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Quantum chemical study of the structure and properties of isotopically pure lead chalcogenides

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Abstract. In the present work the theoretical methods B3LYP/SDD, GGA and BP86/TZ2P were used for quantum-chemical calculations of lead chalcogenides. It is shown that these levels of theory are applicable for assessment of their geometric parameters, Raman and IR spectra and thermodynamic characteristics. It is shown that there are correlations between the experimental and calculated characteristics of lead sulphide, selenide and telluride. The influence of different isotopes of lead, sulphur, selenium and tellurium on the thermodynamic parameters and the Raman spectra for the lead chalcogenides is shown.

1. Introduction

Lead chalcogenides compounds of PbS, PbSe, PbTe are narrow band-gap semiconductors used in infrared detectors, thermoelectric devices and photoresistors. In spite of the fact that the electronic and optical properties of lead chalcogenides were studied long ago and are rather well known, in these materials they continue to reveal interesting properties. For example, PbSe semiconductors display unusually high temperatures of continuous emission that are of great interest for engineering infra-red lasers that work at room temperatures [1]. Data from recent research indicates that elements of high-sensitivity receivers in the distant infra-red range (20–200 microns) based on lead alloy chalcogenides can successfully compete with germanium and silicon [2]. Unlike those elements, lead chalcogenides possess considerable radiation resistance caused by their high density, stabilizing Fermi's level. Moreover lead chalcogenides are interesting as objects of research, namely studying the influence of isotope composition of semi-conductor materials on their physical properties. Recently interesting results in this direction were obtained in papers [3, 4].

Several attempts have been made to develop theoretical settlement models using various approaches, in order to accurately reproduce the properties of lead chalcogenides. Previously, geometrical, spectral and thermodynamic characteristics of sulphur and lead were calculated by density functional method using various values of functionals and basic conditions, such as B3LYP (GAUSSIAN), BP86 (ADF), GGA (FLAPW) [5].

The purpose of this work is the analysis of applicability of the theory of a functional of density to an assessment of frequency shifts in Raman spectra and thermodynamic characteristics of chalcogenides with various isotope compositions of lead, selenium and tellurium, and also an elementary cell PbS, PbSe and PbTe.

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2. Experimental part

For carrying out quantum and chemical calculations we used the standard software package GAUSSIAN'03W [6]. Calculations were carried out using a hybrid method of a functional of density of B3LYP, with an exchange functional to Becke B3 and a correlation functional Lee, Wang and Parr (LYP) [7, 8]. This method is now generally accepted to be the best for describing thermodynamic properties and vibrational spectra [9]. As a basic condition we used the SDD pseudopotential for an atom of lead and the D95 double-dzeta as the basis for other atoms [10]. Calculated geometries of the molecules were fully optimized; the absence of imaginary vibration frequencies confirmed the stationary character of the structures. Energy calculations were corrected for zero-point vibrational energy and reduced to normal conditions (298.15K, 1 atm) using thermal corrections to enthalpy and free energy. We have also calculated the ADF'2004 (Amsterdam density functional) program [11]. The OPTX exchange functional was used in combination with the PBE correlation functional using an all electron triple-ζ + polarization basis set of Slater orbitals (BP86/TZ2P+) [12]. To estimate the enthalpy of formation the semi-empirical method PM3 was used [13].

All the above-stated calculations were carried out for compounds of PbS, PbSe and PbTe in the gaseous phase. The calculations of electronic structure and characteristics of PbSb, PbSe and PbTe, were in the crystalline state through the full-potential linear augmented plane wave method (code WIEN2k [14]) with the generalized gradient approximation of exchange and correlation potential [15], and full structural optimization. The density of electronic conditions was calculated by the method of tetrahedrons [16]. In this case cubic monosulphide, monoselenide and monotelluride of lead PbS, PbSe, PbTe (the B1 type, spatial group № 225, Fm-3m) with atomic coordinates: Pb (0; 0; 0) and S, Se, Te (1/2; 1/2; 1/2) were used for calculations.

3. Results and discussion

To assess the "quality" of the calculations it is necessary to rely on some physico-chemical properties of similar compounds, for which sufficiently accurate experimental values are known. As experimental values, we used the bond lengths of compounds of lead, the frequency of stretching and deformation vibrations in the IR spectra of two- and four-coordinated lead compounds, as well as the band gap of crystalline halides, and the entropy and enthalpy of formation and dissociation energies of compounds of lead in the gas phase (Table 1).

