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Study of Spectroscopic and Vibrational Properties of the Phthalocyanine Molecule ($C_{32}H_{18}N_8$) and Magnesium Phthalocyanine ($C_{32}H_{16}MgN_8$) by Using Quantum Programs

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Abstract

In this paper calculation spectroscopic and vibrational properties using Semi-empirical method, through the results showed the IR spectra, the value of the lowest amount of total energy for H_2Pc molecule was equal to ($-7049.071\,\mathrm{Kcal/mol}$) for ($C_{16}$-$H_{41}$) and ($-7049.07\,\mathrm{Kcal/mol}$) for ($C_{27}$-$H_{43}$), for MgPc molecule is equal to ($-6974.54\,\mathrm{Kcal/mol}$) for ($C_{17}$-$H_{42}$) and ($-6974.55\,\mathrm{Kcal/mol}$) for ($C_{28}$-$H_{44}$), and after that equilibrium distance is ($\mathrm{r} = r_{\mathrm{eq}} = 1.09\mathrm{A}^{\circ}$) for each molecule. The theoretical and experimental results were compared to the energy gap, for H_2Pc (5.67 eV), (5.04 eV), for MgPc (5.043 eV), (2.73 eV), respectively.

Keywords: Phthalocyanine (H_2Pc), PM3 Method, Spectroscopic and Vibrational Properties.

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دراسة الخصائص الطيفية والاهتزازية للجزيئات الفثالوسيانين $(C_{32}H_{18}N_8)$ و الفثالوسيانين–المغنيسيوم $(C_{32}H_{16}MgN_8)$ باستخدام برامج الكم

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الملخص

في هذه الدراسة تم حساب الخصائص الطيفية والاهتزازية باستخدام طريقة الشبه التجريبية، من خلال النتائج التي اظهرت طيف IR، اقل قيمة الطاقة الكلية لجزيئة (H_2Pc) $(-7049.071\,\mathrm{Kcal/mol})$ للآصرة $(C_{16}\text{-}H_{41})$، $(-7049.07\,\mathrm{Kcal/mol})$ للآصرة $(C_{27}\text{-}H_{43})$، لجزيئة (MgPc) تساوي $(-6974.54\,\mathrm{Kcal/mol})$ للآصرة $(C_{17}\text{-}H_{42})$ و$(-6974.55\,\mathrm{Kcal/mol})$ للاصرة $(C_{28}\text{-}H_{44})$، والمسافة المتوازنة لكل جزيئة تساوي $(r = r_{eq} = 1.09\mathring{A})$. تمت مقارنة النتائج النظرية والعملية لفجوة الطاقة، للجزيئة H_2Pc كانت (5.67 eV)، (5.04 eV)، لجزيئة MgPc (5.043 eV)، (2.73 eV) على التوالي.

الكلمات الدالة: الفثالوسيانين (H_2Pc)، طريقة (PM3)، الخصائص الطيفية والاهتزازية.

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1.Introduction:

Phthalocyanine is an organic semiconducting material which is widely used for transistor fabrication sensor and applications [1]. Phthalocyanine is porphyry derivatives and includes a comprehensive range of different molecules with similar structure [2]. Afterward of its discovery, phthalocyanine was widely applied as green and blue light resistant dyes and pigments in textile and paper industries for their high chemical, thermal, and photochemical stabilities [3-4].

The researchers Zhang Xianxi, Zhang Yuexing and others in (2004) have calculated infrared frequencies and intensities for the magnesium phthalocyanine complex MgPc at density functional B3LYP level by using the 6-31G(d) basis set. Consequently, Cross shifts are perceived from H_2Pc to MgPc. The vibrational mode expected at 757.3 cm^{-1} for H_2Pc was found to shift to 720.8 cm^{-1} for MgPc, while the vibrational modes which predicted at 717.2 and 722.4 cm^{-1} for H_2Pc were found to shift to 740.3 cm^{-1} for MgPc [5].

The researchers Seoudi R. , El-Bahy G.S and others in (2006) have studies thin films of Phthalocyanine and its complexes [magnesium, manganese, iron, cobalt, zinc and lead Phthalocyanine] by vacuum evaporation technique. The $\pi \rightarrow \pi^*$ transition exists in the region of the Soret band. This band was determined at 346 nm of phthalocyanine and shifted to 350, 353, 326, 315, 346 and 351 nm for MgPc, MnPc, FePc, CoPc, ZnPc and PbPc respectively. Consequently, there was the Q-band $n \rightarrow \pi^*$ transition which appeared in the visible region at about 600–735 nm. This band has a doublet for the all models, and new band existed at (538.5, 561.5 and 444.2 nm) for (MnPc), (FePc) and (PbPc), respectively [6].

The researchers Li Fang, Zheng Qiguang and others in (2008) have investigated the spectrum of copper Phthalocyanine (CuPc) both experimentally and theoretically, which is a potential laser protective organic absorbing dye By using semi-empirical quantum chemical calculations. The study presents the visible spectrum of CuPc solution. As a result, there is a sharp and intense absorption peak at 658 nm with a small shoulder at 597 nm, and there is nearly no absorption during the band of 400–600 nm, which is appropriate for being used as a potential infrared dye for laser protective technology [7].

