Structure of Rare-earth/Alkali Halide Complexes

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Vapour complex formation of rare-earth halides with alkali halides strongly increases the volatility of these compounds. We evaluate the structure taken by such complexes having the chemical formulas MRX_4, M_2RX_5 and M_3RX_6, where X = F or Cl and typically M = Li or Na and R = La. The roles played by the two types of metal atom is investigated in MRX_4 complexes by also taking M = K, Rb or Cs and R = Gd or Lu. The main predictions that emerge from our calculations are as follows: (i) in MRX_4 a fourfold coordination of the rare-earth atom is accompanied by twofold or threefold coordination of the alkali atom, the energy difference in favour of the twofold-coordination state being about 0.3 eV in the case of the LiF complexing agent but even changing sign as the ionic radius of either the alkali or the halogen is increased; (ii) in M_2RX_5 a fivefold coordination of the rare-earth atom is energetically more stable than a fourfold one, by again not more than about 0.3 eV; (iii) in M_3RX_6 the fivefold and sixfold coordinations of the rare-earth atom are energetically competitive; and (iv) in both M_2RX_5 and M_3RX_6 each coordination state can be realized in various forms that differ in detail but are close in energy. Bond fluctuations and disorder around the rare-earth atom can be expected to be a general feature at elevated temperatures, both in the vapour and in liquid rare-earth/alkali halide mixtures.

Key words: Ionic Clusters; Molten Salts.

1. Introduction

The vapour complexes that are formed in binary systems of rare-earth halides with alkali halides are characterized by large volatility enhancement factors over the pure rare-earth compounds, this property being essential for a number of technical applications of rare-earth materials (see Boghosian and Papatheodorou [1] and references given therein). A large number of these vapours have been studied by Knudsen effusion mass spectrometry at high temperature, allowing identification of gaseous species and determinations of partial pressures and other thermodynamic properties. Other methods such as torsion-mass-effusion, gas phase spectrophotometry, and chemical analysis of quenched vapours have also been applied to a considerable extent. The most common species is the MRX_4 vapour complex (where M denotes an alkali atom, R a rare-earth atom, and X a halogen atom), but the M_2RX_5 complex is also a common component of these vapours.

In contrast with the abundance of thermodynamic data, very little seems to be known about the structure of rare-earth vapour complexes. Papatheodorou [2] has noted that there are three possible configurations for the MRX_4 molecule: given a fourfold coordination of the rare-earth atom surrounded by halogens in a tetrahedral arrangement, the alkali atom may be situated at an apex (C_{3v} symmetry), an edge (C_{2v} symmetry), or a face (C_{3v} symmetry) of the tetrahedron. No diffraction experiments nor theoretical calculations seem to have been carried out, however, to ascertain these possibilities and to discriminate among them in dependence of the three atomic species entering the complex. In fact, the alkali atom may fluctuate among these various configurations. The structure of the R_2MX_5 complexes seems to be totally unknown.

In the present work we carry out calculations of the structure for a number of these molecules, selected in such a way as to allow us to expose the structural trends holding across the whole series of compounds. We also evaluate the structure of M_3RX_6

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Table 1. Relative energy (in eV) of the edge-bridged (II) and face-bridged (III) geometries for MRF_4 and $MRCl_4$. The ground state is taken at zero energy.

Complex	II	III	Complex	II	III
$LiLaF_4$	0	0.32	$LiLaCl_4$	0	0.16
$NaLaF_4$	0	0.10	$NaLaCl_4$	0.03	0
$KLaF_4$	0	0.03	$KLaCl_4$	0.06	0
$RbLaF_4$	0	0.01			
$CsLaF_4$	0.03	0			
$LiGdF_4$	0	0.34	$LiGdCl_4$	0	0.16
$NaGdF_4$	0	0.10	$NaGdCl_4$	0.04	0
$LiLuF_4$	0	0.32	$LiLuCl_4$	0	0.15
$NaLuF_4$	0	0.10	$NaLuCl_4$	0.04	0

molecules, for reasons that will become apparent in the following. Our calculations are based on an ionic model that was originally developed for Al chloride molecules and molecular ions entering Al chloroaluminates [3] and was thoroughly tested for these Al chloride complexes against experimental data and by comparisons with the results of first-principles calculations. The basic model has already been applied by us to study a number of other compounds of trivalent and tetravalent metals, and in view of all past experience we believe that the predictions given below are quantitatively reliable. Especially relevant in the present context will be our previous work on Al-alkali fluoride compounds [4 - 6].