From the results of the calculation it follows that the valent angles of Hal-Pb-Hal optimized in the GAUSSIAN program are close to the experimental values [10] (about 98–100 °), and the bond lengths of Pb-Hal (Hal=F, Cl, Br, I, Me) Pb (II) and Pb (IV) compounds have a good correlation ratio (fig. 1).

Table 1. The calculated and experimental [12] enthalpy of formation (kJ/mol), entropy (J/mol·K), dissociation energy (kJ/mol) of lead halides

Compound	ΔH°, PM3	ΔH°, exp.	S°, calc.	S°, exp.	$-D_o$, calc.	$-D_o$, exp.
PbF_2	-375	-435.14	293	292.66	484	388
$PbCl_2$	-166	-174.05	318	317.19	388	304
$PbBr_2$	-119	-104.39	346	339.39	353	262
PbI_2	-18	-3.18	362	359.55	315	209
PbF_4	-617	-1133.45	345	333.52	341	327
$PbCl_4$	-259	-552.41	399	381.65	260	252
$PbBr_4$	-109	-456.36	445	426.20	229	199
PbI_4	56	-224.47	477	466.26	200	164

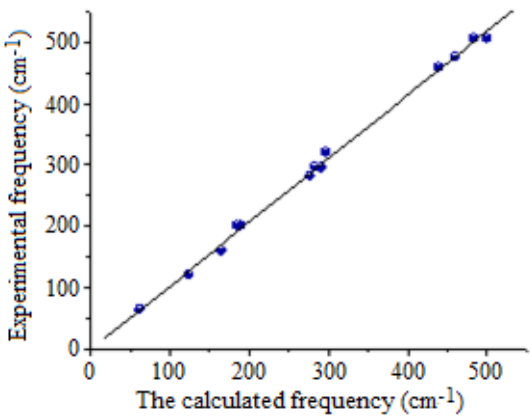

Figure 1. The relationship between experimental bond lengths of compounds of Pb (II) and Pb (IV) and those calculated by the B3LYP/SDD method.

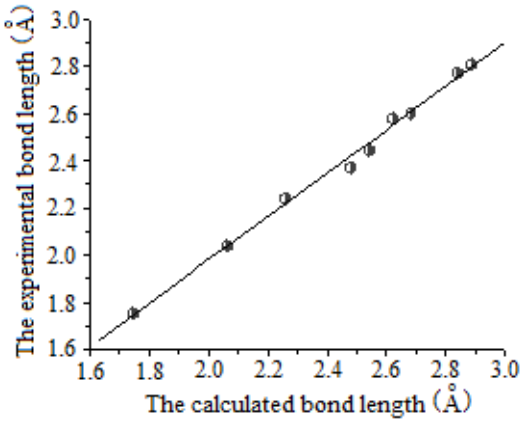

Figure 2. The relationship between experimental IR-frequencies of lead halides and those calculated by the B3LYP/SDD method.

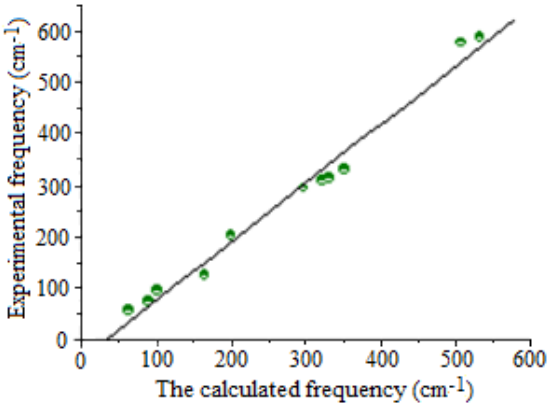

Figure 3. The relationship between experimental IR-frequencies of lead halides and those calculated by the ADF method.

In addition, the frequencies calculated by the two methods of IR and Raman spectra of lead halides are close to the experimental values (Fig. 2, 3) with a coefficient of correlation of 0.998 and a standard deviation of 9 %.

We observed quite reliable linear correlation (1–8), which showed that the calculations for lead halides by the PM3 and B3LYP/SDD methods correctly describe not only the geometry, but also the thermodynamic parameters such as enthalpies (ΔH°) and entropies (S°) of formation, and the dissociation energies (D_0). The dissociation energy of the lead compounds was determined as the difference between the energy of the compound and the energies of their constituent atoms, as amended by the enthalpy of formation.

