

## CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

# Formation Energies of Molecules and Anions of Europium Bromides

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**Abstract**—The content of saturated vapors above europium dibromide and Eu–EuBr<sub>2</sub>, Eu–Ba–BaBr<sub>2</sub>, EuBr<sub>2</sub>–LaBr<sub>3</sub> systems is investigated by means of high-temperature mass-spectrometry in the electron ionization and thermoionic emission regimes. On the basis of the measured equilibrium constants for reactions with participation of molecules and negative ions, the enthalpies of formation  $\Delta_f H_{298}^\circ$  (kJ/mol) are determined using the method of the third law of thermodynamics:  $-59 \pm 13$  (EuBr),  $-349 \pm 19$  (EuBr<sub>2</sub>), and  $-861 \pm 24$  (EuBr<sub>3</sub><sup>−</sup>).

**Keywords:** high-temperature mass-spectrometry, electrons, thermoionic emission, saturated vapor, formation enthalpy, europium dibromide.

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## INTRODUCTION

The energy characteristics of lanthanide halides are of interest in modeling the processes of numerous modern technologies [1]. The reliability of the modeling is in turn determined by the precision of preset parameters. So far, the literature data on thermochemical data for europium bromides are of an estimative character or do not exist at all. In this work, the experimental determination of enthalpies of formation for EuBr, EuBr<sub>2</sub> molecules and EuBr<sub>3</sub><sup>−</sup> ions is performed using ion-molecular equilibria [2]. Measurable quantities of gaseous molecules and ions were synthesized in situ in a Knudsen effusion cell. This method was used earlier by the authors of [3] to determine the enthalpies of formation of EuCl<sub>2</sub><sup>−</sup>, EuCl<sub>3</sub><sup>−</sup>, and EuCl<sub>4</sub><sup>−</sup> ions found during investigations of the thermoionic emission of europium dichloride. Detection of EuCl<sub>4</sub><sup>−</sup> ions in this case indicated a disproportionate reaction [4] whose products in the vapor phase could be Eu atoms and EuCl<sub>*n*</sub> (*n* = 1–3) molecules.

The aims of the present investigation included (1) gathering information on the stability of EuBr<sub>2</sub> with respect to disproportionation, based on the analysis of the vapor phase content; (2) determining the enthalpies of formation of EuBr<sub>*n*+1</sub><sup>−</sup> ions and the electron (bromide ion) affinity of the corresponding molecules.

## EXPERIMENTAL

Experiments were performed on an MI 1201 magnetic mass-spectrometer (angle 90°; radius of curvature, 200 mm) reequipped for high-temperature effusion measurements. A combined ion source allowed us to work in the electron ionization (EI) and thermoionic emission (TE) regimes, and thus to investigate, respectively, neutral and charged vapor components. The experimental method is described in detail in [5]. In the EI regime, mass spectra were recorded at the energy of ionizing electrons  $E_{\bar{e}}$  in the range of 6.5–130 eV and cathode emission current  $I_{\bar{e}} = 1$  mA. In the TE regime, negative 3 kV potential was applied to the cell. To extract ions from the cell, negative potential in the range 2850–2950 V was applied to the collimator. The sensitivity of the registration system for direct current at the level of  $10^{-17}$  A was ensured by the combination of a secondary emission electron multiplier and a digital picoammeter. The effusion cell temperature was measured by a calibrated tungsten–rhenium thermocouple (GOST 8.585-2001, type A-1). Temperature corrections were determined from melting points of pure substances (NaBr and Ag). Measurements of the sensitivity constant of the device were performed in experiments on silver evaporation. The software module in [6] enabled us to record automatically ionic current, cell temperature, and energy of ionizing electrons during the measurements.

EuBr<sub>2</sub> sample was synthesized using the NH<sub>4</sub>Br technique [7, 8], which includes the following stages: (a) the dissolution of Eu<sub>2</sub>O<sub>3</sub> in HBr and the addition of ammonium bromide in a Eu : NH<sub>4</sub>Br ratio of 1 : 3.5

