7990 J. Phys. Chem. A **1998,** *102,* 7990−7995

Theoretical Study of the Molecular Properties of Cerium Trihalides and Tetrahalides CeX_n ($n = 3, 4$; X = F, Cl)

Giuseppe Lanza[‡] **and Ignazio L. Fragalà***[,§]

Dipartimento di Chimica, Università della Basilicata, Via N. Sauro 85, 85100 Potenza, Italy, and Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6, 95125 Catania, Italy

Received: February 4, 1998; In Final Form: June 24, 1998

Relativistic effective core potential quantum chemical investigations of molecular geometries, vibrational frequencies, and bond dissociation energies of cerium tri- and tetrahalides CeX_3 and CeX_4 (X = F, Cl) are presented. At RHF, MP2, and CASSCF levels of theory, CeF_4 and $CeCl_4$ possess stable tetrahedral (T_d) geometries, and the calculated bond distances and vibrational frequencies lie very close to available electron diffraction and vibrational spectroscopy data. There is evidence of different stabilities of present tetrahalides toward the reductive elimination to CeX_3. Thus, the very strong CeF_3−F bond can be contrasted with the easier chlorine elimination to $CeCl_3$. Five possible lower-lying electronic states are associated with open-shell CeX_3 halides, depending on the 4f orbital occupancy. The $(4f_{z^3})^1$ configuration represents the ground state, mostly due to the nonbonding nature of the corresponding atomic orbital whose electron density, perpendicular to the molecular plane, minimizes the electrostatic repulsion between the unpaired 4f metal electron and the halogen pairs. In agreement with experimental results, pyramidal structures (C_{3v}) are found for CeF_3 for any of $4f^1$ state at all levels of theory. By contrast, the relative stability of the planar and pyramidal structures of $CeCl_3$ strongly depends on the adopted basis set, as well as on the effects of correlation terms.

Introduction

Recent advances in quantum chemistry have spurred state-of-the-art theoretical studies of molecular properties of 4f-metal systems, and several investigations have recently appeared in the literature.[1] Particular attention has been devoted to lanthanide trihalides, and ab initio calculations have provided information on geometrical structures, vibrational frequencies, dissociation energies, thermodynamic functions, and chemical bonds.[2−7] The reason behind the large interest is associated with the great relevance, in various fields of the applied chemistry and physics,[8−12] of rather simple 4f molecular systems as well as to the large variety of experimental measurements which can be compared and contrasted with very high-level theoretical calculations. Despite the numerous theoretical studies reported so far for the lanthanide trihalides, few investigations have been devoted to lanthanide metals having oxidation states other than +3.[2,13] Nevertheless, the +2 state represents an important oxidation state for Sm, Eu. and Yb, while +4 is important for Ce, Pr, and Tb.

The CeF_4 is a well-characterized molecule, it is stable in the gas phase, and it has application as a fluorinating agent[14] and IR-reflecting coating on halogen lamps.[15] There are reports for $CeCl_4$, even though its existence has not been unambiguously demonstrated.[16]

In this perspective, the present study focuses on molecular structures of CeX_4 and CeX_3 (X = F, Cl) to throw light on some controversial experimental data. The reductive dissociation of $CeCl_4$ to $CeCl_3$ has been also analyzed and contrasted with CeF_4 to provide insights on those effects which ultimately affect the different stabilities.

Computational Methods

The RECP of Stevens et al.[17] (which explicitly treats 5s, 5p, and 4f electrons) and a basis set contracted as [4sp,2d,2f], were used for the cerium atom. The standard all-electron 6-31G* basis sets were used for the fluorine and chlorine atoms.[18] Since the halogen atom basis set may play an important role in molecular properties, larger basis sets (11s,6p) and (13s,10p), contracted as [5s,3p] and [6s,5p] (Dunning's Triple zeta) and added with two "d" polarization functions (TZ2P), were used for fluorine and chlorine atoms, respectively.[3,19]

The geometry and vibrational frequencies of all the systems investigated, were determined using the RHF and ROHF methods for closed-shell and open-shell systems, respectively. For degenerate states, the average configuration states multiconfigurational formalism was adopted in order to obtain a symmetric charge density.

The correlation effects were considered through the second-order Møller−Plesset (MP2) method using the single reference RHF and ROHF determinants. Complete active space self-consistent field (CASSCF) calculations were also carried out for CeX_4 systems. Two different active spaces were adopted: (i) the eight electrons associated with the four Ce−X σ bonds were distributed among the four σ^* antibonding orbitals ($4\sigma/4\sigma^*$); (ii) the six electrons (one σ and two π orbitals) associated with a Ce−X bond were distributed among one σ^* and two π^* antibonding orbitals ($\sigma 2\pi/\sigma^* 2\pi^*$). The $4\sigma/4\sigma^*$ CASSCF wave function was used to investigate the geometry and vibrational frequencies of the CeX_4 ground state, while the $\sigma 2\pi/\sigma^* 2\pi^*$ was used to investigate the cleavage of the Ce−X bond.

---

* Corresponding author.

[‡] Università della Basilicata.

[§] Università di Cantania.

