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Study of Spectroscopic and Thermal Properties for PbS Molecule

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Abstract: ***In present work, we studied the spectroscopic and thermodynamic properties for (PbS) molecule. This study included the potential of bonds (Pb-S). The results showed that the spectral dissociation energy for (PbS) molecule which was (11.722(ev)) and the vibration modes for the molecule were studied. From the results, the high occupied molecular orbital (HOMO) calculated equals (-8.9810eV), respectively, also we calculated the total charge density and electrostatic potential in 2-D and 3-D. The Thermodynamic properties behavior have been studied as a function of temperatures in the range (100-1000)K. The results show that the heat of formation, enthalpy, heat capacity and entropy are increasing with increase the temperature, while Gibbs energy was decrease with the increasing the temperature*** .

Keywords: Thermodynamic properties, PbS, molecule, Gibbs energy, HOMO.

1. Introduction

I've dealt with this research study molecule (PbS), which is a type of semiconductor known as Algalina, "body natural mineral of lead sulfide bilateral and ore importantly for the lead, and Algalina of more metal sulfide plentiful and the most widespread, crystallized in the system of crystalline cube showing the form of eight surfaces .The sulfide lead a dark brownish black (non-transparent), and its solubility in acid and Aivob in alcohol or potassium hydroxide.

The most important applications:

1) Algalina used in wireless communication systems because it is the semiconductor.
2) Used in the manufacture of car rims.
3) The main source of lead ore.
4) Used in the manufacture of ammunition and platelets.
5) Excavating for Algalina to extract silver from them.
6) Lead sulfide crystals for electrical conductivity.
7) Sensors are used in Takht-red rays.
8) The ancient Egyptians used kohl in which they put it on their eyes for protection from the sun's rays reflected from the desert, and the expulsion of flies has been studying the geometry of the molecule painted Program (chem Hyper) As in Figure 1.

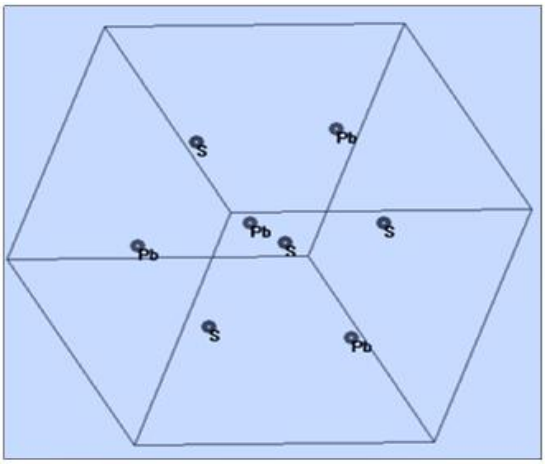


Figure 1: Illustrates the molecule (pbs) painted using Hyperc

The other form of the molecule has been drawn by the program (Winmopac) as in Figure 2. In this molecule has a dipole torque and then can be effective in the region (IR), a molecular form, which was adopted at the expense of spectral properties as frequency each style vibratory [M.Clyde Day, JR and Joel Sel-bin (1983), R.B. Wood Wards an R. Hoffmann (1970)].

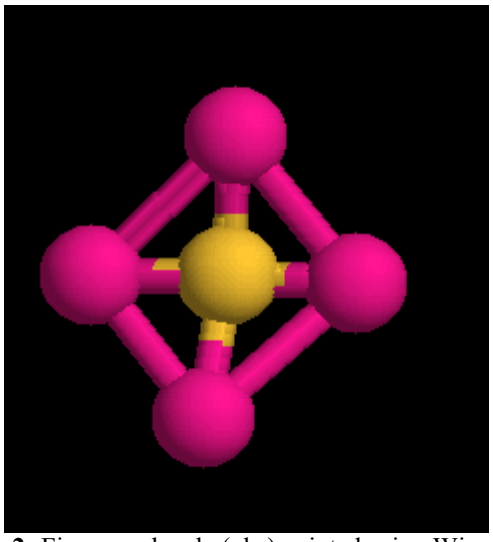


Figure 2: Figure molecule (pbs) painted using Win mopac.

