Structural and Thermochemical ab Initio Studies of Lanthanide Trihalide Molecules with Pseudopotentials

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Structural and vibrational frequency studies have been carried out for 30 lanthanide trihalide molecules LnX_3 (Ln = La−Lu; X = Cl, F) using ab initio quasi-relativistic effective core potentials at Hartree−Fock and Møller−Plesset post-Hartree−Fock levels of theory. A planar D_{3h} geometry was obtained for all trichloride molecules. In accordance with previous theoretical works, a C_{3v} structure was clearly established for the majority of the trifluorides. Calculated bond lengths and vibrational frequencies are in good agreement with the experimental data. Therefore, thermochemical functions have been estimated from thermostatistics calculations combined with our quantum mechanics results. The electronic partition function is crucial in order to be in accordance with experimental data tables, especially for temperatures higher than 500 K. A simple example of thermochemical equilibrium clearly proves the validity of the estimated functions in the case of the lanthanum halides.

Introduction

Today, the materials sciences are devoted to the synthesis of new products or compounds with controlled properties. For most of them, thermochemical data are not available from common databases. As a matter of fact, the experimental determination of these data is difficult for some compounds since it may depend on purity or lead to dangerous handlings. This is prejudicial, since these data are needed in order to develop synthesis processes. One way to obtain them is based on quantum calculations, which allow us to obtain enthalpies and vibrational frequencies at 0 K for geometrically optimized structures. These data, combined with classical thermostatistic relationships,[1] lead to the heat capacities, entropies, enthalpies, and free energies of the considered molecule. For example, this procedure has already been used in the case of light and heavy metal chlorides.[2−5] For systems with heavy elements, relativistic effects have to be taken into account. This can be done by either Dirac−Fock-type calculations or Hartree−Fock calculations using relativistic pseudopotentials.[6] The purpose of this paper is to check the consistency of this last procedure with lanthanide chlorides and fluorides whose thermochemical data are already known.

The industrial interest of the lanthanide halides (chlorides and fluorides) is very important. These molecules are involved in the industrial production of very reactive metals, through an electrodeposition process in alkali halide melts.[7−10] Therefore, numerous experimental or theoretical works have been undertaken on these molecules. They were studied experimentally using several methods: rotational, vibrational, and electronic studies, electron diffraction, and electric deflection of a molecular beam.[11,12]

The first important theoretical works began in the early seventies. One of the most important was carried out by Myers et al. on lanthanide trihalides.[6,13−17] Then, thanks to the creation of the lanthanide pseudopotentials during the eighties, ab initio calculations were performed on these molecules.[18−29] The major work at this time was carried out by Dolg et al. They studied

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lanthanide halides, lanthanide oxides, and other derivatives.[6,18−24] A similar very complete structural work was recently realized by Cundari et al. on 56 LnX_3 molecules[26] (Ln = Ce−Lu; X = F, Cl, Br, and I) based on the pseudopotentials created by Stevens and Cundari, which include the f orbitals in the valence shell.[27] Finally, Di Bella[28] et al. and Lanza et al.[29] calculated the equilibrium geometries and vibrational frequencies of six trihalide molecules. To our knowledge, no theoretical thermochemical study has been carried out to date using quantum mechanics data.

Procedure

It's commonly admitted that, in a first approximation for the rare earths, the 4f orbitals may be treated as core orbitals and that only 5d and 6s valence orbitals are important for a chemical study. The various studies realized in Stuttgart by Dolg et al.[6,18−24] confirm this assumption. The same authors also published a paper concerning pseudopotentials which attribute the 4f orbitals explicitly to the valence space and use a spin−orbital coupling correction.[24] However, these calculations were not feasible for any molecules other than the diatomic rare earth molecules. Therefore, it seemed to be acceptable in our calculations to use pseudopotentials which explicitly include the 4f orbitals in the lanthanide's core. That is why we chose a set of quasi-relativistic pseudopotentials developed by the Stuttgart team for lanthanides.[21,22] The term "quasi-relativistic" means that spin−orbit effects are omitted and the other one-electron relativistic effects included. This set of pseudopotentials explicitly includes the f orbitals within the core orbitals with a fixed 4f occupation corresponding to the desired valency of the atom. Therefore, for the trihalide molecules, all rare earth elements are modeled as 11-valence-electron systems. The Stuttgart pseudopotentials were also chosen for the halogens,[30] since they will shorten the computational time for larger molecules which will be studied in the future. They are modeled as 7-valence-electron systems, and the *n*s and *n*p orbitals are included in the valence shell ($n = 2$ and $n = 3$ for fluorine and chlorine atoms, respectively). The determination of the quasi-relativistic pseudopotential parameters is described in detail in ref 21.

Concerning the associated valence basis sets, we chose, for both halogens and lanthanides, the corresponding optimized valence basis sets developed at Stuttgart,[21,22,30] adding a polarization function on the halogens in order to describe the anionic nature of the halide ligands. For the trivalent rare earth elements optimized (7s6p5d)/[5s4p3d] valence basis sets were applied; for chlorine and fluorine atoms, optimized (4s5p1d)/[2s3p1d] valence basis sets were used. To improve the results, we also used all-electron 6-31G(d) basis sets for the halogens.

The ab initio software Gaussian94[31] used during this work, was running on both IBM RISC 6000 and SGI R4000 workstations. The geometry optimizations and vibrational frequency calculations were limited to the restricted Hartree−Fock (RHF) level. To improve the computational accuracy, it was necessary to take the electronic correlation by a Møller−Plesset perturbational approach (MP2) into account.