The researchers Hassan Z. Issa, Fat-hulla N. Moayyed and others in (2013) have calculated three transition metal-Phthalocyanines (metals= Co, Ni, Cu) by using semi-empirical methods. PM3 and ZINDO/S maintain transition metal parameters. Nevertheless, ZINDO/S method presented less efficiency when dealing with open shell models especially CoPc. PM3 and ZINDO/S do not apply d-orbitals in their basis sets, therefore; they do not show very accurate results for most d-metal compounds nor for those core group elements where, from ab initio studies, d-orbitals are known to be of importance. As a result, the bond length (C_1- N_1) of CoPc, CuPc and NiPc were (1.442, 1.429 and 1.417 A^o) respectively, and it was found that they are comparable to each other [8].

Arslan Sönmez in (2016) has introduced Phthalocyanines (Pcs) with their derivates, types, synthesis and purification methods and finally stated their applications. Since Phthalocyanines have high electron transfer abilities, Pcs have been utilized in many fields such as molecular electronics, optoelectronics and photonics. As a result of these investigations, it was determined that Pcs are greatly colored, planar 18 π-electron aromatic ring systems corresponding with porphyrins [9].

The researchers Hamam J. Khalil and Alomari I. Mohammed in (2017) have studied the optical band gap of zinc Phthalocyanine nanoparticles by using UV-Vis spectroscopy and DFT function. The shift in the absorption position was determined as a proof of the formation of nanoparticles. Nanoparticles band gap energy recorded higher values at both B-band and Q-band (3.13 and 1.55 eV, respectively) compared to the values for similar bands of bulk ZnPc (2.97 and 1.53 eV respectively) [10].

The aim of this study is to calculate the spectral and vibrational properties of the Phthalocyanine (H_2Pc), and Magnesium Phthalocyanine (MgPc) molecules by using the semi-empirical quantum programs [HyperChem8.0] by (PM3) method.

2. Theoretical Part:

Semi-empirical (SE) methods can be derivative from either Hartree–Fock or density functional theory via applying systematic approximations, leading to efficient computational schemes that are some orders of magnitude faster than ab initio calculations. Such numerical efficiency, in combination with modern computational facilities and linear scaling algorithms, allows application of SE methods to very large molecular systems with extensive conformational sampling [11].

It is in this context that semi-empirical (SE) methods, which take a long history in quantum chemistry, have come back into the spotlight in recent years. The greatest prevalent SE methods are those based on approximations to the Hartree–Fock (HF) theory, leading to methods for instance AM1, PM3 and MNDO/d.

In standard electronic structure methods, the molecular orbitals (MOs, $\{\psi_i\}$) are approximated via a linear combination of basic functions represented via atomic orbitals (AOs, $\{\chi_\mu\}$):[11]

$$\psi_i(\mathbf{r}) = \sum_{\mu} C_{\mu i}\chi_\mu(\mathbf{r}) \qquad (1)$$

The conventional HF theory usually expands all electrons in the AO basis, whereas SE methods typically only treat the valence shell electrons and suppose these in the field of the nuclei and the (unpolarizable) inner-shell electrons. Generally, SE methods expand the valence electron density in a minimal set of Slater-type orbitals [11].

The molecular orbital coefficients $C\mu i$ are acquired via solving the Roothaan–Hall equations, which can be written in the form of a generalized eigenvalue problem, [11]

$$\mathrm{FC} = \mathrm{SC}\epsilon \qquad (2)$$

Where F, C and S are the Fock, MO-coefficient, and overlap matrices, respectively, and ϵ is the diagonal matrix containing the orbital energies [11].

3. Results and Discussion:

3.1 The Molecular Structure:

Phthalocyanine molecule is considered an organic semiconductor and un-linear molecule. It consists of (58) of atom, (32) of carbon, (18) of hydrogen, (8) of nitrogen. However, Magnesium Phthalocyanine (MgPc) consists of (57) of atom, (32) of carbon, (16) of hydrogen, (1) of magnesium atom and (8) of nitrogen. Through using HyperChem8.0 program for semi-empirical (PM3) method, Phthalocyanine and Magnesium Phthalocyanine molecule structures have been illustrated by drawing their figures to obtain a superior, balanced and stable form as it is shown in Fig. 1.

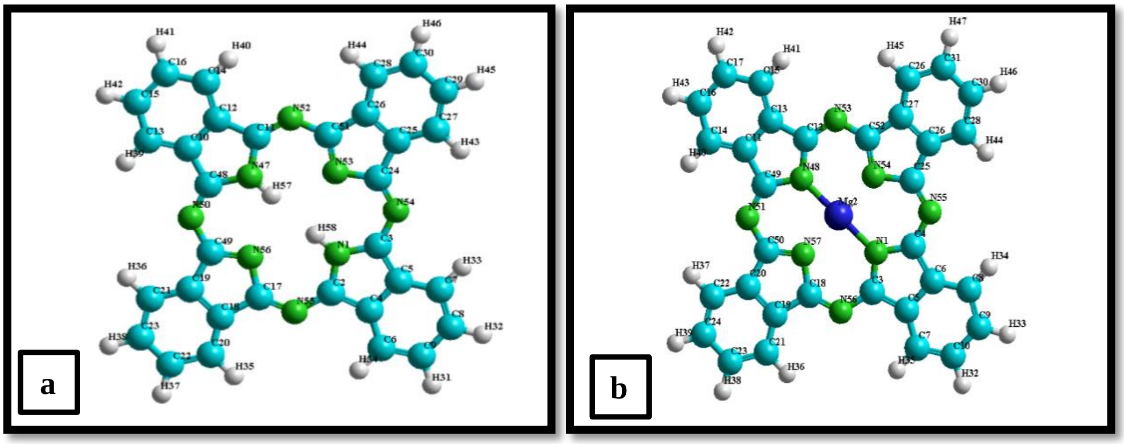


Fig. 1: the molecular structure of the molecule (a) and (b) painted program of the HyperChem8.0.

