Thermochemical Properties (D_0^o and IP) of the Lanthanide Monohalides

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Thermochemical data for the lanthanide monohalides have been combined with recent ligand field theory calculations (A. L. Kaledin, M. C. Heaven, R. W. Field, and L. A. Kaledin (1996). *J. Mol. Spectrosc.* **179,** 310) to estimate the dissociation energies and ionization potentials for all LnX (where $Ln \in$ Ba through Lu, and $X \in$ F, Cl, Br, or I) molecules and the dissociation energies for the LnX^+ ions. Owing to the negligible involvement of the core-like $4f$ electrons in bonding, the dissociation energies and ionization potentials of all LnX molecules, where $Ln \in$ Ba through Lu, and $X \in$ O, S, F, Cl, Br, or I, should vary with Ln atom in a simple linear manner, provided that corrections are made for differences in f-orbital occupancy between the LnX molecule and the free Ln atom or between the LnX molecule and the LnX^+ molecular ion. We provide such a model here and, in so doing, correct several inconsistencies in the thermochemical data. Based on thermochemical data (A. A. Kitaev, I. S. Gotkis, P. G. Val'kov, and K. C. Krasnov (1996). *Russ. Chem. Phys.* **7,** 1685) and recent spectroscopic observations (M. C. McCarthy, J. C. Bloch, R. W. Field, and L. A. Kaledin (1996) *J. Mol. Spectrosc.* **179,** 251), a revised value for the ionization potential of DyF, IP(DyF) = 5.85 ± 0.06 eV, is proposed. © 1999 Academic Press

INTRODUCTION

Processes by which gas phase lanthanide metal atoms are produced from bound systems display a double periodicity in their enthalpy changes as the atomic number varies from 56 through 71. Two classical examples of such processes are the enthalpy of sublimation of the metals (*1*) and the dissociation energy of the gaseous lanthanide monoxides (*2*). Dissociation energies of the other lanthanide monochalcogenides (*3–6*) and carbides (*7*) follow similar trends. The observed double periodicity closely parallels the energy of $4f \rightarrow 5d$ promotion for those elements which have no $5d$ electron in the gaseous atomic ground state, i.e., all but La, Ce, Gd, and Lu. The elements Eu and Yb, which, respectively, have half- and fully-occupied $4f$-shells, deviate considerably from the smooth trend defined by the other elements, as predicted by the $4f \rightarrow 5d$ promotion scheme. Owing to the negligible involvement of the core-like $4f$ electrons in bonding, the dissociation energies and ionization energies of all LnX molecules, where $Ln \in$ Ba through Lu, and $X \in$ O, S, F, Cl, Br, or I, should vary with Ln atom in a simple linear manner, provided that corrections are made for differences in f-orbital occupancy between the LnX molecule and the free Ln atom or between the LnX molecule and the LnX^+ molecular ion.

Recent advances in spectroscopic techniques and the development of ligand field theory (LFT) models (*8, 9*) have made it possible to eliminate the major uncertainties in the dissociation energies of the lanthanide monoxides and have provided a framework for understanding the observed trend in the dissociation energies (*10*). The central features of the electronic structure of the LnO molecules are the assumptions that the lowest lying states are dominated by the ionic structure $Ln^{2+}O^{2-}$ and that the electronic configurations of the ground states near the equilibrium internuclear distance are all $4f^{N-1}6s$, with the exception of EuO and YbO, which have the $4f^N$ type of the ground state configuration due to the extraordinary stability of the half- and fully-occupied $4f$ shells (*8*). It was shown in Ref. (*10*) that the dissociation energies of LaO, CeO, GdO, and LuO, whose gaseous atoms have the $4f^{N-1}5d6s^2$ ground state configuration, correspond to the process

