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Using the Extended-Rydberg Function to Study Some of Spectral Properties of Some Molecules

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ABSTRACT

In this work, (Extended-Rydberg function) has been used to determine the values of the energy and the form of the energy curve and some Spectral characteristics of some Germanium-Tetrahalides ($GeBr_4$ and GeI_4) by depending on dissociation energy, bond length at equilibrium and by changing bond lengths between (Ge-Br), (Ge-I). Our calculation has been done using semi-empirical quantum programs (PC Model, Winmopac7.21, and Hyperchem) with MNDO/PM3 method which takes a short period of time comparing with (ab-initio). The spectral properties as modes, vibration frequencies, intensities and Symmetry have been calculated for each mode at equilibrium. Also, the total energy, dipole moment, zero point energy and molecular weight have been calculated by Winmopac 7.21 program. Also, HOMO energy, LUMO energy, ionization potential and electron affinity have been determined in the results.

1. Introduction

The spectroscopic parameters, potential energy curves, thermal and electronic properties of very heavy halides molecules have been the important subjects of many spectroscopic studies. Many problems centered on how improvement theoretical investigation of diatomic molecules [1]. The potential energy curve represents important relation with bond length: i.e. as a function of changing of the distance between atoms of the molecule from its equilibrium distance. The determination of energy curves is of main importance in the study of diatomic molecular spectra [2,3]. In the calculations of dissociation energy with spectral parameters and thermodynamic parameters etc, the studies of potential energy curves are very necessary. The potential energy functions Varshni [4] and extended Rydberg [5] are usually used and the potential curves are plotted. Naturally to compute the turning points of various vibrational levels the accurate spectroscopic constants are required. The empirical potential energy functions also require these molecular constants as dissociation energy and bond length.

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It is known that the solution of Schrodinger equation is possible in diatomic molecules for the audit of polyatomic molecules, solutions of this equation to be complex and complex mathematical reasons, one of the most important methods used to resolve the complex mathematical questions are semi-empirical quantum programs (PC Model, Hyperchem, and Winmopac7.21) with MNDO/PM3 method. The application of these programs has grown considerably in recent years and introduced and widely in many scientific studies and research, used the Semi-empirical programs unilaterally in account programs and sometimes interfere with the (Ab-initio) program to describe a number of important characteristics and properties of molecular systems [6,7]

The objective of the present work is to determine potential energy curves of some of Germanium tetrahalides using Extended-Rydberg potential and calculate some of the spectral properties in the ground electronic state of these molecules as the modes, vibration frequencies, intensities, Symmetry at equilibrium, the total energy, electronic energy, binding energy, core-core repulsion, ionization potential, dipole moment, molecular weight, moment of inertia and highest occupied and lowest unoccupied molecular orbitals energies, (HOMO, LUMO) respectively, by depending on previous programs [6,7].

2. Methods of calculations :

In our calculation, one of important potential energy functions has been used to determine potential curves and spectroscopic parameters of our polyatomic molecules ($GeBr_4$ and GeI_4), this important function is Extended Rydberg function which was written as [4]:

$$U_{ER} = -D_e\left[\left(1+12\left(\frac{r}{r_e}-1\right)+42\left(\frac{r}{r_e}-1\right)^2 + 140\left(\frac{r}{r_e}-1\right)^3\right)e^{12\left(1-\frac{r}{r_e}\right)}\right]$$

Where U_{ER} is Extended Rydberg potential, and (r), (r_e) and (D_e) are bond length, bond length at equilibrium and dissociation energy receptivity.

Also, the mathematical calculations of spectral properties of our molecules ($GeBr_4$ and GeI_4) in this research have been done with the help of three of the arithmetic programs that belong to the molecular modeling programs:

2.1. PC Model program

A program adopted one of the modalities of molecular modeling by form molecular mechanic (Molecular Mechanic) which use of simple analytical functions f(r,θ,φ) which are represent the Interior coordinates such as the bond length, angle curvature and surface angles (Dihedral angle)[8, 9].