The first thermostatistics calculations were carried out using the MacMaster software developed in the laboratory.[32] It has the advantage of running easily on a simple Macintosh computer. Using the molecular structure and the vibrational frequencies, this software allows the determination of some thermochemical properties: enthalpy, entropy, Gibbs free energy, and heat capacity. An IBM RISC 6000 version of this software (G-Thermo) was also developed. It takes the electronic partition function in thermostatistics studies into account.[33]

Table 1. Experimental and RHF and MP2 Calculated Bond Lengths (in Å) for LnF_3 Molecules[a]

LnF_3	exptl[b] [15]	exptl[b] [11]	RHF[c] calcd	RHF[d] calcd	MP2[c] calcd	MP2[d] calcd
LaF_3	*2.22*	2.14	2.17 (117.5)	2.15 (116.0)	2.18 (115.1)	2.15 (112.9)
CeF_3	*2.18*	*2.13*	2.16 (118.2)	2.13 (116.8)	2.16 (115.7)	2.13 (113.7)
PrF_3	*2.17*	2.09	2.14 (118.6)	2.12 (117.4)	2.14 (116.1)	2.12 (114.1)
NdF_3	2.16	*2.09*	2.13	2.11 (118.0)	2.13 (116.5)	2.10 (114.6)
PmF_3	*2.16*	*2.08*	2.11	2.09 (118.9)	2.12 (117.5)	2.09 (115.5)
SmF_3	*2.14*	*2.07*	2.10	2.08 (119.8)	2.10 (118.2)	2.08 (116.3)
EuF_3	*2.13*	*2.05*	2.08	2.06	2.09 (118.6)	2.06 (118.3)
GdF_3	*2.12*	2.05	2.07	2.06	2.08 (118.9)	2.06 (117.8)
TbF_3	*2.10*	*2.03*	2.06	2.05	2.07	2.05 (119.1)
DyF_3	*2.09*	*2.02*	2.05	2.03	2.06	2.04
HoF_3	*2.08*	2.01	2.03	2.02	2.04	2.02
ErF_3	*2.07*	*2.00*	2.02	2.01	2.03	2.01
TmF_3	*2.05*	*1.99*	2.01	2.00	2.02	2.00
YbF_3	*2.04*	*1.98*	2.00	1.99	2.01	1.99
LuF_3	*2.04*	*1.97*	1.99	1.98	2.00	1.98

[a] The calculated bond angles of nonplanar trifluorides are indicated between parentheses (in degrees). [b] Numbers in italices represent extrapolated values. [c] ECPs for both lanthanides (with optimized (7s6p5d)/[5s4p3d] valence basis sets) and fluorine (with an optimized (4s5p1d)/[2s3p1d] valence basis set). [d] ECPs for lanthanides (with optimized (7s6p5d)/[5s4p3d] valence basis sets) and a 6-31G(d) basis set for fluorine.

Results

A preliminary structural study was necessary to validate for our molecular systems the use of the Stuttgart pseudopotentials (allowing short computational time) before undertaking any rare earth thermodynamical study which is the main purpose of this work. We considered two sources of experimental values.[11,15] Two remarks are to be made: these values do not agree exactly and only a part of them was really experimentally measured (by electronic diffraction). In fact, these data are a mix of experimental and extrapolated values.

First, we used Stuttgart's ECPs for both lanthanides and halogens. A geometry optimization was performed on thirty LnX_3 compounds (Ln = La−Lu; X = Cl, F), starting from a nonplanar C_{3v} geometry (bond angle X−Ln−X equal to 109.5°). All of these optimizations were realized at RHF and MP2 levels and based on a gradient-driven geometry optimization. In Tables 1 and 2, the calculated results are compared to the two sources of "experimental" values.[11,15] Whatever the level of theory, we obtained a final planar D_{3h} geometry for all trichloride molecules. If the electronic correlation is taken into account, pyramidal C_{3v} structures are found for the majority of the trifluoride compounds, that is, LaF_3 to GdF_3. Considering the most recent experimental values,[11] we found between 3 and 5 pm of error on Ln−F bond lengths and between 1 and 6 pm of error on Ln−Cl bond lengths (at MP2 level, using pseudopotentials for both lanthanides and halogens). These errors may

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Table 2. Experimental and RHF and MP2 Calculated Bond Lengths (in Å) for $LnCl_3$ Molecules

$LnCl_3$	exptl[a] [15]	exptl[a] [11]	RHF[b] calcd	RHF[c] calcd	MP2[b] calcd	MP2[c] calcd
$LaCl_3$	*2.62*	2.59	2.67	2.68	2.65	2.66
$CeCl_3$	*2.58*	*2.58*	2.65	2.66	2.63	2.64
$PrCl_3$	*2.57*	2.55	2.63	2.64	2.61	2.62
$NdCl_3$	2.56	*2.54*	2.61	2.61	2.59	2.60
$PmCl_3$	*2.55*	*2.53*	2.60	2.59	2.57	2.59
$SmCl_3$	*2.53*	*2.52*	2.58	2.57	2.56	2.57
$EuCl_3$	*2.52*	*2.50*	2.56	2.56	2.53	2.55
$GdCl_3$	*2.51*	2.49	2.55	2.55	2.53	2.54
$TbCl_3$	*2.50*	2.48	2.54	2.53	2.51	2.52
$DyCl_3$	*2.49*	*2.47*	2.52	2.52	2.50	2.51
$HoCl_3$	*2.47*	2.46	2.51	2.51	2.48	2.50
$ErCl_3$	*2.46*	*2.45*	2.49	2.50	2.46	2.48
$TmCl_3$	*2.44*	*2.44*	2.48	2.49	2.46	2.47
$YbCl_3$	*2.43*	*2.43*	2.47	2.48	2.44	2.46
$LuCl_3$	2.42	2.42	2.46	2.47	2.43	2.46

[a] Numbers in italics represent extrapolated values. [b] ECPs for both lanthanides (with optimized (7s6p5d)/[5s4p3d] valence basis sets) and chlorine (with an optimized (4s5p1d)/[2s3p1d] valence basis set). [c] ECPs for lanthanides (with optimized (7s6p5d)/[5s4p3d] valence basis sets) and a 6-31G(d) basis set for chlorine.

