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Ab-Initio Calculations of the Dissociation Energy and Periodic Properties of the Heavy P-block Dimers

Salem A. Hameed

Chemistry Department, Faculty of Science,
King Abdulaziz University, Jeddah, Saudi Arabia

Abstract. Molecular orbital calculations within the ab-initio frame work using SBK-basis set at the RHF level are reported for heavy P-block dimers of the fourth (Ga_2, Ge_2, As_2, Se_2 and Br_2), fifth (In_2, Sn_2, Sb_2, Te_2 and I_2) and sixth (Tl_2, Pb_2 and Bi_2) rows. The results of the molecular orbital interpreted and correlated in terms of equilibrium bond length, bond order, bonded valence, total valence, total energy, nuclear energy, electronic energy, electron-electron energy, electron-nuclear energy, nuclear-nuclear energy and dissociation energy. The effect of d-orbital on the ground state properties is also reported. The results indicate that method used gives fairly satisfactory predication of the molecular properties.

Introduction

The electronic and spectroscopic properties of small clusters of heavy atoms and metal atoms have been the topics of many experimental[1-15] and theoretical studies[16-31]. Experimental progress in this area has been phenomenal in recent years[32-43] due to the advent of laser vaporization and supersonic jet expansion method. Typically, a sample of a foil or sheet of material containing these elements such as a Ga As crystal, a Si crystal or Pt foil is vaporized with a high energy Nd:YAG laser and passed through a supersonic nozzel. A number of other techniques such as sputtering methods, rare-gas matrix isolation methods, particle bombardment method, ligand-stripping methods and aggregation within zeolites and molecular sieves have been used for cluster generation[44 -53].

Clusters of heavy main group elements comprise a subject themselves, a separate class of unusual compounds whose properties exhibit phenomenal variation as a function of size. Many experimental and theoretical investigation in recent years have demonstrated that the geometries and electronic properties of small clusters containing typically 3-10 atoms have no resemblance at all to the more familiar properties of the bulk. It is this aspect that has made the cluster area perhaps one of the most exciting and challenging areas for both experimental and theoretical activities. Electron affinities and ionization potentials of these species exhibit dramatic alternations as a function of cluster size.

A quick review of the chemical literature, shows that no systematic investigations of the electronic structure and bonding of heavy p-block dimers have been undertaken. Such calculations, together with the experimental of spectroscopic properties could provide a wealth of information on the chemistry of such important class of compounds.

In the present study we reported the calculation of the ground state electronic properties (bond lengths, bond orders, total energies, electronic energies, nuclear energies and dissociation energy) of heavy p-block dimers of the fourth, fifth and sixth rows of the periodic table and correlation of periodic trend.

Method of Calculation

The tremendous cost of ab–initio calculations has motivated many attempts to find computational shortcuts. One such approach is based on the observation that core orbitals are relatively inert to changes in chemical bonding (the so called frozen core approximation)[54]. Another observation is that the effect of core electrons on valence electrons can be treated through the use of potential energy term expressed as sum of local functions multiplied by the projection operators. Based on these two assumptions effective core potentials (ECP's) or pseudo potentials, as they are sometimes called, reduce the computational problem to dealing with valence electrons only. Early results obtained from ECP's compared favorably well with these obtained from all electron calculations. These calculations trended, however, to yield shorter bond lengths and somewhat deeper potential energy curves. Such problems have been

overcome, and calculations using ECP's or all electrons results are in good agreement.

All calculations were carried out using SBK (Stevens/Basch/Krauss) valence basis set[55], as implemented in Gaussian 94[56]. This choice implies an unscaled 3-21G basis.

Results and Discussion

The data obtained using SBK-MO calculations are analysed through three rows, fourth (Ga, Ge, As, Se and Br), fifth (In, Sn, Sb, Te and I) and sixth (Tl, Pb and Bi) and five groups, group III (Ga, In and Tl), group IV (Ge, Sn and Pb), group V (As, Sb and Bi), group VI (Se and Te) and group VII (Br and I).

