IR Spectroscopic Study of Triiodosilane (SiHI$_3$) by Using Semi-empirical Quantum Program

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Abstract. In this research, the more important spectral properties of vibration HSiI$_3$ molecule have been studied and calculated by using the semi-empirical theoretical program (HyperChem) method (MNDO-PM3) (Use the RHF wave function for close - shell systems, the spins are paired). The calculated vibration modes for Triiodosilane (SiHI$_3$) were nine modes in the region (63-1815) cm$^{-1}$, which is located in the far and middle infrared region. Total energy, dipole moment, energy gap, Core-core repulsion, Ionization potential and electron affinity (E.A.) have been calculated. Other properties are also plotted in two and three dimensions, such as electrostatic potential and charge density. In addition, the values of the occupied and unoccupied molecular orbitals were calculated.

1. Introduction

Semiconductor halide molecules are of great importance, which made scientists interested in studying their properties theoretically and practically. Triiodosilane is a precursor compound useful in the atomic layer deposition of silicon onto various microelectronic device structures[1].

Methods of calculating the energy and intensity of vibrational transitions are an effective tool in determining the structure of small and interacting molecules [2-4]. And because the molecules are in a state of permanent vibrational motion even at absolute zero temperature, so studying the vibrational transitions of the molecule is a good source of information about the molecular structure. The aim of this research is to obtain information about Triiodosilane (SiHI$_3$) molecule through spectral properties, dipole moment and other properties. The MNDO-PM3 method was used to calculate the theoretical parameters underlying the studied molecule[5-8]. Which is one of the semi-empirical quantum methods that depend on valence electrons only and assume that they move in a stable basic framework consisting of nuclei and electrons in the inner shell. These electrons are dealt with using a minimum basis set that is simplified by neglecting some electron repulsion integrals that include differential overlap. Then the remaining integrals are equated with the parametric function which includes numerical parameters resulting from the fit of some experimental results. These calculations were performed using the hyperchem 6.0program[9].
2. Theory
The first step was to determine the optimal geometry for Triiodosilane (SiH3). The geometry optimization was completely performed using the restricted Hartree-Fock basis (Use the RHF wave function for close-shell systems, the spins are paired) applying the Polak-Ribiere conjugate gradient algorithm with a limit of approximately 0.01 kcal/Å.mol. These Semi-empirical calculations for this molecule were performed in a vacua. And by using the PM3 method (it uses a minimal basis set of valence Slater type s and p atomic orbitals (AO) to expand valence-electron molecular orbitals (MO))[10], which is one of the methods that provides accurate geometry according to the experimental crystal structure, using a computer with low requirements and a short period of time for the calculation[11-14]. This method uses energy derivatives relative to the coordinates by changing the geometry to reduce the formation temperature, and when the additional change in the geometry does not result in a decrease in the formation temperature significantly, the process of optimization stops. Thus, it follows the same general approach.

The frequencies of the harmonic vibrations were calculated after obtaining the stable geometric fitting. The most common method is the calculation of vibration frequency and normal coordinates from molecular force constants, by solving the abstract equation of Wilson [15]:

\[ \sum_j L_j (F_{ij} - \lambda M_{ij}) \]  

Where \((F_{ij})\) in the equation (1) represents a matrix element of the force constants, and \((M_{ij})\) matrix masses of atoms, \((\lambda)\) Eigen value, \((L_j)\) values of Eigen vector coefficients. From solving the equation (1), we obtain the roots \((\lambda)\) of the abstract equation, from which we obtain the basic vibration frequencies \((3N-6)\) of the molecule by substituting the values of the \((\lambda)\) into the following equation[15]:

\[ \lambda = 4\pi \nu^2 c^2 \]  

Where \((\nu)\) the harmonic frequency is represented by a unit \((\text{cm}^{-1})\), \(c\):The speed of light.

And by using the Born-Oppenheimer approximation to solve the Schrödinger equation[16]:

\[ \hat{H}\Psi = E\Psi \]  

Hamiltonian \(H\) for a molecule consisting of \(m\) nuclei and \(n\) of electrons can be written as follows:

\[ H = H_{\text{nuclear}} + H_{\text{electronic}} = H_{\text{nuclear}} + \sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{R_{Ai}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} \]  

The first term is the energy of the nucleus, the second term is the kinetic energy of the electrons, the third term is the attraction of the nucleus and the electron, and the last term is the electron-electron repulsion. Hence, the total energy can be written as the sum of the nuclear repulsion energy \((E_{\text{core-core}})\) and the electronic energy specified by Hamiltonian \(E_{\text{electronic}}[16,17]\):

\[ E_{\text{total}} = E_{\text{electronic}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}} \]  

In addition, the heat of formation, dipole moment \(\mu\), HOMO and LOMO energies were also calculated.