In this program, molecular structure has been determined for getting initial matrix represents the molecular dimensions in terms of internal axis, also, from this program are obtained on a file that contains the Interior coordinates f(r,θ,φ) still under which the geometrically molecule formation where this matrix of the lengths of the bonds between the atoms and values bonding angles and values of surface angles. Therefore, this matrix becomes the entrance to the second program (Win Mopac 7.21).

(Win Mopac 7.21) Program

Is one of the developments of the Mopac program that use the quantum mechanics which include (AM1,PM3, MINDO and MINDO/3 [10].

The meaning of (Semi-empirical Molecular Orbital Program-MOPAC) is a single program which incorporates many of the function of the segregated.

The calculations of Mopac depend on data inserted into the program, after obtaining the Initial matrix through the program of PC MODEL is copy the matrix and use in Mopac program. Also, after determining one of a semi-empirical method (PM3), the program is reading data and then generates new data represented calculated spectral properties results[10].

Hyperchem Program

This program is one of the advanced programs in the molecular modeling field, where it consists of all molecular modeling programs such as Ab-initio as well as semi empirical methods and method which depend on the molecular mechanic. This program can be used to calculate spectral properties by depending on MNDO/PM3 method. These properties are the total energy in (Kcal/mol), dipole moment in Debye (D), molecular weight, principle vibration modes, vibration frequencies, symmetry and (HOMO, LUMO) energies[6-7].

3. Results and Discussion

The calculations of the potential energy values for $GeBr_4$ and GeI_4 molecules are presented by using Extended-Rydberg potential function which depended on spectroscopic constants (bond length (r_e) and dissociation energy (D_e) at equilibrium distance) for ground state for these molecules which equal to (2.30 Å) and (2.501 eV) for $GeBr_4$ respectively, and (2.49 Å) and (2.550 eV) for GeI_4 respectively [11]. These calculations can be obtained with changing in bond lengths between (Ge-Br) and (Ge-I), therefore, the table (1 and 2) and figures (1 and 2) show the results for potential energy values for these molecules.

After calculating the curves of the potential energy at the equilibrium distance (r_e) also indicate an important properties of above molecules with vibration frequencies and the wave number in (cm^{-1}) have been calculated after taking the final matrix using the program (Winmopac 7.21) and MINDO/PM3 method, then calculation of wavelength at each frequency. Since the $GeBr_4$ and GeI_4 molecules nonlinearity so the number of vibration modes according to rule (3N-6=9) mode. Tables (3 and 4) show fundamental frequencies and the wavelengths, and tables (5 and 6) show some of the spectroscopic properties of these molecules.

The vibration frequencies of molecules in unit (cm^{-1}) have been done using the (Hyperchem) program with giving some spectral properties such as the intensity of each mode (Intensity) in the unit (km/mol.) as well as the type of symmetry for each mode of vibration modes of molecules. The figures (3 and 4) represent one of the steps Hyperchem program which clear mods of fundamental vibration. therefore, as result of the rule (3N-6), there are nine vibrations for each molecule with the clarification of the trends of movement with arrows as well as the value of each

frequency, intensity and symmetry of each mode as shown in the figures (5 and 6).

Also, values of HOMO and LUMO energies of these two molecules have been determined through (Winmopac7.21) program with appearing number of occupied orbitals is (16) and a number of unoccupied orbitals is (4) as shown in the tables . (7 and 8).

At taking the absolute value of HOMO energy of $GeBr_4$ molecule, one get the ionization potential, I.P= - E_{HOMO} [12], (I.P =10.55 eV) and this close to the experimental value from the literature [13]. Also, at taking the absolute value of LUMO energy of $GeBr_4$ molecule, one get the electron affinity, EA= - E_{LUMO} [12], (E.A= 4.60 eV) and this close to the experimental value of the literature [13,14], the energy gap from (LUMO energy – HOMO energy) which equal to (5.95 eV).