Table 1 presents molecular orbitals, molecular states, total energies and dissociation energies of the studied dimers. Among the values given in Table 1 one can reveal the followings:

1. Within fourth row, the most stable dimer formed is Ga_2 as indicated from the drop of the total energy. The order of stability of the fourth row are Ga > Br_2 > Se_2 > As_2 > Ge_2. Hence the Ge_2 dimer is the lowest stable dimer in fourth row.
2. With the fifth row, again In_2 is the most stable dimer whereas, Sn_2 dimer is the lowest stable one. The order of stability are In > I_2 > Te_2 > Sb_2 > Sn_2.
3. Due to the lack of experimental data in sixth row, three dimers are considered Tl_2, Pb_2 and Bi_2. The stability of Bi_2 is greater than Pb_2 by about 3.9au.
4. Within the group III, Ga_2 dimer still the most stable dimer of all heavy p-block elements.
5. Within group IV, Ge_2 is more stable than Sn_2 and Pb_2 whereas, Sn_2 and Pb_2 have the same stability.
6. Within group V, As_2 is the more stable than Sb_2 and Bi_2. The order of stability are As_2 > Bi_2 > Sb_2.
7. Within group VI, Se_2 dimer is more stable than Te_2 dimer by about 2.55 au.
8. Within group VII, Br_2 dimer is more stable than I_2 dimer by about 3.83 au.
9. Thermodynamic studies[57] of Ga_2 revealed that the dissociation energy of Ga_2 is about 1.4eV, whereas, the theoretical dissociation

energy calculated at complete active space self consistent field (CASSCF) is 1.2eV. The difference may be attributed to the using the incorrect partition function of Ga_2.

Table 1. Molecular orbitals, molecular states, total energies and dissociation energies of the studied dimers using SBK-basis set.

Dimer	MO – configuration	Molec. state	E_T, au		D,eV	
			SBK	SBK+d	Exp.	Calc.
Ga_2	$^2 2\sigma_u^2 1\sigma_g 1^2 \sigma_g$	$\sum_g^{1+}$	–514.24	–514.21	1.20	1.40
Ge_2	$^2 \pi_u^2 1\sigma_g^2 2\sigma_u^2 1\sigma_g 1$	$\sum_g^{3-}$	7.28	–7.30	2.29	2.65
As_2	$^4 \pi_u^2 1\sigma_g^2 2\sigma_u^2 1\sigma_g 1$	$\sum_g^{+1}$	–12.06	–12.11	2.71	3.96
Se_2	$^2 \pi_g^4 1\pi_u^2 1\sigma_g^2 2\sigma_u^2 1\sigma_g 1$	$\sum_g^{3}$	–18.22	–18.27	2.91	3.19
Br_2	$^4 \pi_g^4 1\pi_u^2 1\sigma_g^2 2\sigma_u^2 1\sigma_g 1$	$\sum_g^{1+}$	–26.25	–26.28	1.88	1.97
In_2	$^1 \pi_u^1 1\sigma_g^2 2\sigma_u^2 1\sigma_g 1$	$^3\pi_4$	–376.45	–376.4	0.83	0.87
Sn_2	$^2 \pi_u^2 1\sigma_g^2 2\sigma_u^2 1\sigma_g 1$	$\sum_g^{3+}$	–6.66	–6.49	1.86	1.94
Sb_2	$^4 \pi_u^2 1\sigma_g^2 2\sigma_u^2 1\sigma_g 1$	$\sum_g^{1+}$	–10.55	–10.59	2.17	3.09
Te_2	$^2 \pi_g^4 1\pi_u^2 1\sigma_g^2 2\sigma_u^2 1\sigma_g 1$	$\sum_g^{3+}$	–15.69	–15.72	1.69	2.68
I_2	$^4 \pi_g^4 1\pi_u^2 1\sigma_g^2 2\sigma_u^2 1\sigma_g 1$	$\sum_g^{1+}$	–22.42	–22.45	2.06	2.68
Tl_2	$^1 \pi_u^1 1\sigma_g^2 2\sigma_u^2 1\sigma_g 1$	$^3\pi_4$	–34.3.40	–343.41	0.58	0.63
Pb_2	$^2 \pi_u^2 1\sigma_g^2 2\sigma_u^2 1\sigma_g 1$	$\sum_g^{3}$	–6.66	–6.67	0.88	0.86
Bi_2	$^4 \pi_u^2 1\sigma_u^2 2\sigma_u^2 1\sigma_g 1$	$\sum_g^{1+}$	–10.61	–10.63	2.30	2.04

