

## Studying the Physical Properties of Graphite and Diamond Using Molecular Modeling

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**Abstract:** Quantum mechanical semiempirical calculations are used to study some parameters like structure and vibrational characteristics of two carbon forms namely graphite and diamond. PM5 calculations are used to obtain the optimized structure subsequently the vibrational spectrum. Furthermore, the final heat of formation as a function of temperature and dipole moment contribution in X, Y and Z directions for both graphite and diamond in the temperature range from 200 K up to 500 K have been calculated. Obtained results confirm the fact that changing the carbon phase has a subsequent effect in changing carbon physical properties.

**Key words:** Graphite, diamond, PM5, Physical properties and Molecular Modelling.

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### INTRODUCTION

For many years, materials science has used molecular modelling methods to describe the various forms of Carbon.<sup>[1-4]</sup> Ab initio calculations were used to study of cubic diamond, including the calculation of electronic properties.<sup>[5]</sup> Density functional theory, DFT was used to study the surfaces and effects on crystalline stability of diamond nanowire<sup>[6]</sup> Both the structural properties of nanodiamond crystals, and the analogous diamond nanowires, as a function of crystallographic morphology were conducted using ab initio calculations<sup>[7]</sup> Furthermore, semiempirical methods were a subject of our research work for many systems and molecules whereas fast results are needed to describe their behaviour.<sup>[8-10]</sup> Many properties such as electronic, structural as well as spectroscopic properties were investigated with these methods.<sup>[11-15]</sup> This indicate the validity of such methods.

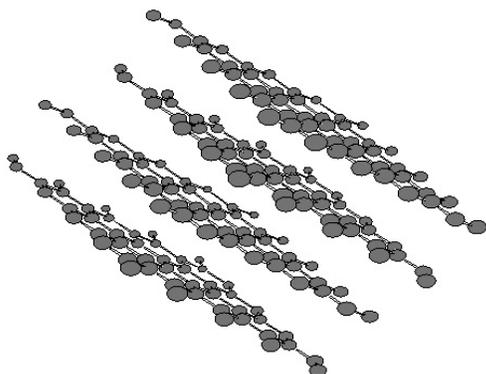
In the present work quantum mechanical methods PM5 was conducted to study some physical as well as vibrational properties of both graphite as well as diamond face centered cubic unit.

**2. Calculations Details:** Molecular modelling calculation was carried out on a personal computer performed using quantum mechanical methods as implemented with the MOPAC 2002 Version 1.33 CAChe Program (by Fujitsu). The geometry optimization of the diamond was optimized by semi empirical methods PM5.<sup>[16]</sup> The calculation was carried out at the RHF level. Vibrational frequencies were calculated at the same level of theory.

### RESULTS AND DISCUSSION

Both graphite as well as diamond was subjected to both geometry optimizations then the results will be discussed as in the following.

**3. 1. Modeling study for Graphite:** Carbon atoms are unique in that they are able to form many different kinds of bonds with other C atoms. The electronic configuration of C is  $1s^2 2s^2 2p^2$ . In the graphite crystal, the  $s$  orbital mixes with two  $p$  orbital only, and each of the new three  $sp^2$  orbital points to one of the three vertices of a triangle which lies in the  $x$ - $y$  plane (for instance). Three electrons occupy these orbital and one electron stays in the  $p_z$  orbital, which is directed, perpendicular to the  $x$ - $y$  plane. Hence, the C atoms are bonded by three  $\sigma$  bonds (the charge density lies between two atoms) and one  $\pi$  bond (the charge density is concentrated above and under the  $x$ - $y$  plane, perpendicular to the atomic bond). Since there is no preference as to which atom the  $p_z$ -electron should bond to, the bond formed ( $\pi$  bond) with all three neighbors is weaker than the  $\sigma$  bonds, this electron is free to move and contributes to conduction. Furthermore, the  $\pi$  bond stabilizes the structure and "locks" it in the plane.<sup>[17]</sup> Describing the bond of C is necessary toward understanding the nature and type of C. Graphite is optimized at semiempirical PM5 method in the optimized structure is indicated as in fig. 1. The model suggests that C atoms are arranged in four-layered lattice as in fig. 1. Graphite is layered. Within each layer, C atoms form strong covalent bonds in a hexagonal pattern (planar). A covalent bond is one



