Ionic Interactions in Lanthanide Halides

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We determine a model of the ionic interactions in RX_3 compounds (where R is a metal in the rare-earth series from La to Lu and X = Cl, Br or I) by an analysis of data on the static and dynamic structure of their molecular monomers. The potential energy function that we adopt is patterned after earlier work on Aluminium trichloride [Z. Akdeniz and M. P. Tosi, Z. Naturforsch. **54a**, 180 (1999)], but includes as an essential element the electric polarizability of the trivalent metal ion to account for a pyramidal shape of RX_3 molecules. From data referring mostly to trihalides of elements at the ends and in the middle of the rare-earth series (*i. e.* LaX_3, GdX_3 and LuX_3), we propose systematic variations for the effective valence, ionic radius and electric polarizability of the metal ions across the series. As a first application of our results we predict the structure of the Dy_2Cl_6 and Dy_2Br_6 molecular dimers and demonstrate by comparison with electron diffraction data that lanthanide-ion polarizability plays a quantitative role also in this state of tetrahedral-like coordination.

Key words: Ionic Clusters; Molten Salts.

1. Introduction

Industrial and technical applications have motivated interest in rare-earth halides for a number of years. Great attention has been given to their vapours and to the volatile vapour complexes that are formed with complexing agents such as the alkali halides or the Al trihalides, in view of a series of potential applications related to new energy sources, energy conservation, and recycling or separation processes [1]. The extraction and processing of rare-earth metals are based on molten-salt technologies, giving incentive to current efforts at determining thermodynamic and structural properties of rare-earth halide melts by both experimental and simulational methods [2].

In attempting to develop a refined model for the ionic interactions in rare-earth halides it seems natural to follow the approach developed by two of us [3] for Al chlorides and alkali chloroaluminates: that is, to start by examining the static and dynamic structure of the simplest molecular units, which are the RX_3 monomers. As evidenced in the work of Molnár and Hargittai [4], the shape of these molecules has been for a number of years a matter of controversy. Although the majority of the data supports slightly pyramidal shapes for RX_3 gaseous molecules, the question as to which of these are planar (D_{3h} symmetry) and which are pyramidal (C_{3v} symmetry) does not seem to be fully settled experimentally [1]. The assignment of vibrational frequencies on the basis of C_{3v} symmetry [1] yields relatively low values for the frequency of the ν_2 mode, indicating that these molecules are quite floppy.

On the theoretical side, extended Hückel calculations by Myers *et al.* [5] predicted a pyramidal configuration for all these molecules, with the X-R-X bond angle increasing both across the lanthanide series and across the halogen series from 91° in LaF_3 to 119° in LuI_3. Attention has also been drawn to the role of ionic polarizabilities in determining the molecular shape [6]. Within a simple ionic model the distortion of an RX_3 molecule from a planar to a pyramidal shape is driven by the energy gain from electric polarization of the rare-earth ion: a pyramidal shape is then favoured by a high polarizability of the rare-earth ion and by a short X-R bond length. This prediction is in accord with the trends revealed by the molecu-

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lar orbital calculations of Myers *et al.* [5]. However, for quantitative purposes the available value of the lanthanide-ion polarizability obtained by Pauling [7] is likely to be much too low. The rare-earth ions do not seem to have been considered in the re-assessments of the Pauling polarizability scale due to Tessman, Kahn and Shockley [8] and to later workers [9]. The work of these authors led to a very sizable increase of the polarizability over the Pauling values for all other positive ions, and in particular to an increase by about a factor of two for the doubly charged alkaline-earth ions.

Therefore, our first task in the present work is to obtain a new estimate for the electric polarizability of the lanthanide ions. We focus for this purpose on those gaseous RX_3 molecules for which electron diffraction data are available to provide evidence for a pyramidal shape and a value for the X-R-X bond angle. These mainly are the chloride, bromide and iodide of La, Gd and Lu (excepting LaI_3), and their study presents two evident advantages: (i) these elements are at the beginning, in the middle and at the end of the rare-earth series, so that their inclusion in the analysis facilitates an assessment of trends ; and (ii) the electron distribution in the f-shell of these elements in the isolated state is spherically symmetrical, thus excluding that f-shell anisotropy may be relevant in driving a pyramidal distortion as discussed by Molnár and Hargittai [4].