10. The theoretical CASSCF De value for the ground state $^3\sum_g^-$ of Ge_2 is 2.29 eV. This is a resamable agreement with the experimental value of 2.65 eV. The small discrepancy between the calculated and observed values could be attributed to the high order correlation correction as well as the effective core potentials.

11. The theoretical CASSCF dissociation energy of the ground state of Se_2 was found to be 2.91eV.A number of experimental De values were obtained (3.41, 3.16 and 3.110eV)[58]. Photoionization and thermo-chemical studies[59] seem to favor the higher value. Balasubramanian[60] thus obtained an upper value for De, eliminating the highest value of the three possible De values. Thus the De value should be about 3.19 eV.

12. The main effect of higher order correlations was found to be on the dissociation energies of Sb_2 dimer. The calculated De increased by 17% due to the higher order correlations. The refined theoretical De (2.17 eV) was still about 30% smaller than an experiment (thermodynamic) value of 3.09eV obtained by Knudsen effusion mass spectrometric method.

13. The theoretical dissociation energy De obtained with the CASSCF method for Te_2 dimer was found to be 1.69 eV. The spin-orbit interaction decreased the De value, since the separated atoms are more stabilized by the spin-orbit interaction compared to the molecule. The experimental value reported for Te_2 is 2.68eV based on a weighted mean of a number of values obtained from spectroscopic and thermochemical methods. The difference between theoretical and experimental may be attributed to limitation of the calculations.

14. The theoretical De for Pb_2 dimer is 0.88 eV was almost in exact agreement with an experimental value of 0.86eV. The agreement of such magnitude on a very heavy dimer such as Pb_2, for which both spin-orbit effects and relativistic effects are large, must be considered impressive.

Periodic Properties

Bond length, bond order, total valence, bonded valence, nuclear energy, electronic energy, electron-electron repulsion energy, electron-nuclear attraction energy and nuclear-nuclear repulsion energy are presented and plotted in Tables 2-5 and Fig. 1-6. The periodicity of the studied dimers explained within a row on going from left to right (increasing of molecular weight) and in the group on going from up to

down (increasing of outer orbital shells). Among the values given in Tables 2-5 and Fig. 1-6 one can reveal the following:

Table 2. Bond length and bond order of the studied dimers.

Dimer	Bond length (A°)		Bond order	
	SBK	SBK+d	SBK	SBK+d
Ga_2	2.5771	2.5780	1.307	1.330
Ge_2	2.2322	2.2004	2.020	2.225
As_2	2.1163	2.0723	2.653	2.815
Se_2	2.2337	2.1527	1.715	1.814
Br_2	2.3920	2.2838	0.871	0.917
In_2	2.8881	2.9001	1.380	1.339
Sn_2	2.5571	2.5382	2.108	2.219
Sb_2	2.4722	2.4349	2.761	2.869
Te_2	2.6351	2.5654	1.801	1.892
I_2	2.7700	2.6750	0.883	0.950
Tl_2	3.0277	3.0344	1.173	1.158
Pb_2	2.6424	2.6342	1.925	2.013
Bi_2	2.5871	2.5645	2.763	2.849

Table 3. Total valence and bonded valence of the studied dimers.