S1089-5639(98)01006-8 CCC: \$15.00

TABLE 1: Calculated Bond Lengths *R* (Å), Vibrational Frequencies (cm^{-1}), and Partial ($\Delta H1$) and Total ($\Delta H4$) Dissociation Energies (kcal/mol)

	R	ν_2 (e)	ν_4 (f_2)	ν_3 (f_2)	ν_1 (a_1)	$\Delta H1$	$\Delta H4$
CeF_4							
HF/6-31G*	2.026	130	144	618	659	53	454
CAS/6-31G*	2.034	135	148	608	645		
MP2/6-31G*	2.024	115	124	620	654	109	609
HF/TZ2P	2.036	133	147	579	630	47	455
MP2/TZ2P	2.041	121	132	571	616	105	621
exptl[a]	1.939−2.080	128[b]	134[b]	561	608		
$CeCl_4$							
HF/6-31G*	2.489	75	84	363	364	2	355
CAS/6-31G*	2.493	78	86	357	360		
MP2/6-31G*	2.449	71	73	375	368	52	431
HF/TZ2P	2.496	78	88	364	365	7	370
MP2/TZ2P	2.470	70	72	376	369	53	454

[a] Experimental values from refs 22 and 24. [b] See text.

Because of the very flat potential energy surface toward the out-of-plane deformation, additional calculations were performed for $CeCl_3$ to analyze the effects of electron correlation and basis set. Therefore, high-order correlation effects were considered through the coupled cluster single and double wave function expansion (CCSD) using the 6-31G* basis set. MP2 calculations were performed employing the TZ2P basis set added with a "g" ($\alpha = 0.35$) polarization function on the cerium atom (TZ2PG) or diffuse "sp" functions ($\alpha = 0.0437$) on the chlorine atoms (TZ2P+).

The geometries of all the involved structure were optimized using gradient techniques at HF, CASSCF, and MP2/RHF levels. For MP2/ROHF and CCSD calculations, the stationary points were derived from a set of single-point energy calculations. The nature of the stationary points was always determined by numerical evaluations of the complete matrix of force constants. Because of the presence of various electronic states very close in energy, the lower molecular symmetry causes state flipping in second derivative calculations. Therefore, vibrational frequencies were evaluated only for certain electronic states.

Presently, calculations do not explicitly include spin−orbit effects. Nevertheless, they should not influence molecular properties since nearly degenerate states have the same spin multiplicity. Thus, for example, spin−orbit effects qualitatively estimated for $An(CH_3)_3$ (An = U, Np, and Pu) have been found small and not significantly affecting stabilities of various electronic states and geometrical structures.[20]

All the calculations were performed using the HONDO95.3[19] code on IBM-SP and Cray C90 computers. The CCSD calculations were carried out using the G94[21] program.

Results and Discussion

Geometrical Structure and Vibrational Frequencies. *CeF_4.* Earlier high-temperature gas-phase electron diffraction studies of CeF_4 have suggested some symmetry lowering from the regular tetrahedral structure to either C_{3v} or C_{2v} symmetries.[22] Electron deflection studies on molecular beams of CeF_4 show very slight refocusing, thus suggesting small distortion from the symmetric T_d equilibrium geometry.[23] IR and Raman spectra and polarization measurements of CeF_4 molecules trapped in various inert gas matrixes have unequivocally pointed to a tetrahedral structure.[24]

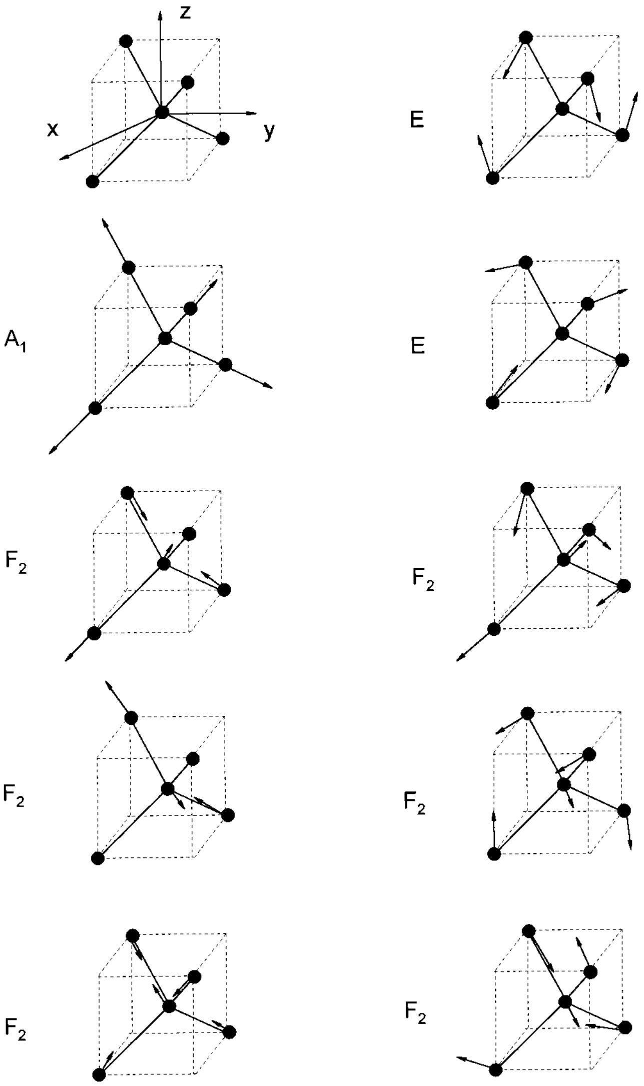

Figure 1. Normal modes of tetrahedral CeX_4 systems.

