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Stability of multiply charged anions of lanthanide hexafluorides LnF_6^{2-} and LnF_6^{3-} (Ln = Ce to Lu)*

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Abstract

The kinetic and electronic stability of a series of free LnF_6^{q-}-type lanthanide hexafluorides (Ln = Ce to Lu; $q = 2, 3$) is studied with the relativistic effective core potentials of Cundari and Stevens. In all complexes (LnF_6^{2-} and LnF_6^{3-}), the octahedral or almost octahedral structure is calculated to be stable through normal mode analyses at the unrestricted Hartree–Fock (UHF) and complete active space self-consistent field (CASSCF) levels. The electronic stability of all complexes is investigated using the state-averaged CASSCF and quasidegenerate perturbation theory with multiconfigurational self-consistent field reference functions (MC-QDPT) schemes. The most electronically stable LnF_6^{q-} is LnF_6^{2-} for Ce, Pr, Nd, Pm, Sm, Tb, Dy, Ho, Er, Tm, Yb. These LnF_6^{2-} anions are found to have an energy barrier with respect to the unimolecular decomposition $LnF_6^{2-} \rightarrow LnF_6^{5-} + F^-$ and are predicted to be long-lived species formally existing in a meta-stable state. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Multiply charged anion; Lanthanide hexafluoride; Electronic stability; Kinetic stability; 4f Orbital

1. Introduction

Many organic and inorganic molecules exist as multiply charged anions in solution phase. However, in the gas phase, few multiply charged anions exist due to their intrinsic instability originating from the Coulomb repulsion between excess minus charges. Thus, it is interesting and important to clarify the electronic structure and chemical bond of the multiply charged anions that are stable or meta-stable in the gas phase, and the design of such anions is a challenging problem in the electronic structure theory.

At present, there are many theoretical studies on the design of such multiply charged anions. Some good review articles, for example references [1–3], are now available. In the present paper we focus on MF_6^{q-}-type multiply charged anions, particularly the lanthanide hexafluorides LnF_6^{q-} (Ln = Ce to Lu). The MF_6^{q-}-type anions have been investigated by several researchers, since the extra charges can be distributed in the electronegative ligands in these molecules and thus they could be promising candidates for the

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anions. Miyoshi et al. [4] studied the electron affinities (EA) of CrF_6^-, MoF_6^-, and WF_6^- using a model potential method and configuration interaction (CI) calculations, and found the CrF_6^- anion has a positive EA and thus the CrF_6^{2-} dianion is the most stable in the CrF_6^{q-} ($q = 0$, 1, and 2) sequence. After several years, Hendrickx et al. [5] studied the stability of the CrF_6^{2-} dianion toward dissociation to $CrF_5^- + F^-$ and concluded that the energy barrier was sufficiently wide and high so as to prevent the dissociation process. Gutsev and Boldyrev [6] found that hexafluorides might possess a second positive EA; namely, their doubly charged anions may be stable to the loss of an electron. Gutowski et al. [7–11] made an intensive study on this type of octahedral species, MX_6^{q-} (X = F, Cl, Br, I; $q = 2,3$), and found several ones might be electronically and geometrically stable in the gas phase.

In our previous study [12], we investigated the electronic structures of lanthanide trifluorides LnF_3 and trichlorides $LnCl_3$ to derive a fundamental insight into the electronic structure, chemical bonding, and geometric structures of the lanthanide complexes. In these molecules, 2.1–2.2 (1.2–1.6) electrons are transferred from Ln to F (Cl), and the Ln–X bonds are dominated by charge-transfer but have a significant amount of covalent character that involves the 5d-orbital on Ln. The spin symmetry of the most stable state coincides with that of the ground state of Ln^{3+}; that is the 4f-electron increases with increasing the atomic number. If three F^-, or two F^- and one F, can be attached to the molecules LnF_3 with the extra charges distributed in the electronegative six F ligands like the above mentioned MF_6^{q-} complexes, LnF_6^{q-} or LnF_6^{3-} can be promising candidates of stable multiply charged anions. Assuming that the 4f-electrons remain not to participate in the chemical bond with ligands, the electronic structure in the chemical bonding region, namely, the occupation in 5d and 6s orbitals in Ln and 2p orbitals in F may be similar to each other in all the LnF_6^{q-}. This indicates the possibility that we can obtain the series of stable or meta-stable LnF_6^{q-}. In the present paper, we examine the stability of LnF_6^{2-} and LnF_6^{3-} for the electron ejection, geometry changes, and the fragmentation to singly charged anions using unrestricted Hartree–Fock (UHF), complete active space self-consistent field (CASSCF) methods [13,14], and the second-order

multiconfiguration quasidegenerate perturbation theory (MC-QDPT) with the CASSCF reference functions [15,16].