Dimer	Total valence		Bonded valence	
	SBK	SBK+d	SBK	SBK+d
Ga_2	1.307	1.330	1.307	1.330
Ge_2	2.020	2.225	2.020	2.225
As_2	2.653	2.815	2.653	2.815
Se_2	1.715	1.814	1.715	1.814
Br_2	0.871	0.917	0.871	0.917
In_2	1.380	1.339	1.380	1.339
Sn_2	2.108	2.219	2.108	2.219
Sb_2	2.761	2.869	2.761	2.869
Te_2	1.801	1.892	1.801	1.892
I_2	0.883	0.950	0.883	0.950
Tl_2	1.173	1.158	1.173	1.158
Pb_2	1.925	1.925	1.925	1.925
Bi_2	2.763	2.849	2.763	2.849

Table 4. Nuclear energy, electronic energy and total energy of the studied dimers.

Dimer	Nuclear energy		Electronic energy		Total energy	
	SBK	SBK+d	SBK	SBK+d	SBK	SBK+d
Ga_2	90.55	90.49	–604.79	–604.70	–514.24	–514.24
Ge_2	3.79	3.84	–11.07	–11.14	–7.28	–7.30
As_2	6.25	6.38	–18.31	–18.49	–12.06	–12.10
Se_2	8.52	8.84	–26.75	–27.11	–18.22	–18.26
Br_2	10.83	11.35	–37.08	–37.63	–26.24	–26.27
In_2	80.80	80.46	–457.25	–456.92	–376.45	–376.46
Sn_2	3.31	3.33	–9.79	–9.82	–6.47	–6.49
Sb_2	5.35	5.43	–15.90	–16.02	–10.55	–10.58
Te_2	7.22	7.42	–22.91	–23.14	–15.68	–15.71
I_2	9.36	9.69	–31.78	–32.14	–22.42	–22.44
Tl_2	77.07	76.90	–420.49	–420.32	–343.41	–343.41
Pb_2	3.20	3.21	–9.86	–9.88	–6.66	–6.67
Bi_2	5.11	5.15	–15.72	–15.78	–10.60	–10.62

Table 5. Electron-electron energy, electron- nuclear energy and nuclear-nuclear energy of the studied dimers.

Dimer	E_{e-e}		E_{e-N}		E_{N-N}	
	SBK	SBK+d	SBK	SBK+d	SBK	SBK+d
Ga_2	498.40	498.35	–1452.67	–1452.38	90.55	90.46
Ge_2	7.55	7.67	–21.20	–21.20	3.79	3.84
As_2	13.11	13.37	–35.62	–36.08	6.25	6.38
Se_2	19.83	20.25	–52.83	–53.64	8.52	8.84
Br_2	28.14	28.72	–74.00	–75.16	10.83	11.35
In_2	371.07	370.70	–970.27	–969.52	80.80	80.46
Sn_2	6.64	6.72	–18.47	–18.59	3.31	3.33
Sb_2	11.31	11.50	–30.33	–30.64	5.35	5.43
Te_2	16.89	17.19	–44.44	–44.97	7.22	7.42
I_2	23.96	24.37	–62.14	–62.92	9.36	9.69
Tl_2	337.48	337.32	–867.16	– 866.81	77.07	76.90
Pb_2	6.55	6.60	–18.50	–18.57	3.20	3.21
Bi_2	11.05	11.18	–29.90	–30.08	5.11	5.15

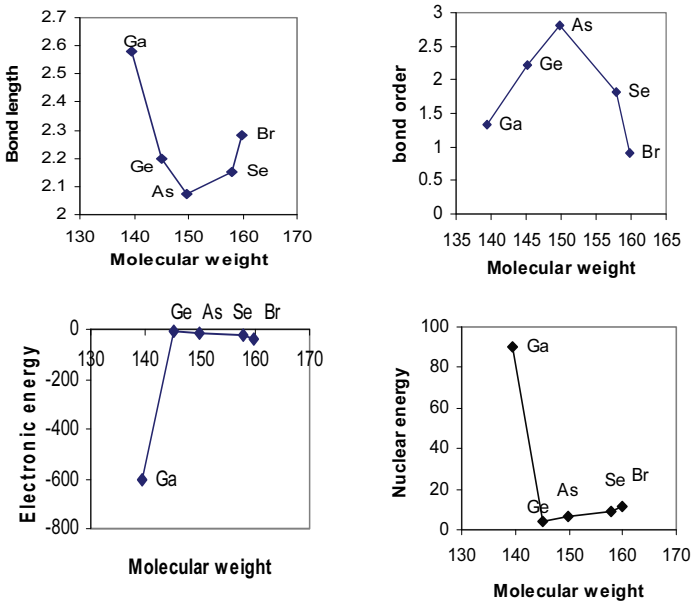

Fig. 1. The variations of bond length, bond order, nuclear energy and electronic energy of the fourth row with molecular weight.