The calculated dissociation energy was related to the number of bonds, compared with the experimental average binding energy of lead-halogen [15]. It should be noted that if the entropy falls on the curve for compounds Pb (II) and Pb (IV), then the relationship between the calculated and experimental enthalpies of formation and dissociation energies are observed separately for the coordination of various lead compounds on the basis of the two methods of calculation GAUSSIAN and ADF programs:

$$\text{GAUSSIAN: } S^\circ\,(\text{exp.}) = -23 + 0.914S^\circ\,(\text{calc.})\quad r = 0.996;\ s = 5;\ n = 8 \qquad (1)$$

$$\text{ADF: } S^\circ\,(\text{exp.}) = 10.6 + 0.97S^\circ\,(\text{calc.})\quad r = 0.998;\ s = 4;\ n = 7 \qquad (2)$$

For Pb(II):

PM3: ΔH° (exp.) = 29 +1.23 ΔH° (calc.) r = 0.999; s = 12; n = 4 (3)

GAUSSIAN: D_o (exp.) = -108 +1.04 D_o (calc.) r = 0.993; s = 11; n = 4 (4)

ADF: D_o (exp.) = -44 +1.54 D_o (calc.) r = 0.990; s = 13; n = 4 (5)

For Pb(IV):

PM3: ΔH° (exp.) = -289 +1,35 ΔH° (calc.) r = 0.997; s = 35; n = 4 (6)

GAUSSIAN: D_o (exp.) = -62 +1.14 D_o (calc.) r = 0.992; s = 11; n = 4 (7)

ADF: D_o (exp.) = -28 +0.83 D_o (calc.) r = 0.986; s = 14; n = 4 (8)

Here and below, r - correlation coefficient, s - standard deviation, n - number of compounds.

The values of the energy distance between the occupied and unoccupied molecular orbitals ΔE(B3MO-HCMO) calculated by both methods agree well with the band gap in crystalline chloride, bromide and iodide of lead [17], with a coefficient of correlation 0.999 and a standard deviation of 0.02 eV.

By analogy with the sulphur compounds [5], for selenium and tellurium compounds were used as a "quality assessment" on the base on the bond lengths, frequencies in the vibrational spectra, and experimental values of the band gap of crystalline chalcogenides, as well as the dissociation energy of selenium and tellurium in the gaseous phase (Table 2).

Table 2. The experimental and calculated dissociation energy of selenium and tellurium compounds

Molecule	Experimental bond dissociation energy, kJ/mol	Bond dissociation energy calculated by ADF, kJ/mol	Bond dissociation energy calculated by B3LYP/SDD, kJ/mol
TeB	354	485	477
SeAl	338	468	438
TeAl	268	343	372
SeIn	247	359	414
TeIn	218	326	364
SeP	364	505	574
SeAs	352	490	564
TeAs	312	445	519
SeS	371	547	490
TeS	339	502	469
SeTe	292	468	446
Molecule	Experimental bond dissociation energy, kJ/mol	Bond dissociation energy calculated by ADF, kJ/mol	Bond dissociation energy calculated by B3LYP/SDD, kJ/mol
SeO	465	694	623
SeC	590	869	802
Se_2	333	510	468
SeH	311	493	439
SeSi	534	731	694
SeGe	485	694	673
SeSn	401	635	631
Te_2	260	390	422
TeSi	448	631	623
TeO	376	550	602
TeCu	229	320	351
TeGe	430	610	614

On the other hand, the results of the calculations imply that bond lengths optimized by the B3LYP/SDD method for the compounds of selenium and tellurium are proportional to the experimental values [17], and there is a good correlation between them:

For selenium compounds

$$R(exp.) = 0.957\ R(calc.)\ r = 0.995;\ s = 0.04;\ n = 18 \quad (9)$$

For tellurium compounds

$$R(exp.) = 0.969\ R(calc.)\ r = 0.993;\ s = 0.04;\ n = 10 \quad (10)$$

Table 3. The energy of the unit cell of lead chalcogenides (relative to 5619 u.a.m.u. for PbS, 176 u.a.m.u. for PbSe and 158 u.a.m.u. for PbTe) and isotopic composition