In view of the presumable uncertainties in the measured pyramidal bond angles, our main aim is the assessment of trends in the ionic-model parameters for the trivalent ions across the rare-earth series, rather than their individual values in each system. These parameters are the electric polarizability, the effective valence and the ionic radius entering the core repulsion. In Sect. 2, after a brief reminder of the essence of our model as developed in [3], we list the input values of the other model parameters and the available evidence on bond lengths, bond angles and vibrational mode frequencies in each of the gaseous molecules that we have taken into consideration. The trends of the model parameters for the lanthanide ions across the series of rare-earth trihalides are presented and discussed in Sect. 3. A first test of our results is reported in Sect. 4, by giving a prediction of the structure of the Dy chloride and bromide dimers and comparing it with evidence from electron diffraction experiments. Finally, Sect. 5 ends the paper with a brief summary and outlook.

2. Interionic Force Model and Evaluation of Model Parameters

Following our earlier study of the Al-based chlorides [3], the microscopic model that we use for lanthanide halide clusters incorporates the Born model of cohesion [10] and the shell model for vibrational motions and crystal defects [11]. Electron-shell deformability is described through (i) effective valences z_i subject to overall charge compensation; (ii) the electric and overlap polarizabilities of the halogens (denoted by α_X and α_s, respectively); and (iii) the electric polarizability α_R of the lanthanide ions. Overlap repulsions of exponential form involve ionic radii R_i and stiffness parameters ρ_i. Van der Waals dipole-dipole interactions are included for the halogens.

For convenience we report here the form of the potential energy $U(\{\boldsymbol{r}_{ij}\}, \{\boldsymbol{p}_i\})$ as a function of the bond vectors $\boldsymbol{r}_{ij}$ and of the electric dipole moments $\boldsymbol{p}_i$ carried by the ions. This is

$$U(\{\boldsymbol{r}_{ij}\}, \{\boldsymbol{p}_i\}) = \sum_{i<j} \left[\frac{z_i z_j e^2}{r_{ij}} + \Phi_{ij}(r_{ij}) - \frac{C_i C_j e^2}{r_{ij}^6} \right] + U_{\text{pol}}^{\text{cl}}(\{\boldsymbol{r}_{ij}\}, \{\boldsymbol{p}_i\}) + U_{\text{shell}}(\{\boldsymbol{r}_{ij}\}, \{\boldsymbol{p}_i\}). \quad (1)$$

The overlap repulsive energy in (1) is taken in the Busing form [12]

$$\Phi_{ij}(r) = f(\rho_i + \rho_j)\exp[(R_i + R_j - r)/(\rho_i + \rho_j)]. \quad (2)$$

The reader is referred to our earlier work [3] for expressions of the classical polarization energy $U_{\text{pol}}^{\text{cl}}$ and of the shell deformation energy U_{shell}.

A very helpful aspect of the model (1) is that transferability of the parameters describing the halogen ions and direct proportionality between the characteristic radius R_R and the hardness parameter ρ_R of the metal ion are approximately valid. We expect (and, as we shall see below, find) that the rare-earth compounds of present interest are rather highly ionic

Table 1. Input of interionic force parameters for rare-earth trihalides[a].

X	f (e^2/Å^2)	R_R/ρ_R	α_X(Å^3)	α_s (Å^3)	C_X (eÅ$^{5/2}$)
Cl	0.05	18.6	3.00	0.83	5.50
Br	0.05	18.6	4.17	1.2	7.17
I	0.05	18.6	6.29	1.7	10.1

[a] The polarizability α_X is taken from [9], the other parameters from [13].

Table 2. Bond lengths r_{RX} (Å), bonds angles ∠X-R-X (degrees) and vibrational frequencies (cm^{-1}) of selected RX_3 molecules[a].

Molecule	r_{RX}	∠X-R-X	ν_1	ν_2	ν_3	ν_4
$LaCl_3$[14,22]	2.56	116.5	336.8	52.1	332.5	72.6
			333	26		63
$LaBr_3$[15,22]	2.74	115.5	190	35	220	47
			198	22		39
$PrCl_3$[16,1]	2.55	110.8	(336)	(52)	320	(80)
			337	44		67
PrI_3[17,1]	2.90	112.7	(186)	(28)	(179)	(45)
			164	26		34
NdI_3[17,1]	2.88	111.8	(187)	(29)	195	45
			182	29		37
$GdCl_3$[18,23,1]	2.49	113.0	(338)	64	337	(84)
			358	41		71
$GdBr_3$[19,1]	2.64	113.7	(268)	(44)	(257)	(66)
			244	31		50
GdI_3[17,1]	2.84	108.0	(188)	(31)	194	(46)
			200	37		41
$TbCl_3$[20,1]	2.48	110.4	(339)	(57)	(326)	(84)
			356	49		73
$HoCl_3$[16,1]	2.46	111.2	(339)	(58)	340	(85)
			371	48		76
$LuCl_3$[21,1]	2.42	111.5	(342)	(60)	(331)	(88)
			369	48		77
$LuBr_3$[19,1]	2.56	114.7	(220)	(43)	245	(60)
			241	29		51
LuI_3[17,1]	2.77	114.5	(191)	(34)	198	(49)
			188	26		40