$$Ln^{2+}(4f^{N-1}6s)O^{2-} \rightarrow Ln(4f^{N-1}5d6s^2) + O(^3P), \quad [1]$$
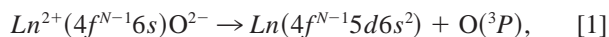
and decrease monotonically across the series. This monotonic behavior is consistent with the Racah method (*11*) which was developed to predict the energy of the lowest levels for the first and second spectra of lanthanide atoms (Ln and Ln^+, respectively) using available experimental data for the third spectra (Ln^{2+}). Racah suggested that differences in energy between the lowest levels of opposite parity (the so-called system differences) in the second and in the third spectra are approximately constant across the lanthanide series. This method is based on the idea that all interactions among the $4f$ electrons and between the $5d$ electron and the $4f$ electrons are cancelled by the differencing procedure, provided that the number of $4f$ electrons remains constant. A detailed examination of the Racah hypothesis was made by Judd (*11*) when more experimental data had become available. Based on experimental data

TABLE 1
Thermochemical Properties of Lanthanide Monofluorides (in units of 10^3 cm^{-1})

Ln	IP(LnF)	$D_0^\circ(Ln\text{-}F)$	$D_0^\circ(Ln^+\text{-}F)$
Ba	38.742 ± 0.003[a]	48.2 ± 0.6[a]	51.5 ± 0.6[a]
La		55.3 ± 1.1[b]	
Nd	39.6 ± 0.6[c]	45.6 ± 1.1[d]	50.3 ± 1.7
Sm	41.6 ± 0.6[e]	46.9 ± 0.7[f]	50.7 ± 1.3
Eu	42.0 ± 0.6[c]	45.1 ± 0.7[f]	48.8 ± 1.3
Gd	49.7 ± 0.6[c]	49.4 ± 1.4[f]	49.2 ± 2.0
Tb	49.4 ± 0.6[c]		
Dy	47.2 ± 0.6[g]	44.1 ± 1.4[h]	44.7 ± 2.0
Ho	48.6 ± 0.6[c]	43.0 ± 1.1[h]	42.9 ± 1.7
Er	50.9 ± 0.6[c]	47.6 ± 1.4[h]	45.9 ± 2.0
Tm	47.3 ± 0.6[c]	42.3 ± 0.7[f]	44.9 ± 1.3
Yb	47.7 ± 0.4[c]	43.6 ± 0.8[f]	46.6 ± 1.2

a. Ref. (18); *b.* Ref. (16); *c.* Ref. (25); *d.* Ref. (19); *e.* Ref. (24); *f.* Refs. (20-22);

g. Ref. (24) and present work. See text for details; *h.* Ref. (23).

it was shown that the system differences are remarkably constant across the lanthanide series (see Table 3 of Ref. (11)). Several authors have successfully used Racah's method to estimate energy differences between electronic configurations of neutral and ionized lanthanide and actinide atoms (12, 13), as well as the ionization potentials of the LnF molecules (14). Their results indicate that the Racah method works reasonably well for most *f*-cores with the possible exceptions of the empty (f^0) and full (f^{14}) *f*-core occupancies (12). Recently, Kaledin *et al.* (15) used this method to estimate the energies for all bound configurations of LnX, where Ln ∈ Ce through Yb, and X ∈ F, Cl, Br, or I.

The gaseous lanthanide monohalides have been the subject of several thermochemical investigations (16–25). In contrast to the pronounced double periodicity in the observed dissociation energies of the lanthanide monoxide

TABLE 2
Thermal Population in the Lowest State of the First Excited
$Ln^+(4f^N 6s)F^-$ Configuration

LnF	IP or D_0°	Reaction	T_{ave} (K)	E_{low} (cm^{-1})	Thermal Population
DyF	IP	DyF(g)+e=DyF$^+$(g)+2·e	1400[a]	2431[b]	0.082
HoF	D_0°	3·HoF(g)=2·Ho(g)+HoF$_3$(g)	1369[c]	1600[b]	0.186
DyF	D_0°	DyF(g)+Ho(g)=HoF(g)+Dy(g)	1446[c]	2431[b]	0.089
ErF	D_0°	ErF(g)+Ho(g)=HoF(g)+Er(g)	1446[c]	7900[b]	0.0004
TmF	D_0°	TmF(g)+Ca(g)=Tm(g)+CaF(g)	1650[d]	1600[b]	0.248

