Ionic Interactions in Alkali – Aluminium Tetrafluoride Clusters

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Z. Naturforsch. **54 a,** 570–574 (1999); received August 20, 1999

Complex anion structures ($(AlF_4)^-$, $(AlF_5)^{2-}$ and $(AlF_6)^{3-}$) coexist in liquid mixtures of aluminium trifluoride and alkali fluorides in composition-dependent relative concentrations and are known to interact with the alkali counterions. We present a comparative study of the static and vibrational structures of $MAlF_4$ molecules (with M = any alkali), with the aim of developing and testing a refined model of the ionic interactions for applications to the M-Al fluoride mixtures. We find that, whereas an edge-bridged coordination is strongly favoured for Li in $LiAlF_4$, edge-bridging and face-bridging of the alkali ion become energetically equivalent as one moves from Na to the heavier alkalis. This result is sensitive to the inclusion of alkali polarizability and may be interpreted as implying (for M = K, Rb or Cs) almost free relative rotations of the M^+ and $(AlF_4)^-$ partners at temperatures of relevance to experiment. The consistency of such a viewpoint with electron diffraction data on vapours and with Raman spectra on melts is discussed.

Key words: Alkali – Aluminium Tetrafluoride; Charged Clusters; Structure of Associated Liquids.

1. Introduction

It has been known for quite some time from Raman scattering experiments [1, 2] that in liquid $(AlF_3)_x{\cdot}(NaF)_{1-x}$ mixtures a gradual shift in cluster populations occurs as the content of AlF_3 is decreased below the equimolar $NaAlF_4$ melt. Special interest is offered in this range of composition by molten cryolite (Na_3AlF_6), because of its role in the industrial electrowinning of Al metal from Al_2O_3 [3]. The interpretation of the evidence obtained from very extensive and detailed measurements of Raman spectra and thermodynamic properties is that in liquid cryolite the $(AlF_5)^{2-}$ complex anion coexists with the $(AlF_4)^-$ and $(AlF_6)^{3-}$ clusters [4 - 6].

In recent calculations on Na_nAlF_{n+3} clusters we have drawn attention to the role of the Na counterions in stabilizing different states of coordination for the Al ion by fluorines [7, 8]. The effect of alkali substitution on the Raman spectra has also been studied experimentally [5]. The characteristic bands of the complexes become sharper in the sequence Li < Na < K, indicating that the perturbation of the anion structures by the alkali counterions weakens in the same order.

In the above background it seems relevant to extend our calculations to clusters with different alkali ions. The aim of the present work is to obtain a refined assessment of the relevant ionic interactions through a study of the $MAlF_4$ molecules (with M = Li, Na, K, Rb or Cs) in conjunction with the $(AlF_4)^-$ anion. The model that we use was first developed to evaluate various neutral and ionized Al chloride clusters [9] and successfully tested in that case against data on molecular structure and vibrational frequencies from experiment and from quantum-chemical and density-functional calculations. In the present context it is relevant that *ab initio* molecular orbital calculations have been carried out both on the $(AlF_4)^-$ species *in vacuo* [10, 11] and on gaseous $LiAlF_4$ and $NaAlF_4$ molecules [12, 13]. Indeed, in the lack of suitable experimental data we make direct use of these theoretical results on $LiAlF_4$ in determining our model parameters for the Li – F interactions.

0932–0784 / 99 / 1000–0570 $ 06.00

The plan of the paper is as follows. In Sect. 2 we give a brief presentation of the essential aspects of the model and the determination of its parameters. Our results for the static and vibrational structures of the $MAlF_4$ molecules are reported in Sections 3 and 4, respectively. Each static structure is obtained as a zero-force configuration of the ionic assembly at zero temperature, and its mechanical stability is then assessed by the evaluation of its vibrational frequencies. Finally, Sect. 5 reports a brief summary and a discussion of the results.

2. Interionic Forces in the $MAlF_4$ Clusters

We start by recalling the essential points of the model that was used in [9] for the potential energy of a metal halide cluster as a function of the interionic bond vectors and of the dipole moments carried by the halogens.

As in the standard Born model for cohesion in ionic crystals [14], the potential energy function is built from Coulomb, overlap repulsive and van der Waals interactions. In addition, polarization energy terms are included. Electron-shell deformability is described through (i) effective valences z_i subject to overall charge compensation ($\Sigma_i z_i = 0$), and (ii) electrical and overlap polarizabilities of the halogens, accounting for electrical dipole induction and for changes in the state of overlap between near-neighbour shells from relative ionic displacements.

