INFORMATION ON STRUCTURE AND BONDING OF MOLTEN CHLOROALUMINATES FROM INFRARED SPECTROSCOPY

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ABSTRACT

The theoretical and experimental basis for obtaining infrared emission and specular reflection spectra of molten salts in general, and particularly of chloroaluminates, has been described. New quantities, $e^*$ and $r^*$, which use a thick (opaque) melt as the reference, give excellent representations of the absorption bands. This method eliminates band splitting due to variations in surface reflectivity or as a result of a cold surface layer of the sample. From the recorded spectra it has been concluded that AlCl$_4$ acts as a tridentate ligand towards Mg$^{2+}$, but as a bidentate ligand towards Zn$^{2+}$. From the direct observation of anion-cation vibrations it has been shown that the interaction increases in the series Cs$^+<\text{Rb}^+<\text{K}^+<\text{Na}^+<\text{Li}^+<\text{Mg}^{2+}<\text{Zn}^{2+}$. Of the alkali ions, only lithium is able to stabilize a bent bridge for AlCl$_7^-$. Another effect of a highly polarizing counterion is a reduction in Cl-Al-Cl bending frequencies as a consequence of more ionic Al-Cl bonds.

INTRODUCTION

In order to obtain infrared (IR) spectra of molten salts, a number of techniques have been described in the literature. The methods include transmission, emission, attenuated total reflection and specular surface reflection. Nevertheless, practical problems due to the corrosive nature, vapour pressures and high melting points of many of the systems have made the construction of a standard experimental set-up difficult. Today, IR spectroscopy of melts has not yet reached the popularity of the much simpler Raman method. Some of the problems can be circumvented in emission or reflection spectroscopy as at least one of the IR windows can be avoided. In the pioneering work of Wilmshurst, however, it was found that band splitting occurred for intense bands presumably due to a too thick sample. We have seen the same effect both in emission and specular reflection. Fortunately, the distortions of the band profiles can be eliminated by using a thick, i.e., IR opaque, melt as the reference.

The emission/reflection technique has in this laboratory so far been applied to neutral and acidic mixtures of AlCl$_3$, with LiCl, NaCl, KCl, RbCl, CsCl, MgCl$_2$, MnCl$_2$, FeCl$_2$, CoCl$_2$, and...
ZnCl$_2$, NaAlOCl$_5$–NaAlCl$_4$, GaCl$_3$ with KCl and CsCl, InCl$_3$ with KCl and GaBr$_3$, and NaAlCl$_5$–NaAlOCl$_5$, GaCl$_3$ with KCl and CsCl, InCl$_3$ with KCl and GaBr$_3$, with RBBr. Addition of Cs$_2$O to acidic and basic melts close to the CsAlCl$_4$ composition and pure AlCl$_3$NH$_3$ also have been studied. It is the intention here to give a short summary of the experimental and theoretical basis for emission and specular reflection spectroscopy of thin films and to demonstrate the types of information that can be deduced from infrared spectroscopy of molten salts. Although the examples are from chloroaluminates, the principles are general.

**PRINCIPLE**

*Specular Reflection Spectroscopy.* The experimental set-up used in the present work consists schematically of a molten sample contained between a window and a reflecting backplate (Fig. 1). The sample property of interest is the internal transmittance (or permeability)

$$P_2 = \exp(-K_2d_2)$$

(1)

where $K_2$ is the absorption coefficient and $d_2$ the thickness.

![Fig. 1. Sample between a non-absorbing window and a reflecting backplate (r$_2$$^2$).](Image)

In reflection spectroscopy, the beam from the source passes the window and the sample before it is reflected at the backplate. The beam thus is transmitted through the sample twice before it reaches the detector. Therefore, the spectrum will be close to the standard transmittance spectrum of a slab with thickness $2d_2$. The spectral intensity of the sample ($I_2$) is measured with an unperturbed beam as reference. In practice, the reference spectrum ($I_0$) is measured using a cell without window and melt, but with a highly reflecting backplate. It turns out, however, that the reflectance obtained,

$$r = I_S/I_0$$

(2)

may give a poor representation of $P_2$ for strong bands. The resulting band distortions are a consequence of the experimental difficulties involved in obtaining a thin enough melt.
The origin of the problem can be understood by studying a thick melt, e.g., with a thickness of a few mm. Then the sample becomes opaque in the IR, and the beam is reflected from the window/sample interphase (giving the IOS spectrum) without ever reaching the backplate. The reflectance approaches the reflectivity (r') of the system and, taking multiple reflections in the window into account,

\[
r' = \frac{I_{OS}}{I_o} = \frac{r'_o + (1-r'_o)^2 r'_o p_1^2 + (1-r'_o)^2 r'_o p_1^2 r'_o r'_1 p_1^2 + (1-r'_o)^2 r'_o p_1^2 (r'_o r'_1 p_1^2)^2 + \ldots}{1 - r'_o r'_1 p_1^2}, \tag{3}
\]