a. Ref. (24); *b.* Ref. (15); *c.* Ref. (23); *d.* Ref. (21).
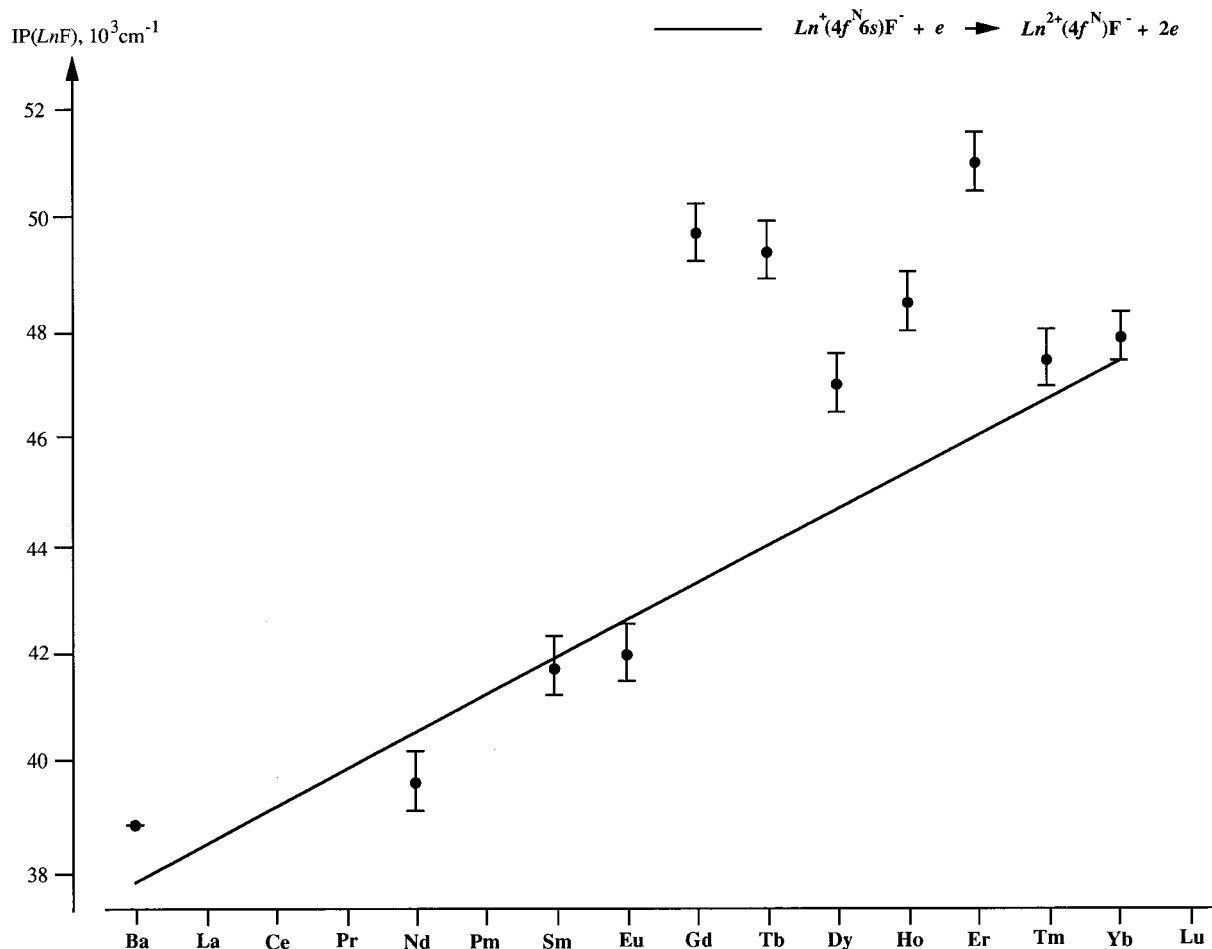
FIG. 1. The ionization potential of the lanthanide monofluorides as a function of atomic number. All of the data for the process described by Eq. [2] were weighted equally in the fitting procedure despite the fact that the ionization potential of BaF is known with considerably better accuracy (± 3 cm^{-1}) from spectroscopic measurements (*18, 34*) than the accuracy of its determination from electron impact measurements [~ 600 cm^{-1}, Refs. (*17, 24, 25*)]. All of the large deviations are due to cases where it is known that Eq. [2] is inapplicable. It is possible to use these deviations and atomic *Ln* configuration energies (*33*) to derive the excitation energy for the lowest state of the $Ln^+(4f^N 6s)F^-$ configuration relative to the *LnF* ground state.