M_{Pb}	M_S	M_{Se}	M_{Te}	E_0, u.a.m.u.
204	32	76	122	0.636289 0.217974 0.611721
206	32	76	122	0.636300 0.217984 0.611731
207	32	76	122	0.636305 0.217989 0.611735
208	32	76	122	0.636311 0.217993 0.611740
204	33	78	124	0.636365 0.218014 0.611746
206	33	78	-	0.636376 0.218024
207	33	78	124	0.636381 0.218029 0.611760
208	33	78	124	0.636387 0.218033 0.611765
M_{Pb}	M_S	M_{Se}	M_{Te}	E_0, u.a.m.u.
204	34	80	126	0.636438 0.218053 0.61177
206	34	80	126	0.636449 0.218062 0.611779
207	34	80	-	0.636454 0.218067
208	34	80	-	0.636460 0.218072
204	36	82	128	0.636575 0.218090 0.611793
206	36	82	128	0.636586 0.218099

				0.611803
207 (204 for PbTe)	36	82	130	0.636591 0.218104 0.611816
208	36	82	-	0.636597 0.218109

In addition, the calculated frequency of the IR and Raman spectra compounds of selenium and tellurium are close to the experimental values [18] (Fig. 4, 5):

For selenium compounds

$$\omega(\text{exp.}) = 59 + 0.996\ \omega(\text{calc.})\ r = 0.993;\ s = 57;\ n = 91 \quad (11)$$

For tellurium compounds

$$\omega(\text{exp.}) = 21 + 1.07\ \omega(\text{calc.})\ r = 0.993;\ s = 27;\ n = 67 \quad (12)$$

It should be noted that correlation coefficients close to one of the calculated parameters in (9–12) indicate the high reliability of the use of the SDD basis set.

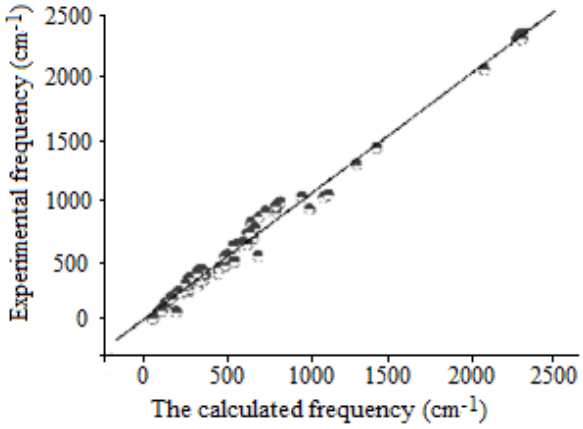

Figure 4. Relationship between experimental IR and Raman frequencies and those calculated by the B3LYP/SDD method for selenium compounds.

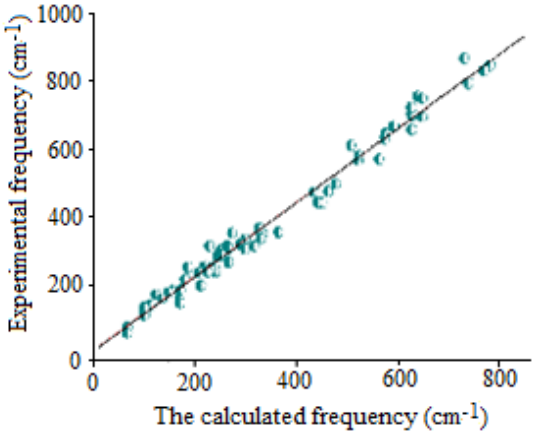

Figure 5. Relationship between experimental IR and Raman frequencies and those calculated by the B3LYP/SDD method tellurium compounds.

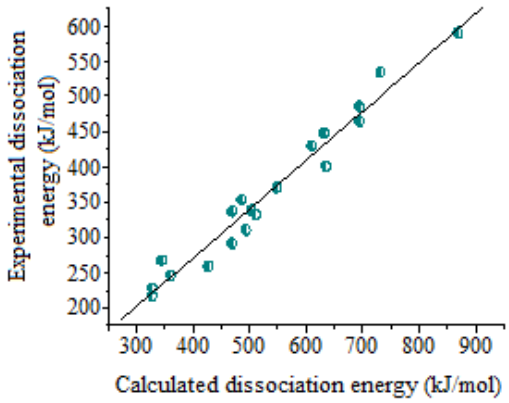

Figure 6. Relationship between experimental dissociation energies and those calculated by the B3LYP/SDD method of selenium and tellurium compounds.