See Fig. 1 for notations. By recognizing the geometric series and assuming that the window is non-absorbing (p_1 = 1), the reflectivity becomes

\[
r' = \frac{r'_o + r'_o - 2 r'_o r'_1}{1 - r'_o r'_1}. \tag{4}
\]

Note that if the window also is non-reflecting (r'_o = 0), then naturally r' = r'_1, the reflectivity of the sample. It was this last quantity that was measured in the work by Wilmshurst.

For strong bands, the reflectivity of the sample varies considerably in the frequency range corresponding to a vibrational transition. In intermediate cases where the sample is not completely opaque, the bands with the highest absorption coefficients reach the r' limit. Thus, distortions and false splittings will occur in the spectra.

For a non-absorbing window, it is seen from eq. (4) that r' is equal for both front and back reflection. Similar to eqs. (3) and (4), the reflectance r for the complete system in Fig. 1 thus may be expressed by

\[
r = \frac{(r' + r'_o p_2^2 - 2 r'_o r'_2 p_2^2)/(1 - r'_o r'_2 p_2^2)}, \tag{5}
\]

which rearranged yields

\[
r'_2 p_2^2 = \frac{r - r'}/(1 - 2 r' + r r'). \tag{6}
\]

Usually, r'_2 is close to unity for a polished metal backplate and therefore may be neglected. The last equation shows that the undistorted internal transmittance p_2 can be calculated by measuring the absolute spectra of a reasonably thin and an opaque melt relative to I_o. Fortunately, however, a simpler procedure that does not require absolute measurements may be employed in practice.

It has been shown experimentally that the new quantity
\[ r^* = 1 - r'/r = 1 - I_{OS}/I_S \]  

(7)

is a good approximation of the internal transmittance (eq. 6).\(^4,8\) A theoretical justification is provided elsewhere.\(^5\) Eq. (7) implies that the reference \( I_0 \) of eq. (2) is replaced by \( I_{OS} \) of a thick melt. Note that only the relative intensities of two single beam spectra determine the band shapes in \( r^* \). The \( 1^- \) term is included to obtain bands pointing downwards as in transmission spectroscopy.

For very thin melts, and generally for weak bands, \( r \) and \( r^* \) work equally well. That the unmodified reflectance spectrum is suitable for weak bands is demonstrated by assuming \( r' \ll r \) in eq. (6), giving \( r_{2D}^2 \approx r \).

**Emission Spectroscopy.** Infrared emission spectroscopy of thin melts is closely related to the reflection method. According to conservation of energy, a light flux which falls upon a body is divided into three fractions: reflectance, absorptance, and transmittance. Since the spectral energy absorbed is equal to the energy emitted, \( \varepsilon \), one has

\[ r + \varepsilon + t = 1. \]

(8)

No energy is transmitted through the system in the present set-up, and hence

\[ \varepsilon = 1 - r = (I_S - I_{BG})/(I_{BB} - I_{BG}) \]

(9)

and

\[ \varepsilon' = 1 - r' = (I_{OS} - I_{BG})/(I_{BB} - I_{BG}). \]

(10)

A blackbody at the same temperature as the melt provides the reference spectrum, \( I_{BB} \). In addition, it is usually necessary to correct for background radiation, \( I_{BG} \).

Spectral distortions are readily avoided if

\[ \varepsilon^* = \varepsilon'/\varepsilon = (I_S - I_{BG})/(I_{OS} - I_{BG}) \]

(11)

is used instead of \( \varepsilon \).\(^3\) An additional advantage of \( \varepsilon^* \) is that the blackbody reference is cancelled out and need not be measured.

Introduction of eqs. (9) and (10) into (6) yields an accurate
expression for the internal transmittance:

\[ \frac{r_{21}^2}{r_{21}^2} = \frac{(\varepsilon' - \varepsilon)}{(\varepsilon' - \varepsilon + \varepsilon\varepsilon')}, \]

now requiring the blackbody spectrum. It is seen that \( (1 - r_{21}^2) \approx \varepsilon \) for weak bands, \( \varepsilon' \gg \varepsilon \). Therefore, the standard emittance spectrum gives sufficient spectral information in this case. Further details have been reported previously.