Through HyperChem8.0 program for semi-empirical (PM3) method, it has presented some spectral characteristics of H_2Pc and MgPc molecule structures by applying geometry optimization. The spectral characteristics were (total energy in term of stable position, binding energy, isolated energy, electronic energy, core-core interaction energy, heat of formation, gradient, molecular point group and zero point energy of vibration) as it is illustrated in **Table 1**.

Table 1: The results of some properties of the molecule H2Pc and MgPc calculated by the program HyperChem8.0.

Quantity	Magnitude (H_2Pc)	Magnitude (MgPc)	Unit
Total Energy	-123635.9518791	-123478.5681510	Kcal/mol
Total Energy	-197.026406321	-196.775599416	a.u.
Binding Energy	-7049.0831331	-6974.5575780	Kcal/mol
Isolated Atomic Energy	-116586.8687460	-116504.0105730	Kcal/mol
Electronic Energy	-1245881.5315890	-1253708.1447767	Kcal/mol
Core-Core Interaction	1122245.5797099	1130229.5766257	Kcal/mol
Heat of Formation	261.2328669	266.5544220	Kcal/mol
Gradient	0.1023176	0.1002682	Kcal/mol/Ang
Molecular point group	C_s	C_s	
Zero point energy of vibration	272.76919	260.01359	Kcal/mol

3.2 The Calculation of un-harmonic Potential Energy:

Fig. 2 and Fig. 3 show the relationship between the total energy of H_2Pc and MgPc respectively and the distance between the two atoms (C_{16}-H_{41}) and (C_{27}-H_{43}) for H_2Pc and the distance between the two atoms (C_{17}-H_{42}) and (C_{28}-H_{44}) for MgPc. The power curves of H_2Pc and MgPc have been plotted the potentiality of the molecules by (C_{16}-H_{41}) and (C_{27}-H_{43}) bonds change for H_2Pc and by (C_{17}-H_{42}) and (C_{28}-H_{44}) bonds change for MgPc and calculated the lowest amount of the total energy for H_2Pc and MgPc as shown in below Figures.

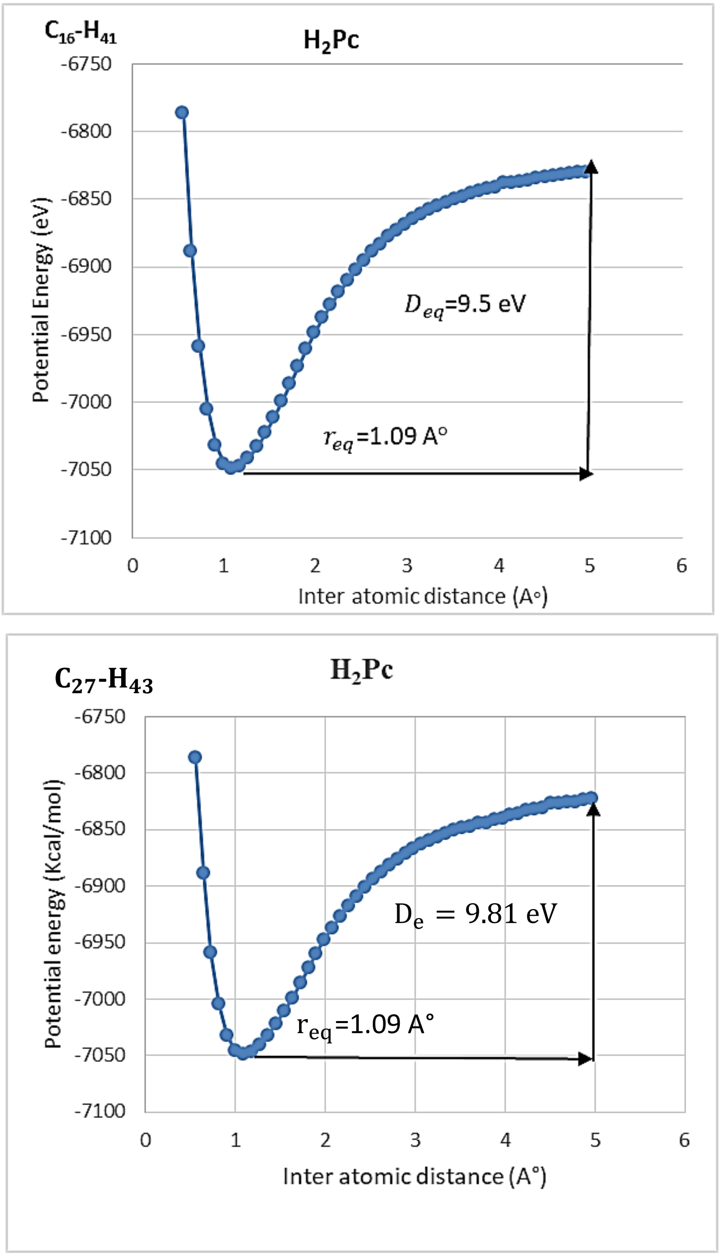
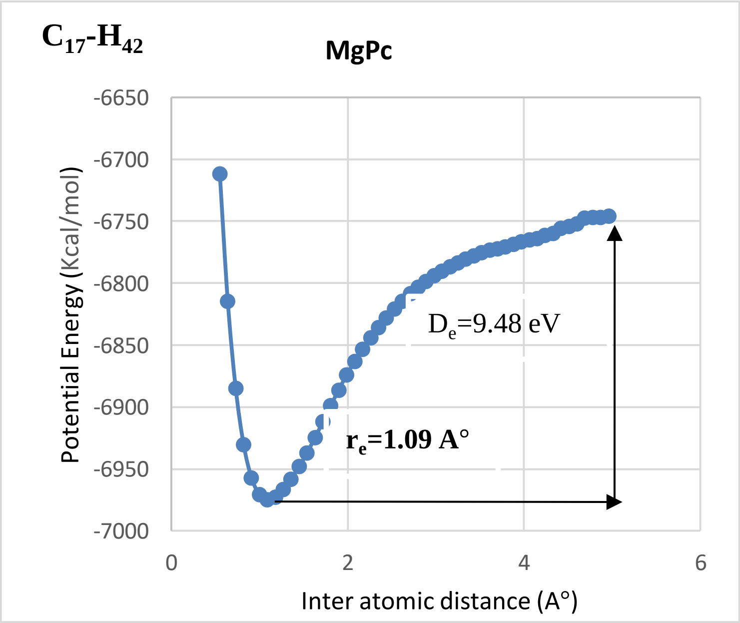