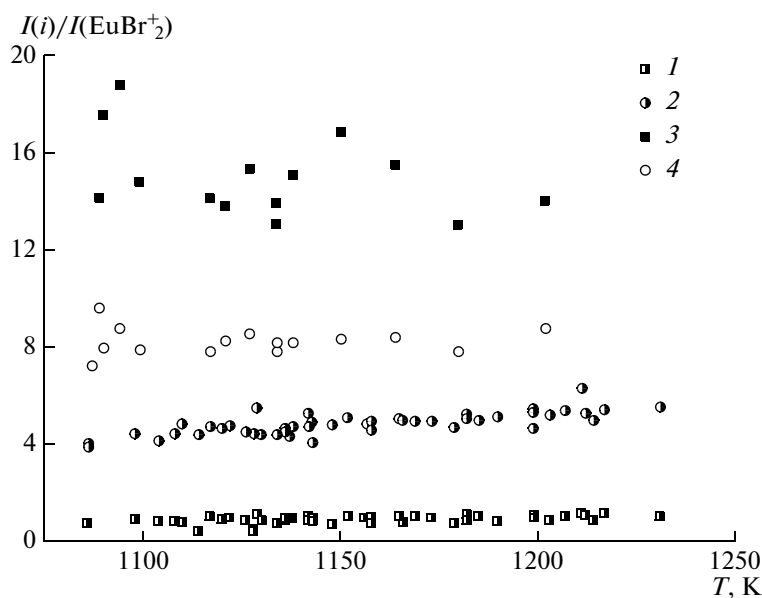


Fig. 1. Temperature dependences of mass spectra.  $I(i)$  is the ionic current of the  $i$ th ion: (1)  $\text{Eu}^+$ , (2)  $\text{EuBr}^+$  (evaporation of  $\text{EuBr}_2$ ), (3)  $\text{Eu}^+$ , (4)  $\text{EuBr}^+$  (evaporation of the system  $\text{Eu}-\text{EuBr}_2$ ).

followed by solution evaporation; (b) the pulverizing of the residue  $(\text{NH}_4)_3\text{EuBr}_6$  and its heating in an argon flow to  $180^\circ\text{C}$  and then in vacuum to  $400^\circ\text{C}$  with the formation of a mixture of  $\text{EuBr}_2$  and  $\text{EuBr}_3$ ; (c) additional vacuum calcination at  $500^\circ\text{C}$  until complete decomposition of  $\text{EuBr}_3$  into  $\text{EuBr}_2$  and  $\text{Br}_2$  is attained. The final product was checked by X-ray and chemical (mercurimetrically for bromine and complexometrically for europium) analysis with the following results: Eu,  $48.74 \pm 0.13\%$  (theoretical value, 48.75%), Br,  $51.26 \pm 0.12\%$  (theoretical value, 51.25%).  $\text{LaBr}_3$  was synthesized by the similar method described in [9].  $\text{BaBr}_2$  preparation included the vacuum dehydration at  $150^\circ\text{C}$  of crystallohydrate  $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$  of reagent grade. The europium and barium metals were of reagent grade.

## RESULTS AND DISCUSSION

### Analysis of Mass Spectra

$\text{Eu}^+$ ,  $\text{EuBr}^+$ , and  $\text{EuBr}_2^+$  ions were detected during our investigation of pure europium dibromide in the regime of electron ionization (temperature range, 1073–1231 K). The relative intensities of ionic currents at different temperatures are presented in Fig. 1.

Negative ions  $\text{EuBr}_3^-$  and  $\text{Br}^-$  were revealed in the regime of thermoionic emission. The absence of  $\text{EuBr}_2^-$  and  $\text{EuBr}_4^-$  ions in the spectra obviously indicates that the disproportionation reactions proceed with a negligibly low yield, in contrast to europium dichloride. The curves of ionization efficiency (CIE) (Fig. 2) support this assumption. Based on our analysis of the near-threshold parts of the CIE, the fractions of

Eu atoms and  $\text{EuBr}$  molecules ( $T = 1130\text{ K}$ ) in vapor lie below 0.05 and 0.3%, respectively.

Considering the formation of negative ions  $\text{EuBr}_{n+1}^-$  in reactions of associative addition of bromide-anion to  $\text{EuBr}_n$  molecules in adsorption layers, we might expect the detection of  $\text{EuBr}_2^-$  ions under the conditions of elevated pressure of europium monobromide inside a Knudsen cell. We therefore investigated