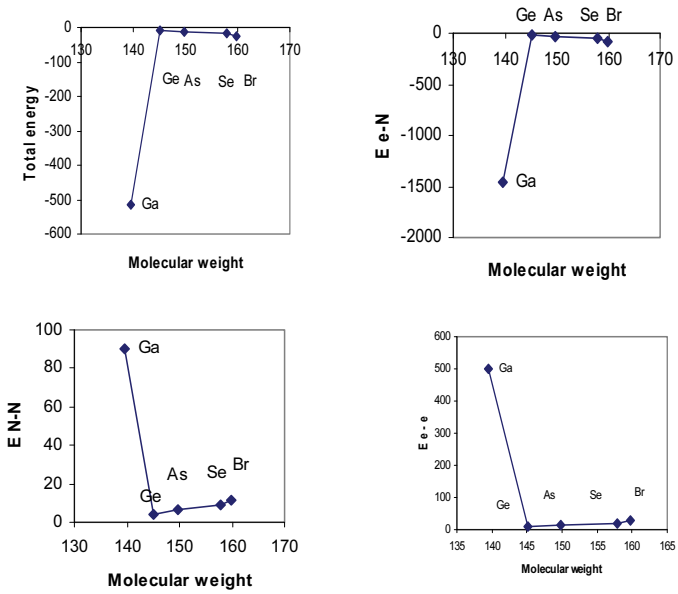

Fig. 2. The variations of total energy, E_{e-N}, E_{N-N} and E_{e-e} of the fourth row with molecular weight.

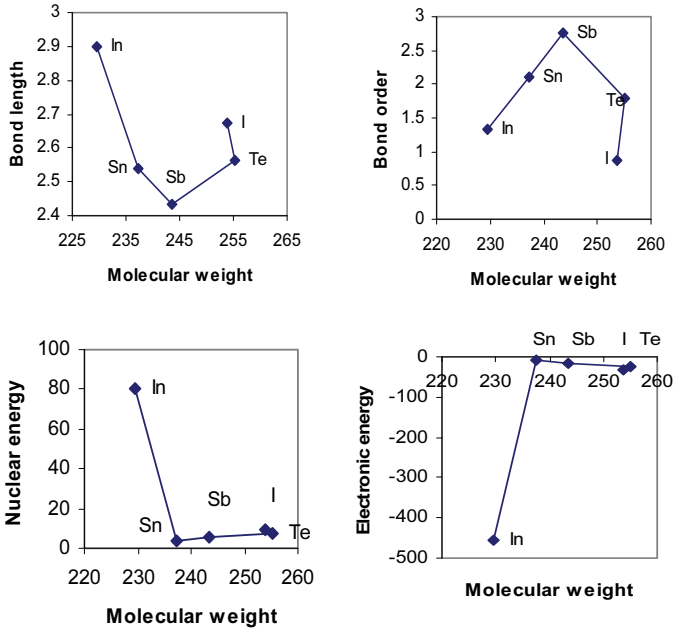

Fig. 3. The variations of bond length, bond order, nuclear energy and electronic energy of the fifth row with molecular weight.