The origin of the splitting of intense emission bands has variably been referred to as dispersion of the sample surface reflectivity, as discussed above, or as self-absorption of emitted radiation by cooler outer layers. We have found that, at least for our emission cell, mainly the former effect is operating. Fortunately, however, theoretical calculations of band shapes based on a damped harmonic oscillator model show that both types of distortions are eliminated by employing \( \varepsilon' \).

EXPERIMENTAL

The cell designed for chloroaluminate melts is shown in Figure 2. It consists of a steel cylinder (I) containing a gold plated support (J), a steel piston (B) and a sample container of nickel (D). The melt (M) is compressed against a 8 mm \( \Phi \), 1 mm thick diamond (type II a) window (G) by a movable piston of nickel (E). Sealing of the system is assured by using steel bolts (A) and a gold gasket (F) between the nickel container and the window. The materials are matched to give a slightly increased sealing pressure at higher temperatures. In recent experiments, the metal parts which come into contact with the melt have been gold plated. The cell design provides a good alignment of the sample container and a resulting
even pressure on the window, reducing the risk of breaking it. Further details, particularly regarding filling and measuring procedures, have been reported by Hvistendahl et al.\textsuperscript{8,12}

The following features of the cell are important for obtaining high-quality spectra of chloroaluminate melts:

a) A closed sample compartment which allows vapor pressures of several atmospheres and assures equilibrium conditions.

b) An available spectral region of $0 - 1800 \text{ cm}^{-1}$ (and $2100 \text{ cm}^{-1}$).

c) A limiting temperature as high as 600°C. At approximately this temperature the diamond turns opaque for infrared radiation.

d) High thermal conductivity of the window resulting in a uniform melt temperature.

e) The formation of thin melt films.

f) Inert conditions for most samples.

g) No spectral influence of the vapor phase.

h) Low background emittance.

The experiments have been performed with evacuable Bruker 114c and 113v Fourier transform spectrometers. In the emission experiments, the furnace was mounted on the standard optical bench of the source compartment. Only a flat mirror had to be added. Reflection required a special reflection unit constructed by Bruker (Fig. 3). The unit provides a focus above the sample compartment, suitable for a horizontal melt layer.

Fig. 3. Optical path in the FTIR sample chamber with the emission cell (E) employed for specular reflection spectroscopy of melts.

Choice of method depends on several factors. Apart from the need for a special optical unit in reflection spectroscopy, the

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reflecting backplate of the cell becomes an integral part of the optical path. Therefore, the cell position must be adjusted accurately, but it turns out that this adjustment is easy to perform. On the other hand, reflection has two major advantages compared to emission spectroscopy. First, the standard alignment of the instrument need not to be altered. The reflection unit is simply placed in the sample compartment. This system also reduces any damage to the instrument in case of leaks in the cell, because the sample will be well removed from the interferometer. Second, the energy of a high temperature source is employed instead of the sample itself, which is at a considerably lower temperature. The energy thus gained may be of particular importance in the lowest frequency range. Up to 80% of the full energy, i.e., without the reflection attachment, has been obtained in reflection experiments.

APPLICATIONS AND DISCUSSION

This section is focused on the special features of IR-spectroscopy and the different types of information that can be deduced, rather than giving a full description of the individual systems that have been investigated. Comparison is specifically made with the Raman technique.

![Emission spectra of molten KAICl₄ at 280°C](image)

**Fig. 4.** Emission spectra of molten KAICl₄. \( \varepsilon \): emittance; \( \varepsilon' \): emissivity (opaque sample); \( \varepsilon^* = \varepsilon / \varepsilon' \).}

**Removal of Band Distortions.** Fig. 4 shows emission spectra of molten KAICl₄ at 280°C. The spectrum depicts a clear asymmetric splitting around 500 cm⁻¹ due to a too thick sample. The asymmetry in
the distortion implies that reflectivity variations prevail over selfabsorption by cooler outer layers. It is evident from the figure that the emittance reaches the maximum level in the region 460 to 550 cm\(^{-1}\) where it follows the emissivity (\(\varepsilon^*\)) of an opaque sample. With the latter sample as the reference, the \(\varepsilon^*\) spectrum is obtained and the high-frequency shoulder disappears. Thus, it is essential to use \(\varepsilon^*\) (or \(r^*\)) to check shoulders and split bands. The resulting spectra may of course become flat at the top of the most intense peaks. This feature corresponds to the flat bottom of the transmission spectrum of a thick sample.

