Orass A. Hussein
Omar F. Abdullah
Sara S. Tawfeek

Department of Physics, College of Education, University of Samarra, Samarra, IRAQ

Determination of Physical and Thermal Properties of Triiodosilane by Semi-empirical Approach

WINMOPAC 7.21 and the MNDO-PM3 software are two semi-experimental theoretical programs used in this work to analyze the thermal and physical properties of the SiI_3H molecule. After adjusting the Si-H bond's length to satisfy the minimal formation energy at standard temperature (298 K), Reaction characteristics such as electronegativity, molecular hardness, electronic affinity, and ionization potential – which equaled 6.912779 eV, 3.37808 eV, 3.534699 eV, and 10.290859 eV – as well as the HOMO-LUMO energy gap were estimated in order to better understand the nature and reactivity of the molecule. Furthermore, an estimate of the molecule's thermal properties was made.

Keywords: Triiodosilane; MNDO-PM 3; Physical properties; Thermal properties
Received: 05 January 2024; **Revised:** 24 March 2024; **Accepted:** 31 March 2024

1. Introduction

Due to their wide range of uses, semiconductor halide compounds are very important from a scientific and industrial standpoint. This has piqued scientists' interest in both theoretical and practical research on these compounds' features. Triiodosilane is a nonlinear silicon halide molecule that is significant because it can be used to deposit silicon atomic layers on a variety of microelectronic device structures. [1]. The molecule has nine vibrational modes, all of which are in the far- and mid-infrared spectrum [2,3]. In this study, the MNDO/PPM3 method was used with the WINMOPAC 7.21 program to calculate and study the thermal properties and some physical properties of the $SiHI_3$ molecule.

The theoretical treatment of molecular spectra for the calculation of thermodynamic properties and balanced geometry (obtaining the best balanced and stable shape of the molecule) and the energy of the molecular levels of the compounds was greatly impacted by the rapid development of software and the incredible speed at which computers could perform calculations. These methods and software were developed using the Schrödinger equation and approximations of its solutions, and they adopted two directions: one that did not rely on quantum mechanics, and the other that did. These treatments are commonly referred to as semi-experimental methods.

2. Approach

By using the molecule's geometrical advantage and altering it multiple times, the length of the Si-H bond at equilibrium can be found by computing the energy for each iteration. One can create a potential curve using this information. The non-harmonic version of true interatomic potential energy resembles the Morse potential [4].

$$V_m = D_e\left[1 - e^{-\alpha(r-r_e)}\right]^2 \quad (1)$$

Equation (1) indicates that the value of V_m approaches D_e as r approaches infinity, which is consistent with the actual behaviour of the diatomic particles. Where α is a constant for the electronic energy levels of the molecule, V_m represents the potential energy of the bond.

The vibrational energy levels are found by [5] when a Morse potential function is used in place of the potential energy in the Schrödinger equation:

$$g(v) = \left(v + \frac{1}{2}\right) w_e - \left(v + \frac{1}{2}\right)^2 w_e x_e \quad (2)$$

where g(v) represents the vibrational energy level, ω_e the vibrational frequency in an harmonic motion, x_e the an harmonic constant

When v = 0 the value of g (v) is equal to the zero point energy [6]:

$$g(v) = \frac{1}{2} w_e \left(1 - \frac{1}{2} x_e\right) cm^{-1} \quad (3)$$

The following relationship can also be used to calculate the molecule's dissociation energy [7]:

$$D_e \cong \frac{w_e^2}{4 w_e x_e} \quad (4)$$

Some physical parameters, such as ionization potential and electronic affinity, are computed using Koopmans' theory [8,9]:

$$IE(\text{Ionization potential}) = -E_{HOMO} \quad (5)$$

$$EA(\text{Electron affinity}) = -E_{LUMO} \quad (6)$$

In which LUMO is the lowest empty molecular orbital and HOMO is the highest occupied molecular orbital. The following formulas [10–15] are used to calculate the electronegativity (χ) and molecular hardness (η), which are vital interacting properties of matter that are defined as the resistance to electron cloud polarisation or deformation of chemical species and a measure of the stability and interactions of molecules, based on these values (IE and EA):

$$\chi \approx \frac{(IP+EA)}{2} \quad (7)$$

$$\eta \approx \frac{(IP-EA)}{2} \quad (8)$$

The statistical thermodynamic equations can also be used to calculate the thermal properties [16,17].