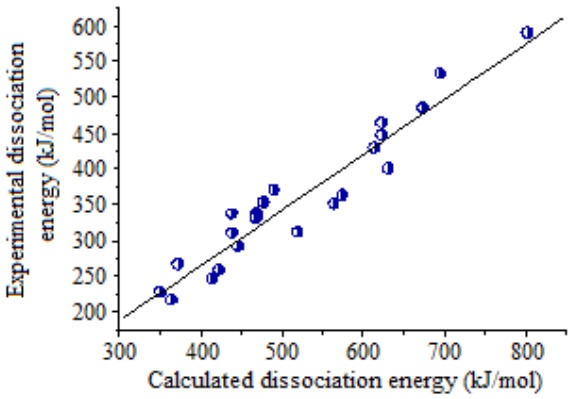

Figure 7. Relationship between experimental dissociation energies and those calculated by the ADF method of selenium and tellurium compounds

We have also obtained quite reliable linear correlation (13 and 14), which suggests that the calculations for compounds of selenium and tellurium by the B3LYP/SDD and BP86/TZ2P+ methods correctly describe not only the geometry, but also the thermodynamic parameters, in particular the dissociation energy (D_0). The energy of dissociation of selenium and tellurium compounds was determined as the difference between the energy of the compound and the energies of their constituent atoms, as amended by the enthalpy of formation. The calculated dissociation energy, relative to the number of bonds, was compared with the experimental average binding energy of selenium- selenium and tellurium-tellurium [19] (Table 3).

As a result we obtained a correlation ratio based on the two methods of calculation using the GAUSSIAN and ADF programs (Fig. 6, 7):

GAUSSIAN:

$$D_o \text{ (exp.)} = -44 + 0.77\, D_o \text{ (calc.)}\quad r = 0.952;\ s = 30;\ n = 23 \tag{13}$$

ADF:

$$D_o \text{ (exp.)} = 6 + 0.68\, D_o \text{ (calc.)}\quad r = 0.982;\ s = 18;\ n = 23 \tag{14}$$

On the basis of optimized structures for PbS, PbSe and PbTe in the gas phase, we have assessed the effect of different isotopes of sulphur (^{32}S-^{34}S), selenium (^{76}Se-^{82}Se), tellurium (^{122}Te-^{130}Te) and lead (^{204}PbS-^{208}Pb) on the spectral and thermodynamic parameters of lead chalcogenides. For the most intense bands of lattice oscillations in the Raman spectra calculated by the B3LYP/SDD method: (~ 120 cm^{-1}) for the lead sulphide; (~ 68 cm^{-1}) for lead selenide; and (~ 81 cm^{-1}) for lead telluride; we obtained multiple correlation ratios between the calculated Raman frequencies (ω) and the masses of the isotopes of lead, sulphur, selenium, and tellurium (M_{Pb}, M_S, M_{Se}, M_{Te}):

$$\omega = 167 - 0{,}26M_S - 0{,}74M_{Pb};\ r = 0.980;\ s = 0.2;\ n = 11 \tag{15}$$

$$\omega = 100 - 0{,}335M_{Se} - 0{,}027M_{Pb};\ r = 0.99996;\ s = 0.017;\ n = 16 \tag{16}$$

$$\omega = 121 - 0{,}25M_{Te} - 0{,}044M_{Pb};\ r = 0.999;\ s = 0.02;\ n = 12 \tag{17}$$

For all chalcogenides the error of calculation does not exceed 0.02 %, indicating that the calculation is correct. For lead chalcogenides we also obtained multiple correlations between the energy of the unit cell PbS (Se) (Te) with a correction to the energy (E_0) and the masses of the isotopes of lead, sulphur, selenium and tellurium:

$$E_0 = 0.63 + 7.13\cdot10^{-5}M_S + 5.46\cdot10^{-6}\, M_{Pb};$$
$$r = 0.999;\ s = 2.96\cdot10^{-6};\ n = 16 \tag{18}$$

$$E_0 = 0.216 + 1.925\cdot10^{-5}M_{Se} + 4.77\cdot10^{-6}\, M_{Pb};$$
$$r = 0.9997;\ s = 8.84\cdot10^{-7};\ n = 16 \tag{19}$$

$$E_0 = 0.6 + 1.19\cdot10^{-5}M_{Te} + 4.77\cdot10^{-6}\, M_{Pb};$$
$$r = 0.9996;\ s = 6.46\cdot10^{-7};\ n = 12 \tag{20}$$