2. The Theoretical Part

The contraction and expansion of the chemical bonds that bind atoms of the molecular system somewhat similar to the behavior of the spring, which is subject to the law of the hook (Hooks Low) [R.Leach Andrew (2001)] As a result of this model is called bold bilateral corn model oscillating simple harmonic (Harmonic Oscillator Model) and the frequency of this oscillating classic is given to the relationship [D. Steel (1971), G.W. King (1964)]:

$$v_{vib} = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \text{ Joules} \quad (1)$$

This equation describes the vibratory motion of the molecule bilateral maize, where k is the force constant, and m represents mass shorthand.

The vibration of the molecules is not really a vibration harmonically simple, when squeezed bond the atoms closer together and increase energy in order to enable the atoms do occupy against the forces of repulsion as that stretch bond lead to a move away atoms from each other, which requires energy to reach the point of losing then ties disintegrate flexibility, and possible writing the energy equation of wobbling non harmonic shaky using the equation and the equation Chrodnker non harmonic effort to Morse for vibratory levels in terms of number of quantitative vibratory V as follows [Gbori: Csonka and Krisztina Elias18,330-342, (1996)]:

$$E_\vartheta=(V+\frac{1}{2})\,\upsilon+(V+\frac{1}{2})^2\,\upsilon X_e-(V+\frac{1}{2})^2\,\upsilon\ X_e \qquad (2)$$

That's where :
V: number of quantitative vibratory and takes values V = 0,1,2,3 .....
Xe: non harmonic constant and have a positive value .
υ: Frequency represents the classic.

Depends gentle vibration of molecules multiple atoms on the relative values of the moments palaces self-Home If we took the molecule number of atoms N, the relationship 3N-6 describes the movement vibrating molecules non-linear, which is known patterns of vibration of the molecule Mode of vibration and so the expense of the energy levels of molecules multi-atoms is given by [SMze, Kwok.Ng (2007)]:

$$\sum_{ij}^{3N} L_j(F_{ij}-\lambda G_{ij}) \qquad (3)$$

Where:$F_{ij:}$ Analqoy constants matrix element represents
Gij: matrix element atomic masses
$L_{j:}$ represents the values of coefficients combined descriptor of the z shaky
λ: function eigenvalues and is given by [M. Revanasiddappa, S.C. Raghavendra (P (1104-1108), (2007)]:

$$\lambda = 4\pi C^2 \upsilon^2 \qquad (4)$$

That's where:
C: the speed of light; ύ: frequency harmonic vibration unit cm^{-1}
The electrostatic voltage is defined as the ratio of electric power to the molecule to the amount of its charge, or that the voltage of the energy molecule, either effort molecule resulting from the distribution of the electron and nuclear shipments petition relationship [E. T. Samulski B 105, 8845, 2001]

$$V=\sum \frac{Z_A}{r-r_A} -\int \frac{\rho(r2)}{r2-r}\,dr^2 \qquad (5)$$

That's where:
r: represents the distance between the point of charge and bitmap ZA
$r_{A:}$ Diameter atom half,p(r′):charge density of the bitmap

As for the properties thermodynamic where concentrated study in this area on the quantitative relationship between thermal energy and other forms of energy, Enthalpy is one of the functions of the situation that can be considered as a function of pressure and temperature and the energy of the Interior, which is given by the following [B 105, 8845, 2001, MJ Frisch (2009)]:

$$H=U+nRT \qquad (6)$$
$$H=U+PV \qquad (7)$$

That PV=nRT

And
P: pressure; V: Size; n: number of moles; R:hard General for gases; T: temperature

The change in enthalpy is known as the amount of heat absorbed or that is to unseal by the system during the process mirrored under constant pressure, and given the relationship [M. J. Frisch (2009)

$$\Delta H = \Delta U+P\Delta V \qquad (8)$$

Also, the heat capacity of the properties thermodynamic mission, which is expressed as the temperature needed to raise the temperature of the system degrees Celsius one and be two heat capacity certified the size C_V and heat capacity certified the pressure C_P. Either entropy is the amount of Thermodynamic same recipe holistic represents one of the functions of the case, and is considered a measure of the degree random mixing in a given system and has the symbol S. Gypsum, as well as free energy as it one of the most important functions where introduced to denote the direction of automatic chemical reaction, and indicate the location and chemical equilibrium is given by:

