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Advantages and drawbacks of the quantum chemistry methodology in predicting the thermochemical data of lanthanide trihalide molecules

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Abstract

DFT calculations have been carried out on six lanthanide trihalide molecules, using Stuttgart ECPs on the lanthanides and a 6-31G* all-electrons basis set on the halogens. These calculations have been compared to previous theoretical and experimental data. Calculated bond lengths and vibrational frequencies are found to be in good agreement with previous theoretical results. The variations observed between experimental and theoretical results are discussed. Therefore, thermochemical data have been derived from such calculations. In this paper, the advantages and drawbacks of this methodology are discussed in the framework of the selected heavy elements. The different factors which influence the estimated thermochemical data have been compared. While molecular parameters seem to have a weak influence on the thermochemical functions, low frequencies (flat energy surfaces along the out-of-plane distortion) and the electronic partition function have been revealed to be the main factors for the accuracy of the predicted thermochemical data. © 1998 Elsevier Science S.A.

Keywords: Lanthanide trihalides; Quantum chemistry methodology

1. Introduction

Lanthanide trihalides are used industrially as intermediate compounds for the production of rare earths metals [1]. During recent years, numerous experimental works have been carried out using complementary experimental techniques such as direct high temperature or differential scanning calorimetry [2]. These studies have given precious information on the thermochemistry and physico-chemical properties of liquid MX–LnX_3 mixtures (M=alkali, Ln=rare earth, X=halide). The corresponding LnX_3 vapor molecules have also been studied from both an experimental and a theoretical viewpoint. Experimental studies have led to controversy with respect to the molecular structure (C_{3v} or D_{3h}) of these molecules [3]. In the last 20 years, theoretical calculations have been undertaken. Using different levels of theory such as semi-empirical or ab-initio methods [4–12], the ground state equilibrium geometries of these species and their corresponding vibrational spectra have been determined. The density functional theory (DFT) approach has very recently been used with success [13] and tends to confirm equilibrium planar geometries for the trihalide lanthanides with the exception of pyramidal trifluorides and the majority of the trichlorides.

Unfortunately, pure experimental thermodynamic data of these vapor complexes are absent from the literature. Thermodynamic data tables give only estimated thermochemical properties [14,15]. These have been calculated by Myers et al. with the aid of experimental and estimated molecular parameters [16]. Moreover, experimental parameters of these species such as their equilibrium geometry or their vibrational frequencies are difficult to obtain. For example, in the case of matrix IR studies [17,18], the values of the experimental vibrational frequencies can be seriously affected by weak interactions with the inert gas matrix.

When combined with thermostatistic calculations, quantum mechanics can also be used to determine estimated thermodynamic data. Successful calculations have already been carried out on aluminum compounds with well established experimental data [19]. We have recently performed such calculations on 30 trichloride and trifluoride lanthanides, using quasi-relativistic pseudopotentials at the SCF and post-Hartree–Fock MP2 level of theory (Møller–Plesset perturbational approach) [12]. The present work presents a systematic comparison between the different parameters which influence the thermochemi-

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cal functions. In order to obtain accurate vibrational frequencies, DFT calculations have been carried out on six selected LnX_3 trihalides (Ln=La, Gd and Lu; X=Cl and F), chosen in order to establish comparisons with the literature.

2. Methods of calculation

Thermodynamical functions may easily be derived from equilibrium structures and vibrational frequencies, using well-known analytical expressions [20] (rigid rotor and harmonic oscillator approximations). Therefore, thermostatistic calculations have been performed on the six selected LnX_3 molecules (Ln=La, Gd, Lu; X=F, Cl) with the thermochemical software G-Thermo, developed in our laboratory. The corresponding f^0, f^7 and f^{14} ground state configurations do not allow us to emphasize the role of the electronic partition function which is crucial for the majority of LnX_3 compounds. In order to point out this particularity, we applied the same methodology to $NdCl_3$, which has been widely studied in our laboratory [21]. The lanthanide trihalide gaseous molecules have energy levels very nearly equal to those observed experimentally for free ions or in crystals [1]. Therefore, these experimental data were used to estimate the electronic partition function of the selected molecules. Only levels below $20\,000\ \mathrm{cm}^{-1}$ were taken into account since higher levels have a negligible effect on the thermodynamic functions in the temperature range of interest.