compounds (*2–7*), no such double periodicity is apparent in the lanthanide monofluorides. The experimentally determined *LnF* D_0° values [BaF (*17, 18*), LaF (*16*), NdF (*19*), SmF (*20–22*), EuF (*20–22*), GdF (*20*), DyF (*23*), HoF (*23*), ErF (*23*), TmF (*21*), and YbF (*22*)] fall within the range $48\,600 \pm 6300$ cm^{-1}, quite different from the D_0° behavior of the *Ln*O molecules. The application of LFT models to all *Ln*F molecules now makes it possible to understand the observed trend in the *Ln*F dissociation energies. Conversely, thermochemical data can be used to determine the energies of the low-lying electronic configurations. From a practical point of view, knowledge of dissociation energies is required for calculations of thermodynamic equilibria by means of statistical mechanics (*26*).

The primary objective of the present work is to estimate the dissociation energy and ionization potential of each *LnX* molecule and the dissociation energy of each *LnX*$^+$ ion.

RESULTS AND DISCUSSION

1. Ionization Potentials of LnF Molecules

Based on the behavior of the ionization potentials of *LnX* molecules (*24, 25*), Gotkis (*14*) suggested the following mechanism for the electron impact ionization process:

$$Ln^+(4f^N 6s) X^- + e \rightarrow Ln^{2+}(4f^N) X^- + 2e, \qquad [2]$$
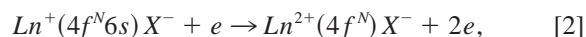
where $Ln \in$ Ba, Nd, Sm, Eu, Dy, Tm, and Yb, and $X \in$ F, Cl, Br, and I. Relevant data for *Ln*F are collected in Table 1 and shown in Fig. 1. Available spectroscopic data are consistent with such assignments for BaF (*27*), EuF (*28*), and YbF (*27*). However, recently McCarthy *et al.* (*29*) determined from spectroscopic measurements that the ground state of DyF belongs to the $4f^{N-1} 6s^2$ configuration, which is in apparent contradic-