**Fig. 1:** PM5 Semiempirical optimized model of graphite which indicates the four layered lattice.

in which one or more pairs of bonding electrons (valence) are shared. C forms a double covalent bond, which means that two pairs of bonding electrons are shared. This type of bond is very strong. The bond length is 1.523 Å. The bonds between atoms of C in the layers of graphite may be strong, but the bonds that are formed by C atoms between layers are quite weak. Van Der Waal's forces hold these atoms together. This kind of attraction is caused by shifts in the cloud of electrons surrounding C nuclei. When the electron cloud shifts in a certain way, the C atom may become slightly negatively charged on one side and slightly positively charged on the other. The C atom becomes a dipole and induces other C atoms to become dipoles, as well. Since the whole crystal according to our model is made of 4 sheets are held together by weak Van der Waals forces, separated by a distance of 3.40 Å. This gives softness to the structure.<sup>[17,18]</sup> Saada stated that, the bond length of graphite is 1.421 Å.<sup>[19]</sup>

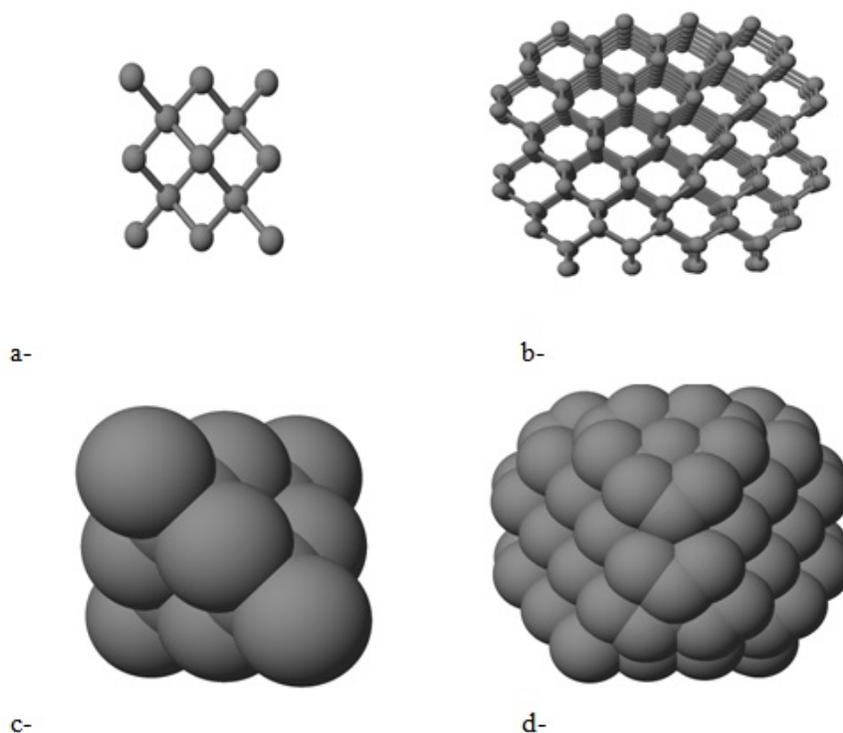
**3. 2. Modeling Study for Diamond:** Diamond was optimized using semiempirical quantum mechanical calculation PM5. First the diamond molecule is optimized then the vibration frequencies are calculated at the same level of theory and no negative frequencies were obtained which indicate that the calculated geometries are corresponding to the energy minimum and hence the structure is the optimized geometry. Figure 2a indicates the optimized structure of diamond unit cell. The optimized structure of diamond showed a face centered cubic unit. A crystal of diamond is indicated also in fig. 2b a simulation represents the surface of both diamond unit cell and diamond crystal is indicated in fig. 2c,d. The molecular point group for the diamond cell is  $C_1$ ; the symmetry number for point

group  $C_1$  is equal to 1. The vibration characteristic of diamond unit cell is indicated in fig. 3. There are 36 calculated vibration modes only 7 of them are active. The active vibration modes of diamond as regarded in fig. 8 are 240.9, 338.6, 628.6, 1022.7, 1252.9, 1397, 1640.8 and 1705  $\text{cm}^{-1}$  respectively. The number of active modes is lower than the calculated because the symmetry of the studied diamond molecule. As stated earlier, the calculated vibration modes indicated that the calculations were carried out upon the optimized structure, which is attributed to the absence of negative frequencies in the calculated spectrum.

**3. 3. Final Heat of Formation:** The final heat of formation for graphite as well as the diamond is plotted as a function of temperature from 200k up to 500k as in fig. 4 as well as table 1. It is relative to the elements in their standard state at 298 K. The figure indicate that the final heat of formation of graphite which is around 3900 Kcal/Mol is decreased sharply as indicated in case of diamond. This proofs that as the form and or phase of C changes its physical parameters is completely changes.