$$G=U-TS \qquad (9)$$

3. Method

It was the rapid development taking place in the software and tremendous speed, it turned Computing greatest impact in the development of theoretical treatment of the spectra of molecular where he developed a lot of researchers, methods and software to calculate the qualities thermodynamic and calculate the geometric shape equilibrium and energy levels of molecular compounds putting in the equation Chrodnker and approximate solutions have a foundation in the formulation of this methods and software, is the most important methods that were used in this research is a method PM3 and characterized by their efficiency relative comparison with other experimental methods [M.Gaylard (1915/2003), Hans Beyer (1955)], it is the most important software used in this research program is PC Model, Win Mopac 7.21 program and the program Hyper Chem. The implementation of these programs has been using an electronic calculator -type Pentium IV. Tables 1 and 2 illustrate the primary version of the matrix and the final molecule (pbs).

Table 1: Primary matrix of elementary molecule (pbs)

Atom	Distance R(Aº)	Opt.	Angle (θº)	Opt.	Dihedral (Φº)	Opt.	A	B	C
Pb	.0000	0	.000000	0	.000000	0	0	0	0
S	1.298519	1	.000000	0	.000000	0	1	0	0
Pb	1.211556	1	175.340800	1	.000000	0	2	1	0
Pb	1.915044	1	45.482480	1	.000000	1	3	2	1
Pb	1.784453	1	46.359310	1	180.000000	1	3	2	1

Table 2: Final matrix of elementary molecule (pbs)

Atom	Distance r(Å)	Opt.	Angle (θº)	Opt	Dihedral (φº)	Opt	A	B	C	Charge
Pb	0.0000000	0	0.000000	0	0.000000	0	0	0	0	.3126
S	2.2586551	1	0.000000	0	0.000000	0	1	0	0	-.4202
Pb	2.8909787	1	171.635269	1	180.000000	0	2	1	1	-1.0859
Pb	2.1499597	1	70.969620	1	-31.648692	1	3	2	1	.5582
Pb	2.7462287	1	60.719574	1	149.603241	1	3	2	1	.6354

4. Results and Discussion

1) Spectral Properties

Been studied curved effort and determine the point of equilibrium and where the value of the total energy is the least that can be Figure 3 shows a curved energy vibration of the molecule (pbs), where the total energy at the position of equilibrium (bottom curve voltage) about ((Emin = -485.229 (eV))), while the length of bond about (r = req = 1.29 (Å)), and notes through the figure approaching the behavior non harmonic in vibration levels, as shown stretch bond and stay away from behavior harmonic for our entry in the vibration levels Supreme greater the value of the distance (Pb- S), where more energy increases until we get to the disintegration of the disintegration of the amount of the molecule card) Deq = 11.722 (ev).

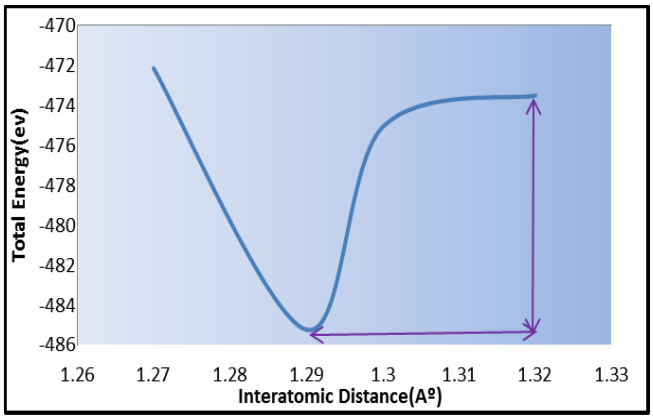


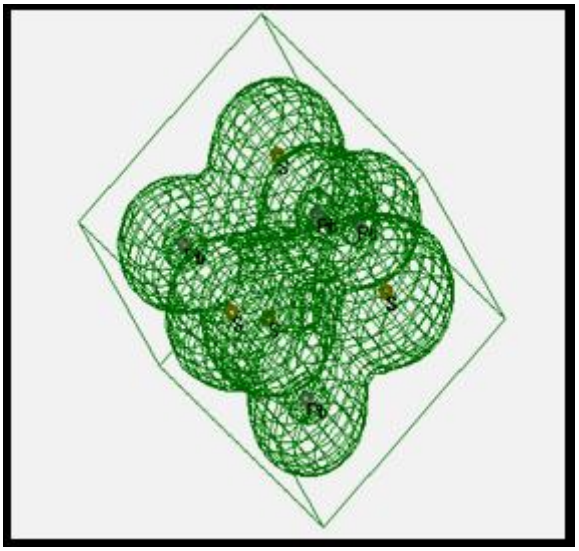
Figure 3: Potential energy curves for the molecule (pbs) when the position of equilibrium to impose that bond pb-S is bond actors