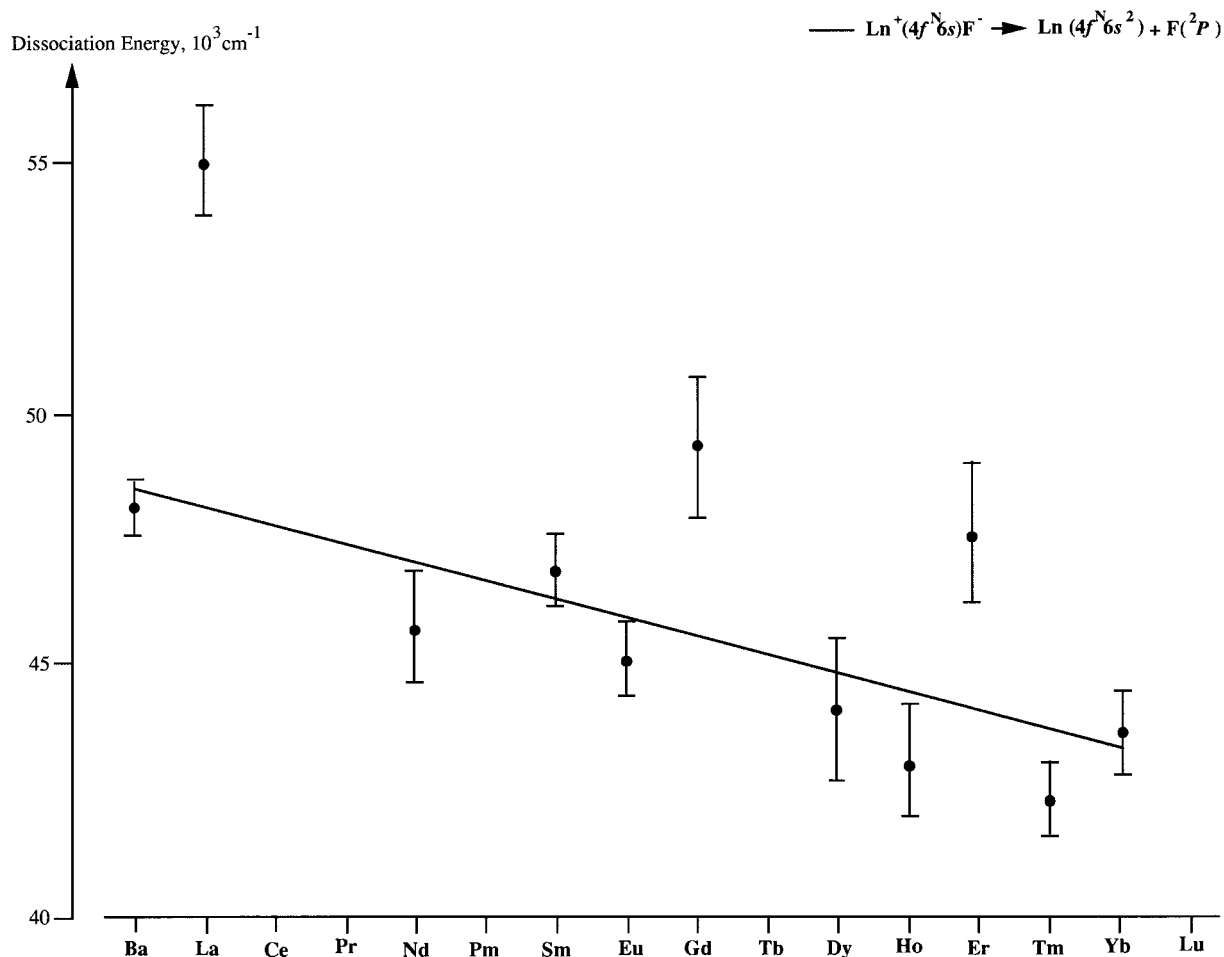
FIG. 2. The dissociation energies of the lanthanide monofluorides as a function of atomic number. The straight line corresponds to Eqs. [4, 5]. All of the large deviations are due to cases where it is known that Eq. [4] is inapplicable. It is possible to use these deviations and atomic *Ln* configuration energies (*33*) to derive the excitation energy for the lowest state of the $Ln^+(4f^N6s)F^-$ configuration relative to the *Ln*F ground state.

tion with the suggestion of Ref. (*14*) that Eq. [2] should apply to DyF.

Kitaev *et al.* (*24*) discussed the possibility that in cases when the first excited configuration of the *LnX* molecule lies low relative to the ground state, the ionization potential of *LnX*, when it is derived from the appearance potential of ionization efficiency curve, could be affected by the relatively high thermal population of this low-lying configuration in the high-temperature experiments (see footnote 1 of Ref. (*24*)). It is likely that this is the case for the DyF molecule where it was found that the lowest state of the $Dy^+(4f^{10}6s)F^-$ configuration lies only 2431 ± 5 cm^{-1} above the $Dy^+(4f^96s^2)F^-$ ground state configuration (*29*). Moreover, the appearance potential of ionization efficiency curve for DyF (Fig. 2 of Ref. (*24*), see curve #2) shows a zigzag behavior with two distinguishable linear segments which correspond, respectively, to the thermal populations of DyF molecules in the $4f^N6s$ and $4f^{N-1}6s^2$ types of configurations. The difference between the

