A spectroscopic and computational study of Al(III) complexes in cryolite melts: Effect of cation nature

Renat R. Nazmutdinov, Tamara T. Zinkicheva, Sergey Yu. Vassiliev, Dmitrii V. Glukhov, Galina A. Tsirlina, Michael Probst

Abstract

Lithium, sodium and potassium cryolite melts are probed by Raman spectroscopy in a wide range of the melt composition. The experimental data demonstrate a slight red shift of main peaks and a decrease of their half-widths in the row Li⁺, Na⁺, K⁺. Quantum chemical modelling of the systems is performed at the density functional theory level. The ionic environment is found to play a crucial role in the energy of fluorocomplexes. Potential energy surfaces describing the formation/dissociation of certain complex species, as well as model Raman spectra are constructed and compared with those obtained recently for sodium containing cryolite melts (R.R. Nazmutdinov, et al., Spectrochim, Acta A 75 (2010) 1244.). The calculations show that the cation nature affects the geometry of the ionic associates as well as the equilibrium and kinetics of the complexation processes. This enables to interpret both original experimental data and those reported in literature.

1. Introduction

The effect of alkali cation nature on the properties of fluoroaluminate melts AlF₃ + MF (M = Li, Na, or K) is an important problem related directly to industrial aluminum electrolysis. This problem was repeatedly addressed at thermodynamical and spectroscopic levels (see Ref. [1] for review), mostly to understand the effects of LiF additives on cryolite properties. LiF is a typical minor component of sodium-based melts used in order to increase their conductivity. Simultaneously it affects melting temperature, vapour pressure, surface tension and alumina solubility. Some data on the influence of lithium ions on sodium intercalation and (feebly) on overvoltage values for both cathodic alumina reduction, and anodic carbon oxidation processes were reported as well. Later an obvious interest in KF additives, as well as in potassium-based fluoroaluminate melts arose due to the problem of low-temperature aluminum production. This important issue should be regarded in connection with a search for an ‘inert’ (low-consumable) anode material, because the melt temperature plays a major role in anode degradation, and acidic potassium fluoroaluminates provide the lowest possible temperature [2]. A deeper insight into melt ionic composition is expected to be helpful to balance useful and harmful effects of additives by combining some of them.

The practical challenges clearly determine the accents and target settings for laboratory research. A number of experimental studies were performed by Raman spectroscopy for molten mixtures (mostly fluoroaluminates with FLiNaK, CsF–KF and NaF–KF eutectics) [3–6]. The results of other studies (where the effect of different cations was addressed separately) have been reported in Refs. [7–11] (Raman spectroscopy) and [12,13] (thermodynamical analysis). Most of the systematic data on cation effects are still available only for rather high cryolite ratios (CR)¹ of ca. 2–3, close to the values typical for industrial scale electrolysis. A thorough investigation of the interplay between CR and cation nature effects is, therefore, a topical issue.

Experimental data obtained for fluoroaluminate melts by Raman spectroscopy are usually discussed using language adopted from coordination chemistry, i.e. the formation of different Al(III) fluoro complexes (including polymeric forms) is assumed. That is why a quantum chemical modelling of fluoroaluminates is very useful to facilitate the interpretation of experimental spectra. Computational approaches at molecular level provide detailed information on the geometry and electronic structure of certain species existing in the melt; ionic equilibria in wide CR intervals and complexation kinetics can be investigated as well. Only a few attempts were made so far to model alkali cation effect on molecular

¹ The cryolite ratio is usually defined as follows [1]: CR = n(XF)/n(AlF₃), where X = Li, Na and K; n notes the number of moles.
structure of cryolite melts considering small neutral associates (see, e.g., Refs. [14–17]). The level of these studies was restricted to ab initio SCF [14] and density functional theory (DFT) [15], Akdeniz et al. [16,17] have performed molecular mechanics calculations using a set of specially devised pair potentials. Raman spectroscopy forms a natural link between molecular modelling and the prediction of microscopic properties of melts, as calculated spectra can be employed to verify model results. In our previous communication [18] we have reported some results on a combined experimental and computational study of sodium cryolite in 1–3 CR intervals, in order to demonstrate the possibilities of such an approach. In what follows we present experimental Raman spectra for lithium and potassium cryolites in the same range and discuss the reasons of cation-dependent spectral behaviour on the basis of molecular-level treatment of assumed equilibria.