2. Computational details

One feature of the lanthanide complexes is that the several 4f-electron configurations are nearly degenerate to each other, resulting from the originally degenerate configurations of Ln^{3+} perturbed by the ligands. Hence methods to treat multiconfigurational electronic structures are required. We therefore used the CASSCF method for geometry optimizations and normal mode analyses and the second-order MC-QDPT with the CASSCF reference functions for more precise energy estimations. For comparison, we also carried out UHF calculations.

The stability of multiply charged lanthanide hexafluoride anions were examined by the following steps: (1) Firstly, we optimize LnF_6^{2-} and LnF_6^{3-} complexes with UHF and CASSCF methods; and (2) then make a normal mode analysis to check if the optimized geometries are really (local) minima. (3) Thirdly, we carry out MC-QDPT calculations with the CASSCF wave functions as references, for LnF_6^{2-} and LnF_6^{3-} and also for LnF_6^- and LnF_6^{4-} to determine the most stable ionic charge. (4) Finally, to verify the stability of the anions for fragmentation, we calculate the potential energy curves (PEC) for the reaction $LnF_6^{q-} \rightarrow LnF_5^{(q-1)-} + F^-$ with CASSCF for optimization and second order MC-QDPT for energy estimation.

We used relativistic effective core potentials (RECP) of Cundari and Stevens [17], such that 46 electrons of Ln (1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, and 4d) and two electrons of F (1s) were replaced with effective potentials. These RECP were determined including the relativistic effects, which are important especially for heavy atoms like lanthanide elements. The basis sets used with the RECP are of double-zeta quality, i.e. (6s6p4d7f/4s4p2d2f) for Ln and (4s4p/2s2p) for F (referred to as DZ) [18]. We also used the DZ basis sets augmented by diffuse p-function ($\zeta = 0.0746$) on F atoms (referred to as DZ + diff).

Equilibrium geometries of the octahedral LnF_6^{2-} and LnF_6^{3-} complexes were first determined for possible highest spin multiplicity states using analytic gradients at the UHF and CASSCF levels, and the

normal mode analysis was performed with the finite difference method of analytic gradients. In the CASSCF calculations, 4f-electrons were distributed among seven 4f-orbitals to construct active spaces.

Then we carried out state-averaged (SA) CASSCF calculations for the respective LnF_6^{2-} and LnF_6^{3-} complexes at the optimized geometries. Since the ligands do not have much affect on the 4f-electron configurations in Ln, 4f-orbitals and electrons were included in the active space, and the number of averaged states for $_ZLnF_6^{2-}$ and $_ZLnF_6^{3-}$ (Z: the atomic number of Ln) was taken to be $(2L_{Z+1} + 1)$ and $(2L_Z + 1)$, respectively, where L_Z is the total-orbital-angular momentum for the ground states of $_ZLn^{3+}$. In complexes with 2, 5, 6, 9, 12, and 13 4f-electrons, the lowest state is calculated to be a degenerate state.

The CASSCF (and SA-CASSCF) calculations were carried out with C_1 symmetry specification on electronic wave functions (in O_h or C_{2v} symmetry molecular structure), and then the O_h symmetry representation was assigned for the respective electronic states.

Further, we compared the second-order MC-QDPT total energies of the lowest states of LnF_6^{q-} ($q = 1 - 4$) to confirm the most stable anion to be LnF_6^{2-}/LnF_6^{3-}. MC-QDPT is a multi-state perturbation theory using several (SA-)CASSCF wavefunctions as reference, which can treat the nearly degenerate electronic states simultaneously.

To check the stability of the anions for fragmentation, we calculated the potential energy curves (PEC) at the UHF and state-specific CASSCF level of theories. The lowest energy fragmentation channel for LnF_6^{q-} anions is the dissociation into $LnF_5^{(q-1)-}$ and F^-. The points on the minimum energy dissociation path were obtained by keeping one of the Ln–F bonds at fixed distance, while optimizing the other distances and angles assuming C_s symmetry.

All the calculations were performed with the electronic structure program package GAMESS [19].

3. Results and discussion

3.1. Electronic and geometric structures

Through the preliminary calculations, it is verified that LnF_6^- and LnF_6^{4-} are much higher in energy than LnF_6^{2-} or LnF_6^{3-} for each central lanthanide atom.

