(RD)^{\frac{1}{2}}(2\beta_1-\beta_2-\beta_3-2\beta_4+\beta_5+\beta_6)\\
S_{4b}(E_u) &= 2^{-\frac{1}{2}}D(\phi_2-\phi_3)
\end{aligned}
$$

The symbols employed have the following significance:

R = X–Y equilibrium distance
D = X–W equilibrium distance
K = $3^{\frac{1}{2}}\cos B/\cos A$
$2A$ = Y–X–Y equilibrium angle
B = Y–X–W equilibrium angle

Force constants. A calculation of fundamental frequencies was performed assuming the D_{3d}-model for $Al_2Cl_7^-$. The force constants f_r and f_{rr} for the Al–Cl terminal stretching, and some of the bending force constants, were transferred from $AlCl_4^-$ and taken from the work of Müller and Krebs [30] (Table 3). The force constants associated with the stretchings, bendings and torsional

motion of the Al–Cl–Al bridge were assumed to be small together with the rest of the bending constants. The following diagonal F-matrix was used, where the numbers in italics denote the constants obtained from the data of Müller and Krebs;[30] all values in mdyne/Å:

2.32	0.10	0.20	*1.48*	*0.17*	0.05	0.00
2.32	0.10	0.20	*1.48*	*0.17*	0.05	0.01

Table 5 gives the calculated frequencies compared with the experimental ones. By refining the force constants within reasonable magnitudes it was possible to obtain quantitative agreement with the observed frequencies. This

Table 5. Raman-active fundamental frequencies (cm^{-1}) for $Al_2Cl_7^-$ assuming D_{3d} symmetry.

Symmetry D_{3d}	Calc.	Observed Frequency	Polarization
A_{1g}	469	394, 425?	?
	272	312	p
	35	–	–
E_g	470	435	dp
	166	164	dp
	83	99	dp

refinement, using the 425 cm^{-1} band rather than the equally possible 394 cm^{-1} band, resulted in the following F-matrix (mdyne/Å units):

$F_{1,1} = 2.092$	$F_{4,4} = 1.220$	$F_{8,8} = 2.092$	$F_{11,11} = 1.220$
$F_{2,2} = 0.050$	$F_{5,5} = 0.169$	$F_{9,9} = 0.050$	$F_{12,12} = 0.169$
$F_{3,1} = 0.172$	$F_{6,6} = 0.072$	$F_{10,8} = 0.172$	$F_{13,13} = 0.072$
$F_{3,3} = 0.258$	$F_{7,7} = 0.000$	$F_{10,10} = 0.258$	$F_{14,14} = 0.010$

The other elements equal zero. Using 394 cm^{-1} as a fundamental rather than 425 cm^{-1} would only result in a slight change in the elements of the F-matrix.

The following IR-active fundamentals are predicted from the present analysis:

A_{2u}: 425, 312, 73 cm^{-1}
E_u: 437, 164, 128, 37 cm^{-1}.

It was also possible to fit the observed frequencies and polarization values to the *eclipsed* (D_{3d}) and *gauche* (D_3) models, but as these models require additional bands not observed experimentally, the analysis will not be given here.

Free internal rotation. The $Al_2Cl_7^-$ model with a linear bridge and two $AlCl_3$ end groups is expected to have a small energy barrier opposing rotation. It is, therefore, of interest to discuss with a basis in group theory the consequences of rotation on the present vibrational spectra. The spectral theories of species with restricted or free internal rotation are not completed, but we will follow the arguments set forth by Howard,[35] Longuet-Higgins,[36] Hougen,[37] and recently Turrell.[38]

Table 6. Raman-active fundamental frequencies of $Al_2Cl_7^-$ (cm^{-1}) using the abstract symmetry group D'_{3h}. Force constants are taken from the D_{3d} calculations after fitting the frequencies exactly to the observed values. The D'_{3h} group gives results identical to that of D_{3h}.

Species of D_{3h}	Calc.	Observed	
		Frequency	Polarization
A_{1g}	425	425	?
	312	312	p
	25	–	–
E'	437	435	dp
	164	164	dp
	128	–	–
	37	–	–
E''	435	435	dp
	164	164	dp
	99	99	dp

Group theory is usually applied to molecules by considering the transformation of the equilibrium configuration to a physically *indistinguishable* configuration. The present theories for structures with internal rotation point out that this is a too restrictive procedure and that symmetry operations must transform the *displaced* configuration of the molecule into a physically *equivalent* configuration; *i.e.* a configuration which keeps the energy invariant.