Table 3. Experimental and RHF and MP2 Calculated Vibrational Wavenumbers (in cm^{-1}) for $LaCl_3$ and LaF_3 with Several Basis Sets

	$LaCl_3$				LaF_3			
	ν_1	ν_2	ν_3	ν_4	ν_1	ν_2	ν_3	ν_4
RHF[a] calcd	292	27	313	71	529	50	517	128
RHF[b] calcd	288	33	310	67	554	59	543	125
MP2[a] calcd	294	16	317	67	521	65	507	121
MP2[b] calcd	289	24	313	60	554	72	539	114
RHF[c] calcd	278	65	316	57	553	113	543	110
exptl (±10) [15]	335	51	316	79	540	82	511	125

[a] Using ECPs for both lanthanum and halogens (with optimized valence basis sets). [b] Using ECPs for lanthanum (with optimized valence basis sets) and a 6-31G(d) basis set for halogens. [c] Using a MINI basis set for lanthanum and a 6-31G(d) basis set for halogens.

seem important. In fact, that corresponds to a maximum error of 2.4% for both Ln−F and Ln−Cl bonds. Using a 6-31G(d) basis set for halogens greatly improves the results for trifluoride lanthanides. RHF and MP2 geometry optimizations have been carried out with this all-electron basis set while keeping pseudopotentials on the lanthanides. We obtained a very good agreement between theory and experiment for the bond lengths of the trifluorides. In comparison with the experimental results of ref 11, we found up to 3 pm of error on Ln−F bond lengths (MP2 level), thus corresponding to a maximum error of 1.4%. Moreover, the pyramidal C_{3v} structures are also more pronounced since the bond angles decrease. However, it does not modify the previous results in the case of the trichloride lanthanides. The planarity of these molecules is certainly due to the fact that the Cl^- ions have a greater π-donor capability than the F^- ions.[28]

It is interesting to notice that Cundari et al.[26] and Dolg et al.[23] found similar results, respectively, with MCSCF (multiconfiguration SCF) and CI-SD (configuration interaction single and double excitations) calculations. Cundari et al. treated explicitly 4f orbitals in the valence shell, while Dolg et al. included them in the core of the atom. These results verify the hypothesis that the 4f orbitals can be explicitly included in the core without loss of accuracy. Although the present results are slightly different from the data calculated by Cundari et al., they are rather similar to those obtained by Dolg et al.

As yet, the exact structure of these compounds was not clearly established. The first experimental studies allowed us to think that these molecules adopt a planar D_{3h} geometry.[34] Then, the planarity or nonplanarity problem became a subject of controversy.[11,17,35−41] The present work, like the studies realized by Cundari et al., seems to indicate a D_{3h} lowest-energy structure at 0 K for the trichloride compounds. They used ECPs for both lanthanides and chlorine atoms with a polarization function on the halogens at the MCSCF level of theory. With the same MCSCF calculations, they found planar structures for all 56 of the lanthanide halide molecules. They also realized a structural study on trifluorides at UHF level using ECPs for lanthanides and a 6-31G* basis set for fluorines. All 14 of the structures converged to a planar geometry except three molecules (CeF_3, PrF_3 and PmF_3). As precised by Cundari in his paper, it is strongly probable that these "floppy" molecules are fluxional at ambient temperature. Recent works realized by Di Bella et al.[28] and Lanza et al.[29] indicate C_{3v} structures for LaF_3, GdF_3, and LuF_3 molecules when correlation effects are taken into account. They found that the electron correlation seems to play a crucial role in predicting the trigonal shape of fluorides as it has been confirmed by our study. However, the C_{3v} structures they found are very close to the planar geometry ($\theta = 118.9°$ and 118.7°, respectively, for GdF_3 and LuF_3 molecules at MP2 level, using a very large TZ2P basis set on fluorines[29]). Moreover, the bond angles are still far from experimental bond angles for trifluoride molecules. It is clear that the structural problem of these compounds still subsists. However, finding a very accurate structure is not our main purpose, as it will be emphasized in the thermochemical part of this paper.

Following the structural analysis, a vibrational study of these compounds was carried out. The vibrational frequencies were first calculated at the RHF level, using ECPs for both lanthanides and halogens. The results seem to be more accurate without the use of the classical 0.9 scaling factor[42] on the frequencies. The second time, we calculated the same frequencies at a Møller−Plesset post-Hartree−Fock MP2 level of theory. Rather similar frequencies were obtained. Finally, RHF and MP2 calculated frequencies were estimated by using a 6-31G(d) basis set on the halogens.

The calculation of experimental frequencies is based on the matrix isolation data of Hastie et al.[43] and corrected by the empirical relation $\nu(\text{gas}) \approx \nu(\text{Ne}) + 0.8(\nu_{\text{Ne}} - \nu_{\text{Ar}})$ given by these authors. Vibrational frequencies of lanthanide halides were not measured in all cases. Most of them were extrapolated from experimental values, using an empirical formula which assumes a linear progression of the frequencies throughout the rare earths family.

Table 3 illustrates the differences between the experimental[15] and RHF and MP2 calculated vibrational frequencies for LaF_3

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Table 4. Calculated and Experimental LnX_3 Vibrational Wavenumbers (Except PmX_3 Compounds)