In the complex LnF_6^{q-} ($q = 2, 3$), three electrons are expected to be transferred from Ln to six F atoms, forming ionic bonds between Ln^{3+} and six F^-. The triple-charged cation Ln^{3+} is known to have the electron configuration, $(4f)^m(5s)^2(5p)^6$ with m ranging from 1 (for Ce^{3+}) to 14 (for Lu^{3+}), in the ground state (no electrons in 5d and 6s orbitals), indicating that the electron is occupied one by one in 4f-orbitals according to the increase in the atomic number. Since the seven 4f-orbitals form a nearly degenerate orbital set, the n electrons should occupy f-orbitals according to the Hund rule in the complex. Thus the spin multiplicity of LnF_6^{q-} can be specified by the number of f-electrons, n. Through the preliminary calculations, it is verified that the other spin states have a relatively high energy for the respective LnF_6^{q-} at the Hartree–Fock level. In the following, our discussions will be focused on the most stable spin states; only 4f-orbitals of Ln can be open-shell orbitals in the electron configuration.

In the LnF_6^{q-}, the seven originally degenerate 4f-orbitals of Ln split into a_{2u}, t_{2u}, and t_{1u} orbitals in the O_h symmetry, or a_2, a_1, b_2, and b_1 in the C_{2v} symmetry. The electronic states of LnF_6^{q-} depend on how n electrons occupy these seven 4f-orbitals, namely the *4f-electron configuration*. Taking into account the Jahn–Teller instability of degenerate electronic configurations, we located equilibrium structures of O_h symmetry or C_{2v} symmetry at the UHF level of theory for all the possible non-degenerate 4f-electron configurations for the respective in LnF_6^{2-} and LnF_6^{3-}. Table 1 shows their total energies, Ln–F bond length, Mulliken charges on Ln, and expectation values of the square of the spin operator, $\langle S^2 \rangle$, for the lowest state. Equilibrium structures of complexes that have 2, 5, 6, 9, 12, and 13 4f-electrons were calculated to be close to O_h under the C_{2v} symmetry constraint. The spin contamination is found to be negligible in all cases (the largest deviation of $\langle S^2 \rangle$ from the theoretical value is about 0.05). In the respective LnF_6^{2-} and LnF_6^{3-}, the Ln–F bond length and Mulliken charge are almost constant among the different electron configurations, suggesting that the f-electrons have no relation to the chemical bonding of Ln–F.

We also located equilibrium structures of O_h or C_{2v} symmetry for the lowest state of LnF_6^{2-} and LnF_6^{3-} by the CASSCF method (including seven 4f-orbitals and related electrons in the active space), and evaluated

Table 1

Total energies, Ln–F bond lengths, Mulliken charges on Ln, the expectation value of the square of the spin operator $\langle S^2 \rangle$ and vibrational frequencies calculated by the UHF method for the equilibrium structure (O_h) in the ground state of LnF_6^{2-} and LnF_6^{3-}