The present calculations indicate a tetrahedral structure at all levels of theory with no evidence of any lower symmetry (Table 1). The calculated Ce−F bond length is slightly influenced by both basis sets and correlation effects and ranges from 2.024 to 2.041 Å, compared to experimental values ranging from 1.9393 to 2.0802 Å.[22]

The CeX_4 molecules in the T_d point group have four fundamental vibrations: the symmetric $\nu_1(a_1)$ and asymmetric stretching ν_3 (f_2) and the double and triple degenerate bending modes ν_2(e) and $\nu_4(f_2)$ (Figure 1). Only the triple degenerate fundamentals are IR active, but all vibrations are Raman active.

Calculated harmonic vibrational frequencies (Table 1) are satisfactorily in agreement with experimental IR and Raman data. Note that, although the ν_2(e) and $\nu_4(f_2)$ frequencies have been found experimentally coincident (134 cm^{-1}),[24] present calculations indicate an energy separation of 10 cm^{-1}. This separation is probably too small to be clearly detectable in Raman experiments. Nevertheless, a careful analysis of the Raman peak at 134 cm^{-1} (see ref 24) reveals an asymmetric shape (not observable in IR spectra) that resembles a doublet structure with two maxima at 134 and 128 cm^{-1}. This suggests that the low energy absorption can be associated with the ν_2(e), leaving the remainder for $\nu_4(f_2)$. The calculated stretching frequencies $\nu_1(a_1)$ and $\nu_3(f_2)$ are moderately overestimated (10%) with respect to experimental values adopting the 6-31G* basis set. They, however, compare well with vibrational data using the TZ2P basis set (average error less than 2%).

$CeCl_4$. The $CeCl_4$ system has never been characterized in the gas phase. There is, however, some indication of its

TABLE 2: Calculated Bond Lengths *R* (Å), Bond Angles *θ* (deg), Relative Energies Δ*E* (kcal/mol), Vibrational Frequencies (cm^{-1}), and Total Dissociation Energy Δ*H*3 (kcal/mol) for CeF_3

metal configuration	state		R^a	θ^a	ΔE^a	ν_2	ν_4	ν_3	ν_1	$\Delta H3$
6-31G*	D_{3h}	C_{3v}								
$4f_{z^3}$	$^2A_2''$		2.106 [2.090]	120 [120]	0.02 [0.9]					
$4f_{z^3}$		$^2A_1$	2.104 [2.080]	119.3 [112.7]	0.0 [0.0]	50	130	556	571	401 [504]
$4f_{y(x^2-3y^2)}$	$^2A_2'$		2.101 [2.086]	120 [120]	2.3 [3.7]					
$4f_{y(x^2-3y^2)}$		$^2A_2$	2.098 [2.076]	117.1 [110.9]	2.1 [2.2]	61	134	554	575	
$4f_{x(3^x2-y^2)}$	$^2A_1'$		2.101 [2.086]	120 [120]	2.8 [3.3]					
$4f_{yz^2}$, $4f_{xz^2}$	$^2E'$		2.105 [2.091]	120 [120]	1.3 [1.4]					
$4f_{yz^2}$, $4f_{xz^2}$		^2E	2.100 [2.078]	117.1 [111.8]	1.2 [0.1]					
$4f_{xyz}$, $4f_{z(y^2-x^2)}$	$^2E''$		2.101 [2.086]	120 [120]	1.1 [0.9]					
$4f_{xyz}$, $4f_{z(y^2-x^2)}$		^2E	2.100 [2.075]	119.2 [113.6]	1.0 [0.1]					
TZ2P										
$4f_{z^3}$	$^2A_2''$		2.128 [2.122]	120 [120]	0.0 [0.1]	42	131	515	534	408 [522]
$4f_{z^3}$		$^2A_1$	[2.115]	[117.1]	[0.0]					
$4f_{y(x^2-3y^2)}$	$^2A_2'$		2.126 [2.120]	120 [120]	2.3 [2.7]					
$4f_{y(x^2-3y^2)}$		$^2A_2$	2.124 [2.110]	118.6 [115.8]	2.2 [2.3]	56	137	512	533	
$4f_{x(3x^2-y^2)}$	$^2A_1'$		2.125 [2.115]	120 [120]	2.9 [2.8]					
$4f_{yz^2}$, $4f_{xz^2}$	$^2E'$		2.127 [2.122]	120 [120]	1.3 [0.6]					
$4f_{yz^2}$, $4f_{xz^2}$		^2E	2.127 [2.114]	119.2 [115.7]	1.2 [0.2]					
$4f_{xyz}$, $4f_{z(y^2-x^2)}$	$^2E''$		2.124 [2.116]	120 [120]	1.2 [0.5]					
$4f_{xyz}$, $4f_{z(y^2-x^2)}$		^2E	[2.112]	[117.6]	[0.3]					
experimental values[b]						86	116	483		463
						78	134	505	537	

[a] MP2 values are given in parentheses. [b] Vibrational frequencies from refs 25 and 26, while dissociation energy from ref 28.

existence.[16] Present calculations indicate that $CeCl_4$ possesses a regular tetrahedral geometry with a Ce−Cl bond length of 2.47 Å. The calculated harmonic vibrational frequencies are almost unaffected by both the basis set and the correlation effects as commonly found in lanthanide trihalides.[3,4] Therefore, they represent a reliable estimation of experimental frequencies that can be useful for spectral identification of $CeCl_4$ complex in the gas phase or inert matrix.

