Ionic Interactions in Actinide Tetrahalides

Z. Akdeniz, A. Karaman, and M. P. Tosi[a]

Department of Physics, University of Istanbul, Istanbul, Turkey
[a] INFM and Classe di Scienze, Scuola Normale Superiore, I-56126 Pisa, Italy

Reprint requests to Prof. M. P. T.; Fax: +39-050-563513; E-mail: tosim@sns.it

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We determine a model of the ionic interactions in AX_4 compounds (where A is an atom in the actinide series from Th to Am and X = F, 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 taken from earlier work on rare-earth trihalides [Z. Akdeniz, Z. Çiçek and M. P. Tosi, Z. Naturforsch. **55a**, 861 (2000)] and in particular allows for the electronic polarizability of the actinide ion. This polarizability quantitatively determines the antisymmetric-bending vibrational mode, but its magnitude remains compatible with a symmetric tetrahedral shape of the molecule at equilibrium. The fluorides have an especially high degree of ionic character, and the interionic-force parameters for each halide of the U, Np, Pu and Am series show regular trends, suggesting that extrapolations to the other transuranic-element halides may usefully be made. The Th compounds show some deviations from these trends, and the interionic-force model that we determine for $ThCl_4$ differs somewhat from that obtained in a previous study. We therefore return on the evaluation of the relative stability of charged oligomers of $ThCl_4$ and $ZrCl_4$ and find confirmation of our earlier results on this problem.

Key words: Ionic Clusters; Molten Salts.

1. Introduction

Molten salt technology has found applications in the fields of nuclear fuel recycling and of transmutation processes for minor actinide elements. The physical and chemical properties of molten actinide halides, and especially of chlorides, are important in these contexts. Little is known, however, about their liquid structure, justifying an effort to develop interionic-force models that may help in complementing diffraction experiments with simulation studies [1].

In fact, for actinide tetrahalides even the structure of the molecular monomer in the vapour phase has been a matter of repeated studies and interpretations. Any deviation from T_d symmetry would result in at least a partial lifting of the triple degeneracy of the ν_3 and ν_4 modes, *i. e.* the antisymmetric stretching and bending vibrations of the tetrahedron. As summarized in the review by Hargittai [2], the evidence from vapour-phase and matrix-isolation infrared spectra, electron diffraction, and photoelectron spectra has at long last converged towards attributing a regular tetrahedral structure to the ThF_4, UF_4, $ThCl_4$ and UCl_4 molecules. The conclusion drawn from renewed thermochemical analyses of vapour-pressure data, using infrared spectroscopic measurements in calculations of the entropy of the vapour from molecular vibrational frequencies, also is that these molecules offer no evidence for deviations from tetrahedral symmetry [3]. These analyses have been extended to the other tetrahalides of Th and U and to tetrahalides of some transuranic elements, from measurements of the gaseous entropy and accurate estimates of vibrational frequencies based on empirical correlations [3]. Quantum-chemical calculations on actinide halides [4, 5] and more recently a theoretical study of the Th tetrahalides by density functional methods [6] have consistently predicted a regular tetrahedral structure for these molecules. There nevertheless is evidence from the vibrational spectra of $ThCl_4$ molecules inside inert-gas matrices [7] that the molecular structure is sensitive to the environment, with a C_{2v} model giving an excellent account of the data for a krypton matrix against a T_d model being appropriate for a neon matrix.

Within an ionic molecular model, a distortion of a high-symmetry structural configuration of the molecule would be driven by the energy gain from the polarization of the metal ion in the electric field that the distortion induces at its site. The distortion would then be favoured by a high electric polarizability of the metal ion in combination with a short bond length. A case in point is that of the rare-earth trihalide monomers, for which a trigonal-pyramid configuration of the ground state has been explained by precisely this mechanism [8, 9]. It is natural, therefore, to adopt a similar approach in the determination of the ionic interactions in the actinide tetrahalides.