Howard [35] applies this to C_2H_6 which is symmetrically similar to the $Al_2Cl_7^-$ group with a linear Al – Cl – Al bridge. $Al_2Cl_7^-$ will only have D_3 symmetry if the two end groups are twisted by an arbitrary angle with respect to each other. But regardless of the forces restricting internal rotation, reflection through a plane of symmetry perpendicular to the threefold axis will not change the potential energy, and this symmetry element should be included. Hence, the proper symmetry group is obtained as the direct product of D_3 and C_s. This direct product is identical with the symmetry group D_{3h}, and Howard denotes the abstract group which includes all symmetry operations keeping the energy invariant for D'_{3h}. The characters of the irreducible representations are identical with that of D_{3h}. The optical selection rules are independent of restrictive forces and the rotational angle between the two end groups, except when the symmetry goes over to D_{3d}. In Table 6 are given the

Table 7. Vibrational frequencies of $Al_2Cl_7^-$ (cm^{-1}) tentatively assigned to the symmetry group D'_{3h} and D_3[2]. Predicted Raman active bands in italics.

D'_{3h}	σ/cm^{-1}				D_3[2]	σ/cm^{-1}		
3 A_1'	*425*	*312*	*25*		3 A_1	*425*	*312*	*25*
3 A_2''					3 A_4			
4 E'	*437*	*164*	*128*	*37*	3 E	128	99	37
3 E''	*435*	*164*	*99*		2 G	*436*	*164*	

calculated frequencies, using the same force constants as found by fitting the observed frequencies to D_{3d}. A complete correspondance with the observed spectra is not obtained as the predicted band with frequency 128 cm^{-1} is lacking. This band will be active in IR as well, and a definite conclusion about the non-appearance of this band can only be done after the IR spectra are studied, especially also because the location is close to the strong $\sigma_2(E)$ band of $AlCl_4^-$.

Longuet-Higgins [36] has introduced the molecular symmetry groups being composed of all feasible permutations and inversion-permutations. The symmetry operators are not operated on the atoms, but on their relative coordinates, and this is achieved by permuting the positions of the atoms. Only feasible transformations, those not passing over an insuperable energy barrier are used. For $Al_2Cl_7^-$ the resulting symmetry group will be $D_3 \times D_3 = D_3^2$, the same group as Longuet-Higgins [36] found for ethane and Hougen [37] applied to dimethylacetylene. The symmetry group has 36 elements in 9 classes. Hougen gives as the probable set of irreducible representations for dimethylacetylene:

$$\Gamma_{(CH_3)_2C_2}(D_3^2) = 4A_1 + 3A_4 + 2E_1 + 2E_2 + 2G$$

The total number of vibrational modes are $3 \times 10 - 7 = 23$, as the torsional vibrational mode has been removed. We have not been able to determine the irreducible representations for $Al_2Cl_7^-$ directly, but using analogy between D'_{3h}, for dimethylacetylene, $Al_2Cl_7^-$ and ethane, and D_3^2 for dimethylacetylene and ethane, we arrive at the following probable irreducible representations for $Al_2Cl_7^-$ in the group D_3^2.

$$\Gamma_{Al_2Cl_7^-}(D_3^2) = 3A_1 + 3A_4 + 3E + 2G$$

In Table 7 an assignment for $Al_2Cl_7^-$ to D'_{3h} is compared with a tentative assignment according to D_3^2. The point we will make at this stage is that the D_3^2 assignment transforms two of the accidental degeneracies of D'_{3h} (the pairs 435 – 437 and 164 – 164) to true degeneracies. However, neither of the models fit perfectly. D'_{3h} disagrees because of the non-observed 128 cm^{-1} frequency, while the E representation will not be Raman-active in D_3^2 so that the frequency of 99 cm^{-1} should not have been observed.

In a recent article, Turrell [38] points out the difficulties in determining the vibrational states for molecules with free internal rotation using the method of Longuet-Higgins [36] as the rotational angle is not defined. Turrell [38] develops a theory for determining the proper set of irreducible representations and applies it to toluene and diphenyl ether. Applying this method for dimethylacetylene and $Al_2Cl_7^-$ results in the following characters of reducible representations for the D_3^2 group of Longuet-Higgins.[36]

$\chi_{((CH_3)_2C_2)}$: 30, 60, 0, 60, 120, 0, 0, 0, 54.
$\chi_{(Al_2Cl_7^-)}$: 27, 54, 3, 54, 108, 6, −3, **−6**, 45.

Using standard methods [29] the representations are found to consist of the following irreducible representations:

$$\Gamma_{((CH_3)_2C_2)}: 9A_1 + 6A_2 + 6A_3 + 9A_4$$
$$\Gamma_{(Al_2Cl_7^-)}: 8A_1 + 6A_2 + 5A_3 + 8A_4$$

Here translational, rotational, and torsional modes are included. Turrell's method hence results in a correct number of irreducible representations, but the representation of $(CH_3)_2C_2$ differs from that given as the probable representation by Hougen.[37] The two examples treated here, and toluene and diphenyl ether discussed by Turrell, also result in one-dimensional representations only. The presence of only one-dimensional representations may be considered physically improbable, as one would expect some modes for $Al_2Cl_7^-$ and $(CH_3)_2C_2$ to be degenerate. There are also difficulties with subtraction of the translational, rotational, and torsional modes.