This paper is organized as follows. Experimental and computational details are given in Section 2. The experimental Raman spectra and results of quantum chemical modelling are reported in Section 3. Concluding remarks are listed in Section 4.

2. Experimental and computational details

Spectroscopic measurements were performed using a fiber-optics Raman spectrometer RamanRXN1 with a long-focal-length optics (work distance is 430 mm). The laser wavelength was 532 nm. The reagents (X2AlF6 and AlF3 of ‘pure’ grade, and XF (X = Li, K) of ‘extra pure’ grade, ChimMed, Russia) were used to prepare melts at different temperatures (see Table 1). For XF containing crystal-pure grade, the preliminary heat treatment in platinum crucible at 500°C was applied. This procedure, as well as any additional purification of all reagents, demonstrated no effect on the spectra. We can assume that all volatile impurities could be deleted in the course of melting, and the traces of other (less volatile) impurities could not affect spectral behavior of predominating fluoroaluminate components.

The water IR filter prevented the spectrometer optics from IR radiation and destructive vapor of the melt. Test measurements in one and the same melt at different temperatures showed that overheat of 100 grades reckoned from the melting temperature does change slightly the form and ratios of peaks. For a quantitative analysis of spectra we employed a deconvolution of the experimental Raman spectra using a set of specially devised pair potentials. Raman spectroscopy forms a natural link between molecular modelling and the prediction of microscopic properties of melts, as calculated spectra can be employed to verify model results. In our previous communication [18] we have reported some results on a combined experimental and computational study of sodium cryolite in 1–3 CR intervals, in order to demonstrate the possibilities of such an approach. In what follows we present experimental Raman spectra for lithium and potassium cryolites in the same range and discuss the reasons of cation-dependent spectral behaviour on the basis of molecular-level treatment of assumed equilibria.

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The water IR filter prevented the spectrometer optics from IR radiation and destructive vapor of the melt. Test measurements in one and the same melt at different temperatures showed that overheat of 100 grades reckoned from the melting temperature does change slightly the form and ratios of peaks. For a quantitative analysis of spectra we employed a deconvolution of the experimental Raman spectra (Gaussian-Lorendzian fit, ThermoGrams/Al 8.0 software). The accuracy of band maxima determination is strongly dependent on the degree of bands overlap. Namely, for a separate band in the vicinity of 620 cm−1 this accuracy is surely below 1 cm−1. For two other bands, the accuracy is estimated as ca. 5 cm−1. The shift of bands resulting from overheat never exceeded 1–2 cm−1, i.e. it is comparable with the accuracy of determination of maxima positions.

For ca. 10 g portions of melt and ca. 4 cm2 area of melt/air interface, changes of melt composition with time (induced by evaporation) were not drastic. This can be concluded from comparison of spectra registered subsequently with 10 min long intervals (at least three spectra were collected for each sample). Typical time interval between temperature stabilization (after melting) and registration of spectra never exceeded 20 min. The changes of spectra with time (if any) were negligible as compared to observed CR effects. To say more quantitatively, the intensity of the most characteristic band at 620 cm−1 decreased for <5% after 1 h.

Other pertinent details of experimental setup can be found in [18,19].

The quantum chemical calculations were performed at the DFT level by using the B3LYP hybrid functional as implemented in the Gaussian 03 program package [20]. Our calculations are related to neutral ensembles, with the charge excess of anionic Al(III) complexes compensated by the cations. We thus assume that the formed ion pairs (small clusters) address the short – range effects of the ionic environment (a similar model was used in [18]). For the description of Al, F, Li and K atoms the standard triple-zeta 6-311G valence basis set augmented by polarization (d) functions was employed. The free energy of the model processes was computed taking into account vibrational, translational, and rotational contributions. The free energy calculations of model processes were performed at a given temperature. Therefore, the temperature dependences of enthalpy and entropy terms were directly addressed. The long-range medium effects were taken into account in terms of the continuum Conductor-like Screening Model (COSMO) [21]. When estimating equilibrium constants, we used a high value of ca 500 for the dielectric constant in order to model the strong Coulomb screening present by the dense ionic melt.