Fig. 2: The Change of the Total Energy with Distance of H_2Pc Molecule.



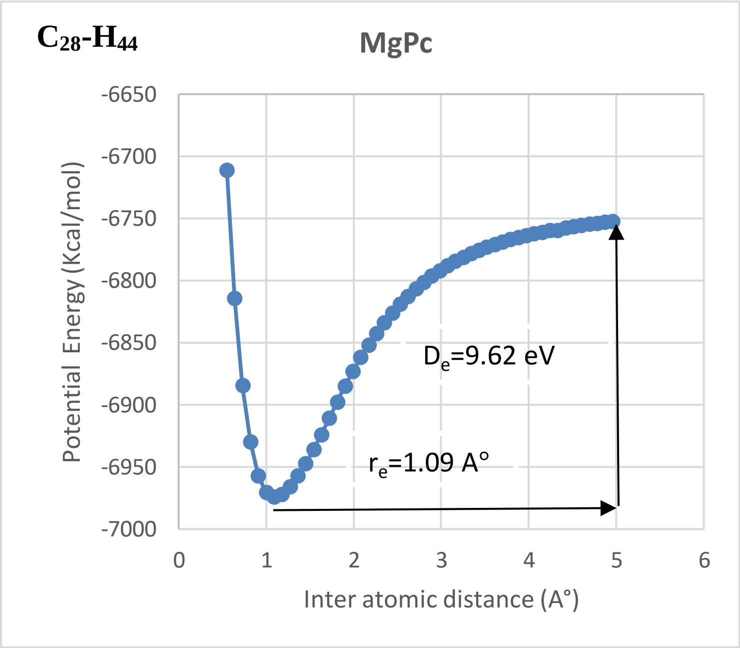


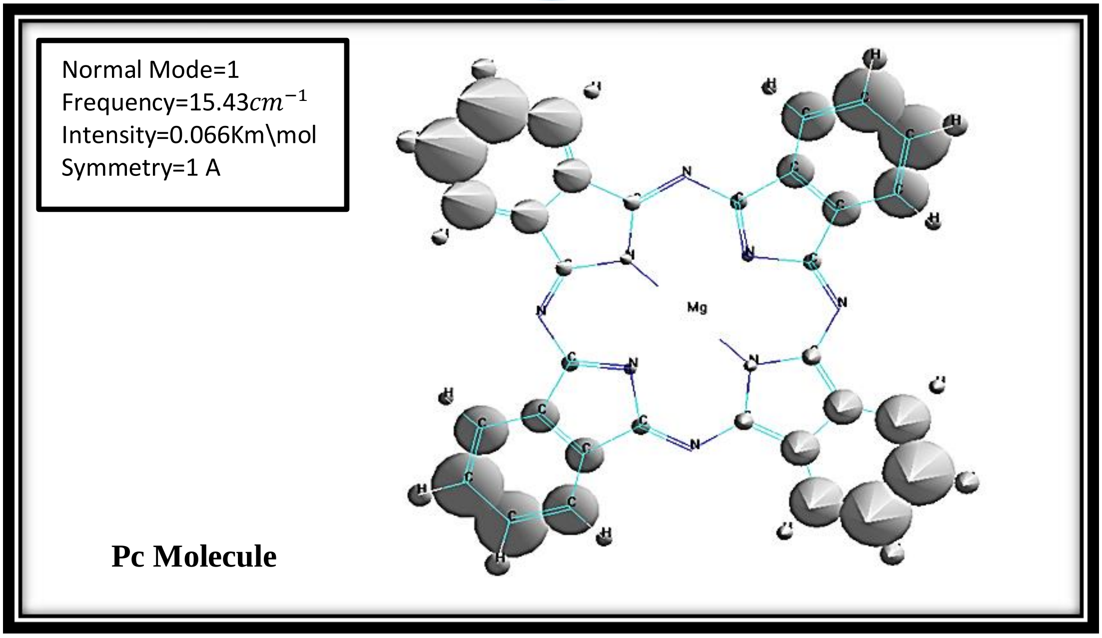
Fig. 3: The Change of the Total Energy with Distance of MgPc Molecule.