Although a model of $Al_2Cl_7^-$ with free internal rotation physically may be considered a plausible model, the present investigation and theories are not decisive about this point. It is planned to study the IR spectra as well, particularly looking for the 128 cm^{-1} band, and we hope with further developments of the theories to be able to reach more specific conclusions on the problem of free internal rotation of $Al_2Cl_7^-$.

DISSOCIATION EQUILIBRIUM

Addition of KCl to molten $AlCl_3$ may be described by the successive equilibria:[5,8]

$$Al_2Cl_6 + Cl^- = Al_2Cl_7^- \qquad K_1 \tag{1}$$

$$Al_2Cl_7^- + Cl^- = 2\,AlCl_4^- \qquad K_2 \tag{2}$$

The dissociation equilibrium of $Al_2Cl_7^-$ is obtained by combination of eqns. (1) and (2):

$$2\,Al_2Cl_7^- = Al_2Cl_6 + 2\,AlCl_4^- \quad K = K_2/K_1 \tag{3}$$

As the relative intensities of the $AlCl_4^-$ bands to the $Al_2Cl_7^-$ bands are determined at two different compositions, this information can be used to obtain a semi-quantitative value for the stoichiometric dissociation constant K.

The following assumptions are made. The mixtures are considered as ideal mixtures of the anionic and neutral species. This represents a modified Temkin model, and K is independent of temperature within the temperature range 240 to 170°C. The last assumption is justified because of the spectral invariance to the temperature change from 300 to 240°C for the mixture with 58 mol% $AlCl_3$. Stoichiometric relations give:

$$n_{KCl}^{\circ} = n_{Cl^-} + n_{Al_2Cl_7^-} + n_{AlCl_4^-} \tag{4}$$

$$n_{AlCl_3}^{\circ} = 2n_{Al_2Cl_6} + 2n_{Al_2Cl_7^-} + n_{AlCl_4^-} \tag{5}$$

For 1 mol of mixture:

$$n_{KCl}^{\circ} = X_{KCl}^{\circ}, \quad n_{AlCl_3}^{\circ} = X_{AlCl_3}^{\circ}$$

$$X_{KCl}^{\circ} + X_{AlCl_3}^{\circ} = 1 \tag{6}$$

From spectral as well as electrometric studies [5,8,9,39], one may assume $n_{Cl^-} \ll n_{AlCl_4^-}$, and $n_{Al_2Cl_7^-}$ in the concentration range studied, $0.58 < X_{AlCl_3}^{\circ} < 0.66$. By then introducing the ratio

$$P = \frac{n_{Al_2Cl_7^-}}{n_{AlCl_4^-}} \tag{7}$$

one may express the amount of different species as:

$$n_{AlCl_4^-} = \frac{X_{KCl}^{\circ}}{1+P} \tag{8}$$

$$n_{Al_2Cl_7^-} = \frac{P\,X_{KCl}^{\circ}}{1+P} \tag{9}$$

$$n_{Al_2Cl_6} = \frac{1+P-(2+3P)\;X_{KCl}^{\circ}}{2\,(1+P)} \tag{10}$$

Total number of anionic and neutral species in moles:

$$\sum n = n_{Al_2Cl_6} + n_{Al_2Cl_7^-} + n_{AlCl_4^-} + n_{Cl^-} = X_{KCl}^{\circ} + n_{Al_2Cl_6} \tag{11}$$

Expressing the stoichiometric equilibrium constant K in mol fractions and ignoring $n_{Al_2Cl_6}$ with respect to X_{KCl}°:

$$K = \frac{n_{Al_2Cl_6}}{P^2 \cdot X_{KCl}^{\circ}} = \frac{1+P-(2+3P)X_{KCl}^{\circ}}{2P^2(1+P)X_{KCl}^{\circ}} \tag{12}$$

Assuming the mol fractions of $AlCl_4^-$ and $Al_2Cl_7^-$ to be proportional to the intensity of the strongest band for each species, one obtains

$$P_{58} = k(I_{58}^{D}/I_{58}^{\beta}), \quad P_{66} = k(I_{66}^{D}/I_{66}^{\beta}) \tag{13}$$

Eliminating the constant:

$$P_{58} = P_{66}\,(I_{58}^{D}/I_{58}^{\beta})/(I_{66}^{D}/I_{66}^{\beta}) \tag{14a}$$

Inserting the measured intensity ratios (see Results):

$$P_{58} = P_{66} \times 5.8 \tag{14b}$$

By then combining eqn. (14b) with eqn. (12) for the two compositions studied, P and K are determined, and the number of moles of each species is then given by eqns. (8 – 10). The results are given in Table 8.