On the other hand, the absolute value of HOMO energy of GeI_4 molecule has been taken and the ionization potential according that was (I.P =10.05 eV) and this close to the experimental value from the literature [15]. Also, at taking the absolute value of LUMO energy of GeI_4 molecule, one get the electron affinity (E.A=4.70 eV) and this close to the experimental value from the literature[14,15], the energy gap equal to (5.35 eV) From these results, the Germanium behaves as insulator material that due to energy gaps equal to (5.95 eV) and (5.35 eV) for $GeBr_4$ and GeI_4 molecules respectively.

4. Conclusion

The important conclusions from this work focused on the importance of finding some spectral properties of our molecules ($GeBr_4$ and GeI_4) depending on potential energy curves and using Extended Rydberg function with some of the semi empirical programs. The total energy for $GeBr_4$ was (-2.5 eV) and for GeI_4 was (-2.55 eV) this means that the stability of $GeBr_4$ molecule more than the stability of (GeI_4). Also, in this study, because the dissociation energy of $GeBr_4$ is larger than GeI_4 that leads us to concluding that the Germanium atom is the common element between the molecules and it is going to speak on (Br and I) atoms and the atomic number (35) for (Br) while the atomic number for (I) (53), and therefore when the atomic number less whenever one need to high energy to separate the electrons from the nucleus.

The important conclusion from our results is there are (9) mods of vibration for each molecule according to the rule (3N-6) as well as the value of each frequency, intensity and symmetry of each mode were clear. Another conclusion is the two molecules ($GeBr_4$ and GeI_4) have the same number of occupied orbitals which is (16) and the same number of unoccupied orbitals which is (4). Also, the ionization potential for $GeBr_4$ is large than the ionization potential for GeI_4. The Germanium behaves as insulator material after treatment its by (I and Br) that due to the energy gap of $GeBr_4$ equal to (5.95 eV) and equal to (5.35 eV) for GeI_4 molecule.

Table 1. Extended Rydberg potential energy values with bond lengths of $GeBr_4$ molecule.

Distance (Å)	Potential energy (eV)
2	1.93
2.1	-1.29
2.2	-2.3
2.3	-2.5
2.4	-2.39
2.5	-2.16
2.6	-1.87
2.7	-1.58
2.8	-1.28
2.9	-1.03
3	-0.8
3.1	-0.62
3.2	-0.46
3.3	-0.34
3.4	-0.25
3.5	-0.18
3.6	-0.13
3.7	-0.09

Table 2. Extended Rydberg potential energy values with bond lengths of GeI_4 molecule.

Distance (Å)	Potential energy (eV)
2.1	6.46
2.2	0.5
2.3	-1.69
2.49	-2.55
2.5	-2.54
2.6	-2.43
2.7	-2.21
2.8	-1.95
2.9	-1.67
3	-1.4
3.1	-1.14
3.2	-0.92
3.3	-0.72
3.4	-0.56
3.5	-0.43
3.6	-0.32
3.7	-0.24

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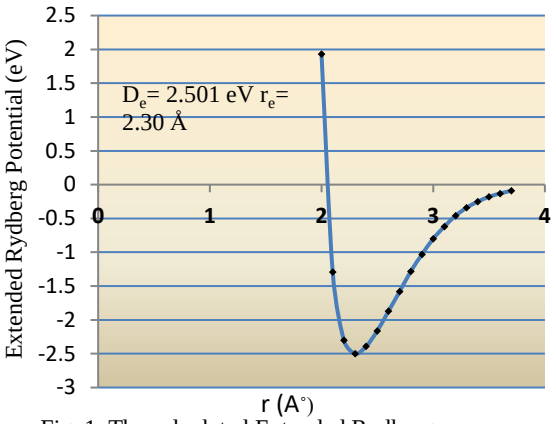


Fig. 1. The calculated Extended Rydberg potential curve for $GeBr_4$ molecule.