Previous quantum calculations confirmed the assumption that only the 5d and 6s valence orbitals are essential in the characterization of the lanthanide–halogen bond. The very recent theoretical orbital analysis of Adamo et al. (with pseudopotentials using explicitly 4f orbitals in the valence shell) confirmed this hypothesis [13]. Therefore, we chose a set of quasi-relativistic pseudopotentials (Stuttgart pseudopotentials) for lanthanides which include the f orbitals within the core orbitals with a fixed 4f occupation corresponding to the desired valency of the atom [22]. In the case of the trihalides, all the lanthanides are modeled as 11-valence-electron systems. The determination of the quasi-relativistic (including major relativistic effects) pseudopotential parameters A_{kl} and a_{kl} is described in detail in Ref. [22]. Optimized (7s6p5d)/[5s4p3d] valence basis sets were applied to the trivalent rare earth elements. In order to obtain accurate results, we used all-electron 6-31G(d) basis sets for the halogens; the d polarization function has been revealed to be primordial to take the anionic nature of the halogens into account.

All the calculations were performed with the ab-initio/DFT Gaussian94 [23] code using IBM RISC 6000 and SGI R10000 workstations. Geometry optimization and a vibrational analysis were carried out using a DFT approach with a B3LYP hybrid functional [24–26].

3. Thermostatistic calculations parameters

The results of the thermostatistic calculations are only influenced by the accuracy of the rotational, vibrational and electronic partition function. Two molecular parameters influence the entropy rotational contribution: the inertia moments and the symmetry number of the considered molecule. In the case of the trihalide lanthanides, the inertia moments are not perturbed by a small change in the molecular structure. We have previously demonstrated that it is possible to modify the bond lengths and the bond angles, respectively, by up to 8 Å and 10° without any change in the entropy rotational contribution [12]. On the other hand, the symmetry number can slightly affect the entropy. $R\ln(2)$ ($\approx 5.8\ \mathrm{J\,K^{-1}\,mol^{-1}}$) is the amount by which entropy values using symmetry numbers 3 and 6 would differ. Therefore, an accurate equilibrium geometry is needed to determine the correct symmetry number and hence to perform a rigorous vibrational analysis. In Table 1, DFT calculated equilibrium geometries of the selected LnX_3 molecules (Ln=La, Gd and Lu; X=Cl and F) are

Table 1
Experimental, ab-initio and DFT calculated bond lengths (Å) and bond angles (deg) for the six selected molecules

	LaF_3		GdF_3		LuF_3		$LaCl_3$		$GdCl_3$		$LuCl_3$	
	R	θ	R	θ	R	θ	R	θ	R	θ	R	θ
SCF[a]	2.16	118.3	2.04	120	1.97	120	2.66	120	2.52	120	2.44	120
SCF[b]			2.04	120	1.97	120						
SCF[c]	2.15	116.0	2.06	120	1.98	120	2.68	120	2.55	120	2.47	120
CASSCF[a]	2.16	118.2	2.05	119.9	1.97	119.8	2.66	120	2.53	120	2.45	120
MCSCF[b]			2.06	120	2.00	120			2.53	120	2.45	120
MCSCF[d]	2.18	118.6	2.05	119.9	1.97	119.8	2.64	120	2.53	120	2.45	120
MP2[a]			2.02	115.2	1.94	117.9			2.46	120	2.38	120
MP2[c]	2.15	112.9	2.06	117.8	1.98	120	2.66	120	2.54	120	2.46	120
DFT[d]	2.16	115.1	2.06	117.7	1.99	118.9	2.63	118.6	2.52	119.0	2.45	120
DFT (This work)	2.14	110.8	2.04	113.6	1.97	118.4	2.65	118.1	2.53	118.8	2.44	119.9
EXP.[e]	*2.14*		2.05	108.4	*1.97*		2.59	112.5	2.49	113.0	2.42	111.5

[a] Refs. [9,10]. [b] Ref. [11]. [c] Ref. [12]. [d] Ref. [13]. [e] Ref. [3] (values in italics are estimated).