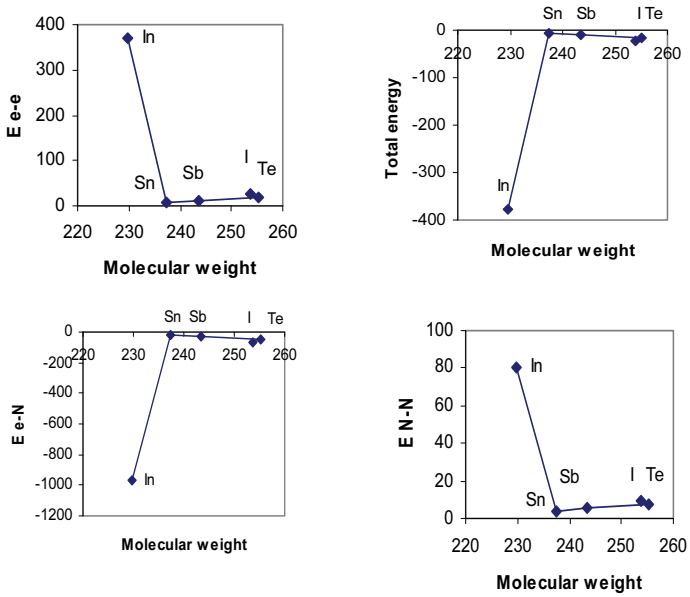

Fig. 4. The variations of total energy, E_{e-N}, E_{N-N} and E_{e-e} of the fifth row with molecular weight.

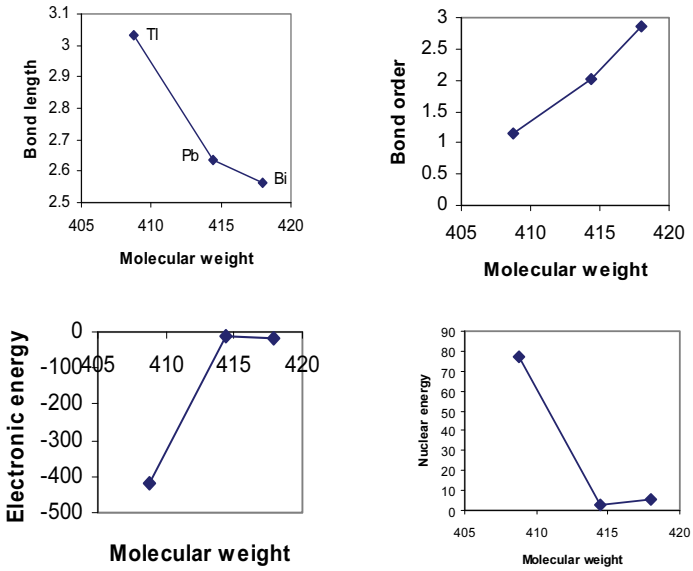

Fig. 5. The variations of bond length, bond order, nuclear energy and electronic energy of the sixth row with molecular weight.

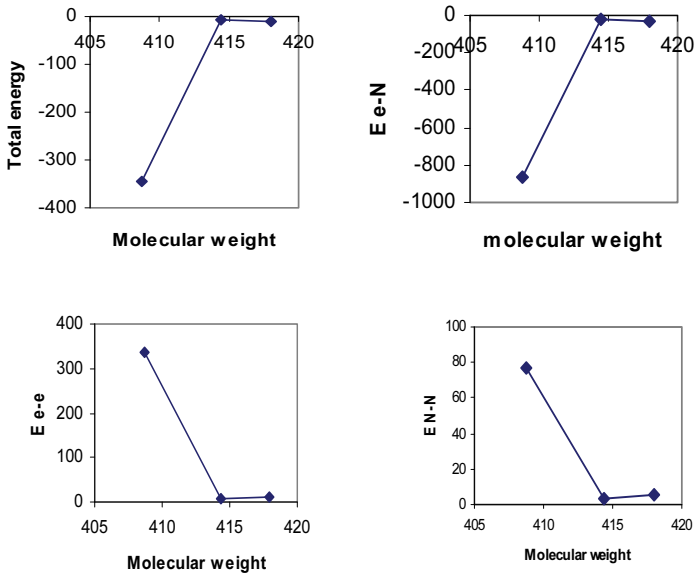

Fig. 6. The variations of total energy, E_{e-N}, E_{N-N} and E_{e-e} of the sixth row with molecular weight.