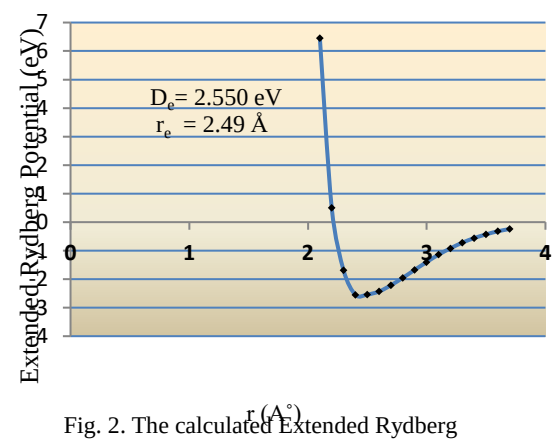


Fig. 2. The calculated Extended Rydberg potential curve for GeI_4 molecule.

Table 3. vibration frequency with a wave length of the GeBr4 molecule.

No. of vibration	Vibration frequency ω (cm^{-1})	Wave length λ(μm)
1	13.53	739
2	18.18	550
3	29.06	344
4	55.55	180
5	158.73	63
6	222.22	45
7	256.4	39
8	344.82	29
9	370.37	27

Table 4. Vibration frequency with the wave length of the GeI4 molecule.

No. of vibration	Vibration frequency ω (cm^{-1})	Wave length λ(μm)
1	36.65	271
2	40.16	249
3	111.10	90
4	125.00	80
5	161.29	62
6	212.76	47
7	250.00	40
8	322.58	31
9	344.82	29

Table 5. Some of the spectral properties of GeBr4 molecule.

Quantity	Magnitude
Total energy	-2.5 eV
Molecular weight	390.222 a.m.u
Zero point energy	1.700 Kcal/mol
Dipole moment	3.801D

Table 6. Some of the spectral properties of GeI_4 molecule.

Quantity	Magnitude
Total energy	-2.55 eV
Molecular weight	581. 001 a.m.u
Zero point energy	1.900 Kcal/mol
Dipole moment	0.0080 D

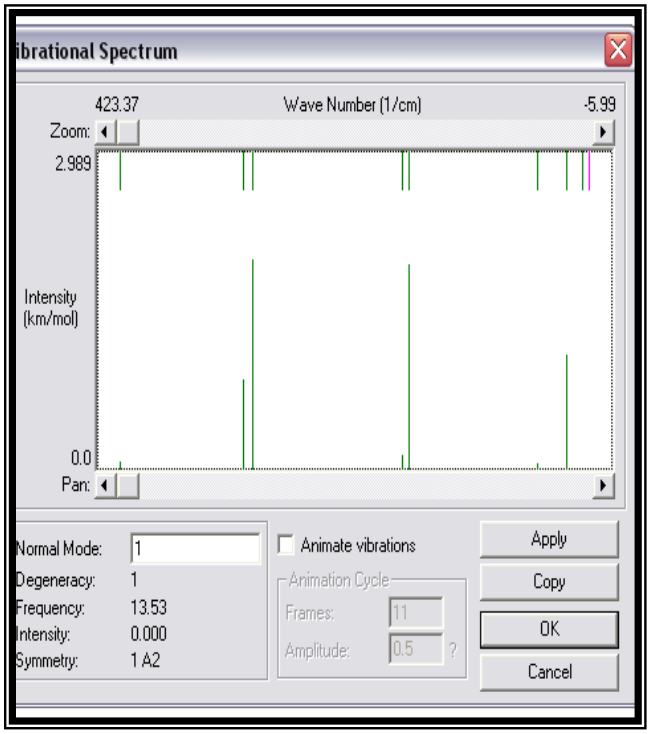


Fig. 3. One of the steps of Hyperchem program which clear mods of fundamental vibration of $GeBr_4$ molecule.