Such an ionic model is evaluated in the present work for all those actinide tetrahalides on which basic input on bond lengths and molecular vibrational frequencies is available from the study of Konings and Hildebrand [3]. These include AX_4 systems with A = Th, U, Np, Pu and Am and X = F, Cl, Br and I. We anticipate from our results that the frequency of the ν_4 vibrational mode of the molecular tetrahedron is especially sensitive to the inclusion of the metal-ion polarizability and that the available values of these frequencies allow us to obtain an assessment of this molecular parameter within limits that do not lead to breaking the T_d symmetry of the ground state. Whereas the Th halides show some deviations from the general behaviour, for each halide the other actinide ions are found to have essentially the same effective valence and to show some reduction of the ionic radius with increasing number of 5f electrons, the latter being a manifestation of the well-known actinide contraction, which from a fundamental viewpoint appears to be mainly due to relativistic effects [10].

2. Interionic Force Model

We follow our earlier studies of trihalides [9, 11 - 13] and tetrahalides [14, 15] to construct a microscopic model for actinide tetrahalide clusters, which incorporates the Born model of cohesion and the shell model for vibrational motions and crystal defects in ionic compounds [16, 17]. Electron-shell deformability is described through (i) effective valences z_i subject to overall charge compensation; (ii) electric and overlap polarizabilities for the halogens (denoted by α_X and α_s, respectively); and (iii) the electric polarizability α_A of the actinide 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.

Table 1. Interionic force parameters for halogen ions in actinide tetrahalides [19].

X	R_X (Å)	ρ_X (Å)	C_X (eÅ$^{5/2}$)	α_X (Å^3)	α_s (Å^3/e)
F	1.32 [19]	0.215 [19]	2.08 [19]	0.88 [19]	0.2
Cl	1.71 [19]	0.238 [19]	5.50 [19]	1.36 [14]	0.46 [14]
Br	1.84 [19]	0.258 [19]	7.17 [19]	1.70	0.76 [13]
I	2.02 [19]	0.289 [19]	10.1 [19]	3.04	1.24

For convenience we report here the form of the potential energy $U(\{\boldsymbol{r}_{ij}\},\{\boldsymbol{p}_i\})$ of a molecular cluster in an arbitrary configuration 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

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

$$+ U_{\text{pol}}^{\text{cl}}(\{\boldsymbol{r}_{ij}\},\{\boldsymbol{p}_i\}) + U_{\text{shell}}(\{\boldsymbol{r}_{ij}\},\{\boldsymbol{p}_i\}).$$

The overlap repulsive energy in Eq. (1) is taken in the Busing form [18]

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

where f has the standard value f = 0.05 e^2/Å^2. The reader is referred to our earlier work [11] for expressions of the classical polarization energy $U_{\text{pol}}^{\text{cl}}$ and of the shell deformation energy U_{shell}.

The potential energy function in (1) is handled by a computer programme which first searches for zero-force configurations corresponding to extrema in the total energy of the molecule, and then evaluates deformations of each zero-force structure in order to assess its mechanical stability and its vibrational frequencies.

A helpful aspect of the model (1) is that transferability of parameters describing halogen ions and direct proportionality between the characteristic radius R_A and the hardness parameter ρ_A of the metal ion are approximately valid. We have taken R_A/ρ_A = 18.6 and the values of R_X, ρ_X and C_X from earlier work [19]. These values are collected in Table 1 together with the values of the halogen polarizabilities α_X and α_s. Some readjustment of halogen polarizabilities to actinide halide data was needed, as will be described in the next sections together with the details of the determination of the actinide parameters z_A, R_A and α_A.

3. Determination of Ionic Parameters for the Actinide Series Excluding Th

For the halides of U, Np, Pu and Am we find simple regular trends in the model parameters, while some quantitative deviations from these trends appear in the Th halides. We shall turn to the latter compounds in the next section. Here we present our results for the other members of the actinide series. To save space we shall, however, include in the Tables reported in the present section also our results for Th and Zr halides.