1. The total energy of row IV dimers increases on going from left to right, *i.e.* from Ga_2 to Br_2. The increase in energy are systematic in case of Ge_2, As_2, Se_2 and Br_2 in which a single double and triple bonds are formed. The order of stability follow $Br_2 > Se_2 > As_2 > Ge_2$.

2. In case of Ga_2-dimer a dramatic change in the total energy reaches up to ≈ 480 au *i.e.* the most stable dimer in row IV is Ga_2.

3. The addition of d-orbitals as polarized function does not affect the total energies of all dimers, this may be attributed to the filling of d-orbitals.

4. The same trend were observed in case of electronic energy and electron-nuclear attraction energy but it reverse in case of nuclear energy, nuclear-nuclear repulsion and electron-electron repulsion energies. (*c.f.* Fig. 1 and 2).

5. The bond length of fourth row heavy dimers varies in a systematic way on going from left to right (*i.e.* increasing of molecular weight). It is found that the smallest value is As_2 (triple bond) and the largest value is Ga_2 (single bond).

6. The variation of bond lengths are supported by the variation of the bond order values, As_2 dimer have the largest bond order and Br_2 dimer (single bond) have the smallest bond order. The same trend can be observed in case of total valence and bonded valence.

7. The bond order, total and bonded valence are affected by the addition of d-orbitals to the SBK-basis set (*c.f.* Tables 2-5).

8. The same trend observed in the fifth row dimers at which In_2 is the most stable dimer. The rest of the fifth row dimers follows the order $In_2 > Te_2 > Sb_2 > Sn_2$.

9. The largest bond order dimer of fifth row is Sb_2-dimer (smallest bond length), this may be attributed to the formation of triple bond. On the other hand, the smallest bond order is I_2.

10. The variation of energy components of the fifth row follow the same trend as that of the fourth row.

11. In case of the sixth row Tl_2-dimer is the most stable one, whereas, Bi_2-dimer is more stable than Pb_2-dimer by about 4au. Due to the lack of experimental data and parametrization in SBK-basis set, the rest of sixth row (Po and At) cannot be studied.

12. Tl_2-dimer (single bond) is the largest bond length (smallest bond order) whereas, Bi_2-dimer (triple bond) is the smallest bond length (largest bond order).

13. Within the groups (III → VII) the stability as measured by the total energy decreases on going from up to down. This may be attributed to the increase of the total valence and bonded valence. Ga_2-dimer is more stable than In_2 and Tl_2-dimer by ≈ 138 and ≈ 171au respectively.

14. In case of group IV and V Ge_2 and As_2 are more stable than (Sn_2 and Pb_2) and (Sb_2 and Bi_2). Both (Sn_2 and Pb_2) and (Sb_2 and Bi_2) dimers have the same stability.

15. In group VI and VII, Se_2-dimer is more stable than Te_2 and Br_2 than I_2 by about 3 au and 4 au respectively.

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طاقة التفكك والخواص الدورية لثنائي العناصر الثقيلة باستخدام حسابات Ab-Initio

سالم عبود حميد

قسم الكيمياء، كلية العلوم، جامعة الملك عبدالعزيز

جدة- المملكة العربية السعودية

المستخلص. تمت دراسة الخواص الدورية وطاقة التفكك لثنائي العناصر الثقيلة، وذلك باستخدام قاعدة المجموعة SBK عند مستوى RHF والثنائيات المستخدمة هي ثنائيات الدورة الرابعة (Br_2, Se_2, As_2, Ge_2, Ga_2)، وثنائيات الدورة الخامسة (In_2, Sn_2, Sb_2, Te_2, I_2)، وثنائيات الدورة السادسة (Tl_2, Pb_2, Bi_2). وقد نوقشت نتائج الحسابات المدارية في ضوء كل من: طول الرابطة، ورتبة الرابطة، والتكافؤ الكلي، والتكافؤ الرابط، والطاقة النووية، والطاقة الإلكترونية، والطاقة الكلية. كما تمت دراسة تأثير المدار (d) على خواص الثنائيات. وقد أظهرت نتائج الطريقة المستخدمة قدرتها على تحليل الخواص الدورية لهذه الثنائيات.