The potential curve represents the force between the atoms (C_{16}-H_{41}) and (C_{27}-H_{43}) for H_2Pc and (C_{17}-H_{42}) and (C_{28}-H_{44}) for MgPc and these forces illustrate the sum of the forces of repulsion and attraction. When the distance between the atoms is reduced, each electron starts to be effected by the force of attraction by the other nucleus. At the same time, both electron and nuclei start to repel each other [12]. When the atoms are separated from each other by increasing the distance the gravitational force will present that the total energy decreases due to the decrease in the potential energy and the (electron-nucleus) attraction, thus; increasing the energy reduction until it reaches the lowest total energy value. The dissociation energy of the molecule is calculated from the difference between the lowest energy value and its value when the (r) is infinity. And, the potential energy becomes zero when the distance between two atoms is infinite [12], and the value of dissociation energy is illustrated in Fig. 2 and Fig. 3.

3.3 Calculate Frequencies and Vibrational Modes:

The basic values of the vibration frequencies for (H_2Pc) and (MgPc), and their values have been calculated by Infrared Region of the Phthalocyanine (H_2Pc) and Magnesium Phthalocyanine (MgPc) molecules. The number of vibrational mode which were (168) mode for H_2Pc and (165) mode for MgPc according to the relationship (3N-6), where N represents the number of atoms of the molecule. Furthermore, the vibration frequency values of H_2Pc were convergent to the wave number of MgPc by using HyperChem8.0 program for semi-empirical (PM3) method.

Fig. 4 shows the description of number of vibration modes for H_2Pc and MgPc molecules, where the vibration patterns of the molecules are describe in the program HyperChem8.0 for semi-empirical (PM3) method with some other spectral characteristics such as the intensity in unit (Km/mol) and symmetry for each type of vibration patterns of the molecules. This figure show these types with the description of molecular patterns, and (168) mode for H_2Pc and (165) mode for MgPc vibrating patterns of the molecules according to the rule (3N-6). The non-ring molecules include N of atoms and its bond numbers are equal to (N-1). Consequently, the vibrational freedom degrees are divided to (N-1) from the expanded vibrations. The other freedom degrees would be related to the bending vibrations and these numbers are equal (2N-5) of non-linear molecules [12].



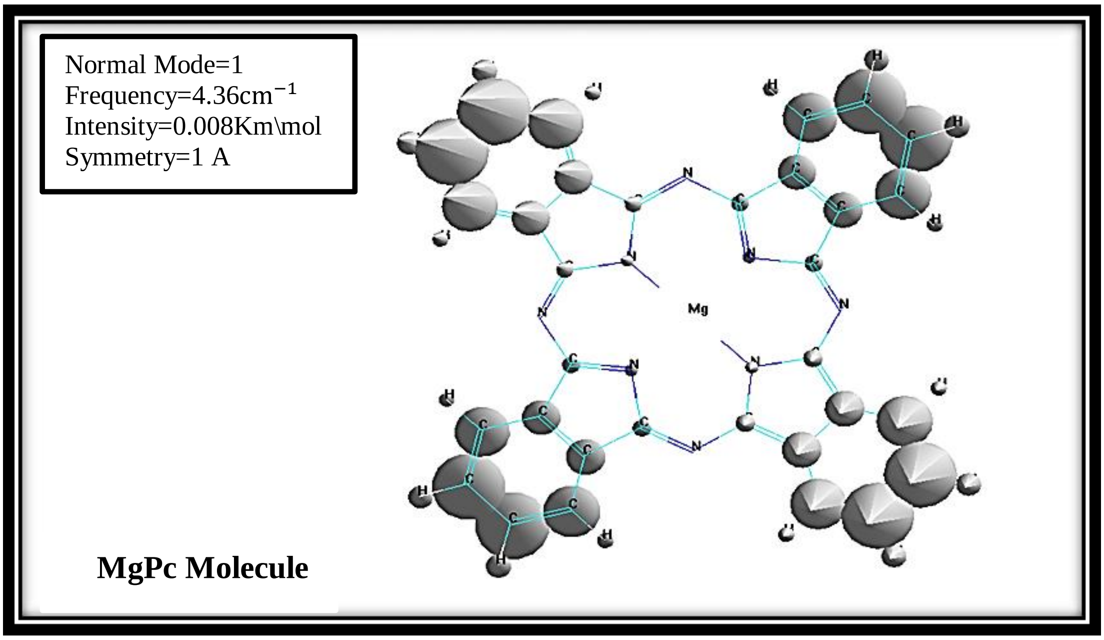


Fig. 4: The basic mode of vibration of H_2Pc and MgPc molecules.

