Study of Spectral and thermal properties of Selenium Diatomic Halides by Semi-empirical Treatment

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Abstract:-

The spectroscopic properties, potential energy curve, dipole moments, total charge density, Electrostatic potential as well as the thermodynamic properties of selenium diatomic halides have been studied using code Mopac.7.21 and hyperchem, semi-empirical molecular orbital of MNDO-method (modified neglected of differential overlap) of parameterization PM_3 involving quantum mechanical semi-empirical Hamiltonian. The relevant molecular parameters like interatomic distance, bond angle, dihedral angle and net charge were also calculated.

Introduction:-

The spectroscopic properties, potential energy curve, dipole moments, and transition moments of very heavy main group halides molecules containing p.block element (4p, 5p and 6p) have been the topics of many investigations [(1)]. Much of the problems centered around have not any theoretical calculations or insight into the electronic energy levels of heavy molecules. However, in recent years, with the advant of relativistic quantum mechanical methods, theoretical calculations of almost any molecule in the periodic table have been made possible .

The halides such as MF, MCL, etc. are generated in chemiluminscent reactions of the type $M+X_2 \longrightarrow MX^-+X$. Some of the heavier halides have been investigated by parson and co-workers . In the chemiluminscent reactions the MX_2 triatomic (C_2) is generated, which eventually forms MX^- in the excited state .

The excited MX^- chemiluminesces, emitting photons. The photoionization of such halides have been the topic of many investigations .Berkowitz and chupks have examined the ion. Pair processes and the high-energy process that ionize the molecule.

There are many recent experiment investigations on group IIIA halides, and in particular Incl in the recent investigation on Incl, Hoeft and Nair obtained the rotational spectra of Incl. from these data, the vibrational constants and Dunham-potential constant are derived for Incl.

Glenewinkel- Meyer et. al. have studied the emission spectra of group IIIA monohalides ions, MX* (M=Bi, Al, Ga, In; X=F, CL, Br) in the visible and near UV regions. The emission spectra of all these species were obtained through the following chemiluminscent reaction:

$$M^+ + X_2 \longrightarrow MX^*+X$$

On the basis of the observed spectra, the excited states of these ions are considerably displaced compared to the ground states. Although there are many experimental investigations on halides such as GeF, Gecl, Sncl, etc., concerning the spectral properties, potential energy curves, and discussion of agreement and differences between theory and experimental, the literature does not seem to contain any systematic investigations of the electronic structure and bonding characteristic of heavy p-block diatomic halides.

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Therefore, the theoretical calculations together with the experimental spectroscopic properties have provided a wealth of information which needs to be collected together and understood.

The objective of the present work is to calculate the ground state electronic properties (bond length, heat of formation, total energy, core-core repulsion energy, dipole moment, net charge on heavy metal, ionization potential. electron affinity and energy gap). Involving molecular modeling and quantum mechanical semi empirical Hamiltonian Using pc model, mopac 7.21 and hyperchem program with MNDO/PM3 method [2-4].

Result & Discussion:

1. Spectroscopic study:

The potential energy of Se_2Cl_2 as shown in fig.1 which show the lowest energy (- 1024.984 eV) at the equilibrium distance (1.557 $\overset{o}{A}$)the dissociation energy D_{eq} is equal to (4.524 eV). At equilibrium distance the vibrational frequency was calculated with intensity and symmetry for each frequency as shown in table (1).

The modes of vibrations as shown in fig.(2).The values of the high occupied molecular orbital (Homo) and low unoccupied molecular orbital (lumo) as shown in fig(3) and dimension as shown in fig.(4). The energy gap between Lumo and Homo was calculated which is equal to 5.544 eV and the value of Ionization potential is equal to the 9.537 eV and electron affinity is 3.993 eV. fig (5) show the electrostatic potential and total charge density in two and three dimension.