[a] For each molecule the first row reports data from the literature, the first reference being to the source of the structural data and the following one(s) to the source of the spectral data; the second row gives the values that we obtain for the ν_1, ν_2, and ν_4 modes, having fitted the other data. Estimated values are in parentheses.

– compared, say, with the Al or Fe halides. We therefore rely for the choice of the above-mentioned model parameters on the results obtained by Wang Li and Tosi [13] for the alkaline-earth halides. These values are reported in Table 1.

The remaining model parameters (*i.e.* the effective valence and the ionic radius and polarizability of the rare-earth ions) are determined from the available data on bond lengths, bond angles and ν_3-mode frequencies in RX_3 molecules. These parameters will be presented and discussed in the next section. Here we report in Table 2 the list of the RX_3 molecules that we have considered, together with their structural and vibrational properties. The data on bond lengths and bond angles in Table 2 are from electron diffraction experiments on the gaseous state [14 - 21] and the vibrational frequencies are mostly from the review article of Boghosian and Papatheodorou [1], except for $LaCl_3$ [22], $LaBr_3$ [22] and $GdCl_3$ [23].

Table 2 also includes the values that we have obtained for the other vibrational frequencies of these molecules. It should be noted that many of the mode frequencies reported in the literature are mere estimates and that there is a very appreciable spread in the frequencies from different experiments and different sources, as discussed for instance by Kovács *et al.* [22] in connection with $LaCl_3$ and $LaBr_3$. The comparison between our results and the data for the ν_1, ν_2 and ν_4 modes in Table 2 should not be taken to have quantitative meaning. We may nevertheless remark from Table 2 that the model gives a rather good account of the ν_1 (breathing) mode and tends to underestimate somewhat the ν_2 and ν_4 (bending) modes.

3. The Rare-earth Ionic Parameters

Our results for the effective valence, the core-repulsive radius and the polarizability of the rare-earth ions included in Table 2 are shown in Figs. 1 to 3. We have denoted by different symbols for each element the values appropriate to its chloride, bromide and iodide (a triangle, a circle and a lozenge, respectively).

The effective valences shown in Figure 1 all lie within the range from 2.4 to 2.8. These are rather high values compared to the nominal valence $z = 3$, indicating that these compounds are quite close to the ideal ionic model. No clear trend is discernible, so that the scatter is presumably just due to uncertainties in the input and inaccuracies of the model. Notice that the scatter is much smaller if only the chlorides are included. From these results we propose

$$z_R = 2.6 \tag{3}$$

as an approximate effective valence for all trivalent lanthanide ions.

Figure 2 shows our results for the overlap-repulsive radii of these ions. We emphasize that these are model parameters to be used in (2) for the overlap repulsive energy, in which the pre-exponential parameter f can be arbitrarily chosen: therefore, only the relative magnitudes of the radii have physical meaning as reflecting the relative ionic sizes [24]. Figure 2 shows a very clear trend for chlorides and apparently similar trends for bromides and iodides: the radii decrease as the occupation number n_{4f} of the $4f$ shell increases (from $n_{4f} = 0$ for La to $n_{4f} = 14$ for Lu). The straight lines drawn inside Fig. 2 and marked Cl, Br and I