In relation to the $MAlF_4$ clusters, however, it should be noticed that the electrical polarizability of the K^+, Rb^+ and Cs^+ ions is actually larger than that of the F^- ion [15]. In this work we have therefore extended the model to include the classical polarization energy of the alkali ions. Only for the Li^+ ion is the polarizability completely negligible. For the other alkalis we have used the polarizabilities reported in the work of Jaswal and Sharma [16].

The other new aspect of the model concerns the overlap repulsive interactions between the alkali ions and the fluorine ion. As in [9] we write the overlap potentials in the form proposed by Busing [17], namely

$$\Phi_{ij}(r) = f(\rho_i + \rho_j)\exp[(R_i + R_j - r)/(\rho_i + \rho_j)], \quad (1)$$

where f is chosen to have the standard value f = 0.05 $e^2/Å^2$, while R_i and ρ_i are characteristic radii and hardness parameters which for metal ions can be taken to be proportional to each other. For the alkali ions we have taken the ratios R_M/ρ_M from work on alkali halides and tested the sensitivity of the results by two alternative choices. These are denoted in the following as FT [18] and TF [19].

Table 1. Interionic force parameters (the other parameters are as in [8]). The symbols FT and TF indicate the source used for the ratio R_M/ρ_M (see [18], [19]).

	$-z_F$	R_{Al} (Å)	ρ_{Al} (Å)	R_M (Å)	ρ_M (Å)
$LiAlF_4$ (TF)	0.941	0.997	0.0536	0.747	0.0769
$NaAlF_4$ (TF)	0.945	1.000	0.0538	0.996	0.0979
$NaAlF_4$ (FT)	0.945	0.998	0.0537	1.012	0.120
$KAlF_4$ (TF)	0.946	1.011	0.0539	1.300	0.109
$RbAlF_4$ (TF)	0.948	1.002	0.0539	1.402	0.0998
$CsAlF_4$ (TF)	0.949	1.005	0.0541	1.562	0.0608

Further simplification is achieved by assuming transferability of potential-energy parameters for halogens between different compounds [9]. Adopting, therefore, the parameters for the fluorine ion used in earlier studies of fluorides [8], the potential energy function for each $MAlF_4$ cluster involves three disposable parameters which are the radii R_{Al} and R_M of the two metal ions and the effective valence of the fluorine ion. These have been determined by fitting the measured values of (i) the Al-F bond length in $(AlF_4)^-$ (1.69 Å [10]), (ii) the M-F bond length from molecular-orbital calculations in $LiAlF_4$ [13] and from experiment in the other $MAlF_4$ molecules [20], and (iii) the Al-F bond stretching frequency (the topmost B_1 vibrational mode) of the $MAlF_4$ molecules from IR matrix data [21].

Table 1 reports the values of the effective fluorine valence and the metal-ion repulsive parameters that we have obtained. The effective valences are smaller than the full nominal valences by only about 5% in all cases, so that these molecules are seen to conform closely to the ideal ionic model. A reduction of the nominal valence by 7% was found for the fluorine ion in NaF crystals from dielectric constant studies [22]. The repulsive parameters of Al are also essentially constant through the family of clusters. The results of the alternative choices of repulsive parameters for the alkali ions (FT *versus* TF) are illustrated in Table 1 for $NaAlF_4$. Their consequences will be tested in the calculations of the static structure that we report in the next section.

3. Structure of $MAlF_4$ Clusters

We comparatively discuss in this section the edge-bridged (two-fold coordinated) and face-bridged

Table 2. Equilibrium structure of $MAlF_4$(II) (bond lengths in Å, bond angles in degrees; F* denotes a fluorine bonding the M ion).

		M-F*	Al-F*	Al-F	∠F*-Al-F*	∠F-Al-F
$LiAlF_4$(II):	TF:	1.77	1.75	1.65	88.3	117.7
	QC [13]	1.77	1.737	1.639	88.4	118.2
$NaAlF_4$(II):	TF:	2.11	1.74	1.65	92.8	116.8
	FT:	2.11	1.74	1.65	92.8	116.7
	QC [13]	2.12	1.721	1.646	93.6	116.4
$KAlF_4$(II):	TF:	2.51	1.73	1.66	96.5	116.0
$RbAlF_4$(II):	TF:	2.64	1.73	1.66	97.3	115.8
$CsAlF_4$(II):	TF:	2.84	1.725	1.67	98.3	115.6

Table 3. Equilibrium structure of $MAlF_4$(III) (bond lengths in Å, bond angles in degrees; F* denotes a fluorine bonding the Na ion).