**IR vs. Raman.** During the 70's Raman spectroscopy became a standard method for structural investigations of molten salts, particularly for the identification of complex ions and other structural entities. In alkali chloride - aluminium chloride mixtures, the \(\text{Al}_2\text{Cl}_6^-\) ion and higher polymers have been recognized and approximate equilibrium calculations have been performed for the reaction

\[2 \text{Al}_2\text{Cl}_7^- = 2 \text{AlCl}^- + \text{Al}_2\text{Cl}_6^- \quad (13)\]

Cation-anion interactions have been inferred from the relative abundance of the chloroaluminate species \(\text{Al}_2\text{Cl}_6^-\), \(\text{Al}_2\text{Cl}_{10}^-\), \(\text{Al}_2\text{Cl}_7^-\) and \(\text{AlCl}_4^-\).

In order to obtain a more complete comprehension of the melt structure, it is important that the complementary IR technique is used in addition to Raman. Apart from giving a more detailed vibrational picture of the melt together with the Raman spectra, IR has several particular advantages:

- a) Only small sample amounts are needed and ultra-purity is not required (in Raman problems with fluorescence frequently occur). Attention, however, must be given to the homogeneity of the sample and possible composition changes due to vaporization.
- b) Coloured melts do not cause problems, cf. the investigation of \(\text{MnCl}_2\), \(\text{CoCl}_2\), and \(\text{FeCl}_2\) mixtures with \(\text{AlCl}_3\).
- c) Perturbation of high symmetry species may be detected by the activation of the totally symmetric stretching mode. This feature is demonstrated in Fig. 4 with the appearance of the \(\nu_1\) totally symmetric stretching mode of \(\text{AlCl}_4^-\) at 350 cm\(^{-1}\). For a perfect tetrahedron, this mode is inactive in the IR. Similar arguments are valid for most highly symmetric entities, e.g., \(\text{MX}_2\) (linear \(D_{\infty h}\) ), \(\text{MX}_3\) (planar \(D_{3h}\)), \(\text{MX}_4\) (tetrahedral \(T_d\) or planar \(D_4h\)), \(\text{MX}_5\) (trigonal bipyramidal \(D_3h\)), \(\text{MX}_6\) (octahedral \(O\)), tetragonally distorted octahedron \(D_{4h}\), or planar \(D_6h\) and \(\text{MX}_7\) (linear bridge \(D_3\), \(D_3h\) or \(D_{3d}\)). The detection of \(\nu_1\), however, does not tell anything about the nature or magnitude of the perturbation.
- d) Degenerate stretching modes of symmetric species give rise to intense bands in the infrared, as shown by the \(\nu_3\) band of \(\text{AlCl}_4^-\).
at ca. 490 cm\(^{-1}\) (Fig. 4). It follows that strong anion-cation interactions should be detected as descent in symmetry and band splitting.

e) Chemical bonds with a high degree of ionity give bands in the infrared spectra with reasonable intensities. An example is Al-O (and Al-N) bonds which clearly are seen in the infrared, but are not detected in Raman because the polarizability fluctuations involved are extremely small. Thus, apart from obtaining important structural information on oxide systems, a test of the preparational procedures automatically is performed. Strong oxide bands found at 680 and 800 cm\(^{-1}\) in pure NaAlCl\(_5\) and its mixtures with AlCl\(_3\) or NaAlCl\(_4\) have been attributed to a vibrating unit of the following type:

\[
\begin{array}{c}
\text{Al} \\
\text{O} \\
\text{Al} \\
\text{O} \\
\text{Al}
\end{array}
\]

The AlCl\(_4^–\) Unit. From Raman spectroscopy and other methods it is well known that aluminum is coordinated to four chlorine atoms in chloroaoluminate melts. An AlCl\(_4^–\) unit with tetrahedral symmetry has four fundamental vibrations, observed in Raman at 350 (\(v_1\), A\(_1\)), 122 (\(v_2\), E), 487 (\(v_3\), F\(_2\)) and 182 cm\(^{-1}\) (\(v_4\), F\(_1\)) for KAlCl\(_4\). As demonstrated by the correlation diagram in Table 1, only \(v_3\) and \(v_4\) are IR-active, although it has been mentioned that \(v_1\) is activated by perturbations.