Species	4f Electron configuration	Total energy (hartree)	Bond length (Å)	Mulliken charge	$\langle S^2 \rangle$	Frequencies (cm^{-1})					
						t_{2u}	t_{1u}	t_{2g}	e_g	t_{1u}	a_{1g}
CeF_6^{2-}		−181.63862	2.204	2.60		93	178	187	375	415	498
PrF_6^{2-}	$(a_{2u})^1$	−189.83219	2.186	2.59	0.77	99	182	192	381	423	505
NdF_6^{2-}	$(a_{2u})^1(t_{1u})^1$	−199.42892	2.174	2.58	2.02	108	190	200	392	429	509
PmF_6^{2-}	$(t_{2u})^3$	−210.49635	2.162	2.58	3.76	103	190	200	392	422	510
SmF_6^{2-}	$(a_{2u})^1(t_{1u})^3$	−223.03159	2.158	2.49	6.01	101	190	200	393	429	518
EuF_6^{2-}	$(a_{2u})^1(t_{2u})^2(t_{1u})^2$	−237.17472	2.140	2.52	8.77	109	199	209	413	434	519
GdF_6^{2-}	$(t_{2u})^3(t_{1u})^3$	−253.01104	2.125	2.48	12.05	114	203	213	414	437	524
TbF_6^{2-}	$(a_{2u})^1(t_{2u})^3(t_{1u})^3$	−270.63820	2.117	2.52	15.77	106	202	213	427	439	528
DyF_6^{2-}	$(a_{2u})^2(t_{2u})^3(t_{1u})^3$	−289.76509	2.101	2.50	12.01	112	207	218	430	441	532
HoF_6^{2-}	$(a_{2u})^1(t_{2u})^3(t_{1u})^5$	−310.72215	2.098	2.50	8.76	111	209	220	432	443	533
ErF_6^{2-}	$(a_{2u})^1(t_{2u})^3(t_{1u})^6$	−333.86519	2.079	2.47	6.01	99	203	217	447	449	543
TmF_6^{2-}	$(a_{2u})^2(t_{2u})^6(t_{1u})^3$	−358.93776	2.078	2.48	3.75	124	220	231	440	452	542
YbF_6^{2-}	$(a_{2u})^2(t_{2u})^6(t_{1u})^4$	−386.00511	2.062	2.46	2.00	123	221	232	435	459	546
LuF_6^{2-}	$(a_{2u})^2(t_{2u})^6(t_{1u})^5$	−415.49770	2.055	2.44	0.75	119	220	232	450	453	549
LaF_6^{3-}		−174.42173	2.472	2.24		82	162	161	263	280	342
CeF_6^{3-}	$(a_{2u})^1$	−181.45699	2.430	2.33	0.75	86	165	165	251	271	344
PrF_6^{3-}	$(a_{2u})^1(t_{1u})^1$	−189.67040	2.409	2.32	2.01	90	169	168	253	273	347
NdF_6^{3-}	$(t_{2u})^3$	−199.35611	2.411	2.32	3.76	93	173	171	257	276	349
PmF_6^{3-}	$(a_{2u})^1(t_{1u})^3$	−210.42679	2.395	2.31	6.02	93	175	173	262	281	354
SmF_6^{3-}	$(a_{2u})^1(t_{2u})^2(t_{1u})^2$	−222.98363	2.384	2.29	8.76	93	177	175	266	281	356
EuF_6^{3-}	$(t_{2u})^3(t_{1u})^3$	−237.15650	2.367	2.27	12.02	94	180	177	269	283	358
GdF_6^{3-}	$(a_{2u})^1(t_{2u})^3(t_{1u})^3$	−253.04359	2.336	2.26	15.77	92	181	178	280	292	369
TbF_6^{3-}	$(a_{2u})^2(t_{2u})^3(t_{1u})^3$	−270.39757	2.320	2.26	12.02	101	185	182	259	272	351
DyF_6^{3-}	$(a_{2u})^1(t_{2u})^3(t_{1u})^5$	−289.48920	2.312	2.26	8.76	96	186	183	269	289	367
HoF_6^{3-}	$(a_{2u})^1(t_{2u})^3(t_{1u})^6$	−310.67123	2.294	2.25	6.01	97	187	184	279	289	369
ErF_6^{3-}	$(a_{2u})^2(t_{2u})^6(t_{1u})^3$	−333.72562	2.284	2.24	3.75	100	191	187	280	289	368
TmF_6^{3-}	$(a_{2u})^2(t_{2u})^6(t_{1u})^4$	−358.69930	2.271	2.24	2.00	103	194	190	268	304	376
YbF_6^{3-}	$(a_{2u})^2(t_{2u})^6(t_{1u})^5$	−386.00223	2.262	2.23	0.75	97	192	189	288	293	375
LuF_6^{3-}	$(a_{2u})^2(t_{2u})^6(t_{1u})^6$	−415.43329	2.248	2.22		105	198	194	282	291	372

vibrational frequencies for the respective structure at the same level of theory. In the complexes GdF_6^{2-}, EuF_6^{3-}, which have 4 4f-electrons, and LuF_6^{2-}, YbF_6^{3-}, which have 13 4f-electrons, the lowest state is calculated to be a triply degenerate state at the SA-CASSCF level. Table 2 gives SA-CASSCF orbital occupancies of principal configuration state functions and their weights for the ground state of LnF_6^{2-} and LnF_6^{3-}, where the orbitals are represented by symmetry representations in O_h. Since there is only one electron configuration in the complexes that have 1, 6, 7, 8, and 13 4f-electrons, the CASSCF method coincides with the restricted open-shell Hartree–Fock method in these cases.

Table 3 gives total energies (at SA-CASSCF and MC-QDPT levels), Ln–F bond lengths (at the CASSCF level) and Mulliken charges on Ln (at the SA-CASSCF level) for the ground state of LnF_6^{2-} and LnF_6^{3-}. The lowest state at the SA-CASSCF level is different from that determined by the UHF method. In all the complexes, the CASSCF geometries and Mulliken charges are almost the same as those at the UHF level, supporting that the f-electron has very little relation to chemical bonds.

3.2. Stability for electron ejection

Table 4 gives vibrational frequencies of normal modes calculated for the optimized structures at the CASSCF level.