In calculations of clusters of larger size all electrons of Li and F atoms were described using the Dunning/Huzinaga valence double-zeta basis set. A basis set of DZ quality was employed to describe the valence electrons of Al, K and Na atoms, whereas their inner electrons were replaced by the effective core potentials developed by Hay and Wadt [22]. The geometries of the Al(III) complexes were fully optimised in the gas phase without symmetry constraints. We used the program ChemCraft [23] for the visualisation of model Raman spectra; the calculated frequencies were not scaled.

3. Results and discussion

The experimental Raman spectra are shown in Fig. 1. Deconvolution of the spectra for potassium and especially lithium melts is ambiguous, thus in contrast to sodium melts [18], any quantitative analysis of equilibrium constants is impossible. We can maintain, however, the most important qualitative trends: (1) a slight shift of νmax towards lower values takes place in a sequence Li...Na...K, i.e. the energy of Al-F vibrations tends to decrease in this sequence; (2) band width ∆ν decreases in the same sequence. A conclusion similar to (2) was made earlier in [9,11]. One should mention that even approximate fitting is enough to determine the frequencies for the maxima of the principle bands with high accuracy. For assignment of these three bands (Table 2) we used the same approach as applied earlier for sodium melts [18].

It also follows from our approximate fitting of potassium melt data that K+ cations favour the stability of AlF3 complexes; their concentration starts increase at higher CR as compared with decrease in sodium melt. The maximum of AlF32− concentration, therefore, appears to be lower in the presence of potassium. This observation agrees qualitatively with results reported in [7].

As a first step in quantum chemical modelling we considered monomeric forms of complexes AlF3−, AlF32− and AlF63− with alkali metal cations to keep model systems neutral. Two local energy minima were found for AlF3−-X+(X = Li and K), where the cation X is projected either to the face of tetrahedral Al(III) complex (i), or to its ridge (ii). The geometrical structures are shown in Fig. 2. The same conformations were found previously for an AlF4− · Na+ pair [18]. The free energy of (i) =⇒ (ii) process corrected for medium effects (∆G(0)/(0)) was calculated to be −7.9, −5 [18].

Table 1

<table>
<thead>
<tr>
<th>CR</th>
<th>Li⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1219</td>
<td>1143</td>
<td>1075</td>
</tr>
<tr>
<td>2</td>
<td>1013</td>
<td>1233</td>
<td>1218</td>
</tr>
<tr>
<td>3</td>
<td>1055</td>
<td>1303</td>
<td>1253</td>
</tr>
</tbody>
</table>
2.1 kcal mol$^{-1}$ for Li, Na, K, respectively. Using $\Delta G_{i/i}$ values we estimated the equilibrium constant:

$$K_{eq} = \exp(-\Delta G_{i/i}/k_B T).$$

One can obtain the following sequence for the $K_{eq}$ values using the data presented in Table 1: 27–52 (Li); 6.9–9.1 (Na); 2.2–2.5 (K); thus the stability of form (i) increases in row Li$^+$ < Na$^+$ < K$^+$. The high probability of "ridge" orientation for AlF$_4^-$ - Li$^+$ associate was also maintained in [16]. Calculated Raman spectra$^2$ are shown in Fig. 2; it can be seen that structure (i) yields the best agreement with the positions of main peaks for all cations.

The position of main peaks of the model Raman spectra for the structure (i) (see the data for tetrafluoroaluminate in Table 2) is in a good agreement both with experimental data and with computational predictions reported earlier. For conformation (ii) the main peaks are shifted to the left by 31, 18 and 12 cm$^{-1}$, see also [18]. A competition between two different structures might result in additional tailing the main peak.