CeF_3. Low-temperature IR spectra of CeF_3 trapped in inert gas matrixes have been independently reported by two authors. Wesley and DeKock[25] assigned the vibrational data on the basis of a planar structure. By contrast, Hauge et al.[26] pointed to a pyramidal structure. High-temperature electric deflection studies have shown a substantial refocusing of the molecular beam, thus indicating a permanent dipole moment and, hence, a pyramidal structure.[27]

The CeX_3 halides possess $4f^1$ electron configurations, and various electronic states can be populated. In the D_{3h} symmetry of the planar structure, the seven 4f orbitals transform as a_1', a_2', a_2'', e′, and e″. In the pyramidal geometry (C_{3v}) they correspond to the A_1, A_2, A_1, E, and E representations, respectively. In both cases, five states (two of which are degenerate) can be therefore found close lying in energy.

The calculated relative energy as well as geometrical data associated with the above-mentioned electronic states are reported in Table 2. As expected, they lie very close in energy, and the energy sequence ($^2A_2'' < {}^2E'' \approx {}^2E' < {}^2A_2' \sim {}^2A_1'$) is almost insensitive to both basis set and electron correlation. In any case, the $^2A_2''$ state [$(4f_{z^3})^1$ configuration] represents the ground state. The $^2A_2''$, $^2E''$, $^2E'$, and $^2A_2'$ states appear unstable toward out-of-plane bending and, therefore, have associated slightly pyramidal structure. No conclusion can be drawn as far as the $^2A_1'$ state is concerned since it collapses into a more stable state with a different metal electron configuration upon out-of-plane distortion (Table 2). However, considering the trend observed for all other CeF_3 states, a pyramidal structure is also expected.

The analysis of bond angles associated with various $4f^1$ states provides evidence of a clear correlation between the out-of-plane bending and the angular shape of the involved 4f orbital (see also Table 3 for $CeCl_3$). Therefore, the $^2A_2'$, $^2A_1'$, and $^2E'$ states favor the pyramidal geometries. The naive VSEPR theory can account for this observation in simple terms of minimization of the electrostatic repulsive metal−ligand interactions. Therefore, in the $^2A_2''$ and $^2E''$ states, the halide ligands lie in a nodal plane (xy) of the a_2'' (f_{z^3}) and e″ ($f_{y(3x^2-y^2)}$, $f_{x(x^2-3y^2)}$) metal orbitals. The planar D_{3h} geometry is therefore preferred. By contrast, the $^2E'$, $^2A_2'$, and $^2A_1'$ states favor C_{3v} arrangements since the a_2', a_1', and e′ orbitals have a maximum of density on the D_{3h} molecular plane. The pyramidal structures become more stable.

The dispersion of the Ce−F bond lengths associated with the various electronic states is 0.01 Å due to the minor participation of 4f orbitals in the bonding. As a consequence, the related vibrational frequencies are almost identical for all of the possible states. Moreover, the calculated vibrational frequencies can be satisfactorily compared to experiments (Table 2). In particular, the ν_2 and ν_4 frequencies are very close to experimental measurements, while the ν_1 and ν_3 stretching modes appear overestimated (≈10%) at the HF/6-31G* level. This deviation, however, is largely reduced using the TZ2P basis set (average error ≈ 1%). Interestingly enough, the IR spectrum of CeF_3 shows a multiplet feature extending from 819.5 to 842.5 cm^{-1}.[25] Two possible assignments have been proposed: (i) to a vibrational transition of CeF_4 whose formation might be associated with some CeF_3 disproportionation, and (ii) to an electronic transition of CeF_3. Experimental[24] and calculated highest vibrational frequencies of CeF_4 are consistently (≈200 cm^{-1}) below these values, while calculations provide evidence of CeF_3 electronic excited states lying ≈800 cm^{-1} above the ground state. This suggests that the mentioned absorption can be associated with a CeF_3 $4f^1$ electronic transition.

$CeCl_3$. Earlier electron diffraction studies have indicated a pyramidal C_{3v} geometry with a 2.569 Å average bond length and a $\theta = 111.6°$ bond angle.[28] Gas-phase IR studies do not provide, however, conclusive evidence with respect to the molecular symmetry.[5,29] Presently, calculated bond distance and vibrational frequencies are very close to the experimental values. The calculated energy sequence ($^2A_2'' < {}^2E' < {}^2E'' < {}^2A_2' < {}^2A_1'$) of the possible $4f^1$ states is slightly different than that found

TABLE 3: Calculated Bond Lengths R (Å), Bond Angles θ (deg), Relative Energies ΔE (kcal/mol), Vibrational Frequencies (cm^{-1}), and Total Dissociation Energy $\Delta H3$ (kcal/mol) for $CeCl_3$