extrapolated values of these two linear regions (=0.30 ± 0.05 eV or 2400 ± 400 cm^{-1}) is in good agreement with the energy of the lowest state of the first excited $Dy^+(4f^{10}6s)F^-$ configuration (=2431 ± 5 cm^{-1}, Ref. (*29*)). Table 2 presents the equilibrium population in the lowest state of the first excited configuration at the temperature of the experiment ($T = 1400$ K for the Dy-F system, Ref. (*24*)). This excited state population (≈ 0.082) is within the sensitivity range of the experimental setup of Ref. (*24*). Therefore, we propose that the low-energy segment of the appearance potential of ionization efficiency curve for DyF corresponds to the process described by Eq. [2], while the adiabatic ionization potential corresponds to the high-energy segment of the curve. This leads us to propose that the value of the adiabatic ionization potential for DyF reported in Ref. (*24*) should be increased by 0.3 eV. Based on data of Ref. (*24*), we recommend the value for the ionization potential of DyF to be

$$Ip(DyF) = 5.85 \pm 0.06 \text{ eV or } 47|200 \pm 500 \text{ cm}^{-1}. \quad [3]$$

TABLE 3

Dissociation Energies of *LnX* (in units of 10^3 cm^{-1})

| *Ln*	$D_0^°$(*Ln*-F)[a]	$D_0^°$ (*Ln*-Cl)	$D_0^°$(*Ln*-Br)	$D_0^°$ (*Ln*-I)
Ba	48.2 ± 0.6	36.5 ± 0.7[b]	29.9 ± 0.8[b]	26.7 ± 0.5[b]
La	55.3 ± 1.1	43.6	37.3	34.5
Ce	51.7	38.2	31.2	27.9
Pr	48.4	35.4	28.8	25.6
Nd	45.6 ± 1.1	35.0	28.4	25.2
Pm	46.6	34.6	28.0	24.8
Sm	46.9 ± 0.7	35.0 ± 1.1[c]	27.7	24.5
Eu	45.1 ± 0.7	33.9	27.3	24.1
Gd	49.4 ± 1.4	37.7	31.1	27.9
Tb	53.7	39.3	32.0	28.1
Dy	44.1 ± 1.4	32.8	26.2	23.0
Ho	43.0 ± 1.1	34.2	26.9	23.0
Er	47.6 ± 1.4	37.5	30.2	26.4
Tm	42.3 ± 0.7	31.6	25.0	21.8
Yb	43.6 ± 0.8	31.3	24.7	21.5
Lu	43.5	31.8	25.2	22.0

a. See footnotes to Table 1; *b.* Ref. ([17](underline)); *c.* Ref. ([24](underline)).

It should be noted that this value agrees with the value for the appearance potential of DyF (IP = 6.0 ± 0.3 eV) reported in Ref. (*23*).

2. Dissociation Energies of LnF Molecules

The LFT model (*15, 30*) and *ab initio* calculations (*31*) predict that the electronic ground state belongs to the $4f^N6s$ configuration for those *Ln*F molecules where *Ln* ∈ Ba, Nd, Pm, Sm, Eu, Yb. To get a coherent set of values for the dissociation energies of *Ln*F molecules with the same number of *f*-electrons in the ground states of *Ln* atoms and *Ln*F molecules, as is required by the Racah (*11*) method, we consider the following process:

$$Ln^+(4f^N6s)F^- \rightarrow Ln(4f^N6s^2) + F(^2P), \qquad [4]$$
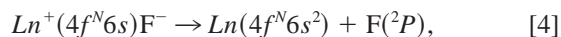
where *Ln* ∈ Ba, Nd, Pm, Sm, Eu, and Yb.