It will be convenient to separately discuss the cases of the fluorides and the chlorides, for which the available experimental evidence is more abundant. We shall then use the results on chlorides to examine bromides and iodides at the end of the section.

3.1. Tetrafluorides

A good overall account of the data on the tetrafluorides of U, Np, Pu and Am is obtained by the following choice of the metal-ion parameters:

$$z_\mathrm{A} = 3.6,\ R_\mathrm{A} = (1.50 - 0.01 n_{5\mathrm{f}})\ \text{Å},\ \alpha_\mathrm{A} = 1.2\ \text{Å}^3 \quad (3)$$

with $n_{5\mathrm{f}}$ being the number of 5f electrons in the ion. In parallel the short-range polarizability of the fluorine ion had to be reduced to α_s = 0.2 Å^3/e (see Table 1), a sizably lower value than found earlier [19] for di- and trifluorides.

The effective valence that we find for fluorides is close to the ideal nominal value, indicating that they conform quite closely to the ideal ionic model. In all cases the calculated equilibrium shape of the tetrafluoride monomer is a regular tetrahedron. For these and all other tetrahalides, the calculated value of the ν_4 mode frequency is very sensitive to the inclusion of the metal-ion polarizability: for instance, setting α_A = 0 typically raises ν_4 by about 30%.

Table 2. Bond lengths $r_\text{A-F}$ (Å) and vibrational frequencies (cm^{-1}) of tetrahedral AF$_4$ molecules [a].

Molecule	$r_\text{A-F}$	ν_1	ν_2	ν_3	ν_4
UF$_4$	2.055	628	137	543	118
	2.059	(625)	(123)	539	114
NpF$_4$	2.042	633	139	543	118
	(2.04)	(635)	(125)	(560)	(120)
PuF$_4$	2.029	638	141	543	116
	(2.03)	(635)	(125)	(565)	(120)
AmF$_4$	2.017	643	143	543	115
	(2.02)	(640)	(125)	(570)	(120)
ThF$_4$	2.140	618	131	551	116
	2.14	(618)	(121)	520	116

[a] For each molecule the first row gives our results and the second row reports the data from [3], estimated values being shown in parentheses.

The extent to which the modelling reported in (3) accounts for the available data and estimates on the bond length and the vibrational frequencies as reported by Konings and Hildebrand [3] can be seen from Table 2. The agreement with the data is evidently very good. These authors estimate the uncertainty on the measured frequencies to be ±3 cm^{-1} and that of the estimated frequencies to be ±15 cm^{-1} for ν_3, ±10 cm^{-1} for ν_1 and ν_4, and ±5 cm^{-1} for ν_2.

3.2. Tetrachlorides

For the tetrachlorides of U, Np and Pu we find

$$z_\mathrm{A} = 3.25,\ R_\mathrm{A} = (1.38 - 0.01 n_{5\mathrm{f}})\,\text{Å},\ \alpha_\mathrm{A} = 2.0\,\text{Å}^3. \quad (4)$$

Evidently, these compounds are somewhat further away from the ideal ionic models, this being a common feature found in earlier work on trichlorides relative to trifluorides [11, 12].

The overall agreement with the available data and estimates for tetrachlorides is again very good, as can be seen from Table 3. The Table also includes our predictions for AmCl$_4$, on which no data seem available.

3.3. Tetrabromides and -iodides

Building again on previous experience on trihalides [13], we have adopted the model parameters shown

Table 3. Bond lengths $r_\text{A-Cl}$ (Å) and vibrational frequencies (cm^{-1}) of tetrahedral ACl$_4$ and ZrCl$_4$ molecules [a].

Molecule	$r_\text{A-Cl}$	ν_1	ν_2	ν_3	ν_4
UCl$_4$	2.509	335	70	329	71
	2.506	327	62	337	72
NpCl$_4$	2.498	337	71	330	72
	(2.49)	(340)	(80)	(330)	(70)
PuCl$_4$	2.486	339	71	330	72
	(2.48)	(340)	(80)	(335)	(70)
AmCl$_4$	2.474	342	72	332	72
ThCl$_4$	2.567	325	66	323	70
	2.567	(325)	(60)	335	(70)
ZrCl$_4$	2.32	375	85	405	100
	2.32	375	(100)	418	(100)

[a] For each molecule the first row gives our results and the second row reports data from [3] or (for Zr halides) from [20] and [22], estimated values being shown in parentheses.