compared with the most recent experimental data [3] and theoretical results [9–13]. For various reasons, comparisons with experiments are often difficult for such compounds. Some experimental properties are often missing, especially in the case of the fluorides (corrosiveness problems). Therefore, in some cases, we can only compare our theoretical results with estimated values (e.g., LaF_3 and LuF_3 bond lengths). Although ab-initio values are in good agreement for the Ln–X bond lengths, these results clearly prove that the DFT calculations better predict the X–Ln–X bond angles. As already stated, the 4f orbitals do not seem to play any role in chemical bonding since very good results are obtained with the Stuttgart pseudopotentials which include explicitly the 4f orbitals in the valence shell. As confirmed in this study, recent theoretical works tend to demonstrate that we can expect a pyramidal geometry for trifluoride rare earth molecules, whereas the trichlorides tend to planar structures. This can easily be explained by the greater π-donor capability of Cl^- (than F^-). In this work, slightly pronounced C_{3v} structures (118°1 for $LaCl_3$) were obtained for the trichlorides with increasing bond angle throughout the lanthanide series. More pronounced pyramidal geometries (110°8 for LaF_3) have been established for the trifluoride compounds, but with the same linearity in the increase of the bond angle. On the other hand, it appears that the electronic correlation seems to play a crucial role in predicting a pyramidal structure. Previous SCF (see Table 1) calculations have systematically established planar structures for GdF_3, LuF_3 and all the trichloride compounds, whereas different post-Hartree–Fock methods favor C_{3v} structures in the case of the trifluorides. A DFT approach confirms this tendency. Furthermore, DFT calculations seem to be more effective in taking the electronic correlation into account and thus with a lower computational effort. Nevertheless, it has already been demonstrated that a very accurate calculated geometry is not essential to predict relevant thermodynamic data [12].

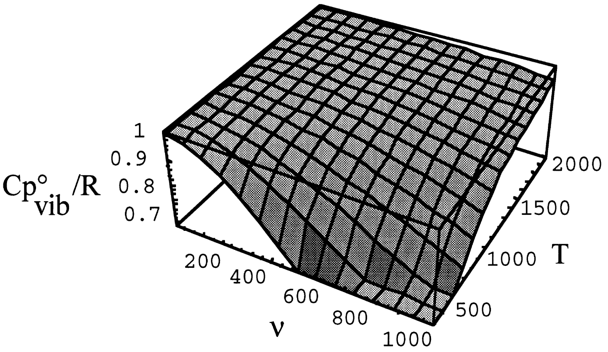

Fig. 1. Variation of the vibrational contribution of the heat capacity ($C_p°/R$, dimensionless) versus temperature T (K) and a single vibrational frequency ν (cm^{-1}).

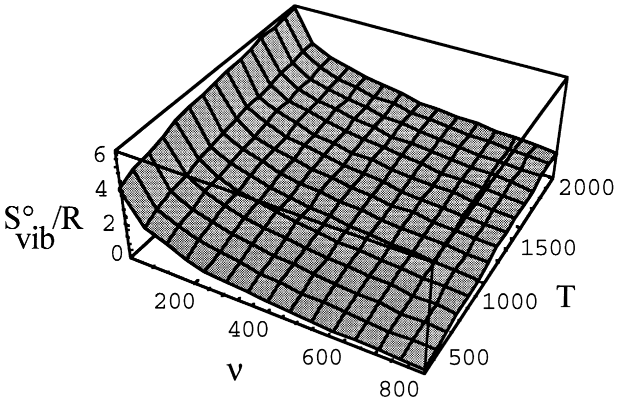

Fig. 2. Variation of the vibrational contribution of the entropy ($S°/R$, dimensionless) versus temperature T (K) and a single vibrational frequency ν (cm^{-1}).

The vibrational frequencies are certainly the most important parameters in thermostatistic calculations. For a single frequency, the vibrational contributions of heat capacity and entropy vary with temperature and frequency as depicted, respectively, in Figs. 1 and 2. Fig. 1 clearly demonstrates that, for a sufficiently high temperature, the vibrational contribution of the heat capacity tends towards an asymptotic limit, i.e. $6R \approx 49.9\ J\ K^{-1}\ mol^{-1}$ for trihalide lanthanides. In this case, accurate vibrational frequencies are not required to obtain a good estimation of the heat capacity. However, at ambient temperature, good precision is needed for the highest vibrational frequencies, whereas approximated low frequencies values are adequate. A similar study reveals that the relative enthalpy depends on the frequency to a lesser extent. This function obviously tends towards a temperature dependent limit (RT for a single vibration or 6RT for the selected molecules). On the other hand, we can see from Fig. 2 that the entropy is strongly influenced by the precision of small vibrational frequencies, whatever the temperature. The selected molecules are often referred to as ''floppy molecules'' in the literature, thus indicating a fluxional capability at ambient temperature. Performing a vibrational analysis effectively reveals a small vibrational frequency (ν_2) which is associated with the out-of-plane bending mode. This small frequency is a direct consequence of the flat energy surface (double-well potential) along the out-of-plane distortion (see Figs. 3 and 4). A problem appears when theoretical ''quasi-planar'' structures are obtained (Fig. 4: case of $LuCl_3$). In this particular case, the excessively flat energy surface leads to an abnormally small calculated frequency and hence alters perceptibly the estimated entropy. In Tables 2 and 3, DFT calculated vibrational frequencies are compared with experimental data [16] and recent theoretical vibrational analyses [9,10,12,13]. Our results are in good agreement with experimental data. However, the small ν_2 frequency is slightly underestimated (especially for GdF_3 and LuF_3) but better than those obtained with ab-initio methods. We find an exception with $LuCl_3$, the out-of-plane frequency of which is unrealistic in comparison with the experimental