The statistical thermodynamics of ideal gas laws and the standard case were used to calculate the thermal properties using the following equations:

$$U^0_{total} = U^0_{trans} + U^0_{rot} + U^0_{vib} + U^0_{elec} + U^0_{nucl} \quad (9)$$

$$U^0_{trans} = U^0_{rot} = 1.5RT \quad (10)$$

$$U^0_{vib} = \sum_{i=1}^{3N-6} \frac{RTX_i}{e^{X_i}-1} \quad (11)$$

$$X_i = \frac{hc\bar{\upsilon}}{KT} = \frac{1.44\bar{\upsilon}}{T} \quad (12)$$

$$H^0 = U^0_{total} + RT \quad (13)$$

$$S^0_{total} = S^0_{trans} + S^0_{rot} + S^0_{vib} + S^0_{elec} + S^0_{nucl} \quad (14)$$

$$S^0_{trans} = R\left[\frac{5}{2} + \ln\frac{(2\pi mKT)^{\frac{3}{2}}RT}{N_0 h^2}\right] \quad (15)$$

$$S^0_{rot} = R\left[\frac{3}{2} + \ln\frac{8\pi^2(8\pi^2 I_X I_Y I_Z)^{\frac{1}{2}}(KT)^{\frac{3}{2}}}{\sigma\hbar^3}\right] \quad (16)$$

$$S^0_{vib} = R\sum_{i=1}^{3N-6}\left[\frac{X_i}{e^{X_i}-1} - \ln(1-e^{-X_i})\right] \quad (17)$$

$$G^0 = H^0 - TS^0 \quad (18)$$

$$A^0 = U^0 - TS^0 \quad (19)$$

3. Results and Discussion

The curve of potential When we reach the lowest energy level at which the molecule is stable at a specific distance, known as the equilibrium distance (re=1.4758 AO), the total energy starts to increase due to the repulsion (nucleus - nucleus), until the bond is broken, at which point it is known as the energy of dissociation (De=6.76785 eV). Figure (1) illustrates how the total energy decreases as the distance between the atoms (Si - H) increases due to the drop in potential energy, which is caused by the attraction (electron - nucleus).

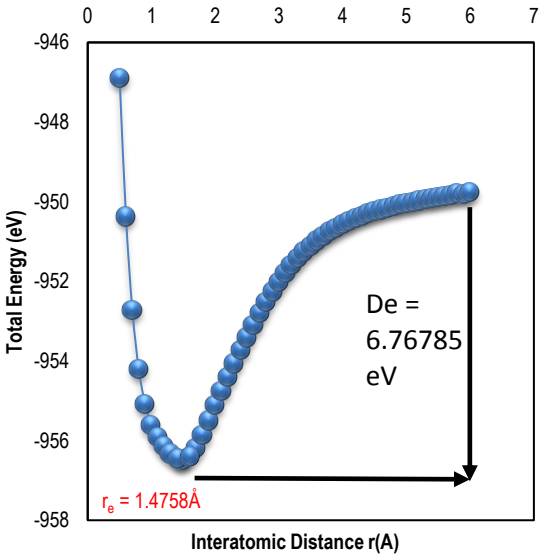

Fig. (1) Nonharmonic potential curve of $SiHI_3$ molecule calculated by Winmopac software (MNDO-PM3)

Some important physical properties of the studied molecule that were also calculated at equilibrium are shown in table (1).