metal configuration	state		R^a	θ^a	ΔE^a	$\nu_2(a_2'')$	$\nu_4(e'')$	$\nu_3(e'')$	$\nu_1(a_1')$	$\Delta H3$
6-31G*	D_{3h}	C_{3v}								
$4f_{z^3}$	$^2A_2''$		2.609 [2.554]	120 [120]	0.0 [0.03]	40	69	323	307	352 [381]
$4f_{z^3}$		$^2A_1$	[2.550]	[118.5]	[0.0]					
$4f_{y(x^2-3y^2)}$	$^2A_2'$		2.605 [2.550]	120 [120]	0.88 [1.3]	37	71	322	307	
$4f_{y(x^2-3y^2)}$		$^2A_2$	[2.545]	[117.9]	[1.2]					
$4f_{x(3x^2-y^2)}$	$^2A_1'$		2.604 [2.549]	120 [120]	1.1 [0.8]	37	68	323	306	
$4f_{x(3x^2-y^2)}$		$^2A_1$	[2.541]	[118.1]	[0.7]					
$4f_{yz^2}$, $4f_{xz^2}$	^2E		2.609 [2.551]	120 [120]	1.0 [0.9]	33	68	323	307	
$4f_{yz^2}$, $4f_{xz^2}$		^2E	[2.549]	120 [118.9]	1.0 [0.0]	33	68	323	307	
$4f_{xyz}$, $4f_{z(y^2-x^2)}$	$^2E''$		2.605 [2.550]	120 [120]	1.7 [0.8]					
$4f_{xyz}$, $4f_{z(y^2-x^2)}$		^2E	[2.546]	[118.1]	1.7 [0.7]					
TZ2P										
$4f_{z^3}$	$^2A_2''$		2.610 [2.570]	120 [120]	0.0 [0.0]	45	73	328	312	363 [403]
$4f_{y(x^2-3y^2)}$	$^2A_2'$		2.608 [2.568]	120 [120]	1.1 [1.4]	44	76	325	309	
$4f_{y}(_{x^2-3y^2})$		$^2A_2$	[2.569]	[119.1]	[1.4]					
$4f_{x(3x^2-y^2)}$	$^2A_1'$		2.607 [2.565]	120 [120]	1.3 [1.1]	44	73	325	309	
$4f_{x(3x^2-y^2)}$		$^2A_1$	[2.565]	[119.2]	[1.1]					
$4f_{yz^2}$, $4f_{xz^2}$	$^2E'$		2.609 [2.571]	120 [120]	1.0 [0.1]	32	71	327	312	
$4f_{xyz}$, $4f_{z(y^2-x^2)}$	$^2E''$		2.607 [2.570]	120 [120]	1.8 [0.9]					
$4f_{xyz}$, $4f_{z(y^2-x^2)}$		^2E	[2.569]	[119.5]	[0.8]					
experimental values^b			2.569	111.6		52	80	319		

^{a} MP2 values are given in parentheses. ^{b} Geometrical structure from ref 22, vibrational frequencies from ref 29, while dissociation energy from ref 28.

TABLE 4: Calculated Bond Lengths R (Å), Bond Angles θ (deg), and Relative Energies ΔE (kcal/mol) for $CeCl_3$

metal configuration	symmetry	state	R	θ	ΔE
MP2/TZ2P+					
$4f_{z^3}$	D_{3h}	$^2A_2''$	2.573	120	0.0
$4f_{y(x^2-3y^2)}$	C_{3v}	$^2A_2$	2.570	119.6	1.4
$4f_{x(3x^2-y^2)}$	D_{3h}	$^2A_1'$	2.569	120	1.1
MP2/TZ2PG					
$4f_{z^3}$	C_{3v}	$^2A_1$	2.555	118.1	0.0
$4f_{y(x^2-3y^2)}$	C_{3v}	$^2A_2$	2.552	117.3	1.6
$4f_{x(3x^2-y^2)}$	C_{3v}	$^2A_1$	2.550	117.6	1.2
CCSD/6-31G*					
$4f_{z^3}$	C_{3v}	$^2A_1$	2.555	119.7	0.0
$4f_{y(x^2-3y^2)}$	C_{3v}	$^2A_2$	2.556	119.6	1.1
$4f_{x(3x^2-y^2)}$	C_{3v}	$^2A_1$	2.558	119.6	0.6

in CeF_3, even though the ground state remains the $^2A_2''$. In addition, the mentioned states are spread in a smaller (than in CeF_3) energy range. This is indication of smaller perturbation of the 4f energy levels, possibly due to reduced electrostatic 4f-X_{np} repulsion, depending, in turn, upon the greater (than Ce−F) Ce−Cl bond lengths. All the states have associated planar geometries at HF level. The planar structures, however, become unstable toward out-of-plane bending (except the $^2A_2''$ and $^2E'$) at MP2 level. These results contrast with previous theoretical studies on $LaCl_3$ (CISD)[4] and $GdCl_3$, $LuCl_3$ (MP2)[3] and CASSCF studies on the entire series of $LnCl_3$ systems.[6] This observation prompted us to probe the problem more deeply, improving both the basis set as well as including high-order correlation effects (Table 4). The inclusion of diffuse “sp” functions on chlorine does not affect results which remain similar to MP2/TZ2P data. A slightly reduced tendency toward pyramidal structure is only observed. The inclusion of one “g” polarization function on the cerium atom increases (relative MP2/TZ2P) the tendency of $CeCl_3$ toward the pyramidal structure, (all the analyzed $4f^1$ states have C_{3v} geometry). Alternatively, the inclusion of high-order correlation effects (CCSD/6-31G*) increases the tendency toward the planar structure. The problem remains, therefore, open to question, even though it is clear that pyramidal geometries might represent an artifact of MP2 calculations.

