

**Thermodynamic Properties of LnX₃ Lanthanide Halide Molecules.
The Role of Vibration Anharmonicity**

L.N. Gorokhov, A.V. Gusarov, and E.L. Osina

V.P. Glushko Thermocenter of RAS, Institute for High Energy
Densities,
Associated Institute for High Temperatures of RAS,
13/19 Izhorskaya St., 125412 Moscow, Russia
E-mail: l.gorokhov@g23.relcom.ru

Lanthanum and lanthanide halides have significant industrial importance. They are used, e.g., as additives in efficient light sources. Reliable thermodynamic information on LnX₃ molecules (Ln = La–Lu), the main constituents of lanthanide halides vapors, is needed for thermodynamic modeling with the aim of optimization of high-temperature processes. The experimental information on the structure and spectra needed for calculation of thermodynamic functions of the LnX₃ molecules is far from being complete and often is contradictory, however. Development of theoretical quantum-chemical *ab initio* and DFT methods of calculation resulted in obtaining more detailed and more complete information on the structure and vibration frequencies of LnX₃ molecules. In particular, it was found that the potential function $V(\rho)$ for the out-of-plane deformation of LnX₃ molecules, with the change of the angle ρ between Ln-X direction and the perpendicular to the third-order symmetry axis, could significantly deviate from that of harmonic oscillator. Quantum-mechanical calculations performed by V.G. Solomonik and O.Yu. Marochko [1-3] show that $V(\rho)$ can be approximated with the expression

$$V(\rho) = a_2\rho^2 + a_4\rho^4 + a_6\rho^6 + a_8\rho^8.$$

This form of potential function demonstrates the fluxional behavior of the LnX₃ molecules and shows that the harmonic oscillator approximation is not adequate for description of the ν_2 out-of-plane low-frequency vibration of LnX₃ molecules. Taking into consideration all experimental and computational information on the structure of the LaF₃ and LaCl₃ molecules (Ln = La–Lu), selection of the most reliable molecular parameters was carried out and thermodynamic functions for these molecules were calculated. To allow for the anharmonicity of the ν_2 vibration, potential functions of Ln out-of-plane motion found in quantum-chemical calculations [1-3] were used. First 10 ν_2 energy levels calculated for LaF₃ and LaCl₃ molecules are given in Table 1. The data presented in this table demonstrate anharmonicity of ν_2 vibration; in the case of LaF₃ irregularity of several ΔE values is connected with a small inversion barrier for out-of-plane deformation. Comparison with the results of calculations using common "rigid rotator-harmonic oscillator" approximation shows significant change of thermodynamic functions values for LaF₃ and several early members of the LnCl₃ series (the anharmonicity contribution diminishes along the lanthanide series). This research was supported by the Russian Foundation for Basic Research (Project № 01-03-32194).

Table 1. Energy levels and transition energy
for ν_2 vibration of LaF₃ and LaCl₃ molecules

ν	E, cm^{-1}		Transition $\nu \rightarrow \nu+1$	$\Delta E, \text{cm}^{-1}$	
	LaF ₃	LaCl ₃		LaF ₃	LaCl ₃
0	19.5	5.0	-	-	-
1	21.9	17.1	0 → 1	2.4	12.1
2	48.6	32.7	1 → 2	26.7	15.6
3	67.1	50.3	2 → 3	18.5	17.6
4	93.5	69.6	3 → 4	26.4	19.3
5	123	90.2	4 → 5	29.5	20.6
6	155	112	5 → 6	32	22
7	190	135	6 → 7	35	23
8	227	159	7 → 8	37	24
9	266.	184	8 → 9	39	25

1. V.G. Solomonik and O.Yu. Marochko, Zhurnal Strukturnoi Khimii, **41**, 885 (2000).
2. V.G. Solomonik and O.Yu. Marochko, Zhurnal Fizicheskoi Khimii, **74**, 2296 (2000).
3. O.Yu. Marochko, Ph.D. thesis, Ivanovo State University of Chemistry and Technology (2001).