Table (1) The physical properties of the Triiodosilane ($SiHI_3$) molecule calculated by MNDO-PM3

Quantity	Magnitude
Heat Of Formation Hf at 298K	-0.39257 eV
E_{LUMO}	-3.534699 eV
E_{HOMO}	-10.290859 eV
Ionization Potential (I.P.)	10.290859 eV
Electronic Affinity (E.A.)	3.534699 eV
electronegativity (χ)	6.912779 eV
molecular hardness η	3.37808 eV

SiI_3H's high ionization energy denotes the molecule's low reactivity. With an electronegativity of 6.912779 eV, the SiI_3H molecule has a notable capacity to draw electrons from neighboring molecules.

The HOMO–LUMO energy gap of SiI_3H is predicted by this study to be 6.75616 eV. It was discovered to be extremely high and, because of the enormous border orbital gap linked to high kinetic stability and minimal chemical interaction, results in more molecular stability and less polarization.

The investigated molecule's heat of production increases with temperature, as seen in Fig. (2).

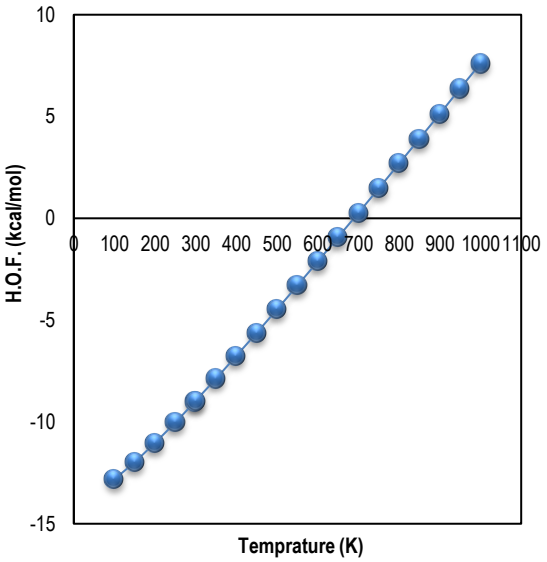

Fig. (2) Heat of formation of $SiHI_3$ molecule at different temperatures

In accordance with [18], figure (3) illustrates how the enthalpy change rises with temperature, suggesting that the reaction is endothermic.

Entropy rises with temperature because it measures how random the atoms that comprise molecules are, as seen in Fig. (4).

Figure (5) illustrates how the system's high thermal resistivity and great thermal stability are demonstrated by Gibbs free energy reductions in SiI_3H [19]. It's also clear that the computed values agree with the real values [18].

See Figure 6 for an illustration of how the heat capacity varies with temperature and rises as a result of an increase in the number of particles at various vibrational energy levels [18].