Table 1. Perturbational splitting of the fundamental vibrations of AlCl\(_4^–\). In \(F_2\) only the splitting of \(v_3\) (487 cm\(^{-1}\)) is given.

| Compound | \(v_1\) | \(v_2\) | \(v_3\) | \(v_4\) |
|----------|---------|---------|---------|---------|
| Zn(AlCl\(_4\))\(_2\) | 344 A\(_1\) | 147 A\(_1\) | 110 A\(_2\) | 482 A\(_1\) |
| KAlCl\(_4\) | 350 A\(_1\) | 122 E | 487 F\(_2\) | 182 F\(_1\) |
| Mg(AlCl\(_4\))\(_2\) | 341 A\(_1\) | 122 E | 573 A\(_1\) | 452 E |

--- IR activity --- Raman activity

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The perturbations may be due to fluctuations in the melt structure in general or to more localized cation-anion interactions. In Table 1 it is shown that the triply degenerate $\nu_3$ vibration of AlCl$_4^-$ (T$_d$) is split into three components when it is a bidentate ligand (C$^{2v}$) and into two components when it is a tridentate ligand (C$^{3v}$). These two cases are found for Zn(AlCl)$_4$ and Mg(AlCl)$_4$ melts, respectively. In Fig. 5 the vibrational spectra of ZnAl$_2$Cl$_8$ are compared. The three components of $\nu_3$ (P$_2$) are very distinct in the IR-spectrum, whereas the Raman spectrum shows a strong resemblance with a nonreacting mixture of ZnCl$_2$ and Al$_2$Cl$_6$. This artifact comes from the vibrational similarity of Al$_2$Cl$_6$ with the more likely structure:

\[
\begin{array}{c}
\text{Cl} \\
\text{Al} \\
\text{Cl} \\
\end{array}
\begin{array}{c}
\text{Cl} \\
\text{Zn} \\
\text{Cl} \\
\end{array}
\begin{array}{c}
\text{Cl} \\
\text{Al} \\
\text{Cl} \\
\end{array}
\]

Thus, it clearly is demonstrated that infrared spectroscopy in addition to Raman is necessary in order to deduce the correct melt structure.

Fig. 6 shows the resemblance between molten and solid MgAl$_2$Cl$_8$, both having tridentate AlCl$_4$ towards Mg$^{2+}$. The weak band at ca. 680 cm$^{-1}$ indicates trace amounts of oxide impurities.
The Al\textsuperscript{2+}Cl\textsuperscript{7-} Unit. Raman spectroscopy has verified the existence of Al\textsubscript{2}Cl\textsubscript{7} in chloroaluminate melts as a chlorine bridged ion. There are, however, discussions as to the structure, particularly regarding a linear or bent Al-Cl-Al bridge. With basis in the available melt data for KAl\textsubscript{2}Cl\textsubscript{7}, it has been possible to perform an assignment of the fundamental modes in terms of a staggered linear configuration (Table 2). The low number of observed bands points to a high symmetry. However, Fig. 7 shows that as the polarizing power of the cation increases, \( \nu \)\textsubscript{11} (E\textsubscript{g}) is split into two components. Since Li is not able to induce a similar band separation in LiAlCl\textsubscript{4}, we conclude that the splitting is due to the formation of a stable bent bridge only for LiAl\textsubscript{2}Cl\textsubscript{7} and Mg(Al\textsubscript{2}Cl\textsubscript{7})\textsubscript{2}. (The splitting for Mg(Al\textsubscript{2}Cl\textsubscript{7})\textsubscript{2} in the figure is somewhat fortuitous as the melt contains a considerable amount of AlCl\textsubscript{4} due to evaporation of Al\textsubscript{2}Cl\textsubscript{6} in the sample container).

Table 2. Vibrational fundamentals of KAl\textsubscript{2}Cl\textsubscript{7} in terms of D\textsubscript{3d} structure.

|        | \( \nu \) (cm\textsuperscript{-1}) | Mode          | \( \nu \) | Symmetry     |
|--------|----------------------------------|---------------|------------|--------------|
| Al\textsubscript{2}Cl\textsubscript{7} | 432    | AlCl\textsubscript{3} stretch | E\textsubscript{g} | AlCl\textsubscript{3} stretch |
|        | 311    | AlCl\textsubscript{3} stretch | \( \nu \) | 97 AlCl\textsubscript{3} def. |
|        | 161    | AlCl\textsubscript{3} def. | \( \nu \) | 10 skel.bend |
|        | i.a.   | torsion | \( \nu \) | 525 AlCl\textsubscript{3} stretch |
| A\textsubscript{1u} | 318    | AlCl\textsubscript{3} stretch | E\textsubscript{u} | \( \nu \) | 158 AlCl\textsubscript{3} def. |
|        | 331    | AlCl\textsubscript{3} stretch | \( \nu \) | 12 skel.bend |
|        | 179    | AlCl\textsubscript{3} def. | \( \nu \) | 14 AlCl\textsubscript{3} AlCl\textsubscript{3} bend |