2. Thermodynamics study:

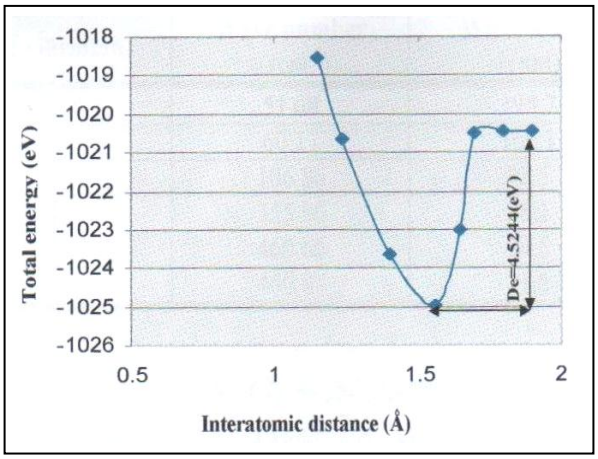
fig (6) show the relation between heat capacity as a function of temperature .The heat capacity increase when the temperature variable from (100-350) K and above the heat capacity unchanged with the temperature .

fig (7) show the relation between enthalpy and temperature

the relation is directly proportional.

fig.(8) show the variation between entropy and temperature which indicate to the stability of the system that change will be very clear between (100-350) K and above will be stable.

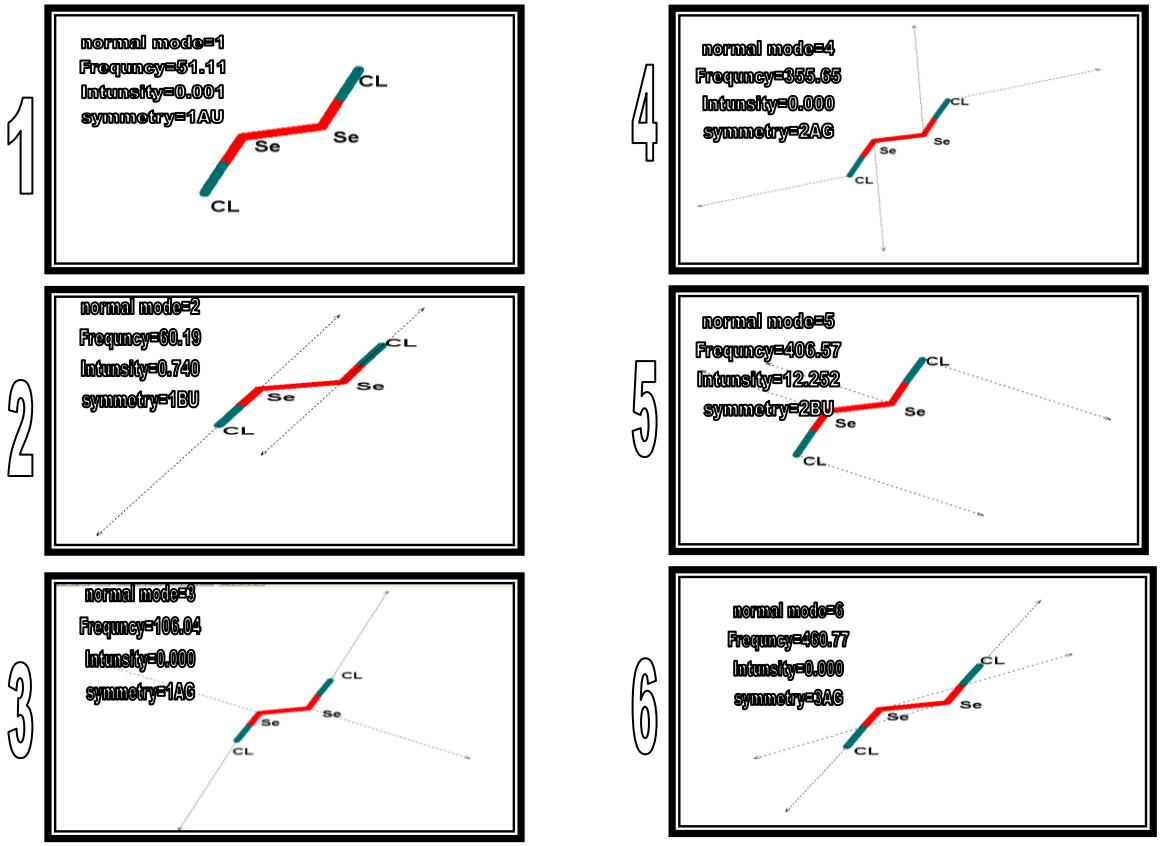
fig (9) show the heat of formation (H.O.F) variable with temperature and the relation is directly proportional and the value of the heat of formation at room temperature was in agreement with the experimental value [5].