Experimental data for *Ln* atoms (*32*) and LFT predictions for *Ln*F molecules suggest that the process described by Eq. [4] is applicable to the ground states of BaF, NdF, SmF, EuF, and YbF. Therefore, the dissociation energies of BaF, NdF,

SmF, EuF, and YbF are approximated by an equation linear in the occupancy of the $4f$ orbitals, *N*,

$$D_0^°(Ln - F) = a + b \cdot N. \qquad [5]$$

Data were weighted according to the inverse square of their stated experimental accuracy. The fit produces $a = 48\,500 \pm 300$ cm^{-1} and $b = -375 \pm 40$ cm^{-1}. The hitherto accepted values for $D_0^°$ of DyF, HoF, and TmF fall into the energy region predicted by Eqs. [4, 5] (see Fig. 2), which would seem to imply that these molecules have the $4f^N6s$ ground state configuration. However, the spectroscopic data for DyF (*29*) and theoretical calculations (*15, 31*) suggest that DyF, HoF, and TmF all have the $4f^{N-1}6s^2$ type of configuration for the ground state. A plausible explanation for this disagreement between trends in $D_0^°$ and the spectroscopic assignments and/or the LFT predictions of the ground state configuration is that the first excited $Ln^+(4f^N6s)F^-$ configuration of DyF, HoF, and TmF lies sufficiently low in energy (*14, 15*) to have significant thermal population. Therefore, the thermal population of the first excited configuration is significant at the temperature of the experiments (see Table 2), and this could lead to an

TABLE 4
Ionization Potentials of LnX (in units of 10^3 cm^{-1})

Ln	IP(LnF)	IP(LnCl)	IP(LnBr)	IP(LnI)
Ba	38.742±0.003[a]	40.0 ± 0.4[b]	40.7 ± 0.2[b]	41.0 ± 0.2[b]
La	45.2	46.5	46.7	46.7
Ce	44.6	46.4	46.9	47.3
Pr	40.9	41.9	42.6	42.8
Nd	39.6 ± 0.6[b]	42.4	43.2	43.6
Pm	41.2	43.0	43.8	44.2
Sm	41.6 ± 0.6[c]	44.0 ± 0.6[b]	44.4	44.9
Eu	42.0 ± 0.6[b]	43.6 ± 0.6[b]	45.1	45.5
Gd	49.7 ± 0.6[b]	53.4	54.2	54.3
Tb	49.4 ± 0.6[b]	51.6	51.9	51.6
Dy	47.2 ± 0.6[d]	46.5 ± 0.4[b]	46.9	47.4
Ho	48.6 ± 0.6[b]	48.4	48.6	48.9
Er	50.9 ± 0.6[b]	52.7	53.0	52.9
Tm	47.3 ± 0.6[b]	48.4 ± 0.4[b]	48.8	49.4
Yb	47.7 ± 0.4[b]	49.2 ± 0.4[b]	49.4 ± 0.4[b]	50.0 ± 0.4[b]
Lu	55.8	60.5	61.8	62.5

a. Ref. (18); *b*. Ref. (25); *c*. Ref. (24); *d*. Ref. (24) and present work. See text for details.

erroneous reduction of the derived value of D_0° in the way that was described above for the ionization potential of DyF. To estimate the degree to which this contribution would skew the thermochemical results, an explicit evaluation of ionization cross section for the $4f^{N-1}6s^2$ and $4f^N6s$ type of configurations is required. Such evaluation is beyond the scope of present work.

The D_0° value for PmF is estimated from Eq. [5] as the lowest configurations for Pm and PmF (14, 15, 31) that correspond to the process defined by Eq. [4]. For the TbF molecule it is necessary to add to the value obtained from Eq. [5] the $f^{N-1}s^2 \rightarrow f^N s$ excitation energy which we take to be the difference between the lowest levels of the Tb$^+$($4f^96s$)F$^-$ and Tb$^+$($4f^86s^2$)F$^-$ configurations (15). Similarly, for the CeF molecule it is necessary to add the $f^{N-1}ds \rightarrow f^N s$ excitation energy for the Ce$^+$($4f^26s$)F$^-$ configuration (15) and to subtract the $f^N ds \rightarrow f^N s^2$ excitation energy for Ce($4f^26s^2$) atom (33). The D_0° value for LuF cannot be estimated from Eqs. [4] and [5] as the appropriate configuration does not exist for the Racah scheme to be applied to the Lu atom. Therefore, we use the following process:

