Journal of Physical and Theoretical Chemistry
of Islamic Azad University of Iran, 8 (3) 199-204: Fall 2011
(J. Phys. Theor. Chem. IAU Iran)
ISSN 1735-2126

AB Initio Study of Molecular Struture, Energetic and Vibrational Spectra of $(GaN)_4$ Nanosemiconductor

E. Pournamdari[1*] and M. khaleghian[2]
[1] Ph.D. Student, Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran
[2] Department of Chemistry, Islamshar Branch, Islamic Azad University, Tehran, Iran

Received November 2011; Accepted November 2011

ABSTRACT

In recent years there has been considerable interest in the structures, energies and thermodynamics of $(GaN)_4$ clusters and it is the subject of many experimental and theoretical studies because of their fundamental importance in chemical and physical process. All calculation of this study is carried out by Gaussian 98. Geometry optimization for $(GaN)_4$ nanocluster are be fulfilled at B3LYP, B1LYP and LSDA levels of theory with LANL2DZ basis set. Calculated are accomplished at 298 K. The structures, energetic and thermodynamic properties and vibrational spectra will be discussed.

Keywords: Nanocluster; Semiconductor; Ab Initio; IR, Vibrational Frequencies; Structure; Energetic

Archive of SID

INTRODUCTION

Recent progress in the synthesis and characterization of one-dimensional nanostructures has been driven by the need to understand the novel physical properties of one-dimensional nanoscale materials, and their potential application in constructing nanoscale electronic and optoelectronic devices [1]. Group III–V semiconductors are promising materials because of the potential applications in optical communications and full colour displays. GaN is a wide and direct band-gap semiconductor, which exhibits less thermal quenching and stronger RE emission at room temperature [2]. The wide-band-gap semiconductor GaN is currently of great interest for development of optoelectronic devices at blue and near-ultraviolet wavelengths as well as high-temperature and -frequency electronics, such as violet light emitting diodes (LEDs). The one-dimensional GaN semiconductor nanostructures are electronic confines systems ideal for fundamental studies of their physical properties and for the fabrications of new optoelectronic nanodevices [3]. Over a past decade, different high performance devices systems with nitride material have been concentrated for intense research [4–6]. These materials represent wide band gaps in the ultraviolet (UV) and visible (VIS) range, i.e. Eg (eV) =6.2 (AlN), 3.4 (GaN) and 1.9 (InN) [7]. Current GaN-based device technologies include light-emitting diodes (LEDs), laser diodes and UV detectors on the photonic side and microwave power and ultra-high power switches on the electronics side [8].

The applications for GaN-based devices include displays and data storage, solar-blind UV detectors, new sensor technologies, wireless communications, solid-state lighting and high power microwave generation for radar [9]. In order to growth of GaN and relative semiconductors

[*] Corresponding author: E. Pournamdari

www.SID.ir

synthesis the most usual techniques are Metalorganic chemical simulavapor deposition and molecular beam epitaxy (MBE). However, in spite of lots of efforts made in the past decades, many fundamental problems related to a growth mechanism still remain unsolved. Even though there are many experimental studies of group IIIA nitrides [10-21], the GaN formation kinetics, for example, is still not well understood. Up to now, Monte Carlo simulation has been widely used for studying GaAs growth mechanisms and its related semiconductors [22, 23]. The information on the structural, energetic and thermodynamics properties of this class of materials was in favour due to our little physical information about them. In this letter, we demonstrated atomic structure of $(GaN)_4$ with ab initio method using density functional theory calculations with LANL2DZ basis set for representing energies, enthalpies, thermochemistry parameters and vibrational spectra. The details of the computational method will be given in the next chapter.