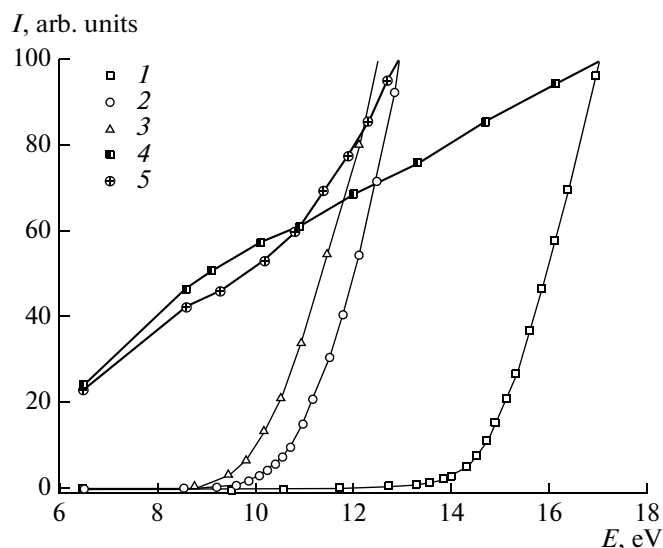
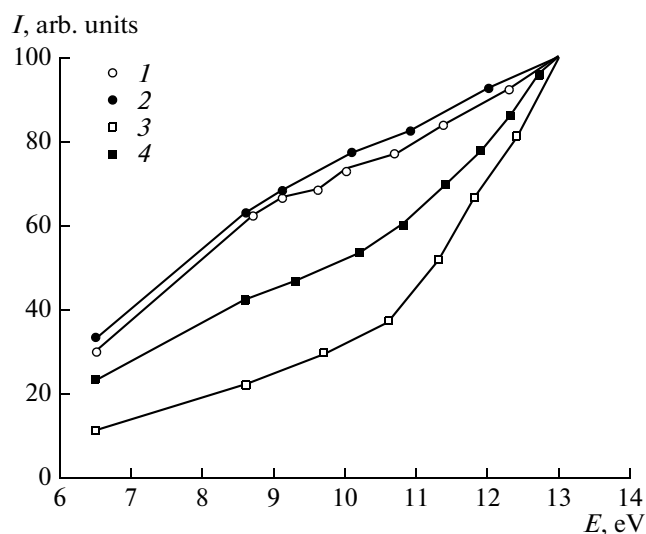


Fig. 2. Curves of ionization efficiency at evaporation of  $\text{EuBr}_2$  (1150 K): (1)  $\text{Eu}^+$ , (2)  $\text{EuBr}^+$ , (3)  $\text{EuBr}_2^+$ . Upon evaporation of the  $\text{Eu}-\text{EuBr}_2$  system: (4)  $\text{Eu}^+$ , (5)  $\text{EuBr}^+$ ;  $I$  is the ionic current;  $E$  is the energy of ionizing electrons.



**Fig. 3.** Curves of ionization efficiency upon evaporation of the Eu–EuBr<sub>2</sub> system for Eu<sup>+</sup>: (1) 1000 K, (2) 1130 K. For EuBr<sup>+</sup>: (3) 1000, (4) 1130 K. The ionic currents of Eu<sup>+</sup> and EuBr<sup>+</sup> are normalized with respect to 13 eV.

the Eu : EuBr<sub>2</sub> (50 : 50 wt %) system. The obtained mass spectra are presented in Fig. 1, and the CIE are found in Fig. 2.

Comparison of the mass spectra for the pure preparation and its mixed system with metallic europium and our analysis of CIE clearly point to additional contributions from Eu<sup>+</sup> and EuBr<sup>+</sup> ions to ionic currents. CIE for Eu<sup>+</sup> ions demonstrate its predominant origin from europium atoms. An inflection point is observed on the CIE for EuBr<sup>+</sup> ions at the 50% value of the relative current, relative to the CIE for pure EuBr<sub>2</sub>. This indicates considerable vapor concentration of europium monobromide molecules. Despite this, however, only EuBr<sub>3</sub><sup>−</sup> and Br<sup>−</sup> ions were found in the regime of thermoionic emission, as in the experiment with pure EuBr<sub>2</sub>. It is obvious that the pressures of EuBr molecules attained under these conditions were still not sufficient for the formation of EuBr<sub>2</sub><sup>−</sup> in measurable quantities. Ions of the LnBr<sub>4</sub><sup>−</sup> type were registered in vapors, especially the thermally stable lanthanide tribromides [10]. The absence of EuBr<sub>4</sub><sup>−</sup> ions in the mass spectra is additional confirmation of the absence of europium tribromide in the condensed phase.