For the details of the ionic model that we use in the calculations presented below, we refer the reader to the above-mentioned studies of Al-alkali halide compounds [3 - 6]. It suffices to specify here the choice of the model parameters entering the interionic force laws. For the interactions between rare-earth ions and chlorine or fluorine ions, we have made use of our results on rare-earth chloride [7] and fluoride [8] molecular monomers. The model thus includes an account of the electronic polarizability of the rare-earth ion, in addition to the electronic and short-range overlap polarizabilities of the halogen. The parameters of the overlap repulsive interactions between alkali and halogen ions are from the work of Tosi and Fumi [9], while the electronic polarizability of alkali ions have been taken from the work of Jaswal and Sharma [10].

2. The MRX_4 Vapour Complex

Among the three possible locations of the alkali atom around the MX_4 tetrahedron proposed by Papatheodorou [2], we find that the single-bonded apex configuration is mechanically unstable. That is, it corresponds to a saddle point in the potential energy surface, rather than to an equilibrium state.

Table 2. Bond lengths (Å) and bond angles (degrees) in MRX_4 at zero temperature. X^* denotes a halogen bonding the alkali atom.

Complex	$r_{M\text{-}X^*}$	$r_{R\text{-}X^*}$	$r_{R\text{-}X}$	$\angle X^*\text{-}R\text{-}X^*$	$\angle X\text{-}R\text{-}X$	$\angle X\text{-}R\text{-}X^*$
$LiLaF_4$(II)	1.83	2.28	2.15	73	117	114
$LiLaF_4$(III)	2.07	2.22	2.18	79	—	133
$NaLaF_4$(II)	2.34	2.25	2.17	81	119	113
$NaLaF_4$(III)	2.57	2.21	2.19	86	—	128
$LiLaCl_4$(II)	2.35	2.72	2.56	87	114	113
$LiLaCl_4$(III)	2.62	2.64	2.59	88	—	126
$NaLaCl_4$(II)	2.90	2.69	2.57	94	114	112
$NaLaCl_4$(III)	3.10	2.64	2.59	94	—	122

Both the twofold (edge-bridged) and the threefold (face-bridged) coordination for the alkali atom correspond, instead, to mechanically stable structures. As is shown in Table 1 (left side), in fluorides of La the twofold configuration is the ground state for Li, Na, K, and Rb, but it is overtaken by the threefold one for Cs. In chlorides of La, as is shown on the right side of the Table, the same inversion of the ground state structure occurs already for Na and K. The results reported in these tables for R = Gd or Lu show that these structural properties of the MRX_4 complex are essentially independent of the rare-earth species.

The above results refer to zero temperature and are reminiscent of those obtained by Curtiss [11] and by Scholz and Curtiss [12] in *ab initio* molecular orbital calculations on complexes formed by Al fluorides. They found that the edge-bridged geometry is the ground state for $LiAlF_4$, while the face-bridged one may become the ground state for $NaAlF_4$ when electronic correlations are approximately included. In our earlier study of the Al tetrafluoride complexes [5] we found the structural inversion occurring between K and Rb, the difference from the case of La that we report here being attributable to differences in ionic size and polarization of the trivalent metal ions.

We should stress, however, that the scale of the energy difference between the two coordination states for the alkali atom in Table 1 is quite small, being at most about 0.3 eV in $LiLaF_4$. This implies, of course, that at elevated temperatures the alkali atom will be essentially free to jump around the tetrahedral core of the complex from one configuration to the other, passing through the saddle point provided by the single-bonded configuration.

Table 3. Excess energy (in eV) of the fourfold-coordinated state of La in M_2LaX_5, relative to the fivefold-coordinated ground state.