3.4 Calculate Eigenvalues of Energy Molecular Orbitals:

Fig. 5 and Fig. 6 presents the molecules H_2Pc and MgPc orbitals and the value of the energy for each term and denotes all levels of the molecule through HyperChem8.0 program for semi-empirical (PM3) method. In addition, the figure is also contains number of orbits which is occupied electrons (9), and (9) orbits are not occupied by electrons. The figure clarifies energy calculation of higher occupied orbit molecules which is symbolized by (E_{HOMO}), and represents energy calculation of lower unoccupied orbit molecules which is symbolized by (E_{LOMO}). Consequently, the energy eigenvalues could be calculated for partial orbits. Otherwise, the energy gap of H_2Pc and MgPc molecules could be calculated through the equation ($E_{gap} = E_{LUMO} - E_{HOMO}$) which are equal to (5.67 eV) and (5.043 eV) respectively. In addition, the experimental results for energy gap of H_2Pc were (5.04 eV) [13], and for MgPc were (2.73 eV) [14], as it is shown in Table 2. As it is shown in Fig. 5, the ionization energy of H_2Pc and MgPc would be taken the absolute value from the highest occupied energy level which are equal to (7.637 eV) and (7.271 eV) and the lowest unoccupied energy level which are equal to $|-1.963\ \text{eV}|$ and $|-2.228\ \text{eV}|$, respectively.

The energy gap of H_2Pc is greater than MgPc because the central metal of the atom is considered as the nearest approach to nitrogen atoms in parallel molecules and this leads to increase in the orbital overlaps among molecule's parallel pairs. Thus, any crystal change would cause an effect to the energy gap between conduction and valence bands [15].