Table 2

Experimental, ab-initio and DFT calculated vibrational frequencies (cm^{-1}) for the selected trifluoride rare earth molecules

	LaF_3				GdF_3				LuF_3			
	ν_1	ν_2	ν_3	ν_4	ν_1	ν_2	ν_3	ν_4	ν_1	ν_2	ν_3	ν_4
SCF[a]	560	42	561	130	594	47	584	137	620	54	614	138
SCF[b]	554	59	543	125								
CASSCF[a]	542	53	545	129	577	116	568	134	596	55	594	135
MP2[a]									629	42	622	141
MP2[b]	554	72	539	114	575	39	564	121	597	44	588	127
DFT[c]	527	83	512	131	569	119	553	138	583	97	569	150
DFT (This work)	553	88	538	117	581	58	564	125	601	61	589	131
EXP[d]	540±10	82±10	511±10	125±10	573±10	97±10	552±10	136±10	598±10	106±10	585±10	147±10

[a] Refs. [9,10]. [b] Ref. [12]. [c] Ref. [13]. [d] Ref. [16].

Table 3

Experimental, ab-initio and DFT calculated vibrational frequencies (cm^{-1}) for the selected trichloride rare earth molecules

	$LaCl_3$				$GdCl_3$				$LuCl_3$			
	ν_1	ν_2	ν_3	ν_4	ν_1	ν_2	ν_3	ν_4	ν_1	ν_2	ν_3	ν_4
SCF[a]	305	26	326	71	318	44	338	75	329	53	348	80
SCF[b]	288	33	310	67								
CASSCF[a]	301	26	323	72	314	45	336	77	323	52	349	87
MP2[a]									342	41	368	78
MP2[b]	289	24	313	60	304	35	328	66	305	60	327	80
DFT[c]	317	43	316	76	333	43	331	77	341	75	318	78
DFT (This work)	294	46	317	68	309	43	328	72	319	8	339	76
EXP.[d]	335±10	51±10	316±10	79±10	338±10	56±10	326±10	84±10	342±10	60±10	331±10	88±10

[a] Refs. [9,10]. [b] Ref. [12]. [c] Ref. [13]. [d] Ref. [16].

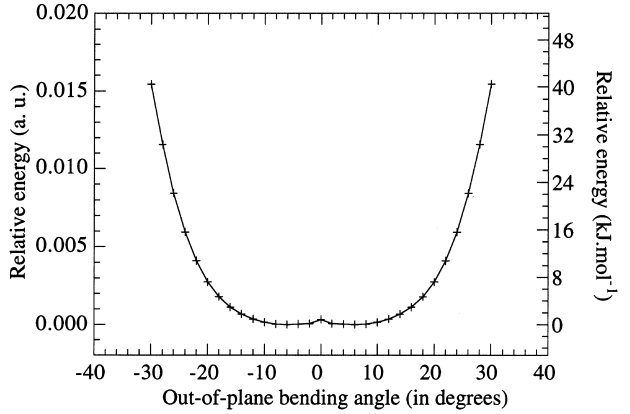

Fig. 3. Variation of the relative energy of LuF_3 (in a.u. and in kJ mol^{-1}) versus the out-of-plane bending angle. This angle is defined as the angle between the plane of the D_{3h} molecular structure and one of the Lu–F bonds.