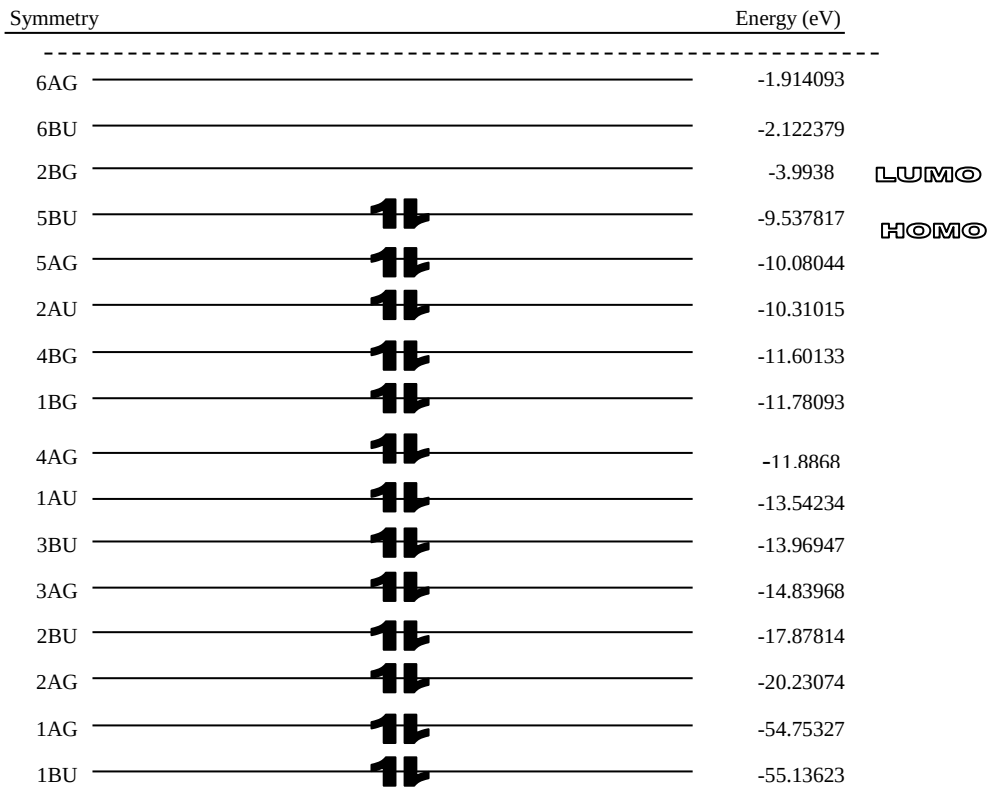
Fig(1) Potential Energy level of [Se_2Cl_2]

Table(1)Vibrational Frequency with intensity and symmetry for [Se_2Cl_2]