Further we investigated a five-coordinated Al(III) fluorocomplex paired with two Li$^+$ or K$^+$ cations. Three different conformations (local energy minima) were found for the associates with Li$^+$ ions, (iii), (iv) and (vi), while only one stable structure is observed for AlF$_5^{2-}$·2K$^+$ (v). According to our previous analysis three local structures exist for a AlF$_5^{2-}$·2Na$^+$, namely (iii), (iv) and (v). In conformation (iii) AlF$_5^{2-}$ forms a trigonal bipyramid, where the cations are located in its face and edge. Structure (iv) looks like a tetragonal pyramid with the cations positioned on its ridges. In conformation (v) the fluoromaluminate also forms a tetragonal pyramid but the cations occupy its faces. Last

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Table 2

<table>
<thead>
<tr>
<th>Single forms (calc.)</th>
<th>Calculation</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li$^+$</td>
<td>Na$^+$ [18]</td>
</tr>
<tr>
<td>AlF$_4^-$</td>
<td>615</td>
<td>597, 626 (613–624)</td>
</tr>
<tr>
<td>AlF$_5^{2-}$</td>
<td>528</td>
<td>532, 537, 552 (528)</td>
</tr>
<tr>
<td>AlF$_6^{3-}$</td>
<td>447</td>
<td>489, 555, 525 (496)</td>
</tr>
</tbody>
</table>

*a* Ref. [17].

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Further...
structure (vi) looks like a trigonal bipyramid and two Li⁺ cations reside on its ridges.

For Li⁺ containing associates our estimations give values of $-5.5$ to $-0.9$ kcal mol⁻¹ for processes (iii) $\leftrightarrow$ (vi) and (iv) $\leftrightarrow$ (vi), respectively. The calculated equilibrium constants range from 9.9–15.5 to 1.44–1.55, so that conformations (vi) and (iv) were found to be the most probable for AlF₅⁻ – 2Li⁺. Earlier we showed [18] that conformations (iii), (iv) and (vi) are strongly competitive for AlF₅⁻ – 2Na⁺ associate; the equilibrium constants amount to 2.0–2.2 for (iii) $\leftrightarrow$ (vi) and ca 1 for (iv) $\leftrightarrow$ (vi) (see Ref. [18] for details). These examples clearly demonstrate the cation effect on the structure of AlF₅⁻ - 2X⁺. The lithium cation favours the “ridge” orientation of associates, while only the “face” orientation is the most probable for potassium ions.

Model Raman spectra for all five-coordinated Al(III) forms are exhibited in Fig. 3 and the symmetric stretching frequencies are presented in Table 2. As can be seen from the Table, the results obtained for structure (v) (Na⁺ and K⁺ associates) agree very good both with experimental data, and with the computational predictions by Akdeniz et al. [17]. The existence of small peaks between 300 and 400 cm⁻¹ also agrees qualitatively with experiment (see Fig. 1). Note that structures (iii), (iv) for AlF₅⁻ – 2Li⁺ (see Fig. 3) and (iv), (vi) for AlF₅⁻ – 2Na⁺ [18] result in very similar Raman spectra, which are difficult to distinguish.

Finally, we modelled ionic associates with a six-coordinated Al(III) fluorocomplex, which reveal two different conformations: (vii) and (viii). Combining our results with those obtained previously [18] one can state that structure (vii) (where three cations are coordinated through the octahedron faces) was found only for Li⁺ and Na⁺ associates. In contrast, structure (viii) with a mixed “face”-“ridge” coordination of cations is observed for Li⁺, Na⁺ and K⁺. A structure similar to (viii) was also found in work [15]. According to our estimations, conformations (vii) and (viii) are rather competitive but yield different model Raman spectra (see Fig. 4).

It can be seen from Table 2 that the computational results obtained for six-coordinated fluorolamines (except for AlF₅⁻ – 3Li⁺) agree worse with experimental data as compared with the other Al(III) complexes. This might be attributed to a more crucial influence of medium effects for highly charged species, which cannot be properly addressed when dealing with small associate species (see also a pertinent discussion in Ref. [18]).