All of the computed vibrational frequencies for LnF_6^{q-} ($q = 2, 3$) are real. Thus, all of LnF_6^{q-} ($q = 2, 3$)

Table 2
SA-CASSCF active canonical orbital occupancies of principal configuration state functions and their weights in the ground state of LnF_6^{2-} and LnF_6^{3-}

Ln	LnF_6^{2-}					LnF_6^{3-}				
	4f	Weight	a_{2u}	t_{2u}	t_{1u}	4f	Weight	a_{2u}	t_{2u}	t_{1u}
Ce	0	1.00	0	0	0	1	1.00	1	0	0
Pr	1	1.00	1	0	0	2	0.464	0	2	0
							0.316	1	1	0
							0.222	0	1	1
Nd	2	0.464	0	2	0	3	0.776	0	3	0
		0.329	1	1	0		0.222	0	1	2
		0.196	0	1	1					
Pm	3	0.819	0	3	0	4	0.545	0	3	1
		0.175	0	1	2		0.223	1	2	1
							0.149	0	2	2
Sm	4	0.546	0	3	1	5	0.524	1	3	1
		0.229	1	2	1		0.347	1	2	2
		0.143	0	2	2		0.128	1	1	3
Eu	5	0.614	1	3	1	6	1.00	1	3	2
		0.249	1	2	2					
		0.098	1	1	3					
Gd	6	1.00	1	3	2	7	1.00	1	3	3
Tb	7	1.00	1	3	3	8	1.00	2	3	3
Dy	8	1.00	2	3	3	9	0.446	1	5	3
							0.325	2	4	3
							0.215	1	4	4
Ho	9	0.443	1	5	3	10	0.767	1	6	3
		0.334	2	4	3		0.235	1	4	5
		0.214	1	4	4					
Er	10	0.792	1	6	3	11	0.542	2	4	5
		0.208	1	4	5		0.254	2	6	3
							0.201	1	5	5
Tm	11	0.527	2	4	5	12	0.498	2	6	4
		0.274	2	6	3		0.278	2	5	5
		0.197	1	5	5		0.175	2	4	6
Yb	12	0.572	2	6	4	13	1.00	2	6	5
		0.203	2	5	5					
		0.132	2	4	6					
Lu	13	1.00	2	6	5	14	1.00	2	6	6

are at local minima of the potential energy surface of O_h symmetry or close to it.

To determine the most stable anion of LnF_6^{q-} for the respective Ln, we compare the total energies for the ground states of LnF_6^{2-} and LnF_6^{3-}. Energy differences between LnF_6^{2-} and LnF_6^{3-} at SA-CASSCF and MC-QDPT levels are listed in Table 5. From the MC-QDPT results in Table 5, one can see that the most stable LnF_6^{q-} is LnF_6^{2-} for Ce, Pr, Nd, Pm, Sm, Tb, Dy, Ho, Er, Tm, Yb and LnF_6^{3-} for Eu, Gd, Lu. To further verify the stability of these 14 anions as

to electron ejection, we performed CASSCF calculations for the lowest states of LnF_6^- for Ce, Pr, Nd, Pm, Sm, Tb, Dy, Ho, Er, Tm, Yb, and LnF_6^{2-} for Eu, Gd, Lu including the triply degenerated t_{1g} highest occupied orbitals in addition to the seven 4f-orbitals in the active space. The CASSCF (including 10 orbitals in the active space) calculations show that the lowest states of LnF_6^- (Ln = Ce, Pr, Nd, Pm, Sm, Tb, Dy, Ho, Er, Tm, and Yb) are higher than the lowest states of LnF_6^{2-} by 40 kcal/mol. However, the energy level of LnF_6^{2-} (Ln = Eu, Gd, Lu) is lower than that of LnF_6^{3-}.

3.3. Stability for fragmentation

To check the stability of LnF_6^{2-} (Ln = Ce, Pr, Nd, Pm, Sm, Tb, Dy, Ho, Er, Tm, and Yb) and LnF_6^{3-} (Ln = Eu, Gd, and Lu) for fragmentation, we first examined PEC of the reaction $LnF_6^{q-} \rightarrow LnF_5^{(q-1)-} + F^-$. Equilibrium geometries of the product molecules $LnF_5^{(q-1)-}$ and transition state geometries of the LnF_6^{q-} anions were determined at the CASSCF level with DZ + diff basis sets and listed in Table 6. Energy changes for the fragmentation path were calculated using SA-CASSCF and MC-QDPT method at the CASSCF optimized geometry and are also listed in Table 6.

The results show that the decomposition of the LnF_6^{q-} anions is exothermic in the reaction. The amount of energy released at the MC-QDPT level is 114, 114 and 125 kcal/mol for the triply charged anions EuF_6^{3-}, GdF_6^{3-}, and LuF_6^{3-}, respectively, and the entropy factor would increase exothermicity. On the other hand, the decompositions of the 11 LnF_6^{2-} anions are predicted to be slightly exothermic. Their energy changes at the MC-QDPT level are 6.4–13.4 kcal/mol.