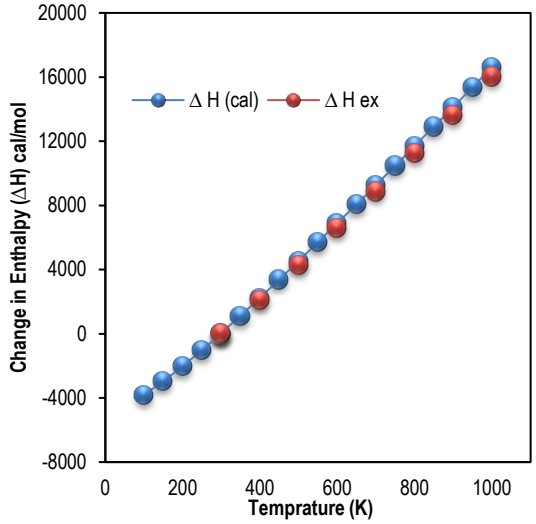

Fig. (3) Enthalpy change of $SiHI_3$ molecule at different temperatures

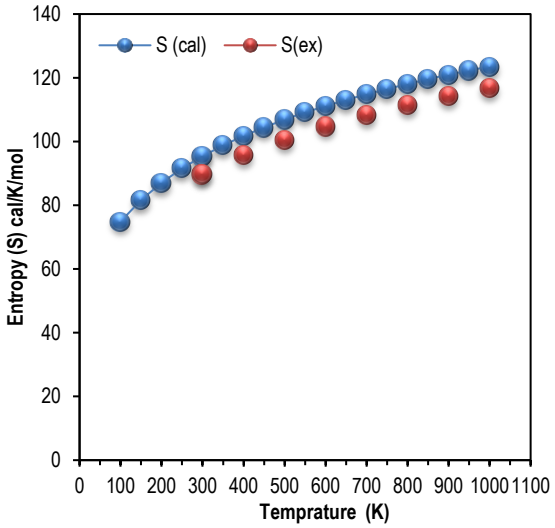

Fig. (4) Entropy of $SiHI_3$ molecule at different temperatures

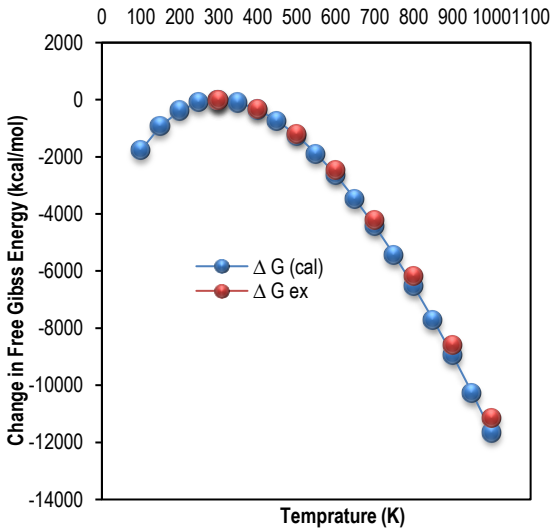

Fig. (5) Change in the Gibbs free energy of $SiHI_3$ at different temperatures

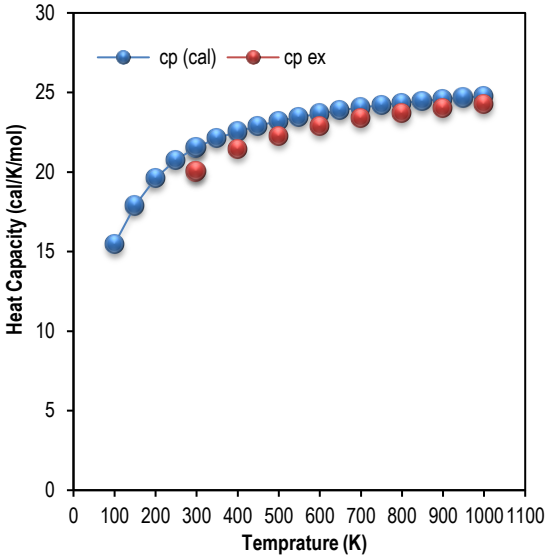

Fig. (6) Heat capacity of $SiHI_3$ molecule at different temperatures

4. Conclusion

A solid grasp of the nature, structure, electrical properties, and chemical reactivity is provided by this study. The molecule is one among those with strong heat resistance, with a bond length (Si-H) equal to r_e=1.4758Å and a dissociation energy of D_e=6.76785 eV. The number of molecules at different vibrational energy levels increases with temperature, which raises specific heat capacity. In addition, the procedure is endothermic.SiI_3H's high ionization energy denotes the molecule's low reactivity. With an electronegativity of 6.912779 eV, the SiI_3H molecule has a notable capacity to draw electrons from neighboring molecules.

According to this study, SiI_3H's HOMO–LUMO energy gap is predicted to be 6.75616 eV. which, since the border orbital gap is big and linked to high kinetic stability and low chemical interaction, was found to be extremely high and results in more molecular stability and less polarization.