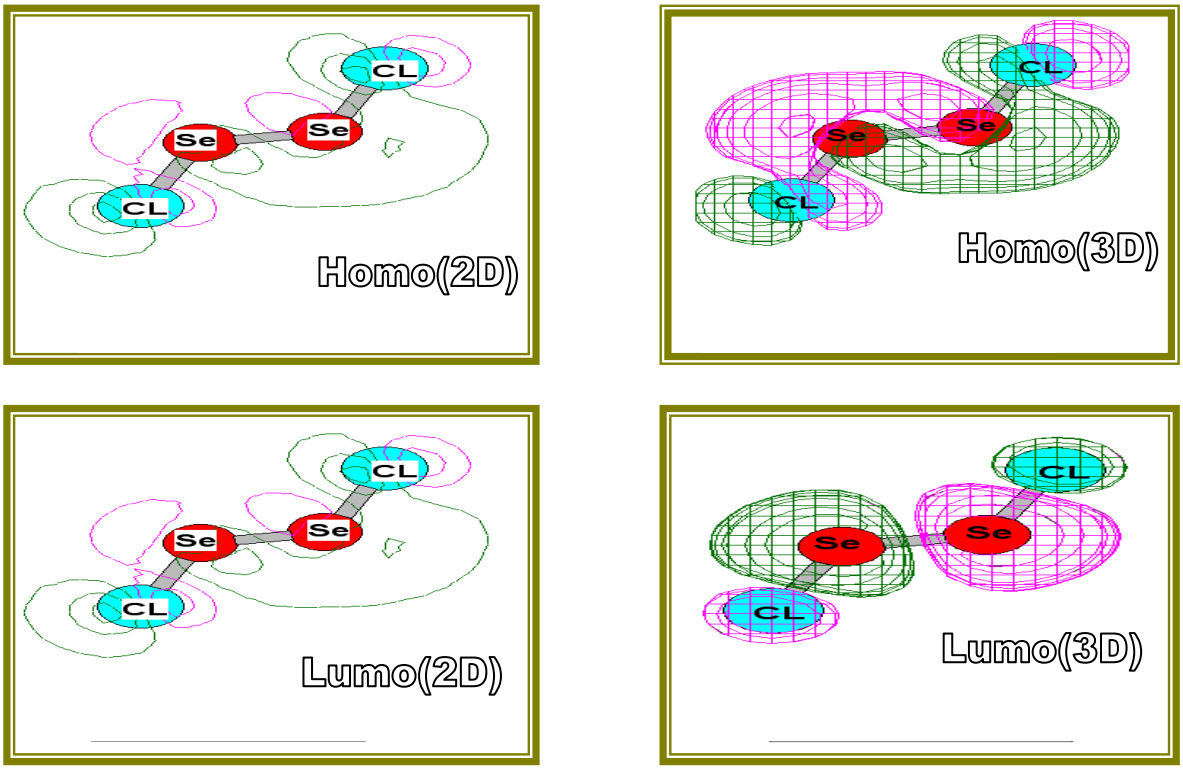
No.	$\upsilon(cm^{-1})$	I(km/ mol)	Symmetry
1	51.10	0.001	1 AU
2	60.19	0.740	1 BU
3	106.04	0.000	1 AG
4	355.65	0.000	2 AG
5	406.57	12.252	2 BU
6	460.77	0.000	3 AG



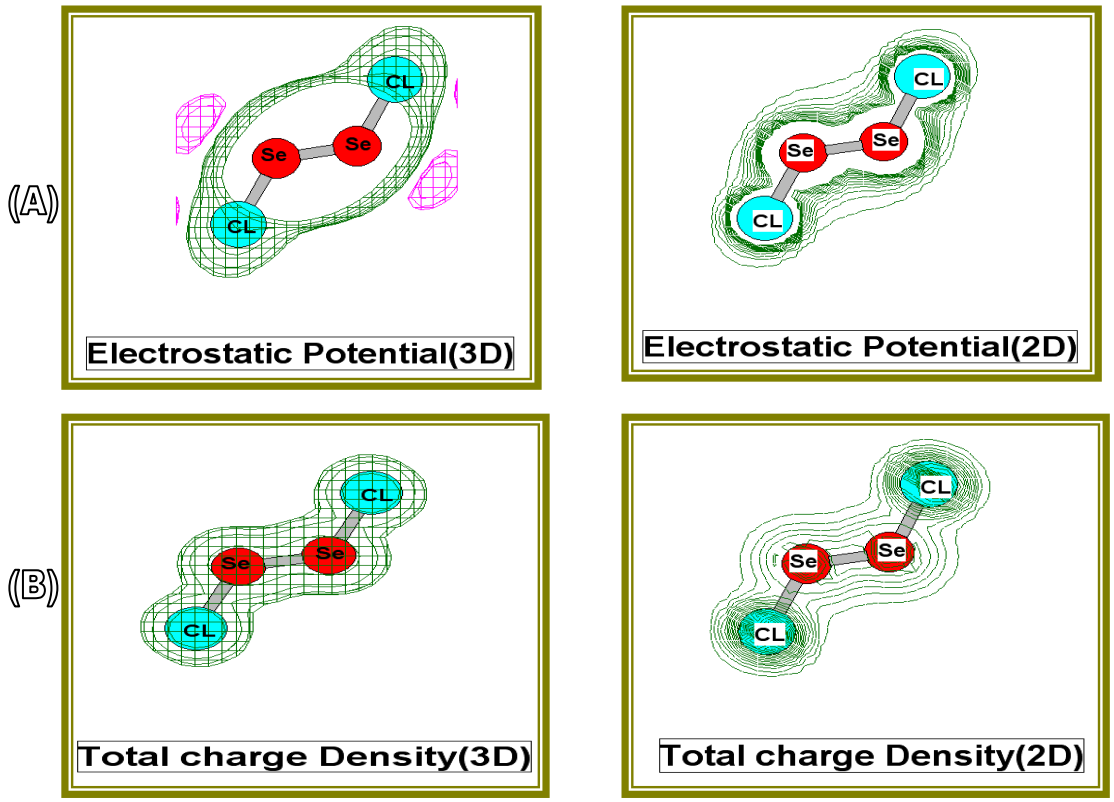
Fig(2) Vibrational Modes of [Se_2Cl_2]