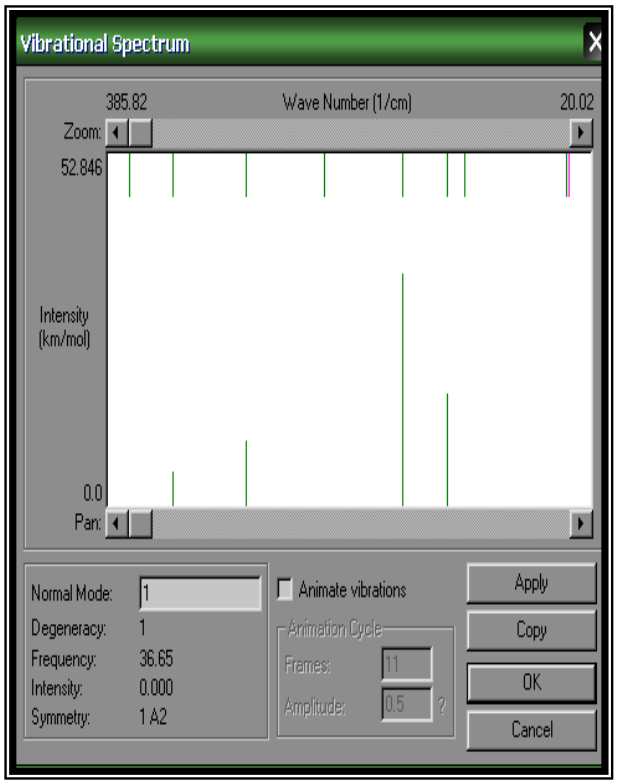
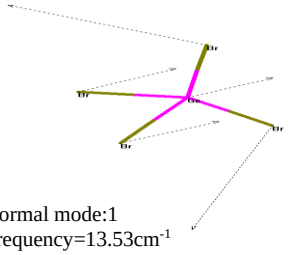
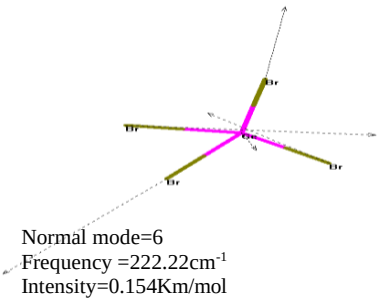


Fig. 4. One of the steps of Hyperchem program which clear mods of fundamental vibration of GeI_4 molecule.



Normal mode:1
Frequency=13.53cm^{-1}
Intensity=0.000Km/mol
Symmetry=1A2



Normal mode=6
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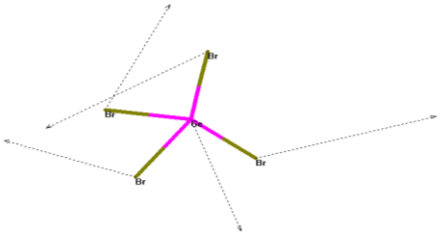
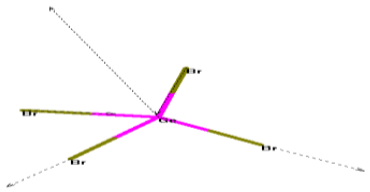
Intensity=0.154Km/mol
Symmetry=2B2



Normal mode=2
Frequency=18.18cm^{-1}
Intensity =0.000Km/mol
Symmetry=1B2



Normal mode=7
Frequency =256.40cm^{-1}
Intensity=1.993Km/mol
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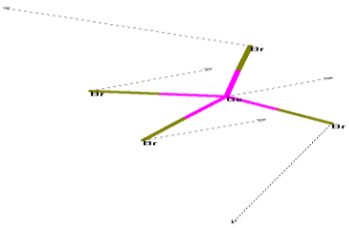

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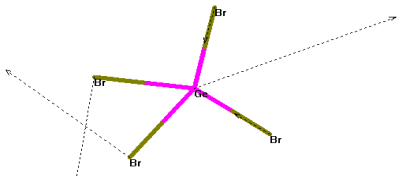

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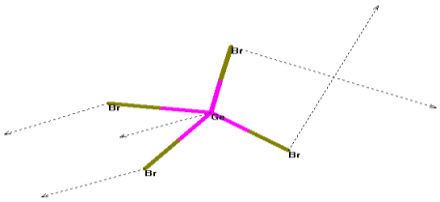
Frequency =322.58cm^{-1}
Intensity=0.870Km/mol
Symmetry=3A1