A deeper insight into the behaviour of Al(III) fluorocomplexes in cryolite melts can be gained from analysis of calculated potential energy surfaces (PES). The PES describing the model process AlF₅⁻ $\leftrightarrow$ AlF₅²⁻ + F⁻ is presented in Fig. 5. One of the Al–F bond lengths was taken as an effective coordinate, which was scanned, while the other degrees of freedom were fully optimized at each step. The energy profile has three local minima separated by barriers. For K⁺ cations both (ii) and (iii) minima correspond to different conformations of penta-coordinated Al(III) fluorocomplexes (Fig. 5b); note that only one stable conformation was predicted earlier (see Fig. 3b) using less number of K⁺ and F⁻ ions in molecular cluster. In opposite, although for Li⁺ associates minimum (ii) (Fig. 5a) relates to a certain conformation of AlF₅²⁻ from those found previously (see Fig. 3a), minimum (iii) describes the formation of AlF₅⁻ (Fig. 5a). If we start from structure (viii) for K⁺ associates, the both minima on the energy surface, (ii) and (iii) are broad and correspond to different conformations of AlF₅⁻ (Fig. 5b); their energy is higher as compared with the first minimum. If the other conformation of K⁺[AlF₄⁻] (structure (vii), Fig. 5b) is used as a starting point to construct the second PES, a molecular structure corresponding to the third minimum (iii) looks very similar to that found at the previous step. Although for this PES the energies of minimum (i) and minimum (iii) are close, the barrier is significantly higher than that calculated for the first PES (Fig. 5b). The PES modeling equilibrium AlF₅⁻ $\leftrightarrow$ AlF₅⁻ + F⁻ (see Fig. 6) has a more simple form and reveals only two local minima. Note that minima (i) and (ii) relate to mixed associates of AlF₅⁻ and AlF₅⁻ with cations and fluoride ions. After Raman spectra for these associates were computed additionally, in order to check the identity of fluoroaluminates, we found that calculated band positions are close to those presented in Table 2.

The potential energy surfaces can be used to estimate the equilibrium constants (see details in [18]²); the results of our calculations are summarized in Tables 3 and 4. One can conclude that the stability of AlF₅⁻ noticeably increases in row Li⁺–Na⁺–K⁺, which confirms the results of work [12]. In contrast, the stability of AlF₅⁻ increases slightly when going from Li⁺ to K⁺ but has a maximum corresponding to sodium cations. Note that we could not reproduce the effect of K⁺ cations on stabilization of less coordinated Al(III) complexes observed in experiment (see the beginning of Section III).

We also performed DFT calculations for neutral clusters of larger size, in order to address environmental effects on the structure of Al(III) fluorocomplexes in a more reliable way. The stoichiometry and composition of clusters modelling cryolite melts with three different alkali cations and CR values are presented in Table 5; the geometry of clusters was fully optimized (see Tables 1S, 2S, 3S). The initial geometry of systems was chosen from analysis of a number of test calculations at the DFT and semiempirical AM1 level. The choice of geometry rested mostly on chemical intuition, i.e. qualitative reproducing changes in coordination numbers of Al atoms in clusters corresponding to different CR values. Of course, ideally many starting configurations should be optimized until a complete set of minima on the very complicated potential energy hypersurface is identified and we are aware of the fact that for certain clusters only one local minimum was found. This, however, is presently impractical due to the size of the systems, and we believe

² Free energies of complex forms corresponding to different minima on the PES were calculated; the medium effect was addressed by using COSMO.

**Fig. 3.** Model Raman spectra calculated for different conformations of AlF₅⁻ – 2Li⁺ (a) and AlF₅⁻ – 2K⁺ (b).
Fig. 4. Model Raman spectra calculated for different conformations of $\text{AlF}_3^-\cdot3\text{Li}^+$ (a) and $\text{AlF}_2^-\cdot3\text{K}^+$ (b).

Fig. 5. Potential energy surfaces describing the equilibrium $\text{AlF}_3^-\cdot3\text{Li}^+$ $\leftrightarrow$ $\text{AlF}_2^+$ $+\text{F}^-$ in $\text{Li}^+$ (a) and $\text{AlF}_3^-\cdot3\text{K}^+$ $\leftrightarrow$ $\text{AlF}_2^+$ $+\text{F}^-$ in $\text{K}^+$ (b) containing associates (the total energy in the deepest minimum is taken as zero energy; the calculated points are connected by a spline function). Black circles (b) refer to the second PES, when structure (viii) is used as a starting point.

Fig. 6. Potential energy surfaces describing the equilibrium $\text{AlF}_2^-$ $\leftrightarrow$ $\text{AlF}_2^+$ $+\text{F}^-$ in $\text{Li}^+$ (a) and $\text{K}^+$ (b) containing associates (the total energy in the deepest minimum is taken as zero energy; the calculated points are connected by a spline function).

Table 3
Equilibrium constants calculated for some model processes in $\text{AlF}_3^+\text{LiF}$ melts at three different CR values.