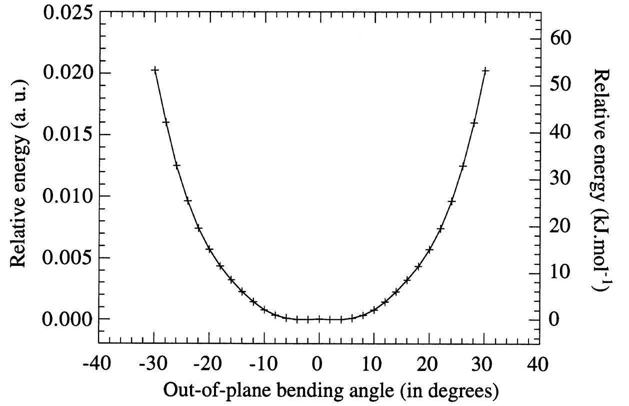

Fig. 4. Variation of the relative energy of $LuCl_3$ (in a.u. and in kJ mol^{-1}) versus the out-of-plane bending angle. This angle is defined as the angle between the plane of the D_{3h} molecular structure and one of the Lu–Cl bonds.

frequency. The other vibrational frequencies (two stretching modes and another bending mode), at all levels of calculation, are in good agreement with experimental data. We should mention that the calculated frequencies are not scaled. In fact, there is no general rule to use scaling factors, although they can be applied with success in some cases [27]. Moreover, we think that they hide several sources of error (e.g., anharmonicity error or Hartree–Fock error in the case of ab-initio methods) and, in our case, they do not bring any additional precision to the calculated frequencies.

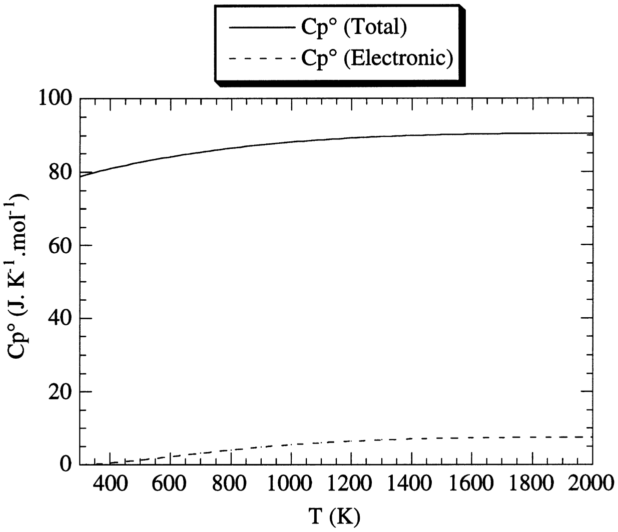

Fig. 5. Variation of the heat capacity of $NdCl_3$ (total and electronic contribution) versus temperature.

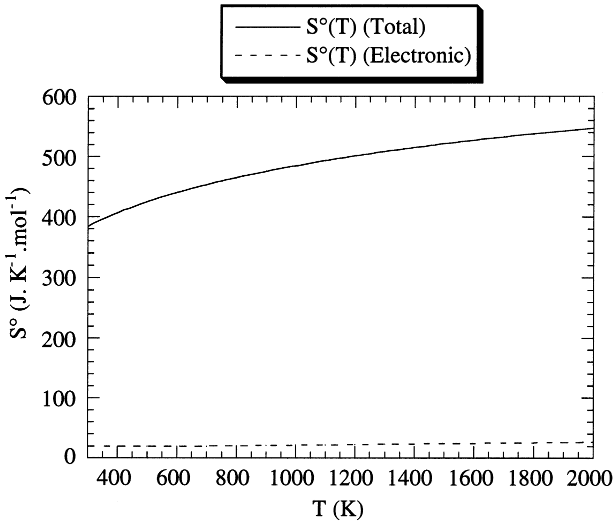

Fig. 6. Variation of the entropy of $NdCl_3$ (total and electronic contribution) versus temperature.

In the case of the rare earths compounds, the electronic partition function plays an important role in predicting accurate thermochemical data. However, the excited electronic states of the selected molecules (f^0, f^7 and f^{14} ground state configurations) lie much higher in energy than the ground state. Therefore, the electronic partition function is no longer needed for these species. In the case of trichloride and trifluoride neodymium molecules (and for the other trihalide lanthanides), we find numerous strongly degenerated electronic excited states lying near the ground state. Figs. 5 and 6 (e.g., heat capacity and entropy) clearly show the strong influence of the electronic contribution on the thermochemical functions of $NdCl_3$. Nevertheless, at low or ambient temperature, the electronic contribution can be neglected for the heat capacity and the enthalpy.