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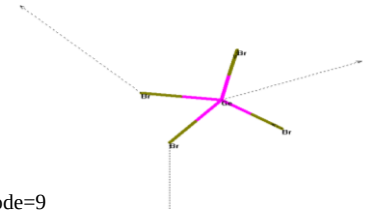
Symmetry=1A1



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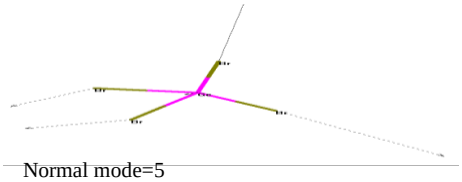
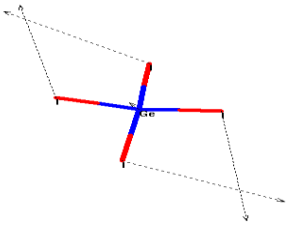
Frequency =370.37cm^{-1}
Intensity=0.094Km/mol
Symmetry=4A1

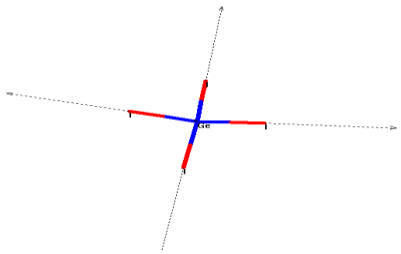


Normal mode=5
Frequency =158.73cm^{-1}
Intensity=1.951Km/mol
Symmetry=2A1

Fig. 5. Mods of vibration with values of each frequency, intensity and symmetry of each mode for $GeBr_4$ molecule.



Normal mode=1
Frequency =36.65cm^{-1}
Intensity=0.000Km/mol
Symmetry=1A2



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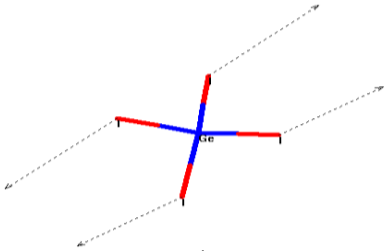
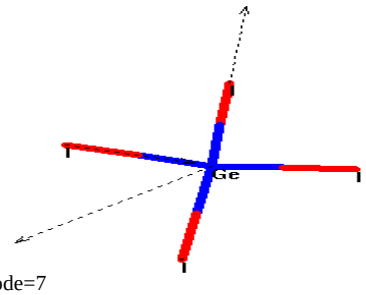
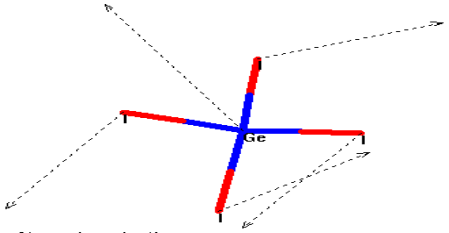
Intensity=0.017Km/mol
Symmetry=2A1



Frequency =40.16cm^{-1}
Intensity=0.031Km/mol
Symmetry=1B1



Normal mode=7
Frequency =250.00cm^{-1}
Intensity=10.313Km/mol
Symmetry=3A1



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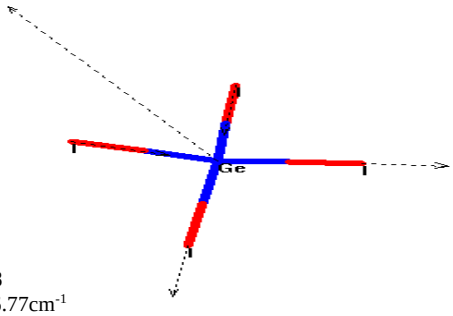
Intensity=0.004Km/mol
Symmetry=1A1



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Frequency =336.77cm^{-1}
Intensity=5.598Km/mol
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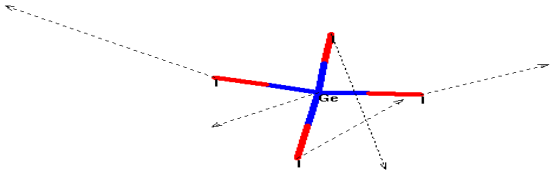