Bond Stability. The total dissociation energies of CeX_4 and CeX_3 have been evaluated in terms of energy difference relative to isolated atoms in their ground states.

$$CeX_3 \rightarrow Ce + 3X + \Delta H3$$

$$CeX_4 \rightarrow Ce + 4X + \Delta H4$$

At HF and MP2 levels of theory, $\Delta H3$ values are very similar, adopting both the 6-31G* and TZ2P bases and can be satisfactorily compared to experimental results (Tables 2 and 3).[30] In particular, HF calculations involve a slight underestimation due to the lack of correlation effects, while MP2 $\Delta H3$ values are moderately overestimated (10%). Note, however, that it is well-known that single-reference MP2 slightly overestimates dissociation energy values of the transition metal complex.[31]

The energy variation associated with reductive elimination processes:

$$CeX_4 \rightarrow CeX_3 + X + \Delta H1$$

appears of particular interest since it provides straightforward information on the relative stabilities of the cerium tetrahalides.

At the HF level of theory, the F ligand is strongly bonded in CeF_4 while a poorer bond is found in $CeCl_4$ (Table 1). The inclusion of correlation effects increases considerably the $\Delta H1$ dissociation energy values for both X = F, Cl even though it becomes evident that CeF_4 remains much more stable (105 kcal/mol) than $CeCl_4$ (53 kcal/mol). Unfortunately, no experimental quantitative thermochemical data have been reported to date for comparison. Nevertheless, the trend presently observed finds counterpart both in the greater stability of CeF_4[27,32,33] and in the well-known difficulties observed in $CeCl_4$ isolation.[32,33]

In this general context it becomes of interest to study the CeX_3−X cleavage from a mechanistic point of view and, in particular, to analyze the energy profiles of the ground state and of first excited states of CeF_4 and $CeCl_4$ along the dissociative pathways. The energies of these relevant states

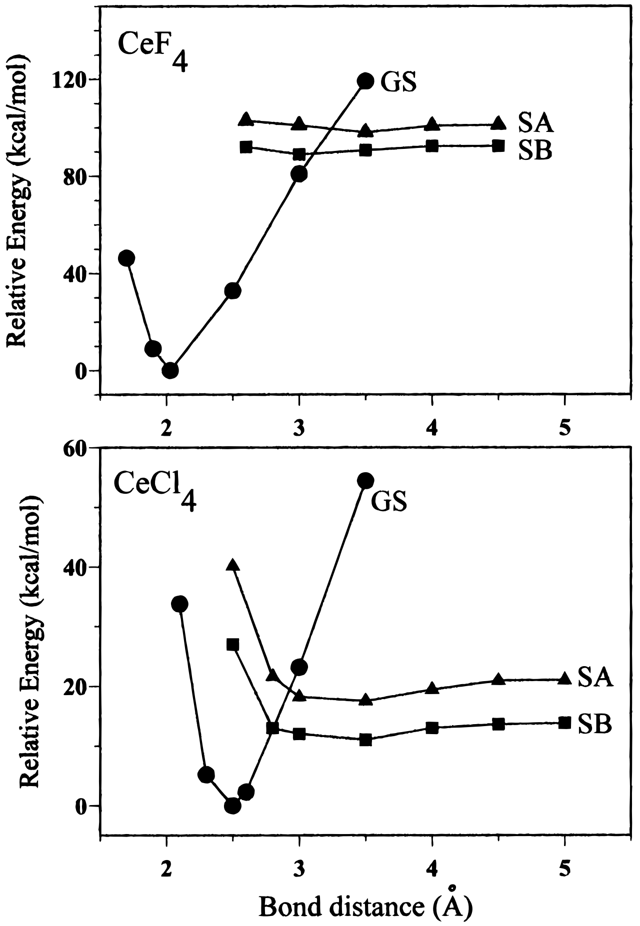

Figure 2. Energy profiles for the CeF_3−F and $CeCl_3$−Cl cleavage.

(Figure 2) have been evaluated, using the CASSCF $\sigma 2\pi/\sigma^* 2\pi^*$ wave function with the 6-31G* basis set upon elongation of a selected Ce−X bond length while optimizing all other geometrical parameters in the appropriate (C_{3v}) symmetry.

The ground state (GS) of present trigonally distorted CeX_4 has a $\sigma^2\pi^4$ configuration (**a**). Low-lying, excited, open-shell states can have either a $\sigma^1\pi^4$,$4f^1$ (**b**) configuration (σ-promotion) or the doubly degenerate $\sigma^2\pi^3$,$4f^1$ configuration due to promotion either from π p_y (**c**) or from π p_x (**d**). Note that the energy values of the degenerate states are averages of **c** and **d** contributions, and they are labeled in the figure as symmetry adapted (SA) states, due to the symmetric charge distribution. All attempts to analyze the configuration **b** failed since it collapses into more stable states which ultimately arise from the degenerate configurations **c** and **d** ($\sigma^2\pi^3$,$4f^1$) upon removal of the symmetry degenerate (symmetry broken SB states). Both SA and SB dissociative states have a very flat profile. It is evident that the ($\sigma^2\pi^3$,$4f^1$) configurations of CeF_4 become more stable than the ground state upon stretching the CeF_3−F bond 1.0 Å beyond the energy minimum through a considerable energy barrier (~90 kcal/mol). Shorter elongation (0.3 Å) as well as only sizable (~15 kcal/mol) barriers are found for $CeCl_4$. This indicates that dissociative states are much more vibrationally accessible in the $CeCl_4$, thus rendering the molecule considerably less stable than CeF_4.