It was also the study of patterns of nonlinear vibration of the molecule as the number of vibration patterns for this molecule is (18) and the pattern of the table shows the values of the frequencies of the molecule expressed in number and waveform measured using the program WinMopac.

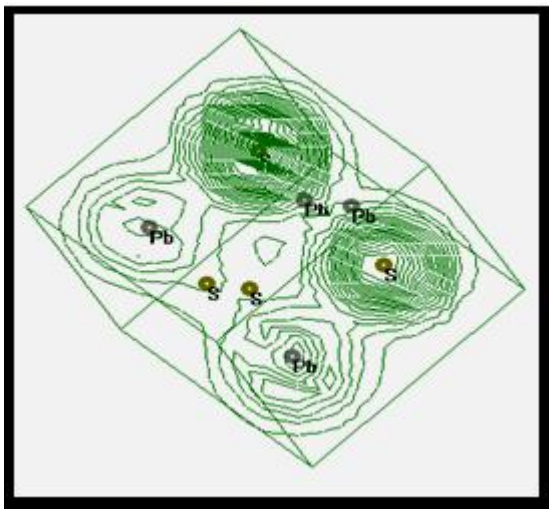
Table 3: Vibrational frequencies of the molecule (pbs) and the corresponding wavelengths

No. Vibration	Wave number ῡ (cm^{-1})	Wave length λ(μ m)
1	56.06	178.3803
2	56.08	178.3166
3	73.07	136.8550
4	73.07	136.8550
5	73.08	136.8363
6	116.54	85.8074
7	267.96	37.3190
8	267.98	37.3162
9	267.98	37.3162
10	276.27	36.1964
11	276.29	36.1938
12	276.29	36.1938
13	289.26	34.5709
14	289.26	34.5709
15	302	33.1125
16	320.21	31.2295
17	320.22	31.2285
18	320.23	31.2275

Add to that the expense of some properties, such as the determination of electric dipole Dipole Moment unit Debye through the program Hyperchem and Win Mopac where (0.0002182D), was calculating the value of a higher orbit molecular busy molecule (-8.9810eV) where the molecule eighteen over the busy HOMO Figure 4 illustrates the intensity shipments overall molecule total Charge Density two-dimensional and three dimensions, where it is noticed that most of the charge is based on the sulfur atom of the most negative lead atom.



Total charge Density (2D)



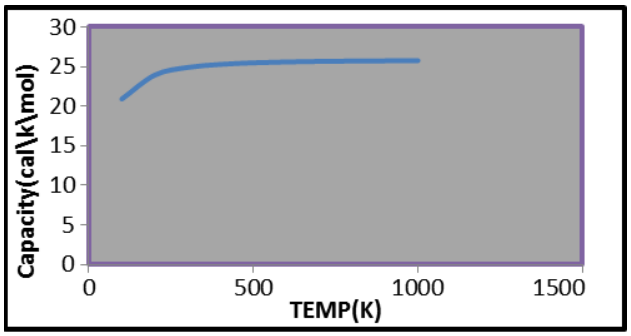
Total charge density (3D)

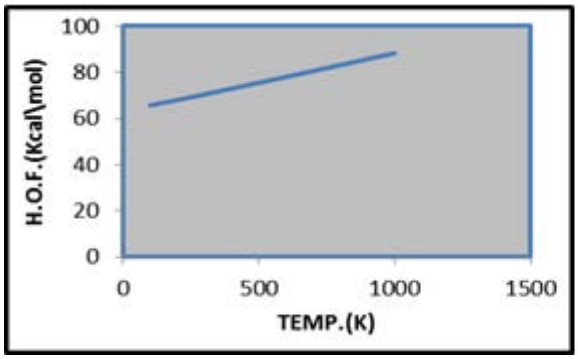
Figure 4: The distribution of the total charge density bold (pbs) two-dimensional and three dimensions