$$Ln^+(4f^{N-1}6s^2)F^- \rightarrow Ln(4f^{N-1}5d6s^2) + F(^2P), \quad [6]$$
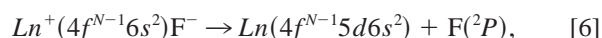
where $Ln \in$ La, Gd, and Lu. The D_0° values for LaF and GdF were taken from Refs. (16, 20). The dissociation energies of LaF and GdF are approximated by an equation linear in the occupancy of the $4f$ orbitals, $(N - 1)$,

$$D_0^\circ(Ln - F) = a + b \cdot (N - 1), \quad [7]$$

where $a = 55\ 300 \pm 1100$ cm^{-1} and $b = -745 \pm 180$ cm^{-1}. The value for LuF is estimated from Eq. [7] as the lowest configurations for Lu and LuF (27) correspond to the process defined by Eq. [6].

3. Dissociation Energies and Ionization Potentials of $LnCl$, $LnBr$, and LnI Molecules

Assuming that the LnX dissociation energies follow similar trends, i.e., the linear terms in Eqs. [5] and [7] are the same for corresponding processes defined by Eqs. [4] and [6] and using the available reliable data for $D_0^\circ(BaX)$ (17, 18), it is straightforward to calculate the dissociation energies for all LnX

TABLE 5
Dissociation Energies of *LnX*$^+$ (in units of 10^3 cm^{-1})

Ln	$D_0^{\circ}(Ln^+$-F$)$	$D_0^{\circ}(Ln^+$-Cl$)$	$D_0^{\circ}(Ln^+$-Br$)$	$D_0^{\circ}(Ln^+$-I$)$
Ba	51.5 ± 0.6	38.5 ± 1.1	31.2 ± 1.0	27.7 ± 0.7
La	55.1	42.1	35.6	32.8
Ce	51.2	35.9	28.5	24.7
Pr	51.1	37.2	29.9	26.5
Nd	50.3 ± 1.7	36.9	29.5	25.9
Pm	50.2	36.4	29.0	25.4
Sm	50.7 ± 1.3	36.4 ± 1.7	28.7	25.0
Eu	48.8 ± 1.3	36.0	27.9	24.3
Gd	49.2 ± 2.0	33.8	26.4	23.1
Tb	51.9	34.9	27.3	23.7
Dy	44.7 ± 2.0	34.1	27.1	23.4
Ho	42.9 ± 1.7	34.3	26.8	22.6
Er	45.9 ± 2.0	34.0	26.4	22.7
Tm	44.9 ± 1.3	34.1	26.1	22.3
Yb	46.6 ± 1.2	33.4	25.7	21.9
Lu	31.5	15.1	7.2	3.4

Note: The uncertainties are those of the combined thermochemical determinations. See Tables 3 and 4 for details.

(where $X \in$ F, Cl, Br, or I). Similarly, the *LnX* ionization potentials were calculated using Eq. [2] and available experimental data. The results of those calculations are collected in Tables 3 and 4.

4. Dissociation Energies of *LnX*$^+$ Molecular Ions

The dissociation energies of *LnX*$^+$, $D_0^{\circ}(Ln^+ - X)$, can be related to $D_0^{\circ}(Ln - X)$, IP(Ln), and IP(LnX) as follows:

$$D_0^{\circ}(Ln^+ - X) = D_0^{\circ}(Ln - X) + \text{IP}(Ln) - \text{IP}(LnX). \quad [8]$$

Table 5 presents the results of the $D_0^{\circ}(Ln^+ - X)$ calculations which have been done with use of Eq. [8] and available data for $D_0^{\circ}(Ln - X)$ (see Table 3), IP(LnX) (see Table 4), and IP(Ln) (*33*).

CONCLUSION

Errors in experimental determination of dissociation energies and ionization potentials of lanthanide monofluorides have been identified, which were due to thermal population the lowest state of the first excited configuration of lanthanide monofluorides. Simple linear relationships enable predictions of the dissociation energies and ionization potentials for all *LnX* (where $Ln \in$ Ba through Lu, and $X \in$ F, Cl, Br, or I) and dissociation energies for *LnX*$^+$ ions. This provides further evidence for the lack of 4*f* electrons participating in bonding.

ACKNOWLEDGMENTS

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