#### Enthalpies of Formation of EuBr and EuBr<sub>2</sub> Molecules

The enthalpy of formation of EuBr molecules was determined by reaction (I) (Table 1) during our investigation of Eu–Ba–BaBr<sub>2</sub> system (30 : 30 : 40 wt %) using the method described in [11]. Measurements of ionic currents were performed at an ionizing electron energy of 9 eV, in order to exclude the dissociative ion-

ization of EuBr, EuBr<sub>2</sub>, BaBr, and BaBr<sub>2</sub> molecules. The measured equilibrium constants  $K_p^\circ(I)$  are presented in Table 1. Thermodynamic functions ( $G^\circ(T) - H^\circ(298.15 \text{ K})/T$ ), which are needed to calculate  $\Delta_f H_{298}^\circ(I)$  (Table 1), were taken from [12] for Ba and Eu atoms and BaBr molecules, while they were estimated for EuBr molecules using the comparative method in [13] and from the data in [14] for EuCl, EuCl<sub>2</sub>, and EuBr<sub>2</sub> [15] molecules. The dissociation energy  $D_{298}(\text{EuBr}) = 346 \pm 11 \text{ kJ/mol}$  was estimated using the obtained formation enthalpy of EuBr (Table 2). This value coincides, within confidence intervals, with the similar value for strontium monobromide  $D_{298}(\text{SrBr}) = 337 \pm 10 \text{ kJ/mol}$  [12]. Such a coincidence confirms the opinion of the authors of [16] as to the physical similarity of valence shells of strontium (5s) and europium (6s), since the resemblance of geometric characteristics of 5s and 6s orbitals, e.g., in the arrangement of their major radial maxima of electron density due to lanthanide contraction for europium.

Formation enthalpy  $\Delta_f H_{298}^\circ(\text{EuBr}_2)$  was determined by reaction (II) (Table 1), which proceeds during evaporation of the Eu–EuBr<sub>2</sub> system (50 : 50 wt %). The phenomenon of dissociative ionization was taken into account in calculating  $K_p^\circ(\text{II})$ ; i.e., the contributions to the current from EuBr<sup>+</sup> (molecular precursors, EuBr and EuBr<sub>2</sub>) and Eu<sup>+</sup> (precursors, Eu, EuBr, and EuBr<sub>2</sub>) ions were separated. The current of EuBr<sub>2</sub><sup>+</sup> ions was considered as a “pure line.” Fragmentation coefficients for EuBr<sub>n</sub> molecules can be presented as the ratio of currents of fragmentary EuBr<sub>i</sub><sup>+</sup> ions ( $0 \leq i < n$ ) and molecular ions EuBr<sub>n</sub><sup>+</sup>:

$$f(\text{EuBr}_i^+/\text{EuBr}_n) = I(\text{EuBr}_i^+/\text{EuBr}_n)/I(\text{EuBr}_n^+/\text{EuBr}_n).$$

Based on the data for EuBr<sub>2</sub> molecules (Fig. 1), it was determined that  $f(\text{Eu}^+/\text{EuBr}_2) = 0.0019T - 1.1939$  and  $f(\text{EuBr}^+/\text{EuBr}_2) = 0.0076T - 3.8902$ , making it possible to calculate  $I(\text{EuBr}^+/\text{EuBr})$  and  $I(\text{Eu}^+/\text{Eu}, \text{EuBr})$ . In order to determine the  $f(\text{Eu}^+/\text{EuBr})$  coefficient, we must estimate the value  $I(\text{Eu}^+/\text{EuBr})$ . Let us therefore consider the CIE of Eu<sup>+</sup> and EuBr<sup>+</sup> ions (Fig. 3). The shape of the CIE for EuBr<sup>+</sup> ions undergoes considerable changes: the contribution from  $I(\text{EuBr}^+/\text{EuBr})$  to the total ionic current rises with an increase of temperature. In contrast, the shape of CIE for Eu<sup>+</sup> ions remains practically unchanged with changes in temperature, within the limits of measurement errors. This indicates that the dissociative contribution  $I(\text{Eu}^+/\text{EuBr})$  is close to zero. On the basis of this conclusion, we accept that  $f(\text{Eu}^+/\text{EuBr}) = 0$ .

The obtained value  $\Delta_f H_{298}^\circ(\text{EuBr}_2)$  is presented in Table 2.