COMPUTATIONAL DETAIL

Ab initio techniques provide detailed information that was unavailable experimentally. Our calculations on $(GaN)_4$ clusters are based on first-principles density functional theory (DFT) [24, 25] because electron correlation effects play an important role on these systems. A DFT study of this system were performed using the GAUSSIAN 98 package of programs [22] by employing B3LYP, B1LYP and LSDA density functional model which exhibits good performance on electron affinities, excellent performance on bond energies and reasonably good performance on vibrational frequencies and geometries of inorganic or ion compounds [23] as well as organic and neutral compounds [24], combined with the Lanl (Los Alamos National Laboratory) basis sets, also known as Lanl2dz (Lanl-2-double zeta) and developed by Hay and Wadt [25] have been widely used in quantum chemistry, particularly in the study of compounds containing heavy elements. Geometry optimizations have been carried out for this cluster. A molecular representation of this system can be found in Fig. 1 and the results are discussed in more details in the next sections. Herein, we report, structures, energetic, thermodynamic investigation and vibrational spectra of this system.

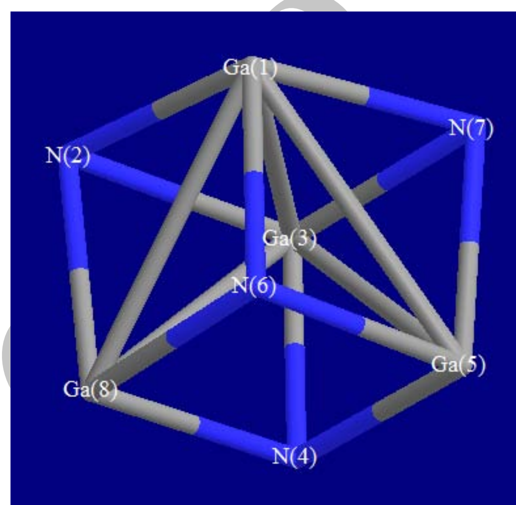

Fig. 1. Atomic structures of $(GaN)_4$ semiconductor with Td point group.

RESULTS and DISCUSSION

Structure

Based on the optimized structure parameters $(GaN)_4$ system is constructed for calculations, which contains 8 atoms in this nanocluster using different methods of density functional theory (DFT) with LANL2DZ basis set. Calculated and observed bond lengths and angles of this system represented in table 1 which the variation and comparison between B3LYP, B1LYP and LSDA methods were demonstrated. It should be noted that there is a little variation between them.

Energies and thermodynamic quantities

As a matter of fact, the energies and thermo chemical parameters can give valuable

Archive of SID

www.SID.ir

information about structures and relative stabilities of these systems. The relative stability of various structures of $(GaN)_4$ nanocluster are computed in DFT methods using B3LYP, B1LYP and LSDA levels of theory which present thermodynamic properties of $(GaN)_4$ and comparison of these different levels with each other's were shown in table 2 . The energetic information is thermodynamically favoured to determine the most stable structure at finite pressure and temperature in which individual terms are refered to 298K, and the Gibbs free energy $G = E+pV-TS$ should be used. To verify structural stability of our system we have optimized $(GaN)_4$. As can be seen in fig. 2, the ΔG value decreased from B3LYP to LSDA, although the relative differences of the ΔG are almost the same as the ΔH and ΔE. Therefore, in this paper, by using ab initio calculations, we analyze the Gibbs free energy of the formation. We found that between these methods, the results obtained at the LSDA level are more negative than those of the other calculations though LSDA shows the best results for $(GaN)_4$ systems which are the most stable one with the minimum at 590.2 kcal/Mol. As can be seen in fig. 3 which display different levels of theory as a function of energy (scf) the lowest value of energy is belong to LSDA levels at the -0.95 kcal/Mol for $(GaN)_4$ systems which indicate that at this point our system have got the most stability.

Table 1. Optimized parameters of Bond length (angstrom) and Bond angle (degree) for $(GaN)_4$ system calculated in B3LYP, B1LYP and LSDA levels of theory using LANL2DZ basis