No
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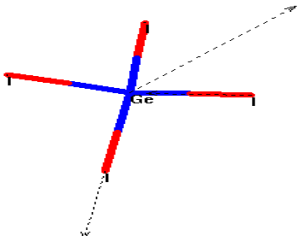
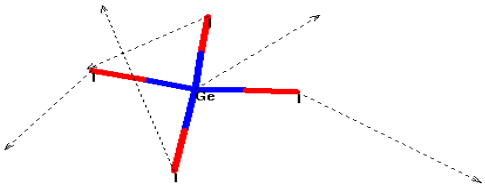
Symmetry=1B2





Normal mode=5
Frequency =161.29cm^{-1}
Intensity=36.133Km/mol
Symmetry=2B2

Normal mode=9
Frequency =344.82cm^{-1}
Intensity=0.531Km/mol
Symmetry=3B2

Fig. 6. Mods of vibration with values of each frequency, intensity, and symmetry of each mode for the GeI_4 molecule.

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Table 7. A number of occupied orbitals and unoccupied orbitals in the $GeBr_4$ molecule.

Eigen values			
HOMO Energy		LUMO Energy	
No. level	Energy (eV)	No. level	Energy (eV)
1	-20.40	1	-4.60
2	-20.22	2	-3.39
3	-19.13	3	-2.80
4	-18.84	4	-2.59
5	-15.43		
6	-13.80		
7	-13.52		
8	-13.18		
9	-12.85		
10	-12.05		
11	-12.01		
12	-11.90		
13	-11.78		
14	-11.55		
15	-11.01		
16	-10.55		

Table 8. A number of occupied orbitals and unoccupied orbitals in the GeI_4 molecule.

Eigen values			
HOMO Energy		LUMO Energy	
No. level	Energy (eV)	No. level	Energy (eV)
1	-18.99	1	-4.70
2	-17.85	2	-4.29
3	-17.62	3	-3.78
4	-17.33	4	0.81
5	-16.77		
6	-16.02		
7	-15.35		
8	-14.61		
9	-13.22		
10	-11.98		
11	-11.34		
12	-11.01		
13	-10.24		
14	-10.23		
15	-10.04		
16	-10.05		

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استخدام دالة ريدبيرك الموسعة لدراسة بعض الخواص الطيفية لبعض الجزيئات

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الخلاصة:

في هذا البحث تم استخدام دالة ريدبيرك الموسعة (Extended-Rydberg function) للتعرف على قيم الطاقة وشكل منحني الجهد وبعض الخواص الطيفية لبعض هاليدات الجرمانيوم الرباعية ($GeBr_4$ and GeI_4) بالاعتماد على طاقة التفكك الطيفية وطول الاصرة عند موضع الاتزان وبتغيير اطوال الاصرة مابين (Ge-Br)،(Ge-I). تمت الحسابات باستخدام برامج الكم شبه التجريبية التي تستغرق مدة زمنية قصيرة للدورات الحسابية قياساً إلى برنامج Ab-inito، اذ تم استخدام برامج PC Model ، Hyperchem و Winmopac7.21 وبطريقة MNDO/PM3.حسبت الخواص الطيفية والخاصة بالانماط (mods) والترددات الاهتزازية(vibration frequencies) للجزيئات و شدة(intensity) كل اهتزاز والتماثل(symmetry) ولكل نمط عند موضع الاتزان، ثم حسبت طاقة الجزيئة الكلية (Total Energy) وجهد التأين (Ionization Potential) وعزم ثنائي القطب (Dipole moment) وطاقة نقطة الصفر (Zero point energy) والوزن الجزيئي (Molecular weight) وباستخدام برنامج WinMopac7.21 بالاضافة إلى ذلك تم حساب القيم الطاقية للمدارات الجزيئية بما فيها اعلى مدار جزيئي مشغول بالالكترونات (HOMO) واوطأ مدار جزيئي خال من الالكترونات (LUMO) وجهد التأين (Ionization Potential) والالفة الالكترونية (Electron affinity) بالاعتماد على القيم الطاقية للمدرات الجزيئية.