A similar dependence is also observed for a lattice of four elemental isotopes of lead:

$$E_0 = -48.2 - 1.5\cdot10^{-5}\, M_{Pb};\ r = 0.995;\ s = 2.9\cdot10^{-6};\ n = 4 \tag{21}$$

To further examine the effect of the isotopes on the physico-chemical properties, we performed optimization of the unit cell of PbS, PbSe and PbTe using the PM3 method. The calculated bond lengths for Pb-S, Pb-Se and Pb-Te totalled 3.5 Å, 3.57 Å and 3,45 Å, close to the experimental values of 2.97 Å, 3.06 Å and 3.23 Å. It should be noted that our calculation using the FLAPW program for crystalline PbS, PbSe and PbTe gave the best value of the lattice constants at 6.01 Å, 6.23 Å and 6.57 Å, close to the experimental values of 5.94 Å, 7.1 Å and 6.75 Å, respectively.

One of the most important characteristics of semiconductors is the value of the energy gap. The calculation in the solid phase for PbS, PbSe and PbTe gave values of 0.5, 0.44 and 0.70 eV and in the gas phase 0.38, 0.36 and 0.28 eV using the GAUSSIAN program. The experimental width of a single-crystal PbS is 0.41 eV [17]. Thus, we can assume that the calculations for the gas phase and crystal lead chalcogenides gave values fairly close to the experimental values for the energy characteristics. Deviation of the calculated energy gap in gas phase from the FLAPW calculation for PbTe apparently is due to the inaccuracy of the parameters for Te by the PM3 method.

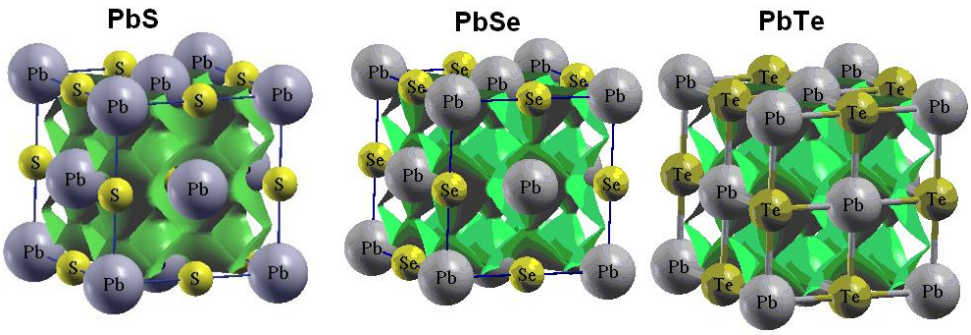

Figure 8. Isoelectronic surfaces (ρ = 0.15 e/Å3) cubic (type B1) PbS, PbSe and PbTe.

Based on the calculations in the solid phase (FLAPW) and in the gaseous phase by ADF we can estimate a bond in terms of ionic (electrostatic) and covalent (orbital) components. FLAPW data indicate a mixed ionic-covalent type (Fig. 8). The ionic component is created by the charge polarization in the direction of Pb → S, Pb → Se and Pb → Te in an ideal ion model of the charge states of $Pb^{2+}Hal^{2-}$. In reality, the effective charges of the atoms are smaller due to the covalent contribution. The covalent constituent is formed by the partially overlapping Halnp - Pb6s, 6p states. The covalent constituent can be illustrated as in Fig. 8, which shows the overlapping of isoelectronic surfaces in the direction Pb-(S, Se, Te). In the ADF program the energy of the molecule is split into several contributions. Energy members can be identified by the three main components of the chemical bond: repulsive Pauli, electrostatic attraction and covalent interactions. Frenking and co-workers [20] suggested that $\Delta E_{elstat.}$ could be used to assess the strength of the electrostatic binding and $\Delta E_{orb.}$ for covalent binding. These results for the calculation of lead chalcogenides in the gaseous phase also indicate that the chemical bond is composed of ionic and covalent components with a predominance of the latter (65% for S, 79% for Se and 56% in the case of Te).

4.Conclusions

Thus, the results suggest that the use of the density functional method in various versions with different functionals and basic conditions, such as B3LYP (GAUSSIAN), BP86 (ADF), GGA (FLAPW) presents an opportunity to evaluate not only the spectral isotope shifts, but also the thermodynamic parameters of the structures of lead chalcogenides containing different isotopes of lead, selenium and tellurium.

Acknowledgements

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