The energy gap \(\Delta E\) between (HOMO) and (LUMO) is defined as [18]:

\[ \Delta E = E_{LUMO} - E_{HOMO} \]
The ability of the elements to be a donor or acceptor is related to the value of the ionization potential (I.P), although there is no formal relationship between them, it has been observed that the small values of I.P give an indication that the element is a donor, while the higher values indicate the opposite. The value of the ionization potential is calculated from the last HOMO:

\[ I.P = |E_{HOMO}| \quad (7) \]

While the absolute values of the first LUMO represent the electron affinity (E.A.).

The sites of the initial attack of protons or other ions can be predicted during the reaction through the results of the electrostatic potential calculations, which can be calculated by evaluating [9]:

\[ V = \sum_{A} \frac{Z_{A}}{|R_{A} - r|} - \int \frac{\rho(r')}{|r' - r|} dr' \quad (8) \]

Where, \( r \) is the location of the positive charge, \( Z_{A} \) represents the charge of the nucleus A at the \( R_{A} \) position, and \( \rho(r') \) is the electronic density. The first term of the previous equation represents the potential produced by the charge of the nucleus and the second term is produced by the electrons.

\[ V(r) = \sum_{A} \left[ \frac{Z_{A}}{|R_{A} - r|} - \sum_{\mu \nu} P_{\mu \nu} \int \frac{\phi_{\mu}(r')\phi_{\nu}(r')}{|r' - r|} dr' \right] \quad (9) \]

The second summation of eq. (9) is over the orbitals of atom A. HyperChem uses this expression to calculate the electrostatic potential of semi-empirical methods. The total dipole moment of a molecule can be calculated using the following formula [19]:

\[ \mu_{tot} = (\mu_{x}^{2} + \mu_{y}^{2} + \mu_{z}^{2})^{\frac{1}{2}} \quad (10) \]

The intensity of the infrared spectral line is proportional to the derivative of the dipole moment of the vibrational pattern [20].

### 3. Results and Discussion

Because the SiHI₃ molecule is nonlinear, it has (3 N - 6 = 9) vibration modes, and the value of the frequencies of these modes is in the region of (1815-63) (cm⁻¹) as shown in Table (1) and it approaches the results calculated by NIST(Gaussian 09 - B3LYP/GENECP) [21]. These modes are divided into five modes of bending vibration and four modes of stretching vibration as shown in Figure (1).

| Vibration Mode | Wave Number (cm⁻¹) calculated by Hyperchem | Wave Number (cm⁻¹) calculated by Gaussian 09 B3LYP/GENECP [15] | error percentage |
|----------------|-------------------------------------------|----------------------------------------------------------|-----------------|
| 1              | 63.19                                     | 74.5706                                                  | 15.26151        |
| 2              | 63.21                                     | 74.6527                                                  | 15.32791        |
| 3              | 98.02                                     | 117.0923                                                 | 16.28826        |
| 4              | 212.20                                    | 267.7332                                                 | 20.74199        |
| 5              | 301.51                                    | 373.4632                                                 | 19.26648        |
| 6              | 301.55                                    | 373.7248                                                 | 19.31229        |
| 7              | 509.61                                    | 741.8988                                                 | 31.47031        |
| 8              | 509.65                                    | 743.6923                                                 | 31.47031        |
| 9              | 1814.74                                   | 2292.0449                                                | 15.26151        |
Vibration Mode : 1  
Frequency : 63.19 cm\(^{-1}\)  
Intensity : 0.468 km/mol  
Type : Bending

Vibration Mode : 2  
Frequency : 63.21 cm\(^{-1}\)  
Intensity : 0.465 km/mol  
Type : Bending

Vibration Mode : 3  
Frequency : 98.02 cm\(^{-1}\)  
Intensity : 1.821 km/mol  
Type : Bending

Vibration Mode : 4  
Frequency : 212.20 cm\(^{-1}\)  
Intensity : 12.241 km/mol  
Type : Stretching

Vibration Mode : 5  
Frequency : 301.51 cm\(^{-1}\)  
Intensity : 28.052 km/mol  
Type : Stretching