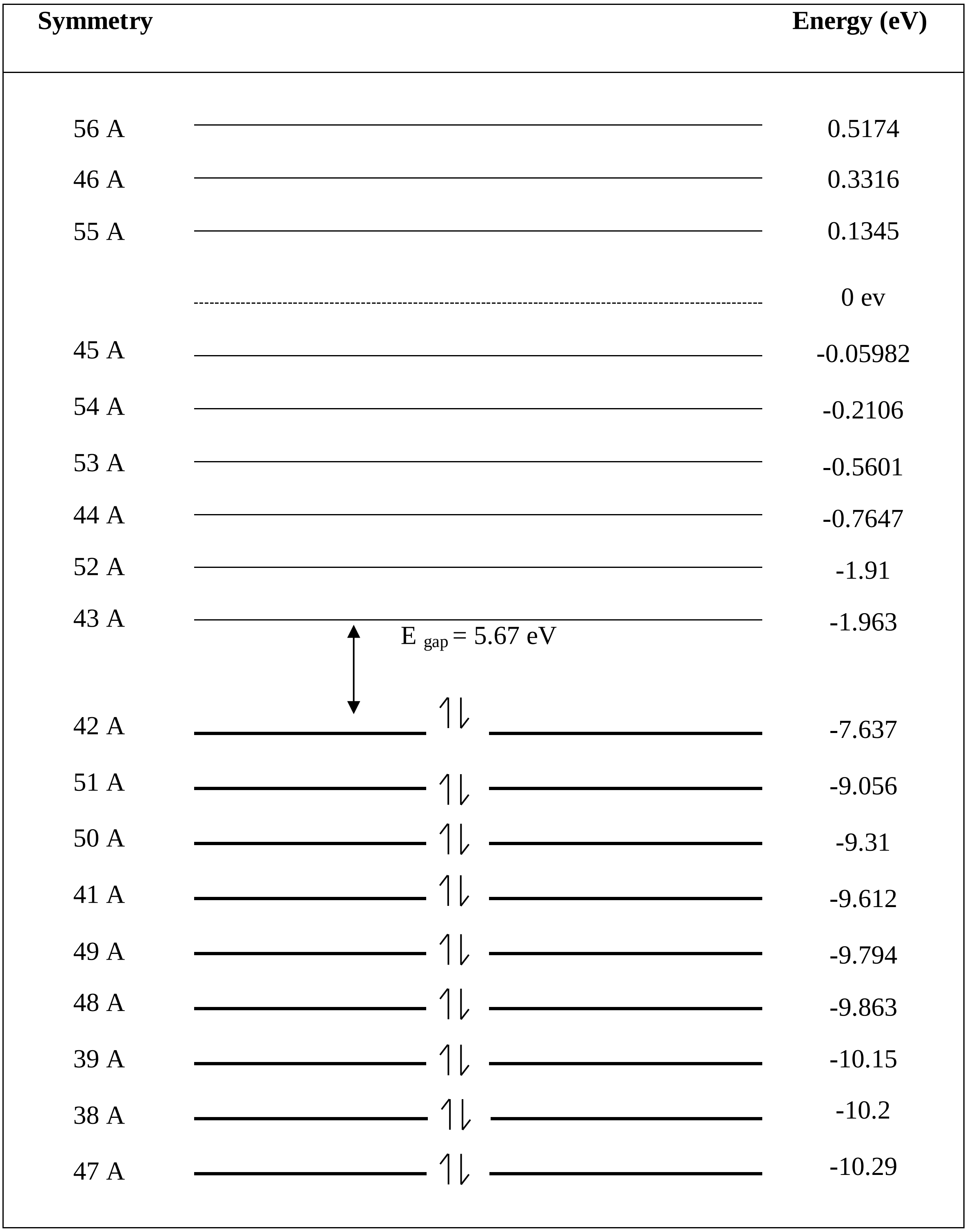


Fig. 5: The values of the energy levels of the molecule H_2Pc.

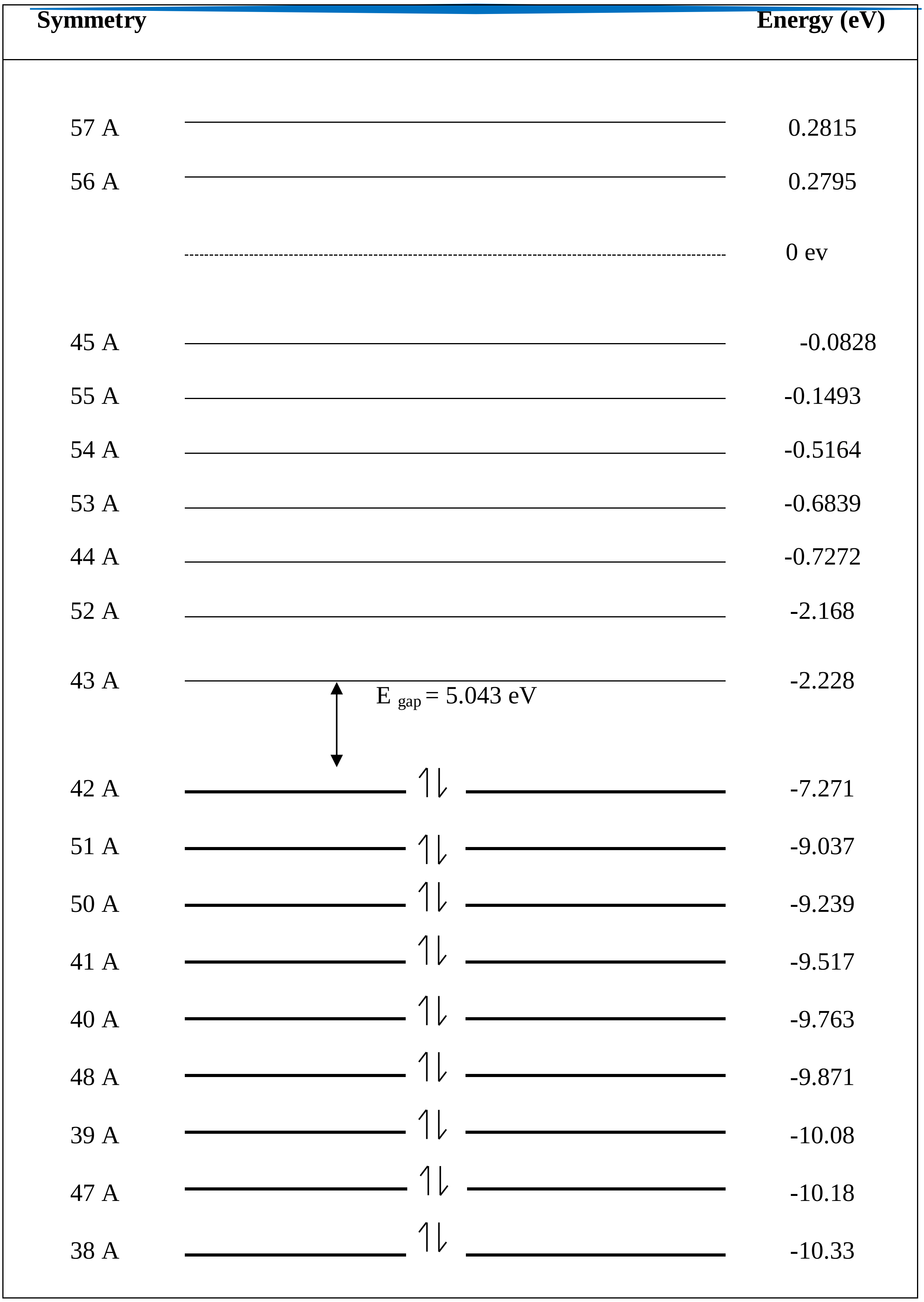


Fig. 6: The values of the energy levels of the molecule MgPc.