Table 4. Bond lengths $r_{\text{A-Br}}$ (Å) and vibrational frequencies (cm^{-1}) of tetrahedral ABr_4 and $ZrBr_4$ molecules [a].

Molecule	$r_{\text{A-Br}}$	ν_1	ν_2	ν_3	ν_4
UBr_4	2.67	201	43	222	52
	2.693	(220)	(50)	233	(45)
$NpBr_4$	2.66	202	43	223	52
$PuBr_4$	2.65	203	44	223	55
$AmBr_4$	2.64	205	44	224	53
$ThBr_4$	2.73	195	41	218	50
	(2.73)	(220)	(50)	(215)	(40)
$ZrBr_4$	2.49	223	52	299	71

[a] For each molecule the first row gives our results and the second row reports data from [3], estimated values being shown in parentheses.

Table 5. Bond lengths $r_{\text{A-I}}$ (Å) and vibrational frequencies (cm^{-1}) of tetrahedral AI_4 and ZrI_4 molecules [a].

Molecule	$r_{\text{A-I}}$	ν_1	ν_2	ν_3	ν_4
UI_4	2.85	149	33	176	43
	(2.85)	(150)	(30)	(150)	(25)
NpI_4	2.84	150	34	176	43
PuI_4	2.83	151	34	176	44
AmI_4	2.82	152	35	177	44
ThI_4	2.91	145	32	173	42
	(2.91)	(145)	(25)	(120)	(20)
ZrI_4	2.66	165	40	248	58

[a] For each molecule the first row gives our results and the second row reports data from Ref. [3], estimated values being shown in parentheses.

in (4) to evaluate the corresponding bromides and iodides of U, Np, Pu and Am. This required some minor adjustments of the polarizabilities of the halogens, relative to earlier studies on di- and trihalides [19], as are shown in Table 1. The results are reported in Tables 4 and 5, where they are compared with available data and estimates from [3].

4. Th and Zr Halides

4.1. Model Parameters for Th Halides

The ThF_4 molecule seems to be even closer to the ideal ionic model than the other actinide fluorides that we have examined in the preceding section. For ThF_4 we find z_{Th} = 3.75, R_{Th} = 1.57 Å and α_{Th} = 1.36 Å^3, while the corresponding values for $ThCl_4$ are z_{Th} = 3.25, R_{Th} = 1.41 Å and α_{Th} = 2.0 Å^3. Comparisons with the values of bond lengths and vibrational frequencies reported for these wo molecules by Konings and Hildebrand [3] are shown in Tables 2 and 3. The discrepancies shown there for the values of ν_3 could be removed by further adjustments of the short-range polarizability of the halogens. The results that we obtain for $ThBr_4$ and ThI_4 with the above choice of parameters are shown in Tables 4 and 5.

The present redetermination of model parameters for $ThCl_4$ has led to somewhat different results from our earlier study [15] (z_{Th} = 3.25 against 3.68 and R_{Th} = 1.41 Å gainst 1.43 Å). These differences are due both to the somewhat different values of the input molecular data and to the present inclusion of the electronic polarizability of the metal ion. The difference between the two values of the ionic valence is appreciable, and we turn below to examine how it may affect the stability of charged oligomers in molten $ThCl_4$. It was a main conclusion of our earlier work [15] that this structural aspect of the melt is sensitive to the degree of ionicity of the compound, the contrast being between the observed structural behaviours of molten $ThCl_4$ and molten $ZrCl_4$ [20, 21].