	MP2[a]				expt (±10 cm^{-1}) [15]			
	ν_1	ν_2	ν_3	ν_4	ν_1	ν_2	ν_3	ν_4
$LaCl_3$	289	24	313	60	335	51	316	79
$CeCl_3$	291	26	316	61	335	52	319	80
$PrCl_3$	294	27	319	62	336	52	320	80
$NdCl_3$	297	27	322	63	336	53	324	81
$SmCl_3$	301	30	326	66	337	55	323	82
$EuCl_3$	313	32	332	70	338	55	324	83
$GdCl_3$	304	35	328	66	338	56	326	84
$TbCl_3$	308	36	333	69	339	57	326	84
$DyCl_3$	310	38	334	70	339	58	327	85
$HoCl_3$	312	39	336	71	340	58	328	85
$ErCl_3$	314	41	338	72	340	59	329	86
$TmCl_3$	316	42	341	73	341	59	330	87
$YbCl_3$	317	43	341	73	341	60	331	87
$LuCl_3$	305	60	327	80	342	60	331	88
LaF_3	554	72	539	114	540	82	511	125
CeF_3	558	68	544	115	549	86	519	115
PrF_3	562	65	548	117	552	86	525	121
NdF_3	566	63	553	118	557	84	536	118
SmF_3	571	50	557	119	564	92	540	126
EuF_3	579	37	571	122	570	92	544	130
GdF_3	575	39	564	121	573	97	552	136
TbF_3	576	24	566	121	579	97	554	131
DyF_3	578	7	569	122	581	98	561	133
HoF_3	582	20	572	123	585	109	569	120
ErF_3	585	27	576	124	589	102	571	137
TmF_3	589	35	580	124	593	103	576	139
YbF_3	592	39	582	125	597	100	579	144
LuF_3	597	44	588	127	598	106	585	147

[a] ECPs for lanthanides and 6-31G(d) basis set for halogens.

and $LaCl_3$ molecules. Compared to experimental data, the calculated values at the RHF level are accurate enough for thermodynamic calculations. However, we found an exception concerning the small frequency associated with the ν_2 out-of-plane bending mode. This frequency is systematically underestimated for all of our compounds. In the case of the trichlorides and for some trifluorides, the small frequencies obtained are the consequence of the flat energy surface along the out-of-plane distortion. From an experimental point of view, weak interactions with the inert gas matrix may strongly affect the smallest frequency associated with the ν_2 normal mode. Nevertheless, if we suppose that the ν_2 frequency is really underestimated, it will induce small errors in the vibrational contributions to the calculated thermochemical functions (see the thermochemical analysis). The next pages provide evidence that these small errors do not spoil the thermodynamics study of these molecules. The best estimated vibrational frequencies are obtained at the MP2 level using the standard 6-31G(d) basis set on the halogens, thus corresponding to a better accuracy on the equilibrium geometry and, hence, on the force constants. These results are summarized in Table 4. We have to notice that the smallest ν_2 frequency is better predicted with an all-electron calculation (using only a simple MINI basis set for lanthanum[44] and a 6-31G(d) basis set for chlorine), which is not very different from the experimental one, though the structure is not well-predicted. This surprising result is certainly due to the cancelation of errors during the calculation.

Recently, vibrational analyses were carried out by Di Bella et al.[28] and Lanza et al.[29] on LnX_3 compounds (respectively $LaCl_3$, LaF_3 and GdF_3, $GdCl_3$, LuF_3, $LuCl_3$ molecules) by using several levels of theory (SCF, CASSCF, and MP2) and large TZ2P basis sets for the halogens. They found frequencies similar to ours except slightly better, but they still underestimated the ν_2 frequency for the GdF_3, $GdCl_3$, LuF_3, and $LuCl_3$ molecules. Jia and Zhang[45] used another method. They evaluated the force constants and fundamental frequencies of the rare earth trihalides by means of the effective nuclear charge model. The results calculated by using this model show that the agreement between the experimental values is moderately good ($LnCl_3$ compounds) but sometimes very satisfactory (LnF_3 compounds, for example). However, this method is an approximate one since it does not take the difference between the electronegativities of the bonded atoms into account.

Some thermodynamical functions may be easily estimated from equilibrium structures and vibrational frequencies, using well-known analytical expressions.[1] Therefore, they may provide a validation of the ab initio calculations using pseudopotentials.

We know that the energy of a molecule is the sum of the contributions of its different modes of motion: translation, rotation, vibration, and electronic. This separation is only approximate because the modes are not completely independent. However, it is satisfactory in most cases and widely used. Therefore, the partition function factorizes into contributions from each mode and we can derive thermodynamical functions in the approximation of a perfect gas.[1]

The translational contributions can be expressed as follows:

$$C_p^\circ(T) = {}^5/_2 R \tag{1}$$

$$S^\circ(T) = R\left({}^5/_2 + {}^3/_2 \ln M + {}^5/_2 \ln T + \ln \frac{k}{p^\circ}\left(\frac{2\pi k}{Nh^2}\right)\right) \tag{2}$$

$$H^\circ(T) - H^\circ(0\ \mathrm{K}) = {}^5/_2 RT \tag{3}$$

where R denotes the gas constant, M the molecular mass, p° the standard pressure, k the Boltzmann constant, N the Avogadro constant, and h the Planck constant.

For a nonlinear molecule, the rotational contributions are as follows:

$$C_p^\circ(T) = {}^3/_2 R \tag{4}$$

$$S^\circ(T) = {}^3/_2 R + \frac{R}{2}\ln\left(\frac{\pi T^3}{\theta_A\theta_B\theta_C\sigma^2}\right) \tag{5}$$

with the following:

$$\theta_A = \frac{h^2}{8\pi^2 I_a k};\quad \theta_B = \frac{h^2}{8\pi^2 I_b k};\quad \text{and}\quad \theta_C = \frac{h^2}{8\pi^2 I_c k}$$

where I_a, I_b, and I_c are the moments of inertia of the molecule and σ its symmetry number.

$$H^\circ(T) - H^\circ(0\ \mathrm{K}) = {}^3/_2 RT \tag{6}$$

The vibrational contributions (nonlinear molecules) can be written as follows:

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(44) Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Radzio-Andzelm, E.; Sakai, Y.; Tatewaki, H. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam, 1984.

(45) Jia, Y. Q.; Zhang, S. G. *Inorg. Chim. Acta* **1988**, *143*, 137.