Molecule:	Li_2LaF_5	Na_2LaF_5	Li_2LaCl_5	Na_2LaCl_5
	0.17	0.33	0.11	0.03

Table 2 reports examples of the structural parameters in both the edge-bridged and the face-bridged geometry for $MLaF_4$ and $MLaCl_4$ in the cases of Li and Na counterions. In the Table we have made a distinction between the structural parameters referring to the alkali-bonding halogens (denoted by X^*) and the other halogens, thus allowing for a small distortion of the tetrahedral unit by the alkali atom. However, averages between these values will become appropriate at elevated temperatures.

3. The M_2RX_5 Vapour Complex

When the M_2RX_5 complex is formed by bringing an MX molecule up to the MRX_4 complex, the additional halogen may enter the coordination shell of the rare-earth atom, bringing it into a fivefold coordination state. This is in fact the ground state configuration that we find for M_2LaX_5 when M = Li or Na and X = F or Cl. The other possible type of molecular geometry is one in which the rare-earth atom preserves its fourfold coordination and the additional halogen acts as a coion in the outer regions of the complex. This type of configuration lies at higher energy (see Table 3), the energy differences being again quite small and therefore expected to become irrelevant at sufficiently high temperature.

The stability of the LaF_5 molecular ion is reminiscent of the structures that have been reported for the coordination shell of the Al ion in liquid mixtures of AlF_3 and alkali fluorides [13]. The Raman scattering evidence in liquid $(NaF)_{1-x}.(AlF_3)_x$ for $x < 0.5$ has been attributed to the presence of AlF_4 and AlF_5 complexes, this interpretation being confirmed by very extensive and detailed measurements of the thermodynamic properties and Raman spectra as functions of composition, temperature, and alkali atom species. Only for $x < 0.25$ has evidence been obtained for the presence of a third species attributed to AlF_6, and these observations have motivated our study of the M_3LaX_6 complex that we report in the next section.

Before proceeding we should emphasize that, while Table 3 reports only the energy difference between the two types of geometry for M_2LaX_5 in their respective lowest-energy states, for each of these coordinations of the La atom we have found a multiplicity of other structures lying at somewhat higher energies. These differ from the lowest-energy geometries simply for re-arrangements of atoms lying in the periphery of the complex. Again, with increasing temperature the outer-lying atoms become quite free to move around the core of the molecular complex. This feature is also present in the M_3LaX_6 complexes, to which we now turn.

Table 4. Relative energy (in eV) of the fourfold (IV), fivefold (V) and sixfold (VI) coordination geometries for M_3RX_6. The ground state is taken at zero energy.

Complex	IV	V	VI
Li_3LaF_6	0.31	0	0.09
Li_3LaCl_6	0.26	0	0.003
Na_3LaF_6	0.76	0.11	0
Na_3LaCl_6	0.44	0.16	0

4. The M_3RX_6 Vapour Complex

In treating the M_3LaX_6 complexes we have considered all possible states of coordination of the La atom for M = Li or Na and X = F or Cl. Our results are reported in Table 4.

We again find the fourfold-coordination state to be energetically unfavoured in all these compounds. On the other hand, the states of fivefold and sixfold coordination are energetically similar, with the former being favoured in the case of Li counterions and the latter in the case of Na. The energy differences between these states are quite small.

While, as far as we know, the M_3RX_6 complex has not been identified in rare-earth/alkali halide vapours, this composition will naturally be met in liquid mixtures of these compounds. From our calculations one may expect that the fivefold and sixfold coordination states (and possibly even higher ones) may arise in such liquid mixtures in appropriate concentration ranges. One should also expect, however, that each local structure will have a relatively short lifetime in the melt, so that its identification may not be easily accessible to techniques such as Raman scattering.

5. Summary

In summary, we have evaluated the structures taken by the first coordination shell of halogens around a

rare-earth ion in the presence of alkali counterions at certain chosen compositions. Although quantitative differences associated with the chemical nature of the halogen and of the alkali exist, two general features of these local structures have emerged. Firstly, given a sufficient supply of halogens, high-coordination structures are favoured with in particular a relevant presence of the rather uncommon fivefold coordination. Secondly, bond fluctuations around each rare-earth atom are expected to occur at the temperatures of interest in the laboratory.

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