The infrared emission spectra of Al\textsubscript{2}Cl\textsubscript{6} and other dimeric aluminium halides are very similar in the liquid and gas phase. Neighbour interactions show up in a slight reduction in stretching frequencies, typically 12-14 cm\textsuperscript{-1} for terminal Al-Cl stretch.

It is worthwhile to compare the calculated stretching and bending force constants for the chloride, bromide and iodide. In Fig. 8 the ratio between a bending constant and the average of the stretching constants of the bonds forming the angle is plotted as a function of difference in Pauling's electronegativities. As might be expected, a more ionic bond gives a reduction in relative resistance against angle bending. A similar situation is found for LiAlCl\textsubscript{4}. Higher ionisity of the Al-Cl bond compared to the melts with larger alkali counterions, results in a reduction in the \( \nu \)\textsubscript{4} bending mode from ca. 180 cm\textsuperscript{-1} to 170 cm\textsuperscript{-1} for Li.
Fig. 7. IR spectra of molten $M(\text{Al}_2\text{Cl}_7)_n$.

Cation Coordination. Apart from giving rise to perturbations of the anion, cation-anion interactions in melts containing $\text{AlCl}_4$ can be observed directly as a broad band below 300 cm$^{-1}$, see Figs. 4, 5 and 6. The comparison with the solid state in Fig. 6 verifies that the 288 cm$^{-1}$ band of the melt indeed is an Mg-Cl vibration. This mode cannot be observed in Raman due to the high ionisity and consequently low polarizability variation during the vibration.

The results for different counterions are compared in Table 3. Calculations of the force constants are for an antisymmetric stretching mode employing the formula (high and low frequency separation)
where $\alpha$ is the ligand-cation-ligand angle between opposite cation-ligand bonds. Tetrahedral geometry and an effective ligand mass of Cl + Al were used for all melts. Introducing different coordination numbers for the cations enhance the trend in the force constant. It can be concluded that the $M\text{-AlCl}_4^-$ frequency shift is not only a mass effect, but is a genuine consequence of the variations in polarizing power.

As the alkali melts may be regarded as ionic $\text{Alk}^+\text{-AlCl}_4^-$ systems, the energy well that determines the force constant may be approximated by a Born type lattice energy expression:

$$\frac{\delta^2U}{\delta r^2} = 4.04 \left(n' - 1\right)/r^3$$

and

$$f_{\text{Alk-Cl}} = \frac{\delta^2U}{\delta r^2}/n$$

when an average Madelung constant of 1.75 is introduced, $n'$ is the exponent in the repulsion term (taken from the pure alkali chlorides) and $n$ is the number of Alk-Cl bonds (taken as 4). The derived anion-cation distances are included in Table 3. Subtracting the cation radii from crystal structure determinations of $\text{AlkAlCl}_4$ yields remarkably constant and reasonable values for the $\text{AlCl}_4^-$ dimension.

Table 3. Cation-anion frequencies, force constants and distances for $M\text{-AlCl}_4^-$ melts.

| Melt       | Frequency ($\text{cm}^{-1}$) | $f$ (mdyn/Å) | $r_{M\text{-AlCl}_4}$ (Å) | $r_{\text{AlCl}_4^-}$ (Å) |
|------------|-----------------------------|--------------|--------------------------|--------------------------|
| Zn(AlCl$_4$)$_2$ | 286                        | 1.324        | 2.92                     | 2.21                     |
| Mg(AlCl$_4$)$_2$ | 288                        | 0.690        | 3.63                     | 2.59                     |
| LiAlCl$_4$ | 300                        | 0.253        | 3.82                     | 2.37                     |
| NaAlCl$_4$ | 140                        | 0.156        | 3.97                     | 2.34                     |
| KAlCl$_4$ | 108                        | 0.137        | 4.71                     | 2.87                     |
| RbAlCl$_4$ | 86                         | 0.138        |                         |                          |
| CsAlCl$_4$ | 64                         | 0.093        |                         |                          |

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