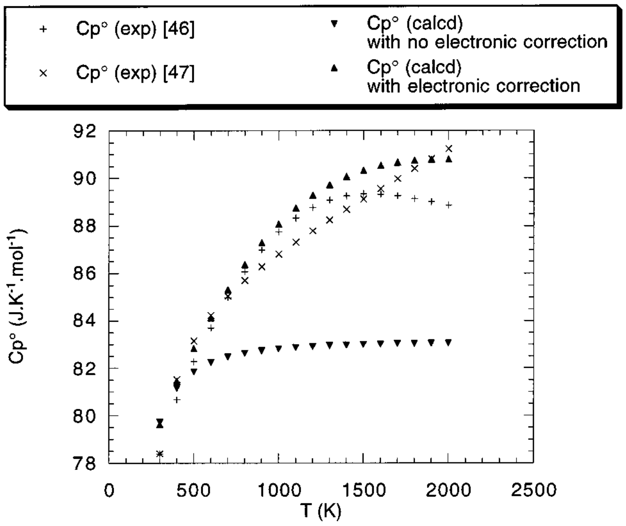

Figure 1. $C_p°$ evolution versus temperature for the $NdCl_3$ molecule between 300 and 2000 K. Calculated (with and without electronic correction with G-Thermo software) and experimental values from two different thermochemical data sources.[46,47]

$$C_p°(T) = R\sum_{i=1}^{3n-6}\frac{a_i^{2}e^{-a_i}}{(1-e^{-a_i})^2} \qquad (7)$$

$$S°(T) = R\sum_{i=1}^{3n-6}\left(\frac{a_ie^{-a_i}}{1-e^{-a_i}} - \ln(1-e^{-a_i})\right) \qquad (8)$$

$$H°(T) - H°(0\text{ K}) = RT\sum_{i=1}^{3n-6}\left(\frac{a_ie^{-a_i}}{1-e^{-a_i}}\right) \qquad (9)$$

with $a_i = \alpha\bar{\nu}_i/T$, $\bar{\nu}_i$ (wavenumbers) in cm^{-1} and $\alpha = hc/k = 1.438786$ cm·K.

Finally, the electronic contributions can be expressed as follows:

$$C_p°(T) = RT^2\frac{d^2\ln q^E}{dT^2} + 2\,RT\frac{d\ln q^E}{dT} \qquad (10)$$

$$S°(T) = RT\frac{d\ln q^E}{dT} + R\ln q^E \qquad (11)$$

$$H°(T) - H°(0\text{ K}) = RT^2\frac{d\ln q^E}{dT} \qquad (12)$$

where q^E is the electronic partition function: $q^E = \sum_{i=1}^{n} g_i e^{-\alpha\epsilon_i/T}$, ϵ_i is the i^{th} electronic level (in cm^{-1}), g_i is its degeneracy, and α is already defined.

As well as Gaussian94, the first software we used (MacMaster) neglects the electronic contribution for polyatomic systems. This approximation can be employed with success in the case of light metal studies.[2] In our concern, we clearly distinguish a high-temperature deviation between the calculated and measured $C_p°$ values for $NdCl_3$ (Figure 1). This important deviation is a consequence of the complexity of the $NdCl_3$ electronic levels spectrum. The G-Thermo software is able to take the electronic partition function (eqs 10, 11, and 12) into account if the electronic levels spectrum of the molecule is available. For the studied molecules, the electronic levels spectra are similar to the Ln^{3+} atomic spectra, experimentally observed for free ions or in crystals.[12] For each rare earth, the electronic spectrum consists of a very large number of electronic levels, strongly degenerated and near the fundamental level. However, some exceptions can be found, like the La^{3+}, Gd^{3+}, or Lu^{3+} ions, the first excited electronic states of which are located beyond 30 000 cm^{-1} above the fundamental state. For the corresponding LnX_3 molecules (Ln = La, Gd, and Lu; X = Cl, F), the electronic contribution is, in this case, equal to 0 in the temperature range of interest (300−2000 K). This result is verified in the thermodynamics data tables.[46,47] This particularity is the consequence of the strong stability of these species in their respective ground-state configurations (f^0, f^7 and f^{14}). The complexity of the electronic spectra of the other lanthanide trihalide molecules does not allow a quantum mechanics approach. Therefore, we calculated all electronic contributions thanks to the experimental Ln^{3+} electronic spectra (using energy levels and their respective degeneracy), available in ref 12. Figure 1 clearly proves that this "electronic correction" is of prime importance for obtaining calculated data in fairly good agreement with the thermodynamics data tables.

The thermochemical functions we chose to compare with tabulated experimental functions are the standard heat capacity $C_p°(T)$ and the standard entropy $S°(T)$. In these thermodynamics tables, the data are given with an unrealistic accuracy: 10^{-3} $J{\cdot}K^{-1}{\cdot}mol^{-1}$ for both $C_p°(T)$ and $S°(T)$. In this work, we preferred to give the coefficients of the adjusted thermodynamics functions with a number of significant digits allowing us to obtain a more realistic accuracy: 10^{-2} $J{\cdot}K^{-1}{\cdot}mol^{-1}$ for $C_p°(T)$ and 10^{-1} $J{\cdot}K^{-1}{\cdot}mol^{-1}$ for $S°(T)$. Instead of giving all of the estimated values, we preferred to give tables collecting the coefficients of the least-squares adjusted curves for $C_p°(T)$ and $S°(T)$ (Tables 5 and 6). For $C_p°(T)$, we used a function which is usually found in thermochemical data tables.[47] Nevertheless, no similar function is provided in these tables for the standard entropy $S°(T)$. Therefore, we interpolated the calculated values with a second-order polynomial function, thus providing a correlation coefficient higher than 0.99. The corresponding $H°(T)$ curve could be easily obtained by a simple integration of the $C_p°$ function versus temperature. All of the calculated coefficients are valid in the temperature range of interest.