**3. 4. Total Dipole Moment:** Dipole moment is defined as the first derivative of energy with respect to an electric field.<sup>[20]</sup> The calculated dipole moment can be expressed in terms of vector in three directions X, Y and Z as indicated in table 2. It is considered as being the measure of asymmetry in the graphite as well as diamond charge distribution. The negative sign of both X and Y-axis indicates that the dipole moment is pointing away from X and Y direction, while the positive sign of Z-axis indicates that it points in Z direction. Regarding table 2 one can conclude that, the total dipole moment and the net contribution of charge in the directions x, y and z are completely changes as one moves from graphite to C. The total dipole moment is decrease sharply from 10.3 to 2.6 debye corresponding to graphite and diamond respectively.

**4. Conclusion:** PM5 model proves that as a result of changing carbon form some physical changes took place. Furthermore, results indicate a change in the final heat of formation as a function of temperature and dipole moment contribution in X, Y and Z directions in terms of the carbon forms either graphite form or diamond form. It could be concluded that diamond properties are quite far from that of graphite which confirm that fact that changing carbon from phase to another leads to a change in physical properties.



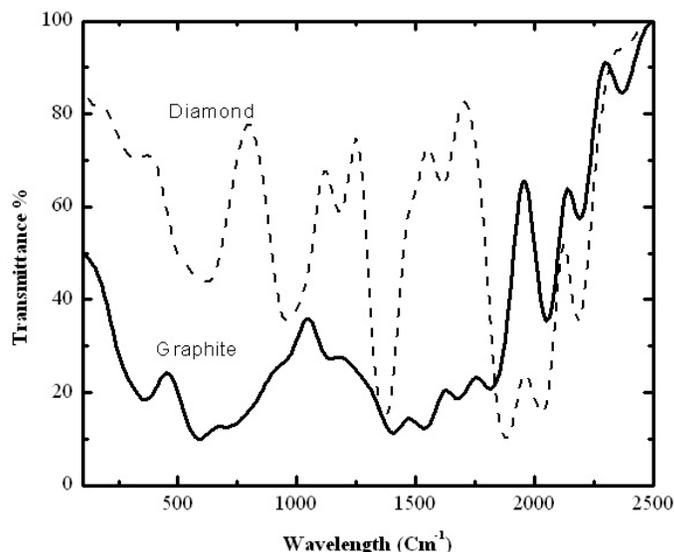
**Fig. 2:** Optimized structure of diamond which has a face-centered cubic arrangement, a- diamond unit cell, b- diamond crystal, c- simulated surface of diamond unit cell and d- simulation of the diamond crystal.

**Table 1:** Calculated final heat of formation in the unit of Kcal/Mol as a function of temperature for both graphite and diamond in the temperature range from 200 k up to 500k.

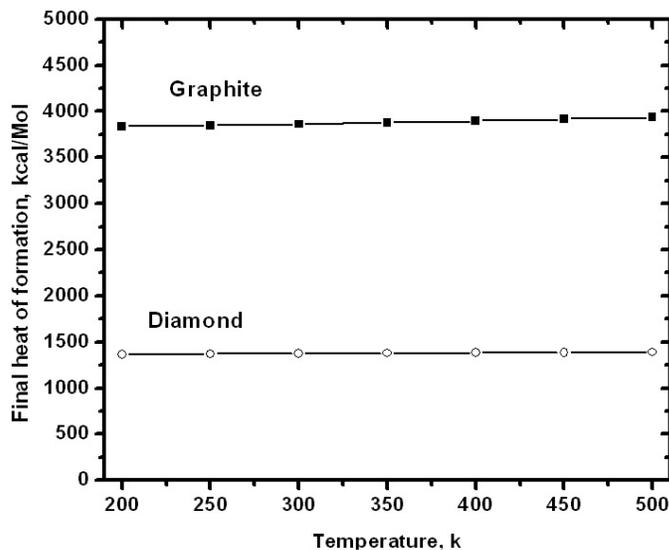
Temperature	Graphite	Diamond
200	3836.176	1365.522
250	3847.882	1368.751
300	3862.046	1372.426
350	3878.460	1376.490
400	3896.923	1380.899
450	3917.247	1385.613
500	3939.254	1390.598

**Table 2:** PM5 calculated dipole moment contribution in X, Y and Z directions for both graphite as well as diamond.

Graphite				
Dipole	X	Y	Z	Total
Point-Charge	-1.865	0.560	-2.421	3.106
Hybrid	-5.518	5.932	-0.782	8.140
Sum	-7.383	6.492	-3.203	10.340
Diamond				
Dipole	X	Y	Z	Total
Point-Charge	1.750	1.136	1.127	2.372
Hybrid	0.273	-1.669	0.496	1.762
Sum	2.023	-0.533	1.624	2.648



**Fig. 3:** Calculated infrared spectrum for both graphite as well as diamond at PM5 semiempirical level of theory.



**Fig. 4:** Final heat of formation in the unit of Kcal/Mol as a function of temperature for both graphite and diamond in the temperature range from 200 k up to 500k.

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