		M-F*	Al-F*	Al-F	∠F-Al-F*
$LiAlF_4$(III):	TF:	2.02	1.72	1.64	122.4
$NaAlF_4$(III):	TF:	2.35	1.71	1.64	119.4
	FT:	2.37	1.71	1.64	119.3
	QC	2.282	1.698	1.634	119.7
$KAlF_4$(III):	TF:	2.74	1.71	1.65	117.2
$RbAlF_4$(III):	TF:	2.85	1.71	1.65	116.8
$CsAlF_4$(III):	TF:	3.02	1.71	1.66	116.2

(three-fold coordinated) configurations for the alkali ion in $MAlF_4$: these are indicated as $MAlF_4$(II) and $MAlF_4$(III), respectively. We exclude a corner-bridged zero-force configuration, which has a very high energy relative to the ground state [13, 8]. We also remark that $LiAlF_4$(III) is obtained in our calculations as a zero-force configuration which is, however, mechanically unstable.

Our results for these two structures are shown in Tables 2 and 3, together with those of the quantum-chemical (QC) calculations reported by Scholz and Curtiss for $LiAlF_4$ and $NaAlF_4$ [13]. Here and in the following Tables we underline the values that have been adjusted in the fitting of the model parameters. Two main remarks are in order: (i) there is little sensitivity to the input on the alkali ion repulsive parameters (FT *versus* TF) and very good agreement with the available QC results in both the bond lengths and the bond angles; and (ii) the alkali ion imparts a small distortion to the basic $(AlF_4)^-$ tetrahedron, by amounts which show little dependence on the nature of the alkali ion and on its bridging configuration.

If we exclude $LiAlF_4$, for which the edge-bridged structure is very definitely the ground state and the face-bridged one is mechanically unstable in our calculations, the two structures for $MAlF_4$ have very similar energies. This fact was already demonstrated for $NaAlF_4$ by Scholz and Curtiss [13], who found that the ground state is edge-bridged in Hartree-Fock but becomes face-bridged after approximate inclusion of correlations, with energy differences at the level of $\pm$ 0.05 eV between the two structures. Our results for the relative energy of the two structures are shown in Table 4. We find that the edge-bridged configuration is the ground state for $NaAlF_4$ by about 0.1 eV, but in the case of $KAlF_4$, $RbAlF_4$ and $CsAlF_4$ the energy difference between the two structures is practically completely negligible. It should be remarked that the inclusion of electrical polarization of the alkali stabilizes the edge-bridged structure relative to the face-bridged one by a very considerable amount – by about 0.3 eV in $KAlF_4$ up to about 0.9 eV in $CsAlF_4$. More precisely, increasing size of the alkali ion favours its three-fold coordination, but this effect is balanced by the accompanying increase in polarizability.

Table 4. Relative energies of $MAlF_4$(II) and $MAlF_4$(III) (in eV). The ground state is taken at zero energy.

		II	III
$LiAlF_4$:	TF:	0	0.30
	QC	0	0.21
$NaAlF_4$:	TF:	0	0.12
	FT:	0	0.14
	QC	0.05	0
$KAlF_4$:	TF:	0	0.02
$RbAlF_4$:	TF:	0.01	0
$CsAlF_4$:	TF:	0.05	0

We believe, therefore, that the energy differences reported in the last three rows of Table 4 are within noise. The conclusion from the above results for the two static structures and for their relative energies is that (excluding again the case of $LiAlF_4$) they are essentially equivalent at the temperatures of interest for experiment. This result seems to be not inconsistent with the experimental evidence from electron diffraction on high-temperature vapours [20]. These experiments have been interpreted in terms of the two-fold structure, but no distortion in the basic $(AlF_4)^-$ tetrahedron has been reported – as if the alkali ion were rapidly moving around it and averaging out the difference between bonding and terminal fluorines. The average Al-F bond length is reported to be in the range 1.69 - 1.696 Å, in excellent agreement with the averages of the calculated bond lengths given in

Tables 2 and 3. In the case of $KAlF_4$ a puckering of the K-F*-Al-F* ring has been reported [23], yielding a position of the K ion which is intermediate between two-fold and three-fold bonding.

The vibrational spectra of the gaseous $MAlF_4$ clusters have not been measured directly, but have been estimated from IR matrix isolation data [21]. The results have been interpreted as indicating a C_{2v} symmetry, which is consistent with the double-bridged structure [21, 24]. Of course, for the heavier alkalis the matrix may be expected to block their motions around the $(AlF_4)^-$ tetrahedron.