Table 2: The results of E_{gap} for molecules of comparison theoretical and experimental results

Molecule	**Theoretical results of E_{gap}** in (eV)	**experimental results of E_{gap}** in (eV)
H_2Pc	5.67	5.04
MgPc	5.043	2.73

3.5 Compare Potential Curves of the Molecules:

Fig. 7 illustrated the equilibrium distance (r_e) and Dissociation energy (D_e) for the bond length (C_{16}-H_{41}) of H_2Pc and the bond length (C_{17}-H_{42}) of MgPc molecules. The figure illustrates the Dissociation energy (D_e) of (H_2Pc $>$ MgPc). Also, the potential energy leads to infinite value when the distance value decreases and reaches to zero because of electrostatic repulsion between two positive charged protons. On the other hand, when the distance value increases and gets higher value, the energy becomes constant because of the dissociation molecule [16]. The total energy of H_2Pc is greater than MgPc molecule. The equilibrium distance (r_e) shows similarity of all molecules which means that the (r_e) of H_2Pc is not shifted when the metal Mg molecule are added to the center of Pc molecule.

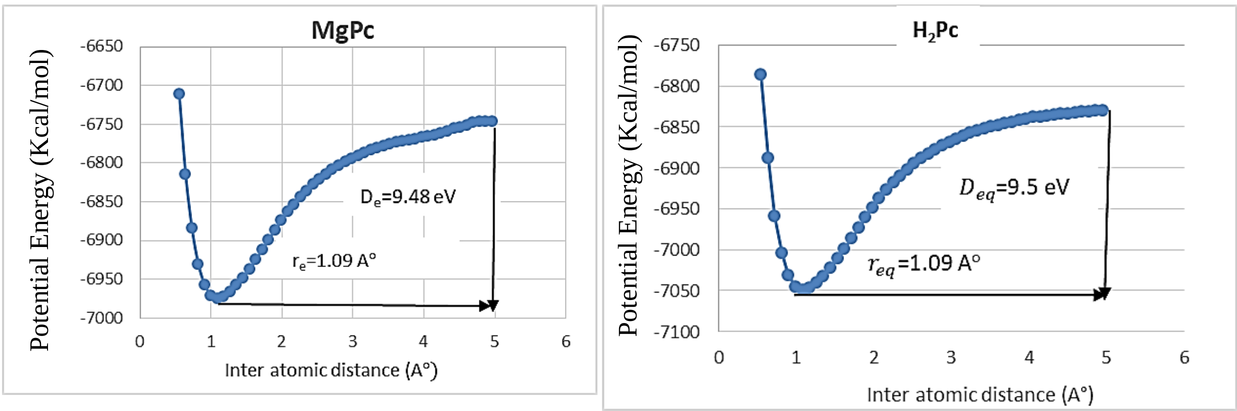


Fig. 7: The Potential Curves of H_2Pc and MgPc.

3.6 Compare the Results with Previous Studies:

The vibrational spectra of IR of all compounds were calculated by the study of (PM3) Semi-empirical method. Table 7 represents the vibration frequency values of H_2Pc and MgPc molecules and the experimental vibration frequency values of MgPc. According to the previous experimental work [5], the vibration frequency of MgPc when the wave number is (502) cm^{-1} was convergent to the results calculation which was equal to (447.73) cm^{-1}. Furthermore, the vibration frequency values of H_2Pc were convergent to the wave number of MgPc as it is shown in Table 3.

Table 3: Vibration frequencies values of the molecule Phthalocyanine calculated through HyperChem8.0 program and compared with the experimental values.

Vibration	This Work		Previous Work
	Wave number Cal. H_2Pc By [HyperChem]	Wave number Cal. MgPc By [HyperChem]	Wave number Exp. [5]
1	15.43	31.64	
2	31.19	42.84	
8	103.73	109.39	
17	201.14	218.18	
26	305.03	294.53	
34	457.75	447.73	502
40	551.68	533.90	
44	570.69	576.93	
59	730.34	726.21	752
63	776.74	774.73	728
70	856.76	856.48	781
72	866.43	874.66	888
75	886.59	904.57	
80	912.97	935.91	956
85	1003.91	968.33	
96	1104.96	1102.59	1060
97	1106.05	1103.09	1084
98	1129.38	1103.36	1114
103	1150.40	1150.64	1163
107	1186.97	1173.63	
110	1221.92	1212.65	

Vibration	**This Work**		**Previous Work**
	Wave number Cal. H_2Pc By [HyperChem]	**Wave number Cal. MgPc By [HyperChem]**	**Wave number Exp. [5]**
112	1246.47	1254.35	1283
117	1298.72	1327.05	
120	1389.84	1380.47	
124	1471.44	1464.29	
130	1565.41	1558.29	

4. Conclusion:

The difference of structural parameters and spectral characteristics of the H_2Pc and MgPc molecules relied on the kind of the central metal. The equilibrium distance (the bond length) for H_2Pc and MgPc molecules is equal to (1.09 A°). Through the calculation of dissociation energy for the molecules, it is observed that H_2Pc molecule requires higher energy than MgPc molecules for bond dissociation at the same equilibrium point. The energy gap of H_2Pc and MgPc molecules were calculated by using IR spectra, the energy gap of H_2Pc was greater than MgPc molecule because the central metal of the atom is considered as the nearest approach to nitrogen atoms in parallel molecules and this leads to increase in the orbital overlaps among molecule's parallel pairs. Thus, any crystal change would cause an effect to the energy gap between conduction and valence bands. It is perceived that Heat of formation of the molecules has positive signals, therefore, these molecules are considered as heat absorbing compounds (Endothermic).

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