In the same perspective, Figure 3 reports the evolution of one-electron MOs of the ground and lower-lying excited states along the CeF_3−F dissociation pathway. Upon moving one fluorine ligand farther away, the related σ and π bonds become less stable. For CeF_3−F distances longer than 3.0 Å (the crossing of curves of ground and SB states), the MO sequence of the SB excited state resembles the combination of those the $4f^1$ of CeF_3 and $2p^5$ F radical while that of the GS resembles the CeF_3^+−F^- ion-pair electron structure.

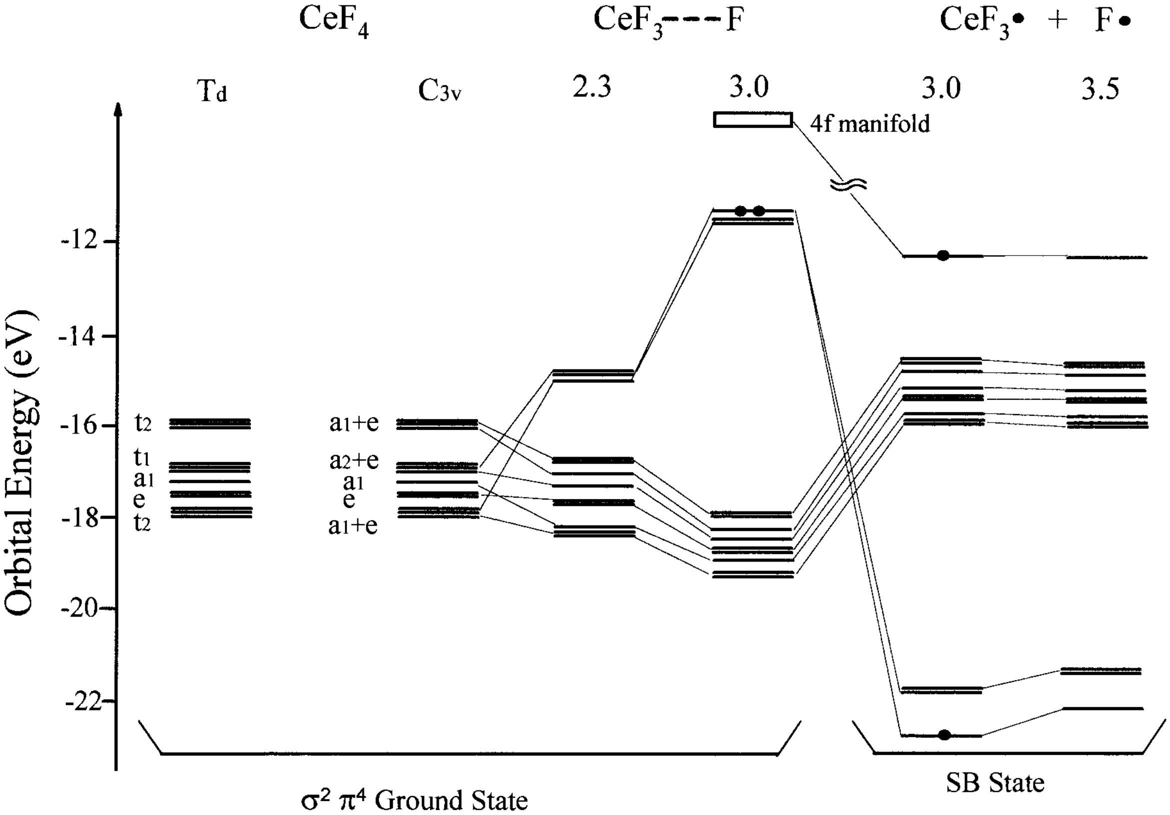

Figure 3. Orbital correlation energy diagram for the ground ($\sigma^2\pi^4$) and SB ($\sigma^2\pi^4$,$4f^1$) states during the CeF_3−F cleavage.

Conclusions

Present calculations provide the first detailed description of molecular properties of CeF_4 and $CeCl_4$. Consistent with experimental data on CeF_4, calculations indicate a tetrahedral geometry in the molecular ground state of both CeF_4 and $CeCl_4$. Energetics associated with the cleavage of a single CeX_3-X bond underscores the inherent thermodynamic and kinetic stabilities of CeF_4 vis-à-vis the $CeCl_4$ analogue. Both calculated bond distances and vibrational frequencies are in good agreement with experimental data of CeF_4. The vibrational frequencies predicted for the still-vanishing $CeCl_4$ may be used as reference for the spectral identification.

The five lowest energy states of the CeF_3 molecule are predicted to have pyramidal geometries. Nevertheless, the bending out-of-the plane of the planar D_{3h} structure strongly depends on the adopted basis set and correlation effects. The influence of basis set and correlation terms on the molecular shape of $CeCl_3$ appears particularly critical, since either planar or pyramidal structures are found, depending on the level of calculations. Further studies adopting a larger basis set as well as including correlation effects through CCSD or large configuration interaction certainly warrant further scrutiny.

The Ce$-$X bond lengths as well as vibrational frequencies of CeX_3 molecular states are both almost insensitive to various $4f^1$ electron configurations, thus suggesting only a marginal involvement of 4f orbitals in the bonding. Nevertheless, effects of nonbonded repulsion among the unpaired 4f metal electron and the halogen electron pairs have an influence on the bond angle due to the very flat potential energy along the out-of-plane deformation.