It was also interesting to test the influence of the vibrational frequencies on the estimated thermochemical functions. According to a recent study on other molecules,[3] in most of the cases a small modification of the geometry does not influence the thermochemical functions. To verify this assumption, we computed the inertia moments of the $LaCl_3$ molecule for different geometries and calculated the modified $S°$ rotational contributions (eq 5). First, we tested the influence of the La−Cl bond length from 2.62 to 2.70 Å with a fixed planar geometry. Figure 2 clearly indicates that the thermodynamic $S°$ function is not affected by such a change in the molecular geometry. Therefore, we fixed the bond length (2.62 Å) and modified the "flap angle" (angle between one of the La−Cl vectors and the plane sustended by the lanthanum and the other two chlorine atoms). As it can be seen in Figure 3, even a strong change in the molecular structure does not influence the $S°$ rotational contribution. Figures 4 and 5 show the variation of the different kinds of thermal contributions (translational, rotational, vibrational, electronic, and total) for the $C_p°(T)$ and $S°(T)$ of $NdCl_3$. However, this study reveals that great precision

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(46) Barin, I.; Sauert, F.; Schultze-Rhonhof, E.; Sheng, W. S. *Thermochemical Data of Pure Substances*; VCH Verlags Gesellschaft: Weinheim, 1989.

(47) Knacke, O.; Kubaschewski, O.; Hesselmann, K. *Thermochemical Properties of Inorganic Substances*, 2nd ed.; Springer-Verlag: Berlin, Heidelberg, New York, 1991.

Table 5. Coefficients of the Least-Squares Adjusted $C_p°(T)$ Functions for LnX_3 Molecules (Except PmX_3 Compounds)

	$C_p°(T)^a$ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)			
LnX_3	*a*	*b*	*c*	*d*
$LaCl_3$	82.83	0.3596	−0.1083	−0.3546
$CeCl_3$	77.58	14.05	−4.838	−0.2279
$PrCl_3$	75.78	16.01	−4.010	−0.1169
$NdCl_3$	77.38	15.40	−4.450	−0.2539
$SmCl_3$	86.39	7.427	−1.978	−0.7304
$EuCl_3$	91.15	3.730	−2.086	−0.2504
$GdCl_3$	82.78	0.4246	−0.1275	−0.3864
$TbCl_3$	75.97	15.90	−4.635	−0.1615
$DyCl_3$	80.10	4.263	0.2959	−0.2588
$HoCl_3$	82.90	−0.7115	1.205	−0.3961
$ErCl_3$	83.56	−1.483	1.073	−0.4421
$TmCl_3$	83.33	−1.290	1.202	−0.4326
$YbCl_3$	82.96	−0.0004262	0.1006	0.4273
$LuCl_3$	82.77	0.4272	−0.1285	−0.3948
LaF_3	80.66	2.822	−0.8428	−0.8357
CeF3	75.35	16.58	−5.591	−0.7100
PrF_3	73.50	18.60	−4.781	−0.5998
NdF_3	75.04	18.05	−5.250	−0.7377
SmF_3	84.00	10.14	−2.787	−1.121
EuF_3	88.60	6.621	−2.947	−0.7302
GdF_3	80.29	3.241	−0.9667	−0.8703
TbF_3	73.49	18.72	−5.475	−0.6353
DyF_3	77.58	7.113	−0.553	−0.7333
HoF_3	80.33	2.205	0.3357	−0.8726
ErF_3	80.92	1.497	0.1855	−0.9208
TmF_3	80.66	1.739	0.3005	−0.9116
YbF_3	80.23	3.086	−0.8184	−0.9104
LuF_3	79.90	3.686	−1.098	−0.1939

[a] $C_p°(T) = a + bT(10^{-3}) + cT^2(10^{-6}) + dT^{-2}(10^6)$.

Table 6. Coefficients of the Polynomial Least-Squares Adjusted $S°(T)$ Functions for LnX_3 Molecules (Except PmX_3 Compounds)

	$S°(T)^a$ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)		
LnX_3	*a*	*b*	*c*
$LaCl_3$	326.6	0.1826	−0.4293
$CeCl_3$	338.9	0.1857	−0.4290
$PrCl_3$	341.7	0.1846	−0.4186
$NdCl_3$	341.3	0.1864	−0.4252
$SmCl_3$	333.7	0.1943	−0.4462
$EuCl_3$	323.9	0.2056	−0.4865
$GdCl_3$	338.0	0.1823	−0.4282
$TbCl_3$	339.5	0.1845	−0.4214
$DyCl_3$	341.9	0.1813	−0.4157
$HoCl_3$	341.8	0.1813	−0.4219
$ErCl_3$	340.4	0.1816	−0.4246
$TmCl_3$	338.2	0.1814	−0.4231
$YbCl_3$	333.8	0.1819	−0.4268
$LuCl_3$	313.2	0.1822	−0.4279
LaF_3	287.2	0.1760	−0.4070
CeF3	300.9	0.1790	−0.4065
PrF_3	304.4	0.1778	−0.3958
NdF_3	304.7	0.1795	−0.4022
SmF_3	300.9	0.1874	−0.4231
EuF_3	295.0	0.1985	−0.4629
GdF_3	308.2	0.1752	−0.4046
TbF_3	315.0	0.1776	−0.3982
DyF_3	323.1	0.1743	−0.3923
HoF_3	314.2	0.1743	−0.3982
ErF_3	310.8	0.1745	−0.4007
TmF_3	307.0	0.1742	−0.3989
YbF_3	301.8	0.1746	−0.4023
LuF_3	283.1	0.1745	−0.4020

[a] $S°(T) = a + bT + cT^2(10^{-6})$.