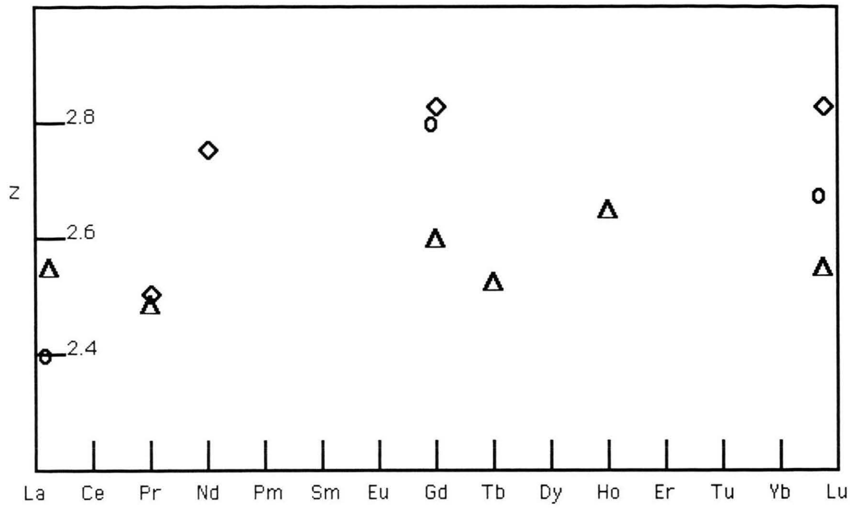

Fig. 1. Effective valence z of rare-earth ions from trihalide monomers (chlorides: Δ; bromides: ○; iodides: $\diamond$).

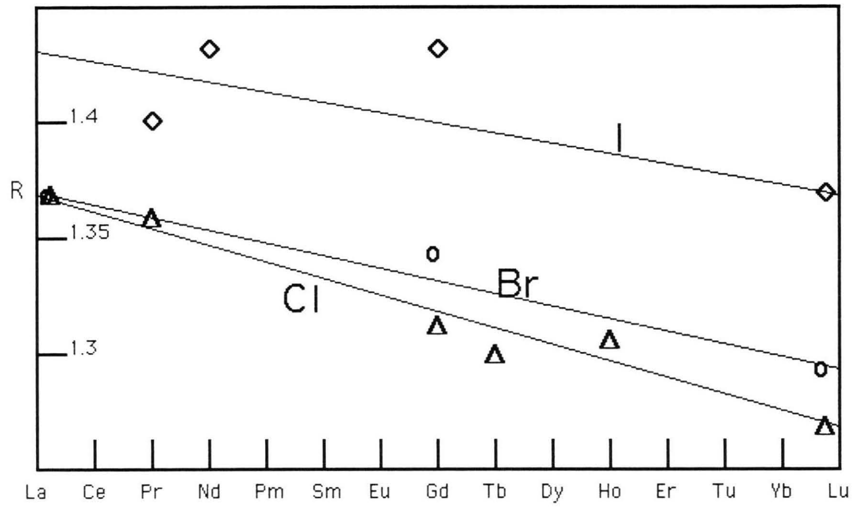

Fig. 2. Ionic radius R (in Å) of rare-earth ions from trihalide monomers. The straight lines are meant to guide the eye through chlorides, bromides and iodides (symbols as in Figure 1).

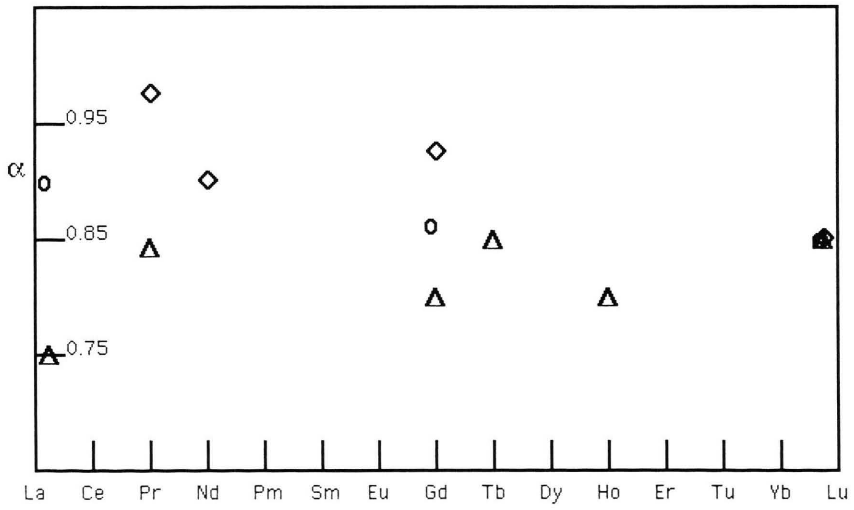

Fig. 3. Same as in Figure 1, for the reduced polarizability $\alpha \equiv \alpha_R / R_R^3$.

are only meant to guide the eye. The differences between chlorides and bromides are almost certainly not significant. We therefore propose the expression

$$R_R = (1.37 - 0.008 n_{4f})\ \text{Å} \qquad (4)$$

for chlorides and bromides, whereas for iodides the expression

$$R_R = (1.43 - 0.005 n_{4f})\ \text{Å} \qquad (5)$$

may perhaps be more appropriate.