<table>
<thead>
<tr>
<th>CR</th>
<th>$(T = 1219 \text{ K})$</th>
<th>$(T = 1013 \text{ K})$</th>
<th>$(T = 1055 \text{ K})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{AlF}_3^+\cdot3\text{Li}^+(\text{min I}) $ $\leftrightarrow$ $\text{AlF}_2^+\cdot3\text{Li}^-\cdot\text{F}(\text{min II})$</td>
<td>1.9 (0.214)$\text{a}$ $0.6^*$</td>
<td>2.0 (0.302)$\text{b}$</td>
<td>2.0 (0.29)$\text{b}$ $0.16^*$</td>
</tr>
<tr>
<td>$\text{AlF}_3^+\cdot2\text{Li}^+(\text{min I}) $ $\leftrightarrow$ $\text{AlF}_2^-\cdot2\text{Li}^-\cdot\text{F}(\text{min II})$</td>
<td>1.9 (0.103)$\text{a}$ $1.1^*$</td>
<td>1.95 (0.125)$\text{b}$</td>
<td>1.97 (0.125)$\text{b}$ $0.53^*$</td>
</tr>
</tbody>
</table>

$\text{a}$ Equilibrium constants for sodium containing cryolite melts calculated in Ref. [18] using the same model as in the present work and at the temperatures listed in Table 1.

$\text{b}$ Fig. 5a.

$\text{c}$ Fig. 6a.

$\text{d}$ Estimates for lithium containing cryolite melt [12].

$\text{e}$ Estimates for sodium containing cryolite melt [12].
**Table 4**

Equilibrium constants calculated for some model processes in AlF₃ × KF melts at three different CR values.

<table>
<thead>
<tr>
<th>CR</th>
<th>(T = 1075 K)</th>
<th>(T = 1218 K)</th>
<th>(T = 1253 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlF₃⁴⁻</td>
<td>3K⁺ (min I) → AlF₃⁵⁻ 3K⁺ F⁻ (min II)⁺</td>
<td>0.06</td>
<td>0.07</td>
</tr>
<tr>
<td>AlF₃⁵⁻</td>
<td>2K⁺ (min I) → AlF₄⁻ 2K⁺ F⁻ (min II)⁺</td>
<td>1.06</td>
<td>1.5</td>
</tr>
</tbody>
</table>

*Fig. 5b.*

**Table 5**

Stoichiometry and composition of clusters used in quantum chemical modeling of AlF₃ × XF melts.

<table>
<thead>
<tr>
<th>CR</th>
<th>Stoichiometry</th>
<th>Type and number of atoms</th>
<th>X = Li, Na, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10XF/10AlF₃</td>
<td>10 40 10 10</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>14XF/7AlF₃</td>
<td>7 35 14</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>18XF/6AlF₃</td>
<td>6 36 18</td>
<td></td>
</tr>
</tbody>
</table>

that nevertheless our limited approach might still be useful to investigate qualitative trends for the effects of CR and cation nature. For large ensembles of molecules on a rather flat energy surface (as it is typical for clusters and biomolecules) often the global minimum, although difficult to find, possesses properties similar to the ones of the large set of the nearby local ones.

The optimized geometry of one of the model clusters containing Li⁺ cations is shown in Fig. 7 as an example.

Model Raman spectra calculated for systems nXF/AlF₃ (X = Li, Na, K; n = 1–3) are displayed in Fig. 8. Ionic environmental effects (partially addressed in such clusters) provide a better description of tailing the peaks of experimental spectra, as compared with small associates. As can be seen from data collected in Table 6, the calculated positions of main band describe experimental spectra with the time scale of the Raman signal (0.1 ps), their half-width even decreases going to higher CR values in apparent contradiction with experiment. Note that the Δν values obtained using the cluster calculations originate from overlaps of different patterns in the model cluster and are, therefore, of static nature. One can assume, however, that the Δν values are determined by kinetics of elementary processes taking part in dynamic equilibria of various labile complex species, i.e. equilibria establishment becomes slower when going from Li- and Na- to K-containing melts. This assumption will be checked further.