Vibration Mode : 6  
Frequency : 301.55 cm\(^{-1}\)  
Intensity : 28.078 km/mol  
Type : Stretching

Vibration Mode : 7  
Frequency : 509.61 cm\(^{-1}\)  
Intensity : 172.368 km/mol  
Type : Stretching

Vibration Mode : 8  
Frequency : 509.65 cm\(^{-1}\)  
Intensity : 172.1 km/mol  
Type : Bending

Vibration Mode : 9  
Frequency : 1814.74 cm\(^{-1}\)  
Intensity : 1.654 km/mol  
Type : Stretching

**Figure 1** Calculated vibrational modes by MNDO-PM3 method
The arrows in Figure (1) indicate the direction of the vibrational movement of the mode, where the length of the arrow relative to another arrow in the same figure indicates the amount of displacement of the atom relative to the displacement of the other atom at the same moment. The lengths of the arrows relative to the distances between the atoms in the figure are exaggerated.

The energies of molecular orbitals were calculated and found 13 occupied molecular orbitals and 4 unoccupied molecular orbitals. Knowing the highest occupied molecular orbit and the lowest unoccupied molecular orbit, we can calculate the energy gap which was equal to 6.756 eV as shown in Figure (2).

| No. level | Energy (eV) |
|-----------|-------------|
| 17        | 0.550267    |
| 16        | -2.332328   |
| 15        | -2.332405   |
| 14        | -3.534699   |

**LUMO**

| Energy (eV) |
|-------------|
| -10.290859  |

**HOMO**

| Energy (eV) |
|-------------|
| -10.383492  |
| -10.411086  |
| -10.411292  |
| -10.468220  |
| -10.468331  |
| -12.460685  |
| -12.461930  |
| -12.715880  |
| -13.481716  |
| -13.541975  |
| -13.543904  |
| -15.905012  |

**Figure 2** Occupied (HOMO) and unoccupied molecular orbitals (LOMO) of SiH₃

Table (2) shows some of the properties of the studied molecule, which are the total energy $E_T$, electronic energy $E_e$, core-core repulsion energy $E_{core-core}$, heat of formation $H_f$, dipole moment $\mu$, ionization potential $I.P.$, electronic affinity $E.A.$, and energy gap $\Delta E$. 
Table 2: The results of the spectral properties of the Triiodosilane (SiHI$_3$) molecule calculated by MNDO-PM3

| Quantity                        | Magnitude  | Unit  |
|--------------------------------|------------|-------|
| Total Energy $E_T$             | -956.4996  | eV    |
| Electronic Energy $E_e$        | -1967.426  | eV    |
| Core-Core Repulsion Energy $E_{core-core}$ | 1011.017 | eV    |
| Heat Of Formation $H_f$        | -0.39257   | eV    |
| Dipole Moment $\mu$            | 1.986      | Deby  |
| Ionization Potential I.P.      | 10.290859  | eV    |
| Electronic Affinity E.A.       | 3.534699   | eV    |
| Energy Gap $\Delta E$          | 6.756      | eV    |

The electrostatic potential is illustrated by drawing it in two (2-D) and three dimensions (3-D) as shown in the Figure (3).

![Figure 3](image)

**Figure 3**: The electrostatic potential of SiHI$_3$ molecule (a) in two and (b) three dimensions.

The electrostatic potential map conveys information about the charge distribution in the molecule.

We notice from the Figure (4) (a) and (b) that the charge is centered around the most electronegative atoms, so we notice that most of the charge is centred around the iodine atoms.

![Figure 4](image)

**Figure 4**: (a) Total Charge Density in two dimensions & (b) three dimensions of SiHI$_3$

4. Conclusions:
We conclude that this molecule is one of the molecules that emit heat because the heat of its formation has a negative signal.

The first three vibration modes of this molecule are located in the far infrared region, while the rest of the modes are within the middle infrared region. Also, the intensity of the stretching modes (4, 5, 6, 7, and 9) is higher than the intensity of the bending modes (1, 2, 3, and 8), this means that the change in the moment of the dipole resulting from the vibration of the molecule in these modes is higher than in other modes. As a result of this change of dipole moment, an absorption band exists in the IR spectrum at these frequencies.
There is a difference in the frequency values of the vibration modes calculated in this study and the theoretical study taken from the literature as a result of the difference in the calculation program and the difference method used in the calculations.

It is also possible to excite the molecule using ultraviolet rays of a wavelength equal to 183.5 nm by calculating the energy gap, which was found to be equivalent to this wavelength.

5. References

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