Let us analyze briefly how the total energy and structure of LnF_6^{q-} change along the fragmentation channel. As an example, the seven-state-averaged-CASSCF PEC for $PrF_6^{2-} \rightarrow PrF_5^- + F^-$ is displayed in Figs. 1 and 2. In the following, we will refer to the minimum of the PEC as the equilibrium structure (EQ) and to the point at the maximum as the transition state (TS). Along the fragmentation path, the C_{2v} (almost O_h) ground state electron configuration of dianion PrF_6^{2-} correlates smoothly with the C_{4v} configuration of the TS and finally with the C_{4v}

Table 3
Total energies (at SA-CASSCF and MC-QDPT2 levels), Ln–F bond lengths (CASSCF), and Mulliken charges on Ln (SA-CASSCF) for the equilibrium structure (O_h) in the ground state of LnF_6^{2-} and LnF_6^{3-}

Ln	LnF_6^{2-}				LnF_6^{3-}			
	Total energy (hartree)		Bond length (Å)	Mulliken charge	Total energy (hartree)		Bond length (Å)	Mulliken charge
	SA-CASSCF	MC-QDPT2			SA-CASSCF	MC-QDPT2		
Ce	−181.63834	−182.57080	2.204	2.614	−181.45407	−182.38172	2.331	2.430
Pr	−189.82924	−190.78469	2.186	2.599	−189.70995	−190.66137	2.327	2.414
Nd	−199.43370	−200.41034	2.177	2.600	−199.36651	−200.35615	2.319	2.398
Pm	−210.50489	−211.49989	2.164	2.596	−210.44014	−211.45178	2.312	2.384
Sm	−223.05216	−224.08416	2.152	2.530	−222.98234	−224.04906	2.294	2.369
Eu	−237.17424	−238.23667	2.140	2.525	−237.14767	−238.24540	2.277	2.351
Gd	−252.99019	−254.05694	2.128	2.512	−253.02660	−254.13770	2.268	2.336
Tb	−270.62098	−271.70919	2.118	2.520	−270.38139	−271.55082	2.259	2.323
Dy	−289.74838	−290.87746	2.101	2.505	−289.57488	−290.78644	2.256	2.307
Ho	−310.82037	−311.99630	2.096	2.505	−310.68308	−311.93557	2.251	2.296
Er	−333.87601	−335.08176	2.083	2.478	−333.73426	−335.03252	2.241	2.283
Tm	−358.96098	−360.21573	2.074	2.477	−358.80100	−360.16109	2.238	2.272
Yb	−386.11462	−387.42673	2.064	2.463	−385.99761	−387.41405	2.229	2.260
Lu	−415.50068	−416.83870	2.055	2.455	−415.43328	−416.87947	2.217	2.248

configuration of the PrF_5^- ion and an F^- ion. The PEC of PrF_6^{2-} system is seen to exhibit an energy barrier to dissociation of F^-. At short distances between PrF_5^- and F^-, the PEC becomes attractive. At larger distances the Coulomb repulsion between the charges of the dissociation products PrF_5^- and F^- dominates the shape of the curve and the curve is repulsive. Owing to this repulsion energy, the PEC of PrF_6^{2-} comes above the dissociation

limit to PrF_5^- and F^- ion as a whole. Thus PrF_6^{2-} formally exists in a meta-stable state due to the existence of an energy barrier to dissociation.

This way the PEC of the other anions were examined. The values of the height of energy barrier to fragmentation calculated at SA-CASSCF and MC-QDPT methods are listed in Table 7. The barrier heights for CeF_6^{2-}, PrF_6^{2-}, NdF_6^{2-}, PmF_6^{2-}, SmF_6^{2-},

Table 4
Vibrational frequencies (in cm^{-1}) by the CASSCF method with DZ + diff basis

	LnF_6^{2-}						LnF_6^{3-}					
	t_{2u}	t_{1u}	t_{2g}	e_g	t_{1u}	a_{1g}	t_{2u}	t_{2g}	t_{1u}	e_g	t_{1u}	a_{1g}
Ce	93	178	187	375	415	498	86	164	165	251	271	344
Pr	99	182	192	382	423	505	90	168	170	256	276	348
Nd	100	187	195	389	425	507	90	169	171	259	277	349
Pm	107	190	199	399	429	510	91	172	174	269	278	357
Sm	94	190	203	419	436	518	145	205	218	265	282	355
Eu	146	232	284	414	435	521	93	174	180	269	283	358
Gd	103	199	208	421	436	525	95	178	182	271	283	361
Tb	106	202	213	428	439	528	97	178	185	271	288	363
Dy	112	207	217	430	442	532	98	181	187	273	285	363
Ho	113	211	219	433	443	533	98	181	188	278	288	368
Er	116	215	231	436	445	536	101	185	191	281	291	368
Tm	117	215	245	458	459	552	104	189	195	279	294	372
Yb	118	219	228	442	454	542	115	197	205	285	306	378
Lu	128	227	236	455	459	549	105	194	198	282	291	372