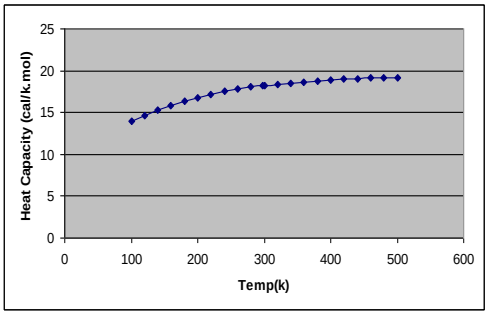
Fig(3) Energy level diagram of Homo & Lumo for [Se_2Cl_2]



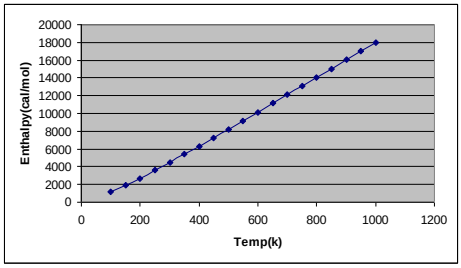
Fig(4) Energy level of Homo & Lumo of (Se_2Cl_2) in (2D and 3D)



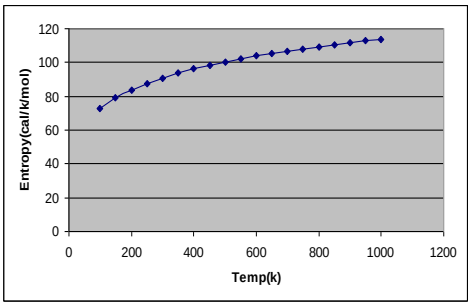
Fig(5)
A . Electrostatic Potential in (2D&3D)
B. Total Charge Density in (2D&3D)



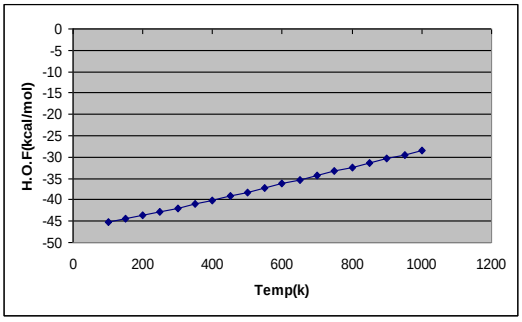
Fig(6)Heat Capacity variation with temperature for $[Se_2Cl_2]$



Fig(7) Enthalpy variation with temperature for $[Se_2Cl_2]$



Fig(8) Entropy variation with temperature $[Se_2Cl_2]$



Fig(9) Heat of formation (H.O.F) variation with temperature $[Se_2Cl_2]$

References:-

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دراسة الخواص الطيفية والحرارية لجزيئة السلينيوم-هالوجين باستخدام برامج الكم الشبه تجريبية

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الخلاصة:

تم دراسة الخواص الطيفية وجهد الطاقة وعزم ثنائي القطب وكثافة الشحنة الكلية و جهد الكهربائية الساكنة بالإضافة للخواص الحرارية لجزيئة سيلينيوم الهالديدات الثنائية باستخدام برامج الكم الشبه تجريبي وبطريقة $MNDO/PM_3$. كذلك تم حساب المعلمات الجزيئة الخاصة بالمسافة بين الذرات والزاوية بين الأواصر و زاوية السطوح ووحدة الشحنة.