Our analysis of the geometry of clusters predicts some important structural features. Particularly, a five-coordinated Al(III) complex is observed as a tetragonal pyramid: –Al–Al– forms linked through double bridged F ions and even a –Al–F–Al–F–Al– cyclic structure were found as well. The latter is distinguished only for a K⁺ containing cluster at CR = 2. One can maintain that the “polymerization” of Al(III) complexes increases in the row Li < Na < K. For example, the number of Al atoms forming a polymeric chain increases from 2 (Li⁺) to 6 (K⁺). Of course, this conclusion should be regarded as preliminary, because only MD simulations enable addressing such features of melts in a proper way. It is interesting to mention the appearance of “branched” tetranuclear bridged fluorooxaluminate complexes at CR = 1 and 3. Earlier the authors of Ref. [9] also concluded that K⁺ cations favour the stabilization of –Al–Al– dimers in comparison with Na⁺ containing cryolite melts. Averaged Al(III) coordination numbers, <n>, are collected in Table 7.

When increasing CR the following features are observed: (1) the growth of <n> and the number of free F⁻ ions; (2) decreasing the number of AlF₄⁻ complexes, till their practical disappearance at CR = 3 (the residual AlF₄⁻ cannot be noticed in the spectra because of low intensity); (3) increasing the <n> values in row Li–Na–K at a given CR (i.e. in this sequence the increase of Al(III) acidity takes place). The latter observation agrees with conclusion made by Roberts and Gilbert on the basis of analysis of experimental Raman spectra [9].

Using the calculated potential energy surfaces (Figs. 5 and 6) one can model the Al(III) complexation kinetics in molten cryolite as well. If the characteristic times of these processes are comparable (or less) with the time scale of the Raman signal (0.1 ps), their kinetics may affect Raman spectra observed in experiment. In the framework of transition state theory the rate constant (k) is defined as follows:

\[ k = v \exp \left( -\frac{\Delta E_a}{kT} \right), \]

where \( v \) is a frequency describing the Al–F bond vibration in the PES minima; \( \Delta E_a \) is the energy barrier.

Then the life time of certain complex form (\( \tau_c \)) can be readily estimated as \( \tau_c = k^{-1} \). One can assume using analogy with radio-spectroscopic methods [26] that the band half-width (Δν) is proportional to 1/\( \tau_c \). Taking the ν and ΔEₐ values obtained from the analysis of PESs (Figs. 5 and 6) and temperatures from Table 1 we estimated the life times for AlF₄⁻, AlF₅⁻, and AlF₆⁻ (see Table 8). The \( \tau_c \) values increase going from Li⁺ to K⁺, which is in accordance with the experimentally observed trend (decreasing Δν in this row). The \( \tau_c \) values decrease, however, in the same sequence. Another important observation is the high stability of tetrahedral complexes, i.e. their complexation kinetics does not affect most

![Fig. 7. Optimized geometry of a model cluster Li₁₈Al₆F₃₆ corresponding to CR = 3.](image-url)
likely the shape of Raman spectra. As the hexa- and penta-coordinated species are noticeably more labile, this may explain increasing \( \Delta v \) values with CR. In low CR interval another physical mechanism may be addressed as well. It follows from Table 1 that at CR = 1 the melting temperature decreases in the row Li > Na > K. According to theory developed in Ref. [25] \( \Delta v \approx \sqrt{T} \), which may explain additionally the cation effect on experimental spectra at acidic fluoroaluminate melts (see Table 6). Of course, this explanation is purely qualitative, as temperature effect predicts only 6% decreasing the \( \Delta v \) values when going from Li\(^+\) to K\(^+\).