In addition to the previously mentioned, the MNDO-PM3 approach results produced with Winmopac 7.21 closely matched the trial outcomes.

References

[1] D. Kuiper et al., "Preparation of Triiodosilanes", Patent No. 20200181178, USA (11 June 2020).

[2] O.A. Hussein, D.M. Khudhair and A.A.A.A. Aljbar, "IR Spectroscopic Study of Triiodosilane ($SiHI_3$) by Using Semi-empirical Quantum Program", *J. Phys.: Conf. Ser.*, 1818(1) (2021) 012014.

[3] www.NIST.gov/Chemistry NIST (2016)

[4] D.V. Shenai-Khatkhate et al., "Environment, health and safety issues for sources used in MOVPE growth of compound semiconductors", *J. Cryst. Growth*, 272(1-4) (2004) 816-821.

[5] J.R. Ferraro, "**Introductory Raman Spectroscopy**", Elsevier, 2003.
[6] G. Henderson, D. Neuville and R Downs, eds., **"Spectroscopic methods in mineralogy and material sciences",** vol. 78, Walter de Gruyter GmbH (2014).
[7] W.S. Struve, "**Fundamentals of molecular spectroscopy**", Wiley (NY, 1989).
[8] R.C. Bingham, M.J.S. Dewar and H.C. Lo, "The Chemistry of Heterocyclic Compounds, Thiophene and Its Derivatives", *J. Am. Chem. Soc.*, 97(6) (1975) 1285-1293.
[9] A. Hinchliffe and H.J. Soscun Machado, "Density Functional Studies of Molecular Polarizabilities. Anthracene and Phenanthrene", *Int. J. Mol. Sci.*, 1(1) (2000) 8-16.
[10] K.R.S. Chandrakumar and S. Pal, "The concept of density functional theory based descriptors and its relation with the reactivity of molecular systems: A semi-quantitative study", *Int. J. Mol. Sci.*, 3(4) (2002) 324-337.
[11] R.G. Parr et al., "Electronegativity: the density functional viewpoint", *The J. Chem. Phys.*, 68(8) (1978) 3801-3807.
[12] A. Rauk, **"Orbital Interaction Theory of Organic Chemistry"**, John Wiley & Sons (2004).
[13] S. Kaya and C. Kaya, "A new equation for calculation of chemical hardness of groups and molecules", *Mol. Phys.*, 113(11) (2015) 1311-1319.
[14] O.A. Hussein and O.F. Abdullah, "Effect of the flow rate of O_2 on SnO_2 thin film properties", *AIP Conf. Proc.*, 2394(1) (2022) 090035.
[15] O.F. Abdullah, O.A. Hussein and T.A. Aswad, "Effect of the Laser Surface Treatment on Properties of the Alloy (Ni-Cu-V) Nanoparticles Prepared by Powder Metallurgy Method", *NeuroQuantology*, 19(12) (2021) 1.
[16] N.A. Jasim, "Theoretical Study of Some Physical and Thermodynamic Properties for some Diclofenac Derivatives by using Semi-Empirical Calculations (PM3 Method)", *Syst. Rev. in Pharma.*, 11(12) (2020) 1294.
[17] K.O. Kzar, "Study the Effect of the Positive (+1,+2) and Negative (-1,-2) Charges on the Geometry and Vibrational Spectra of Bromofulvene Isomers with DFT model", M.Sc. thesis, University of Kerbala, Iraq (2013).
[18] M. Chase Jr., "NIST-JANAF Themochemical Tables", 4th ed., *J. Phys. Chem. Ref. Data*, Monog. 9 (1998) 1-1951.
[19] T. Mathavan et al., "A study on thermochemical properties of ZnS Nanomaterial: A computational Approach", *Int. J. Sci. Eng. Res.*, 5(3) (2014) 33-36.