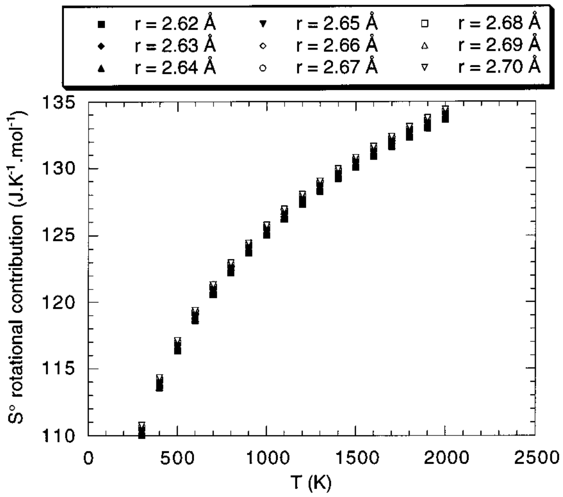

Figure 2. Influence of the bond length on the $S°$ rotational contribution versus temperature (for a fixed $LaCl_3$ planar structure).

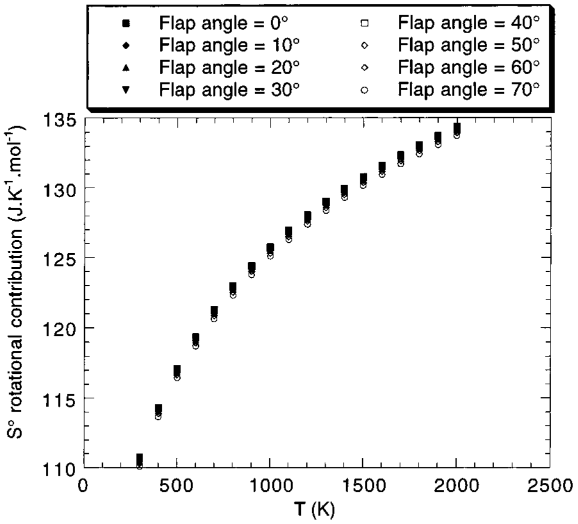

Figure 3. Influence of the "flap angle" on the $S°$ rotational contribution versus temperature (for a fixed bond length (2.62 Å) in $LaCl_3$).

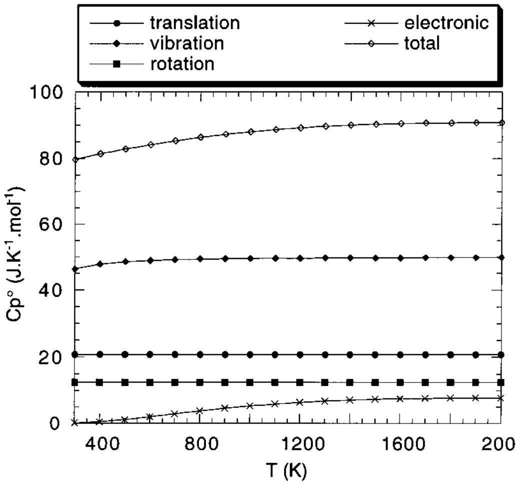

Figure 4. Different $C_p°(T)$ contributions versus temperature (between 300 and 2000 K) for $NdCl_3$: translational, vibrational, rotational, and electronic contributions and total $C_p°(T)$.

is needed for the small frequencies if they exist. Since the rotational contribution is weak, it confirms that the geometry does not significantly influence the thermodynamics functions of these molecules and that the influence of vibrational frequencies is important. Figure 6 illustrates the importance of the small vibrational frequencies on the $S°$ vibrational contribution (eq 8) for $LaCl_3$. We replaced one by one each of the calculated frequencies by its experimental value. We can

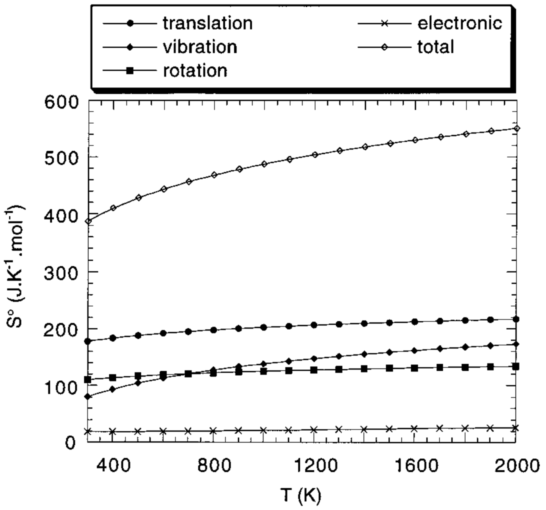

Figure 5. Different $S°(T)$ contributions versus temperature (between 300 and 2000 K) for $NdCl_3$: translational, vibrational, rotational, and electronic contributions and total $S°(T)$.

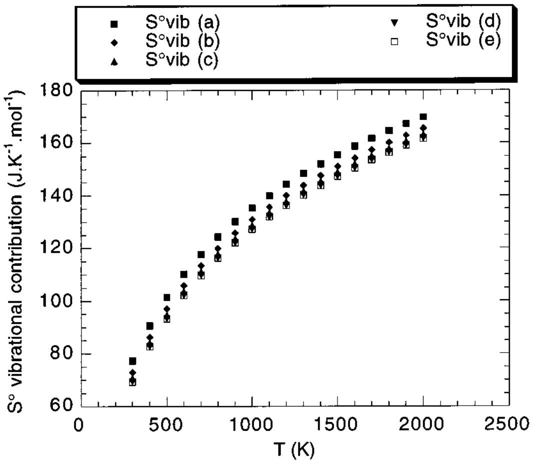

Figure 6. Influence of the smallest frequencies on the $S°$ vibrational contribution versus temperature ($LaCl_3$ molecule). (a) All calculated frequencies: ν_1 (symmetric stretching mode), ν_2 (out-of-plane bending mode), ν_3 (asymmetric stretching mode) and ν_4 (in-plane bending mode). (b) Calculated frequencies: ν_1, ν_3, and ν_4. Experimental frequency:[15] ν_2. (c) Calculated frequencies: ν_1 and ν_3. Experimental frequencies:[15] ν_2 and ν_4. (d) Calculated frequency: ν_1. Experimental frequencies:[15] ν_2, ν_4, and ν_3. (e) All experimental frequencies.[15]

see that the accuracy of the two smallest vibrational frequencies (i.e., the out-of-plane ν_2 (a_1) and in-plane ν_4 (e) bending frequencies) has a significant impact on the thermodynamics functions. It introduces a small difference between the calculated thermodynamics functions and the experimental ones (about 10 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ for $S°(T)$ and less than 0.5 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ for $C_p°(T)$).