4.2. Charged Oligomers in Molten $ThCl_4$ and $ZrCl_4$

As a first step we have redetermined the model parameters for $ZrCl_4$ by the same procedure as the one used in the present work for the other tetrachlorides. The input data are the bond length $r_{\text{Zr-Cl}}$ = 2.32 Å [22] and the vibrational frequencies ν_1 = 375 cm^{-1} and $\nu_4 \approx 100\ \text{cm}^{-1}$ [20]. We find z_{Zr} = 3.27, R_{Zr} = 1.20 Å and α_{Zr} = 1.4 Å^3, the two former values being in excellent agreement with our earlier determination [14]. Results for the other vibrational frequencies of $ZrCl_4$ are shown in Table 3, while Tables 4 and 5 report our predictions for the molecules of $ZrBr_4$ and ZrI_4.

On comparing the model parameters for Th and Zr it is seen that, while the effective valence of the two ions is essentially the same, the Th ion has a sizably larger ionic radius and polarizability. We show immediately below that these differences suffice to stabilize the higher oligomers that were proposed by Photiadis and Papatheodorou [20] to form in acidic mixtures of molten $ThCl_4$ with CsCl and in the pure $ThCl_4$ melt.

The relevant calculations concern, first of all, the incremental energy $\Delta E^{(n)}$ for the binding of the doubly charged M_nCl_{4n+2} polyanions, for M = Th or Zr. $\Delta E^{(n)}$ is defined as

$$\Delta E^{(n)} = E_{\text{b}}^{n} - E_{\text{b}}^{(n-1)} - E_{\text{b}}(\mathrm{MCl_4}), \tag{5}$$

Table 6. Incremental binding energy $\Delta E^{(n)}$ of the $(\mathrm{M}_n\mathrm{Cl}_{4n+2})^{2-}$ series as a function of n (in eV).

	n = 1	n = 2	n = 3
$(\mathrm{Th}_n\mathrm{Cl}_{4n+2})^{2-}$	2.8	2.3	1.5
$(\mathrm{Zr}_n\mathrm{Cl}_{4n+2})^{2-}$	2.0	1.9	1.0

Table 7. Activation energies $E_{\mathrm{M}}(n,m)$ for the reactions (6) *in vacuo* (in eV).

M	$E_{\mathrm{M}}(2, 2)$	$E_{\mathrm{M}}(2, 3)$	$E_{\mathrm{M}}(3, 2)$	$E_{\mathrm{M}}(3, 3)$
Th	–3.8	–2.4	–2.3	–1.4
Zr	–5.0	–3.6	–3.5	–2.6

where E_{b}^n is the binding energy of the n-th member of the series and $E_{\mathrm{b}}(\mathrm{MCl}_4)$ is the binding energy of MCl_4. The results, reported in Table 6, clearly confirm the higher stability of the Th chloride polyanions.

A further question concerns the equilibria described by the formula

$$2\,\mathrm{MCl}_4 \Leftrightarrow \frac{2}{n+m}\left[\mathrm{M}_n\mathrm{Cl}_{4n-2}^{2+} + \mathrm{M}_n\mathrm{Cl}_{4n+2}^{2-}\right] + E_{\mathrm{M}}(n,m) \qquad (6)$$

for the coexistence of doubly charged polyanions and polycations in the pure melt. The results that we obtain for the activation energies $E_{\mathrm{M}}(n,m)$ by taking M = Th or Zr are shown in Table 7. Again, our earlier conclusions are fully confirmed: all these activation energies are significantly larger for the Zr compound, signalling that ion transfer between neutral species is relatively unfavoured in this melt.

Thus, while the present results in Tables 6 and 7 are quantitatively somewhat different from those reported earlier in [15], the present calculations confirm the appreciably greater stability of charged oligomers of Th chloride compared with Zr chloride.

5. Summary

In summary, we have in this work described a model for the ionic interactions in the halides of some tetravalent actinide metals 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 given input on the overlap and polarization parameters of the halogens. We have displayed some simple and reasonable trends of the metal-ion parameters, which could be usefully extended to the whole series of transuranic elements. It is hoped that the results should be useful in computer simulation studies of these compounds in the molten state.

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