The error limits for the calculated K have been set fairly large because of uncertainties in composition, the assumption of spectral intensities being independent of the composition, and since the temperatures of study for the two mixtures were unequal.

The K for the dissociation equilibrium calculated here differs from the dissociation K' calculated previously by Øye and Gruen [8] using the vapour pressure data of Dewing [7] by the factor:

$$K = \frac{K'}{X_{KCl}^{\circ}} = 2.6 \times K'$$

K' for the system NaCl – $AlCl_3$ was found to be 10^{-2}, and for KCl – $AlCl_3$ we now calculate $K = 0.8 \times 10^{-2}$. We see hence that the dissociation constant of $Al_2Cl_7^-$ is quite invariant to the change of cation from Na^+ to K^+, and both

results differ substantially from the K calculated by Morrey and Moore,[5] *viz.* 3×10^{-11}.

Equilibrium calculations have also been performed assuming $\delta\bar{\alpha}/\delta r$ to be equal for $AlCl_4^-$ and $Al_2Cl_7^-$ and using the formula of Chantry and Plane.[40] $\bar{\alpha}$ is the mean molecular polarizability and r the Al – Cl stretching valence coordinate. This method is, however, very sensitive to small variations in the L-matrix, and a consistent K was not obtained.

Table 8. The stoichiometric equilibrium constant K for the dissociation $2\,Al_2Cl_7^- = 2\,AlCl_4^- + Al_2Cl_6$ and number of mol per 1 mol of mixture present of each species at 170 – 240°C.

Mol% $AlCl_3$	$P = \frac{n_{Al_2Cl_7^-}}{n_{AlCl_4^-}}$	$n_{Al_2Cl_7^-}$	$n_{AlCl_4^-}$	$n_{Al_2Cl_6}$	K
58	0.60	0.16	0.26	0.00	$(8 \pm 4) \times 10^{-3}$
66	3.5	0.26	0.08	0.03	

The small value of the equilibrium constant for the dissociation of $Al_2Cl_7^-$, $K = 0.008$ (Table 8) means that $Al_2Cl_7^-$ thermodynamically is a stable species and that the equilibria (1) and (2) may be treated as successive equilibria. $Al_2Cl_7^-$ is then thermodynamically postulated to be the dominant Al-Cl species in the range $0.60 < X_{AlCl_3}^{\circ} < 0.80$. It is interesting to notice that the upper composition corresponds quite closely to the beginning immiscibility gap in the phase diagram.

CONCLUDING REMARKS

We are fully aware of the ambiguity of the species concept in melts where a solvent separating the species is lacking. We would, however, like to point out that we consider the present Raman work to build up a strong case for the species concept in $KCl - AlCl_3$ and $NaCl - AlCl_3$ melts. Both the work of Moore, Morrey and Voiland [4,5] on $U^{3+} - U$ distribution in $KCl - AlCl_3$, and Øye and Gruen's [6] study of Co^{2+} spectra in the same system were given natural explanations by assuming the $Al_2Cl_7^-$ to be present in addition to the more well established species $AlCl_4^-$. Øye and Gruen [8] pointed out that the vapour pressure data of Dewing[7] were most rationally explained by assuming the species $Al_2Cl_7^-$ to be present in the system $NaCl - AlCl_3$.

With respect to the Raman work, we would like to stress the fact that the shift in frequency for the vibrations of the postulated species $Al_2Cl_7^-$ is small when changing the composition from 58 to 66 mol%, and an increase in intensity is observed enabling us to calculate a reasonable equilibrium constant for the dissociation of $Al_2Cl_7^-$. Taking all important force constants directly from $AlCl_4^-$ a good fit both with respect to location and the polarizabilities of the vibrational frequencies was obtained without adjustments, using the D_{3d} model (Table 5).

The $AlCl_4^- - Al_2Cl_7^-$-species must also be expected to be an adequate model for mixtures rich in aluminium chloride with alkali chlorides heavier than KCl.

The existence of $Al_2Cl_7^-$ gives, in spite of no other examples known to the authors, an Al – Cl – Al single bridge, which must be expected to be very weak.

By increasing the ion potential of the cation in a molten $MeCl_x - AlCl_3$ mixture, the Me^{x+} ion will compete more effectively for the Cl^- ions relative to Al^{3+}. A gradual breakdown of the $Al_2Cl_7^-$ and possibly also of the $AlCl_4^-$ species is then expected. Work is now in progress to study the influence of the cation on the vibrational frequencies and to fill the gap to the state when a species concept breaks down and a more total description of the vibrational structure of the whole melt is useful, as put forward by Wilmshurst [41] and recently again by Angell *et al.*[42]

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