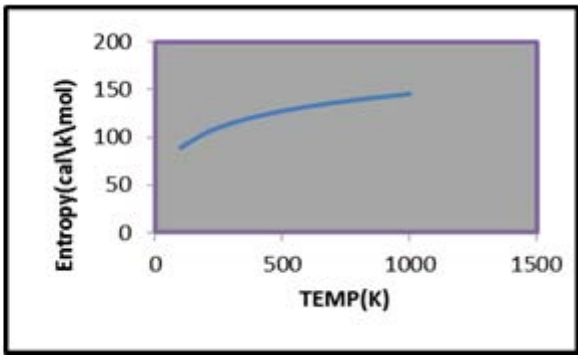
As for the thermal properties, Table 4 shows the values of temperature and composition HfΔ heat capacity CP, enthalpy H, entropy S and free energy Gypsum c for molecules under study, where it was to find these values at room temperature (298 º K).

Table 4: Thermal properties of the molecule (PbS) at room temperature (298 º K).

Thermodynamic properties	*Values at 298ºK, 1atm*	*Unit*
)ΔH_f(composition	70.428	Kcal./mol
)C_p(heat capacity	24.8712	Cal./K/mol.
)H(enthalpy	6256.5835	Cal./mol
)S(entropy	114.4175	Cal./K/mol
)G(free energy Gypsum	-27839.8315	K.Cal./mol







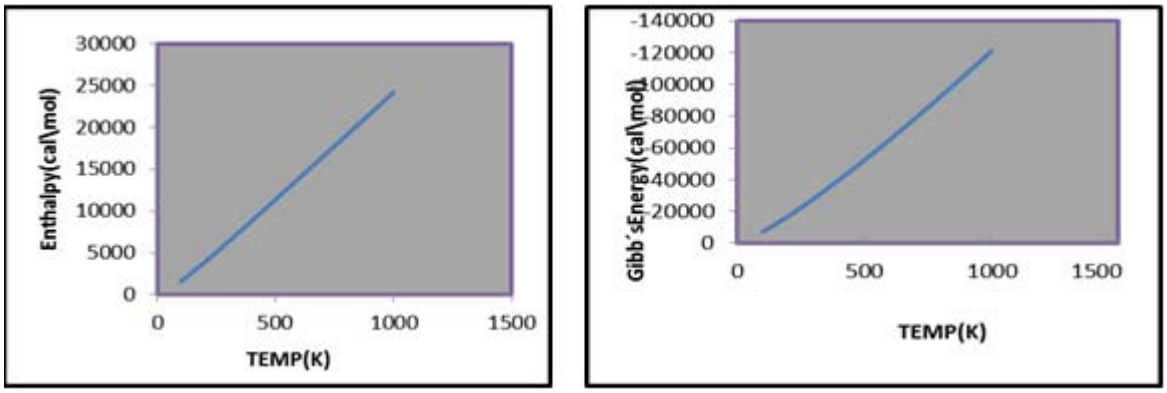


Figure 5: The relationship between the thermal properties and the temperature of the bold (PbS)

Figure 5 shows the exponential proportionality winning each Thermodynamic properties with temperature, except that the free energy Gypsum inversely proportional to the temperature.

5. Conclusions

Through our findings in this research it is clear that bond effective with different values of the absorption is through bond (Pb-S), as the frequencies stretch bending depends largely on the masses of atoms shaky, where whenever atoms lightweight was largest. Vibrations Also note that bond between atoms high be effective Electro negative in the absorption of different values of energy. From the results it is clear that electro negative characterized by high sulfur atom led to an increase in the charge density distribution of the overall molecule near them.

We found the results of properties thermodynamic the molecule under study that there is a direct proportion with the temperatures for each of the HfΔ, Cp, H, S, due to rotational motion and the transition of these molecules, and at high temperatures thus contributing Movement Electronic increase in the values of properties thermodynamic such as heat capacity Cp. And that the negative value of the heat molecule formation (PbS) indicates the stability of this mol

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