**Table 1.** Equilibrium constants, reduced Gibbs energies, and enthalpies of reactions:  $\text{Ba} + \text{EuBr} = \text{BaBr} + \text{Eu}$  (I),  $\text{Eu} + \text{EuBr}_2 = 2\text{EuBr}$  (II),  $\text{EuBr}_2 + \text{LaBrBr}_4^- = \text{LaBr}_3 + \text{EuBr}_3^-$  (III)

$T, \text{K}$	$\ln K_p^\circ$	$-[G^\circ(T) - H^\circ(298.15)]/T, \text{J}/(\text{mol K})$				$\Delta_f H_{298}^\circ, \text{kJ/mol}$
(I)		Ba	EuBr	Eu	BaBr	
1191	2.442	183.3	313.6	201.9	294.5	−24.7
1215	2.518	183.6	314.2	202.2	295.1	−26.0
1208	2.364	183.6	314.0	202.1	295.0	−24.3
1208	2.638	183.6	314.0	202.1	295.0	−27.1
1232	2.656	183.9	314.6	202.4	295.5	−27.8
1227	2.171	183.8	314.5	202.4	295.4	−22.8
						$-26 \pm 3$
(II)		Eu	EuBr <sub>2</sub>	EuBr		
1087	−1.632	200.5	387.9	310.9		51.2
1090	−1.877	200.5	388.0	311.0		53.5
1099	−1.792	200.7	388.3	311.2		53.2
1117	−1.873	200.9	389.0	311.7		54.8
1134	−1.788	201.1	389.7	312.1		54.8
1121	−1.631	201.0	389.2	311.8		52.7
1127	−1.616	201.0	389.4	312.0		52.9
1138	−1.883	201.2	389.8	312.3		55.9
1150	−1.963	201.4	390.3	312.6		57.3
1164	−1.915	201.5	390.8	312.9		57.5
1180	−2.173	201.7	391.4	313.3		60.8
1202	−1.794	202.0	392.2	313.8		58.2
						$55 \pm 5$
(III)		EuBr <sub>2</sub>	LaBr <sub>4</sub> <sup>−</sup>	LaBr <sub>3</sub>	EuBr <sub>3</sub> <sup>−</sup>	
1187	−3.757	391.6	517.0	448.0	437.2	9.3
1197	−3.934	392.0	517.7	448.5	437.7	11.1
1208	−3.716	392.4	518.4	449.1	438.3	9.0
1233	−3.689	393.3	520.1	450.4	439.6	8.9
1258	−3.597	394.2	521.7	451.6	440.8	8.1
1272	−3.337	394.6	522.6	452.3	441.5	5.4
						$9 \pm 3$

Note: Errors for the values calculated by the third law of thermodynamics is an additive value that includes a random error and systematic errors in the thermodynamic functions of reaction participants. Errors in the enthalpies of reactions (I) and (III) were calculated, taking into account the mutual compensation of errors in the functions of compounds in the right- and left-hand sides of the reactions.

### Formation Enthalpy of $\text{EuBr}_3^-$ Ions

Since  $\text{Br}^-$  ions can, along with other halide ions, be partially emitted from the surface of an effusion chamber [17, 18], the internal standard method [19, 20] was used to determine formation enthalpy  $\Delta_f H_{298}^\circ$  ( $\text{EuBr}_3^-$ ) (Table 2). According to this method, ion-molecular exchange reactions with the participation of cluster ions formed directly inside effusion cell are studied. The  $\text{EuBr}_2$ – $\text{LaBr}_3$  system (40 : 60 wt%) was therefore investigated, for which the equilibrium constants and enthalpy of gas-phase ion-molecular reaction (III)

**Table 2.** Enthalpies of formation  $\Delta_f H_{298}^\circ$  of atoms, molecules, and ions, kJ/mol

Obtained data		Used data		Source
EuBr	$-59 \pm 13$	Eu	$176 \pm 3$	[12]
EuBr <sub>2</sub>	$-349 \pm 19$	Ba	$185 \pm 5$	[12]
EuBr <sub>3</sub> <sup>−</sup>	$-861 \pm 24$	BaBr	$-75 \pm 11$	[12]
		LaBr <sub>3</sub>	$-584 \pm 10$	[9]
		LaBr <sub>4</sub> <sup>−</sup>	$-1105 \pm 14$	[24]

were obtained (Table 1). The  $K_p^\circ(\text{III})$  values were measured in the EI and TE regimes during one and the same experiment [21]. These values and the results from calculating reaction (III) enthalpy by the third law of thermodynamics are presented in Table 1. The reduced Gibbs energies of  $\text{EuBr}_3^-$  ions needed for these calculations were taken to be equal to the functions of  $\text{EuBr}_3$ , calculated in the rigid rotator–harmonic oscillator approximation. The molecular constants used in the calculations were taken from [22]. The statistical weight of the ground electronic state of  $\text{EuBr}_3$  molecules was assumed equal to that of the ground electronic state of  $\text{Eu}^{3+}$  ions [23]. The functions for  $\text{LaBr}_3$  and  $\text{LaBr}_4^-$  were calculated in [9, 24].