Finally, Fig. 3 reports the values that we obtain for the quantity $\alpha \equiv \alpha_R / R_R^3$. Again, the scatter is apparently random within an approximate range from 0.75 to 0.95 and would be much reduced if only chlorides were included. From these results we propose

$$\alpha_R = 0.85 R_R^3 \qquad (6)$$

as an approximate expression for the electric polarizability of all trivalent lanthanide ions. Evidently, this expression implies the reasonable assumption of an approximate proportionality between the polarizability and the ionic volume.

The determination of the model parameters is thus completed. Needless to say, we feel more confident with our results for chlorides, in view of the wider basis of input data.

4. The Dy_2Cl_6 and Dy_2Br_6 Dimers

As a further test of the model that we are proposing for rare-earth trihalides, we have evaluated the structure of the gaseous Dy_2Cl_6 and Dy_2Br_6 dimers. The structural parameters of these two molecules have been obtained by electron diffraction (ED) on the vapour phase, in which the dimer content is about 10 % for the chloride and about 20 % for the bromide as reported in the review of Hargittai [25]. Results from *ab initio* quantum chemical (QC) calculations are also available from the same source [25, 26].

We explicitly note that no data for Dysprosium monomers have been used in the foregoing analysis. The input data for our calculation, in addition to those reported in Table 1, are $z_{Dy} \approx 2.6$, $R_{Dy} \approx 1.30$ Å and $\alpha_{Dy} \approx 1.9$ Å^3 from (3) - (6). We find that the geometrical shape of the dimer corresponds to two edge-sharing (and slightly distorted) tetrahedra, as is seen in the ED experiments. Table 3 reports a comparison of our results with the ED data and with the QC calculations. It is evident that we have obtained excellent agreement with the ED experiments.

Table 3. Geometrical parameters of dimeric Dy trihalides (bond lenghts in Å, bond angles in degrees; the indices T and B denote terminal and bonding halogens).

Dymer		$r_{\text{R-X}^\text{T}}$	$r_{\text{R-X}^\text{B}}$	$\angle \text{X}^\text{B}\text{-R-X}^\text{B}$	$\angle \text{X}^\text{T}\text{-R-X}^\text{T}$
Dy_2Cl_6:	IM	2.45	2.70	89	111
	ED [25]	2.449	2.680	84.1	(116.1)[a]
	QC [25]	2.497	2.711	–	116.1
	IM ($\alpha_{Dy} = 0$)	2.47	2.66	87	123
Dy_2Br_6:	IM	2.59	2.84	91	113
	ED [25]	2.594	2.811	91.7	(118.6)[a]
	QC [25, 26]	2.654	2.872	86.8	117.9
	IM ($\alpha_{Dy} = 0$)	2.61	2.81	90	122

[a] The values of these bond angles are "taken over from computation".

The last row for each dimer in Table 3 reports the structural results that we obtain if we arbitrarily set $\alpha_{Dy} = 0$. It is clear that the polarizability of the rare-earth ion plays a quantitative role even in this approximately tetrahedral configuration, although the net electric field on each Dy ion is relatively small. Notice, however, that even this simplified model gives a quite reasonable account of the ED data.

5. Summary and Outlook

In summary, we have in this work described a model for the ionic interactions in the chlorides, bromides and iodides of the trivalent rare earths from an analysis of their gaseous monomers. The main focus has been on the effective valence, the ionic radius and the electric polarizability of these metal ions, for a given input on the overlap and polarization parameters of the halogens. In spite of the sparseness of the data available for the analysis and of some presumed inaccuracies in their values, we have highlighted some simple and reasonable trends which permit a full quantitative assessment of the model for the whole rare-earth series. This statement is supported by very successful predictions of the structure of dimers.

We have been unable to find in the literature similar experimental data on the F-R-F bond angle in trifluoride molecules. We expect that our results in (3), (4) and (6), combined with the results on fluorides in [13], should give a useful first estimate of an ionic model for rare-earth trifluorides. The calculated shape of the trifluoride monomers would again be pyramidal, as is known to be true for a number of these monomers from experimental studies of their vibrational modes [1].

The outlook for applications of our model to further studies of rare-earth halides is in our view quite bright. Of course, it would be interesting to use this model in carrying out computer simulation studies of their melts, for which structural data are currently being obtained by neutron diffraction [2]. A further area of interest would be the gaseous complexes formed with alkali or Al halides, for which a number of remarkable structures have been envisaged [1]. We hope to return to these themes in the near future.

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