In summary, our results are in accord with the *ab initio* molecular orbital calculations on the gaseous $LiAlF_4$ cluster and with the experimental evidence on the gaseous and matrix-isolated $NaAlF_4$ cluster in predicting the two-fold, edge-bridged coordination of the alkali ion as being the favoured one. The trend from $LiAlF_4$ to $NaAlF_4$ is to reduce the energy difference between edge-bridged and face-bridged configurations, again in agreement with the *ab initio* calculations. For the other alkali tetrafluoride clusters we then find that these two configurations have essentially the same cohesive energy and suggest that the $(AlF_4)^-$ tetrahedron may be seen by the heavier alkalis as an almost spherical unit. These results agree with the fact that from Raman scattering studies of melts [5] the perturbations of the $(AlF_4)^-$ anion in the melt are observed to decrease in the sequence Li > Na > K.

4. Vibrational Spectrum of $MAlF_4$ in the Edge-Bridged Structure

As mentioned just above, the vibrational spectra of the $MAlF_4$ clusters have been interpreted from IR matrix isolation data as indicating a C_{2v} molecular symmetry [21, 24]. Table 5 collects our results for the vibrational frequencies of the gaseous $MAlF_4$(II) clusters, in comparison with the data of Huglen *et al.* [21] from the matrix isolation experiments. The values of the highest B_1 mode frequency have been fitted to determine the effective ionic valence and have yielded closely similar values of this parameter in the various clusters (see Table 1).

The overall quality of these comparisons is reasonably satisfactory. The bond-stretching modes in Table 5 are reproduced rather accurately by the model, whereas bond-bending modes are generally more sensitive to the details of the ionic interactions. Nevertheless, we have found only moderate sensitivity of these results to the inclusion of alkali polarizability and to the input on overlap repulsive interactions.

Table 5. Frequencies of vibrational modes (in cm^{-1}) for $MAlF_4$(II). For each cluster the second coulumn reports the values estimated from IR matrix isolation experiments (from [21]; frequencies in parentheses are calculated from a normal-mode analysis).

	$LiAlF_4$		$NaAlF_4$		$KAlF_4$		$RbAlF_4$		$CsAlF_4$	
A_1	823	817	812	808	803	805	803	801	800	798
	612	608	621	613	627	618	630	619	632	620
	476	560	350	378	331	351	330	341	326	330
	310	(361)	293	(291)	243	(284)	231	(281)	231	(280)
	220	220	171	(180)	128	(149)	120	(106)	121	(90)
A_2	231	269	195	269	178	(269)	180	(269)	182	(269)
B_1	911	911	893	893	877	877	874	874	868	868
	330	316	302	304	302	303	304	303	304	303
	115	157	53	(102)	30	(90)	24	(79)	17	(76)
B_2	620	644	635	669	658	695	668	696	677	699
	374	450	314	339	311	317	312	312	313	308
	220	270	172	200	163	(175)	130	(148)	125	(136)

5. Summary and Concluding Remarks

The fundamental and industrial interest presented by the Al-alkali fluorides would justify a special effort to use specific methods in the study of the stable local structures in their liquid phase, *i.e.* diffraction and EXAFS experiments and computer simulations. In this work we have developed a refined phenomenological model of the ionic interactions from the study of the $MAlF_4$ clusters in comparison with data from experiment and from *ab initio* molecular orbital calculations.

We have also proposed an explanation for the observation from liquid-state Raman scattering studies that the interaction of the complex anions in the melt with the alkali counterions is strongest in the case of Li and progressively weakens on substitution with Na and then with K. In the free clusters we have found that the Li ion is fairly strongly bound to two fluorines in the basic $(AlF_4)^-$ tetrahedron, so that it will act as a strong perturbation on the internal modes of the complex anion. As we move to Na and then to the heavier alkalis, the two-fold and three-fold bound states of the alkali effectively become energetically equivalent. This equivalence implies that

for the heavier alkalis the $MAlF_4$ cluster may almost be viewed as a diatomic molecule composed of M^+ and $(AlF_4)^-$ units and that the internal vibrations of the latter unit become almost independent of the alkali partner. Confirmation for this viewpoint can be found through a careful comparison of the frequencies of the various clusters across each row of Table 5.

Acknowledgements

We acknowledge the award of the NATO Grant CRG.CRG.974429. One of us (ZA) acknowledges support from the Turkish Scientific and Technological Research Council (Tubitak) and from the Research Fund of the University of Istanbul under Project Number BA-20/040599.

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