The electron affinity of the  $\text{EuBr}_3$  molecule, equal to  $4.0 \pm 0.3$  eV, and the affinity of  $\text{EuBr}_2$  molecules for bromide ions, equal to  $3.0 \pm 0.3$  eV, were calculated using the obtained values of  $\Delta_f H_{298}^\circ(\text{EuBr}_3^-)$ ,  $\Delta_f H_{298}^\circ(\text{EuBr}_2)$ , and  $\Delta_f H_{298}^\circ(\text{EuBr}_3) = -477 \pm 14$  kJ/mol [1].

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#### REFERENCES

1. A. Kovács and R. J. M. Konings, in *Handbook on Physics and Chemistry of Rare Earths*, Ch. 213 (Elsevier, New York, 2003), Vol. 33, p. 147.
2. L. N. Sidorov, *High Temp. Sci.* **28**, 153 (1990).
3. L. S. Kudin, G. G. Burdukovskaya, M. F. Butman, et al., *Zh. Fiz. Khim.* **67**, 645 (1993).
4. H. A. Eick, *J. Less Common Met.* **127**, 7 (1987).
5. A. M. Pogrebnoi, L. S. Kudin, A. Yu. Kuznetsov, and M. F. Butman, *Rapid Commun. Mass. Spec.* **11**, 1536 (1997).
6. A. M. Dunaev, A. S. Kryuchkov, L. S. Kudin, et al., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **54** (8), 73 (2011).
7. G. Meyer and M. S. Wickleder, in *Handbook on the Physics and Chemistry of Rare Earths*, Ed. by K. A. Gschneidner and L. Eyring (Elsevier, Amsterdam, 2000), Vol. 28, p. 53.
8. G. Meyer, *Inorg. Synth.* **25**, 146 (1989).
9. M. F. Butman, L. S. Kudin, A. E. Grishin, et al., *Russ. J. Phys. Chem. A* **82**, 164 (2008).
10. L. S. Kudin, M. F. Butman, V. B. Motalov, et al., *Vestn. KGTU*, No. 1, 164 (2010).
11. K. F. Zmbov and J. L. Margrave, *J. Chem. Phys.* **45**, 3167 (1966).
12. L. V. Gurvich, V. S. Iorish, I. V. Veitz, et al., *IVTAN-TERMO*, A Thermodynamic Database and Software System for the Personal Computer (2000).
13. M. Kh. Karapet'yants, *Methods of Comparative Calculation of Physical and Chemical Properties* (Nauka, Moscow, 1965) [in Russian].
14. A. D. Chervonnyi, Extended Abstract of Doctoral Dissertation in Chemistry (IPKhF RAN, Chernogolovka, 2010).
15. D. N. Sergeev, V. B. Motalov, M. F. Butman, et al., *Russ. J. Phys. Chem. A* **84**, 554 (2010).
16. V. N. Belyaev and N. L. Lebedeva, *Russ. J. Phys. Chem. A* **84**, 1841 (2010).
17. M. F. Butman, L. S. Kudin, G. G. Burdukovskaya, et al., *Zh. Fiz. Khim.* **61**, 2880 (1987).
18. S. V. Abramov, N. S. Chilingarov, A. Ya. Borshchevskiy, and L. N. Sidorov, *Int. J. Mass Spectrom. Ion Processes* **231**, 31 (2004).
19. L. N. Sidorov, L. V. Zhuravleva, and I. D. Sorokin, *Mass Spectrom. Rev.* **5**, 73 (1986).
20. L. N. Sidorov, *High Temp. Sci.* **29**, 153 (1990).
21. M. F. Butman, L. S. Kudin, V. B. Motalov, et al., *Russ. J. Phys. Chem. A* **82**, 535 (2008).
22. A. Kovács and R. G. M. Konings, *J. Phys. Chem. Ref. Data* **33**, 377 (2004).
23. W. E. Martin, R. Zalubas, and L. Hagan, *Atomic Energy Levels. The Rare-Earth Elements*, NSRDS NBS60 (National Bureau of Standards, Washington, DC, 1978), p. 411.
24. M. F. Butman, L. S. Kudin, A. E. Grishin, et al., *Russ. J. Phys. Chem. A* **82**, 767 (2008).