Table 5
Relative energies of LnF_6^{3-} (kcal/mol) for LnF_6^{2-} with DZ + diff basis

Ln	UHF	CASSCF	SA-CASSCF	MC-QDPT2
Ce	114.0	114.7	115.6	118.7
Pr	101.5	73.3	74.9	77.4
Nd	64.7	43.6	42.2	34.0
Pm	9.3	40.4	40.6	30.2
Sm	−27.9	44.0	43.8	22.0
Eu	8.9	16.0	16.7	−5.5
Gd	−20.4	−24.8	−22.9	−50.7
Tb	151.0	147.8	150.3	99.4
Dy	173.1	108.0	108.9	57.1
Ho	73.5	88.1	86.2	38.1
Er	62.0	88.8	88.9	30.9
Tm	113.9	98.5	100.4	34.3
Yb	1.8	71.9	73.4	8.0
Lu	40.4	39.6	42.3	−25.6

TbF_6^{2-}, DyF_6^{2-}, HoF_6^{2-}, ErF_6^{2-}, TmF_6^{2-} and YbF_6^{2-} are 40.2, 39.7, 40.2, 41.2, 40.5, 43.7, 40.7, 43.9, 37.4, 44.8, and 43.3 kcal/mol, respectively. Energy barriers for the LnF_6^{2-} anions are very close to one another and exhibit substantial width and heights (37.4–44.8 kcal/mol). Owing to the Coulomb repulsion energy of dissociation products $LnF_5^{(q-1)-}$ and F^-, it is obvious that the PEC of the anions are entirely above the

dissociation limit like the PEC of PrF_6^{2-}. Thus these LnF_6^{2-} anions are expected to exist in a meta-stable state with a long lifetime due to the existence of an energy barrier to dissociation. On the other hand, EuF_6^{3-}, GdF_6^{3-}, and LuF_6^{3-} have barriers of 8.8, 9.9, and 3.7 kcal/mol, respectively, to dissociation, and these species are barely meta-stable. However, as indicated in the previous section, these triply charged anions are unstable for an electron ejection.

4. Summary and conclusions

We investigated the electronic and geometric structures of the series of ionic gas phase lanthanide hexafluorides LnF_6^{q-} (Ln = Ce to Lu; q = 2, 3) to obtain an insight into their kinetic and electronic stability. We have found that local minima exist for these species at geometries of octahedral symmetry or close to it. The CASSCF and SA-CASSCF results show that the Ln–F bond length and net charge on Ln are independent of 4f-electron configuration. The most stable electronic structures of LnF_6^{q-} anions for respective central lanthanide atom were investigated using the MC-QDPT method by comparing total energies of LnF_6^{2-} and LnF_6^{3-} in their ground states. The results

Table 6
CASSCF optimized structures (bond lengths in Å; bond angles in °) for the transition state (TS in C_{2v}) and dissociation product (DP in D_{3h}) of LnF_6^{q-} using the DZ + diff basis. (The numbers in (1−2) or (2−1−3) etc. indicate the atoms shown in Fig. 1. R_{ax} and R_{eq} denote distances between Ln and an axial F and an equatorial F, respectively)