4. Conclusion

A quantum mechanics approach, combined with thermostatistic calculations, can be useful for estimating accurate thermodynamic data, especially for the molecules studied, pure experimental thermodynamic data for which are missing. This methodology can also be used to obtain high temperature thermochemical properties which are often unattainable using classic methods. The main difficulty arises from the harmonic approximation used to estimate the vibrational frequencies. However, all quantum chemistry programs have to use this crude approximation to perform a vibrational analysis. In the case of the out-of-plane distortion, the harmonic approximation is not suitable because of the anharmonicity of the potential function (double-well potential) in the vicinity of the minimum. In the future, the one-dimensional problem of the quantization of vibrational motion in a potential of general form has to be solved in order to correct the statistical calculations and more precisely the estimated entropy function. Furthermore, it is necessary to take the electronic contribution for these rare earth compounds into account, whereas it can generally be neglected in the case of light metal compounds.

Moreover, we notice that if only heat capacities or relative enthalpies are needed (e.g., heat exchange fluid experiments), SCF calculations seem to be sufficient to evaluate these thermodynamic functions with good accuracy and little computational effort. In the case of thermochemical equilibrium studies, post-Hartree–Fock or preferably DFT methods are needed to obtain accurate results.

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References

[1] Gmelin Handbuch der Anorganischen Chemie: Sc, Y, La und Lanthanides, Springer, Berlin, 1976.
[2] M. Gaune-Escard, in: R.T. Carlin, M. Matsunaga, J.R. Selman, S. Deki, D.S. Newman, G.R. Stafford (Eds.), Tenth International Symposium on Molten Salts, Los Angeles, Vol. 96-7, 1996, p. 439.
[3] M. Hargittai, Coord. Chem. Rev. 91 (1988) 35.
[4] C.E. Myers, L.J. Norman, L.M. Loew, Inorg. Chem. 17 (1978) 1581.
[5] Y.Q. Jia, S.G. Zhang, Inorg. Chim. Acta 143 (1988) 137.
[6] M. Dolg, H. Stoll, A. Savin, H. Preuss, in: R. Carbó (Ed.), International Workshop on Quantum Chemistry, Girona, Spain, Vol. 62, Elsevier, Amsterdam, 1988, p. 265.
[7] M. Dolg, H. Stoll, H. Preuss, J. Mol. Struct. (Theochem) 235 (1991) 67.
[8] M. Dolg, H. Stoll, Handbook on the Physics and Chemistry of Rare Earths, Vol. 22, Elsevier, Amsterdam, 1996, chapt. 152, p. 607.
[9] S.D. Bella, G. Lanza, I.L. Fragalà, Chem. Phys. Lett. 214 (1993) 598.
[10] G. Lanza, I.L. Fragalà, Chem. Phys. Lett. 255 (1996) 341.
[11] T.R. Cundari, S.O. Sommerer, L.A. Strohecker, L. Tippett, J. Chem. Phys. 103 (1995) 7058.
[12] L. Joubert, G. Picard, J.-J. Legendre Inorg. Chem. (to be published).
[13] C. Adamo, P. Maldivi, Chem. Phys. Lett. 268 (1997) 61.
[14] I. Barin, F. Sanert, E. Schultze-Rhonhof, W.S. Sheng, Thermochemical Data of Pure Substances, VCH Gesellschaft, Weinheim, 1989.
[15] O. Knacke, O. Kubaschewski, K. Hesselmann, Thermochemical Properties of Inorganic Substances, 2nd ed., Springer, Berlin, 1991.
[16] C.E. Myers, D.T. Graves, J. Chem. Eng. Data 22 (1977) 436.
[17] R.H. Hauge, J.W. Hastie, J.L. Margrave, J. Less-Common Met. 23 (1971) 359.
[18] J.W. Hastie, R.H. Hauge, J.L. Margrave, J. Less-Common Met. 39 (1975) 309.
[19] F. Bouyer, Thesis, Université Pierre et Marie Curie, Paris VI, 1995.
[20] M.W. Chase, C.A. Davies, J.R. Downey, D.J. Frurip, R.A. McDonald, A.N. Syverud, J. Phys. Chem. Ref. Data (JANAF Thermochemical Tables) 14 (1985).
[21] C. Zing, Thesis, Umversité Pierre et Marie Curie, Paris VI, 1990.
[22] M. Dolg, H. Stoll, A. Savin, Theor. Chim. Acta 75 (1989) 173.
[23] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheesman, T.A. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, Revision D.4, Gaussian Inc., Pittsburgh, PA, 1995.
[24] A.D. Becke, Phys. Rev. B 38 (1988) 3098.
[25] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[26] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[27] A.P. Scott, L. Radom, J. Phys. Chem. 100 (1996) 16502.