4. Concluding remarks

We have reported experimental Raman spectra obtained for AlF\(_3\) + MF melts (M = Li and K) and compared these data with our previous results (spectra for M = Na [18]). Clear trends in the row Li\(^+\)–Na\(^+\)–K\(^+\) can be observed from a comparative analysis of the experimental data. The cation effect at molecular level on the structure of fluoroaluminates in the melt was addressed using DFT calculations of model clusters and constructing the potential energy surfaces; Raman spectra were calculated and compared with experimental data. Local minima on the energy surfaces are sensitive to the cluster size which is an obvious shortcoming of our approach; this can be overcome in molecular dynamics simulations of melts. We believe that such an approach is robust enough and can be employed to make useful predictions. It is significantly more difficult to estimate possible error bars of calculated model quantities as compared with the experimental data. Errors might result from several sources: computational level, size of clusters, continuum approach to describe medium effects. That is why the main accent of our modeling is put on qualitatively interesting aspects of the problem. As follows from the results of quantum chemical modeling, lithium, sodium and potassium cations entail a number of important differences in the geometry of ionic associates, equilibrium and kinetics of Al(III) complexation. This enables, in turn, to explain qualitatively the main trends in the experimental Raman spectra (band frequency shift and change of band half-width) in the sequence Li\(^+\)–Na\(^+\)–K\(^+\). The molecular nature of stabilization of less-coordinated Al(III) complex forms in K\(^+\) containing melts (observed in experiment) remains, however, a challenge for future studies. A tempting next step would be to devise a set of pair potentials from DFT calculations in order to use them in classical molecular dynamics (MD) simulations of the melts. Some results on MD simulations of cryolite melts have been reported recently [27–30]. Raman spectra were modeled as well [29,30]; the authors [29] addressed structure of bridged –Al–Al–dimers and lifetimes of fluoroaluminates. The molten cryolite was simulated, however, at a very limited number of CR values; no attempts were made so far to compute its ionic conductivity and to investigate the cation effect on the structure and dynamics of the melts with the help of MD simulations.

As for additional experimental support, it can follow from NMR data (see, e.g., Ref. [31]).

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**Table 6**

Experimental and calculated (in parentheses) bands position \( (v_{\text{max}}) \) and half-width \( (\Delta v) \).

<table>
<thead>
<tr>
<th>Cation</th>
<th>Li(^+)</th>
<th>Na(^+)</th>
<th>K(^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CR 1</td>
<td>625 (621)</td>
<td>55 (75)</td>
<td>620 (592)</td>
</tr>
<tr>
<td>CR 2</td>
<td>565 (587)</td>
<td>110 (65)</td>
<td>555 (567)</td>
</tr>
<tr>
<td>CR 3</td>
<td>525 (516)</td>
<td>110 (135)</td>
<td>520 (493)</td>
</tr>
</tbody>
</table>

---

**Table 7**

Averaged coordination number of Al atom in Al(III) fluorocomplexes \( <n_c> \) calculated using the optimized geometry of model clusters (see Table 5).

<table>
<thead>
<tr>
<th>Cation</th>
<th>Li(^+)</th>
<th>Na(^+)</th>
<th>K(^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CR 1</td>
<td>4.5</td>
<td>4.7</td>
<td>4.8</td>
</tr>
<tr>
<td>CR 2</td>
<td>4.7</td>
<td>4.9</td>
<td>5.3</td>
</tr>
<tr>
<td>CR 3</td>
<td>5.7</td>
<td>5.8</td>
<td>5.8</td>
</tr>
</tbody>
</table>

* This quantity is defined as follows: \( <n_c> = (4n[AlF\(_3\)] + 5n[MF\(_2\)] + 6n[AlF\(_4\)] + 138n[A]\)/N_{Al} \), where \( n \) is the number of a certain Al(III) complex; \( N_{Al} \) is the total number of Al atoms.

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**Table 8**

Frequency of the Al–F bond vibration in the PES local minima \( (\epsilon_i, \text{cm}^{-1}) \); the activation barriers \( (\Delta E_s, \text{kJ mol}^{-1}) \) and life times \( (\tau_L, \text{ps}) \).

<table>
<thead>
<tr>
<th>Cation</th>
<th>( (i) ) AlF(_3) + F(^-)</th>
<th>( (ii) ) AlF(_4) + F(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(^+) Figs. 5a, 6a</td>
<td>425 (158)</td>
<td>2.96 (5.78)</td>
</tr>
<tr>
<td>Na(^+) [18]</td>
<td>236 (122)</td>
<td>6.76 (2.87)</td>
</tr>
<tr>
<td>K(^+) Figs. 5b, 6b</td>
<td>187 (124)</td>
<td>7.78 (0.98)</td>
</tr>
</tbody>
</table>

* Calculated data characterizing the reverse model processes \( (i) \) and \( (ii) \) are given in parentheses; arrows indicate direct and reverse processes.
Acknowledgement

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemphys.2012.11.006.

References