|	TS						DP	
	Bond length (Å)				Bond angle (°)		Bond length (Å)	
	(1−2)	(1−3)	(1−5)	(1−6)	(2−1−3)	(2−1−6)	R_{ax}	R_{eq}
CeF_6^{2-}	4.650	2.152	2.148	2.154	82.63	86.56	2.140	2.121
PrF_6^{2-}	4.600	2.135	2.118	2.121	84.41	83.18	2.133	2.107
NdF_6^{2-}	4.650	2.120	2.100	2.114	84.28	82.82	2.117	2.093
PmF_6^{2-}	4.650	2.105	2.087	2.106	84.01	83.01	2.104	2.083
SmF_6^{2-}	4.600	2.092	2.081	2.093	84.13	83.12	2.085	2.073
TbF_6^{2-}	4.500	2.066	2.035	2.066	82.77	82.78	2.068	2.034
DyF_6^{2-}	4.501	2.049	2.021	2.049	82.78	82.79	2.073	2.020
HoF_6^{2-}	4.437	2.037	2.015	2.045	83.35	82.73	2.047	2.012
ErF_6^{2-}	4.400	2.027	2.003	2.036	83.30	82.77	2.035	2.002
TmF_6^{2-}	4.408	2.020	1.993	2.025	83.20	82.43	2.030	1.991
YbF_6^{2-}	4.358	2.012	1.988	2.011	83.33	82.33	2.014	1.983
EuF_6^{3-}	3.500	2.298	2.274	2.292	87.64	87.72	2.276	2.232
GdF_6^{3-}	3.470	2.283	2.253	2.283	87.64	87.71	2.257	2.222
LuF_6^{3-}	3.330	2.199	2.172	2.199	87.24	87.53	2.172	2.139
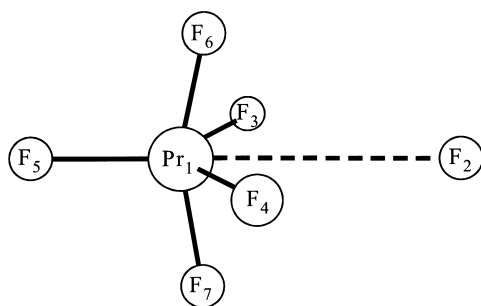
Fig. 1. $PrF_6^{2-} \rightarrow PrF_5^- + F^-$ dissociation. The indices attached to the atoms are used in Table 6.

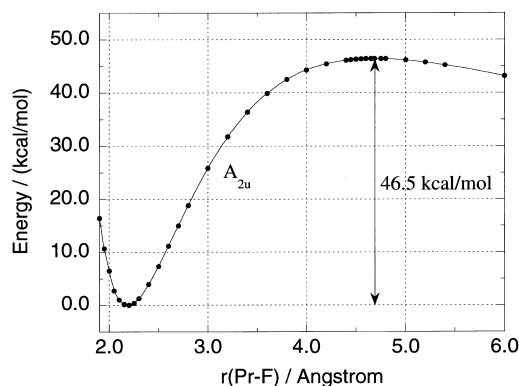Fig. 2. Potential energy curve for $PrF_6^{2-} \rightarrow PrF_5^- + F^-$ dissociation.

show that the most stable LnF_6^{q-} is LnF_6^{2-} for Ce, Pr, Nd, Pm, Sm, Tb, Dy, Ho, Er, Tm, Yb and LnF_6^{3-} for Eu, Gd, Lu. However, the CASSCF (including 10 orbitals in the active space) calculations show that LnF_6^{2-} (Ln = Eu, Gd, Lu) are lower in energy than LnF_6^{3-}.

Stability of the anions LnF_6^{2-} (Ln = Ce, Pr, Nd, Pm, Sm, Tb, Dy, Ho, Er, Tm, Yb) to dissociation is predicted. All of these anions are found to be thermo-dynamically unstable with respect to the fragmenta-tion pathway of LnF_6^{q-} to $LnF_5^{(q-1)-}$ and F^-. The energy released is 6.40–13.4 kcal/mol for 11 LnF_6^{2-} anions. However, the fragmentation pathways of the dianions have been found to exhibit energy barriers and these anions are in a meta-stable state. Values of barrier heights for the LnF_6^{2-} anions are 37.4–44.8 kcal/mol at the MC-QDPT level of theory. We conclude that the ions LnF_6^{2-} (Ln = Ce, Pr, Nd, Pm, Sm, Tb, Dy, Ho, Er, Tm, and Yb) can be new species that are stable to auto-ejection of extra electron and to fragmentation.

Acknowledgements

Table 7
Heat of reaction and barrier height (kcal/mol) for the unimolecular decomposition with DZ + diff basis

Species	Heat of reaction		Barrier height	
	SA-CASSCF	MC-QDPT2	SA-CASSCF	MC-QDPT2
CeF_6^{2-}	−5.67	−11.7	45.4	40.2
PrF_6^{2-}	−4.01	−10.5	46.5	39.7
NdF_6^{2-}	−4.43	−11.3	47.2	40.2
PmF_6^{2-}	−3.81	−10.5	48.2	41.2
SmF_6^{2-}	−4.99	−12.2	47.8	40.5
TbF_6^{2-}	−4.32	−10.9	49.8	43.7
DyF_6^{2-}	−3.37	−6.40	50.0	40.7
HoF_6^{2-}	−5.13	−11.1	49.4	43.9
ErF_6^{2-}	−7.41	−13.4	43.0	37.4
TmF_6^{2-}	−4.99	−11.0	50.4	44.8
YbF_6^{2-}	−5.52	−11.3	49.7	43.3
EuF_6^{3-}	−113	−114	9.77	8.77
GdF_6^{3-}	−113	−114	10.6	9.91
LuF_6^{3-}	−125	−125	4.09	3.73

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