In the aim of future studies on reactions involving rare earth halides, it was necessary to extend this work on free-energy calculations. We chose the following exchange reaction, involving at the same time, chlorides and fluorides:

$$\mathrm{LnCl_3} + \frac{3}{2}F_2 \Leftrightarrow \mathrm{LnF_3} + \frac{3}{2}\mathrm{Cl_2} \tag{13}$$

In our temperature range of interest (300−2000 K), the free energy of this gas-phase reaction can be easily estimated from the thermodynamics data tables. These experimental data will be used to validate our calculated free energy.

According to Kubaschewski and Evans,[48] we can easily verify that, at a sufficiently high temperature, we can neglect the terms involving the heat capacities,

$$\Delta H°_r(T) = \Delta H°_r(0) = \Delta U°_r(0) + \Delta\mathrm{ZPE} \tag{14}$$

where $\Delta U_r(0)$ stands for the difference between the sum of the calculated electronic energies of the products and the sum of the calculated electronic energies of the reactants and ZPE stands for the correction due to the residual vibrational energy at 0 K (or zero-point energy): $\mathrm{ZPE} = {}^1/_2\sum_i h\nu_i$, where h is the Planck constant and ν_i is the i^{th} vibrational frequency. ΔZPE is the difference between the ZPE of the products and the ZPE of the reactants.

So, Gibbs free energy can be easily calculated from the relationship

$$\Delta G°_r(T) = \Delta H°_r(T) - T\Delta S°_r(T) \tag{15}$$

with the above-mentioned hypothesis:

$$\Delta G°_r(T) = \Delta U°_r(0) + \Delta\mathrm{ZPE} - T\Delta S°_r(T) \tag{16}$$

Hence, it is easy to calculate the equilibrium constant:

$$K(T) = \exp\left(\frac{-\Delta G°_r(T)}{RT}\right) \tag{17}$$

For the quantum calculations, ECPs have been used for both lanthanum and the halogens. Therefore, we have replaced the ECPs for the halogens with 6-31G(d) basis sets. The results obtained at the RHF level are accurate enough to determine a good estimation of the Gibbs free energy. Since ΔZPE equals −0.794 $kJ{\cdot}mol^{-1}$ with regard to $\Delta U°_r(0)$ which equals −514.033 $kJ{\cdot}mol^{-1}$ (RHF level), only the electronic energies obtained with Gaussian94 increase the precision on the reaction enthalpy $\Delta H°_r(T)$. This is why we can, in a first and really good approximation, calculate $\Delta U°_r(0)$ with better precision, keeping in the same time the ΔZPE term calculated at the RHF level. We chose a Møller−Plesset perturbational approach as a post-Hartree−Fock method. Therefore, we have calculated the molecular energies at MP2 (with optimized geometry) and MP4 (single-point energy) levels.

We found that the Gibbs free energies have only a small variation throughout the rare earths family. Here, we present only the results on lanthanum:

$$\mathrm{LaCl_3} + \frac{3}{2}F_2 \Leftrightarrow \mathrm{LaF_3} + \frac{3}{2}\mathrm{Cl_2} \tag{18}$$

The small errors in the calculated $C_p°(T)$ and $S°(T)$ values due to the inaccurate smallest vibrational frequency are not important here for two reasons. First, as mentioned above, we neglect thermal contributions such as $C_p°(T)$, then the errors on $S°(T)$ cancel in the considered reaction. Moreover, the ΔZPE term, which involves vibrational frequencies, can be neglected too, as has already been stated. Table 7 gives the obtained results, compared to an experimental thermodynamics table.[46] In the case of all-ECP calculations, we can notice that a RHF calculation is in accordance with the experimental results (2.5% difference), whereas an MP2 or MP4 calculation does not provide any improvement (4.9% and 5.3% difference, respec-

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(48) Kubaschewski, O.; Evans, E. *Metallurgical Thermochemistry*, 3rd ed.; Pergamon Press: Oxford, 1958.

Table 7. Calculated Free Energy (in kJ·mol^{-1}) of the Exchange Reaction

T (K)	ΔG°_r[a] (RHF) (kJ·mol^{-1})	ΔG°_r[b] (RHF) (kJ·mol^{-1})	ΔG°_r[a] (MP2) (kJ·mol^{-1})	ΔG°_r[b] (MP2) (kJ·mol^{-1})	ΔG°_r(exptl) [46] (kJ·mol^{-1})
500	−516	−493	−555	−561	−529
1000	−515	−492	−555	−561	−528
2000	−515	−491	−555	−560	−531

[a] Using Stuttgart's ECPs on both lanthanum and halogens. [b] Using Stuttgart's ECPs on lanthanum and a 6-31G(d) basis set on halogens.

tively). Similar results are found with 6-31G(d) basis sets on the halogens.

Conclusion

The lanthanide trihalide molecules which have been studied in this work were chosen because a research program on the electro deposition of these metals is currently in progress in our laboratory, and we expect to develop a model for these rare earth halide molecules in a molten salt environment. The procedure described in this work is able to provide accurate thermodynamics data up to 2000 K (temperature corresponding to metallization processes and plasmas) and hence to derive thermochemical equilibriums between different lanthanide trihalide molecules within this range of temperatures (300−2000 K). Therefore, it leads to a better understanding of the behavior of these chemical species in such thermal conditions which is of great interest in order to improve the preparation conditions of the lanthanide halides. The pseudopotentials we used will be useful for more complex calculations, allowing one to shorten the calculation time. Calculations on bigger rare earth compounds are actually in progress in our laboratory.

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