Acknowledgment. The authors gratefully thank the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST, Rome) and the Consiglio Nazionale delle Ricerche (CNR, Rome) for financial support. The CINECA computer center (Casalecchio di Reno, BO) is also gratefully acknowledged for a grant of computer time.

References and Notes

(1) Dolg, M.; Stoll, H. in *Handbook on the Physics and Chemistry of Rare Earths*; Gschneider, K. A., Jr., Eyring, L., Eds.; North-Holland Publishing Company: Amsterdam, 1996; Vol. 22, Chapter 152, p 1.

(2) Dolg, M.; Stoll, H.; Preuss, H. *J. Mol. Struct. (THEOCHEM)* **1991**, *235*, 67.

(3) Lanza, G.; Fragalà, I. L. *Chem. Phys. Lett.* **1996**, *255*, 341.

(4) Di Bella, S.; Lanza, G.; Fragalà, I. L. *Chem. Phys. Lett.* **1993**, *214*, 598.

(5) Kovacs, A.; Konings, R. J. M.; Booij, A. S. *Chem. Phys. Lett.* **1997**, *268*, 207; Kovacs, A.; Konings, R. J. M. *Vib. Spectrosc.* **1997**, *15*, 131.

(6) Cundari, T. R.; Sommerer, S. O.; Strohecker, L. A.; Tippett, L. *J. Chem. Phys.* **1995**, *103*, 7085.

(7) Joubert, L.; Picard, G.; Legendre, J.-J. *Inorg. Chem.* **1998**, *37*, 1984.

(8) Caird, J. A.; Carnal, W. T.; Hessler, J. P.; Williams, C. W. *J. Chem. Phys.* **1981**, *74*, 798.

(9) McPhall, D. S.; Hocking, M. G.; Jeffes, J. H. E. *J. Mater. Sci.* **1985**, *20*, 1457.

(10) Hake, D.; Urland, W. *Z. Anorg. Allg. Chem.* **1992**, *613*, 45.

(11) Murase, K.; Ozaki, T.; Machida, K.; Adachi, G. *J. Alloys Compd.* **1996**, *233*, 96.

(12) Murase, K.; Machida, K.; Adachi, G. *J. Alloys Compd.* **1995**, *217*, 218.

(13) Culberson, J. C.; Knappe, P.; Rosch, N.; Zerner, M. C. *Theor. Chim. Acta* **1987**, *71*, 21.

(14) Asovich, V. S.; Kornilov, V. V.; Maksimov, B. N. *Zh. Prikl. Khim.* **1994**, *67*, 107.

(15) Kawakatsu, A. Japanese Patent Applications 94/9,839, August 18, 1995.

(16) Haschke, J. M. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneider, K. A., Jr., Eyring, L., Eds.; North-Holland Publishing Company: Amsterdam, 1979; Vol. 4, Chapter 32, p 89.

(17) Cundari, T. R.; Stevens, W. J. *J. Chem. Phys.* **1993**, *98*, 5555.

(18) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257; Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(19) Dupuis, M.; Marquez, A.; Davidson, E. R. *HONDO 95.3*; CHEM-Station (IBM Corporation) Neighborhood Road, Kingston, NY, 12401, 1995.

(20) Ortiz, J. V.; Hay, P. J.; Marin, R. L. *J. Am. Chem. Soc.* **1992**, *114*, 2736.

(21) Frish, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Che, W.; Wong, M. W.; Andres, J. L.; Repogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, J. D.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A. *Gaussian 94*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(22) Petrov, V. M.; Girichev, G. V.; Giricheva, N. J.; Petrova, V. N.; Krasnov, K. S.; Zasorin, E. Z.; Kiselev, Y. M. *Dokl. Akad. Nauk SSSR* **1981**, *259*, 1399.

(23) Kaiser, E. W.; Sunder, W. A.; Falconer, W. E. *J. Less-Common Met.* **1972**, *27*, 383.

(24) Buchmarina, V. N.; Gerasimov, A. Y.; Predtechenskii, Y. B.; Shklyarik, V. G. *Opt. Spectros.* (USSR) **1992**, *72*, 38.

(25) Wesley, R. D.; DeKock, *J. Chem. Phys.* **1971**, *55*, 3866.

(26) Hauge, R. H.; Hastie, J. W.; Margrave, J. L. *J. Less-Common Met.* **1971**, *23*, 359; Hauge, R. H.; Hastie, J. W.; Margrave, J. L. *J. Less-Common Met.* **1975**, *39*, 309.

(27) Kaiser, E. W.; Falconer, W. E.; Klemperer, W. *J. Chem. Phys.* **1972**, *56*, 5392.

(28) Krasnov, K. S. *Molekulyarn'ie Postoyann'ie Neorganicheskikh Soedineinenii*; Khimiya: Leningrad, 1979.

(29) Kovacs, A.; Konings, R. J. M.; Booij, A. S. *Vib. Spectrosc.* **1995**, *10*, 65.

(30) Myers, C. E. *Inorg. Chem.* **1975**, *14*, 199.

(31) Kozlowski, P. M.; Davidson, E. R. *Chem. Phys. Lett.* **1994**, *222*, 615.

(32) Gibson, J. K.; Haire, R. G. *Thermochim. Acta* **1988**, *133*, 241.

(33) Bayanov, A. P.; Fralov, Y. A. *Zh. Fiz. Khim.* **1977**, *51*, 1567.