Basis set			LANL2DZ								
					Method						
B3LYP				B1LYP				LSDA			
Bond length		Bond angles		Bond length		Bond angles		Bond length		Bond angles	
R(1,2)	2.0558	A(2,1,6)	92.8765	R(1,2)	2.0471	A(2,1,6)	93.7128	R(1,2)	2.0568	A(2,1,6)	88.8756
R(1,6)	1.8817	A(2,1,7)	97.3979	R(1,6)	1.882	A(2,1,7)	98.0034	R(1,6)	1.9016	A(2,1,7)	93.5107
R(1,7)	2.0558	A(6,1,7)	92.8771	R(1,7)	2.0471	A(6,1,7)	93.7126	R(1,7)	2.0568	A(6,1,7)	88.8756
R(2,3)	2.0558	A(1,2,3)	82.3546	R(2,3)	2.0471	A(1,2,3)	81.6455	R(2,3)	2.0568	A(1,2,3)	86.4855
R(2,8)	2.0366	A(1,2,8)	84.3451	R(2,8)	2.037	A(1,2,8)	83.5409	R(2,8)	1.9968	A(1,2,8)	89.162
R(3,4)	1.8816	A(3,2,8)	84.3582	R(3,4)	1.882	A(3,2,8)	83.5467	R(3,4)	1.9017	A(3,2,8)	89.1633
R(3,7)	2.0559	A(2,3,4)	92.8605	R(3,7)	2.0471	A(2,3,4)	93.705	R(3,7)	2.0568	A(2,3,4)	88.8746
R(4,5)	1.9575	A(2,3,7)	97.397	R(4,5)	1.9489	A(2,3,7)	98.0033	R(4,5)	1.9926	A(2,3,7)	93.5106
R(4,8)	1.9575	A(4,3,7)	92.8601	R(4,8)	1.9489	A(4,3,7)	93.7048	R(4,8)	1.9926	A(4,3,7)	88.8747
R(5,6)	1.9576	A(3,4,5)	91.3908	R(5,6)	1.949	A(3,4,5)	90.4873	R(5,6)	1.9926	A(3,4,5)	93.8669
R(5,7)	2.0366	A(3,4,8)	91.3902	R(5,7)	2.037	A(3,4,8)	90.4871	R(5,7)	1.9968	A(3,4,8)	93.867
R(6,8)	1.9576	A(5,4,8)	91.5722	R(6,8)	1.949	A(5,4,8)	90.9723	R(6,8)	1.9926	A(5,4,8)	92.7554
-	-	A(4,5,6)	88.3403	-	-	A(4,5,6)	88.9892	-	-	A(4,5,6)	86.9156
-	-	A(4,5,7)	91.245	-	-	A(4,5,7)	92.041	-	-	A(4,5,7)	88.094
-	-	A(6,5,7)	91.2609	-	-	A(6,5,7)	92.048	-	-	A(6,5,7)	88.0951
-	-	A(1,6,5)	91.3707	-	-	A(1,6,5)	90.4778	-	-	A(1,6,5)	93.8663
-	-	A(1,6,8)	91.371	-	-	A(1,6,8)	90.4776	-	-	A(1,6,8)	93.8662
-	-	A(5,6,8)	91.5681	-	-	A(5,6,8)	90.969	-	-	A(5,6,8)	92.7564
-	-	A(1,7,3)	82.3532	-	-	A(1,7,3)	81.6454	-	-	A(1,7,3)	86.4856
-	-	A(1,7,5)	84.344	-	-	A(1,7,5)	83.5409	-	-	A(1,7,5)	89.162
-	-	A(3,7,5)	84.3571	-	-	A(3,7,5)	83.5467	-	-	A(3,7,5)	89.1634
-	-	A(2,8,4)	91.2442	-	-	A(2,8,4)	92.041	-	-	A(2,8,4)	88.0941
-	-	A(2,8,6)	91.2601	-	-	A(2,8,6)	92.0481	-	-	A(2,8,6)	88.0951
-	-	A(4,8,6)	88.34	-	-	A(4,8,6)	88.9891	-	-	A(4,8,6)	86.9157

Table 2. Relative thermodynamic data for $(GaN)_4$ system in kcal/mol and antropy in cal/mol.kelvin

Basis set			LANL2DZ		
Method	**E(scf)**	***ΔE***	***ΔH***	***ΔG***	***S***
B3LYP	0.00	0.00	0.00	0.00	97.868
B1LYP	-0.16	-101.51	-101.51	-101.47	97.993
LSDA	-0.95	-590.07	-590.07	-590.2	97.444

www.SID.ir

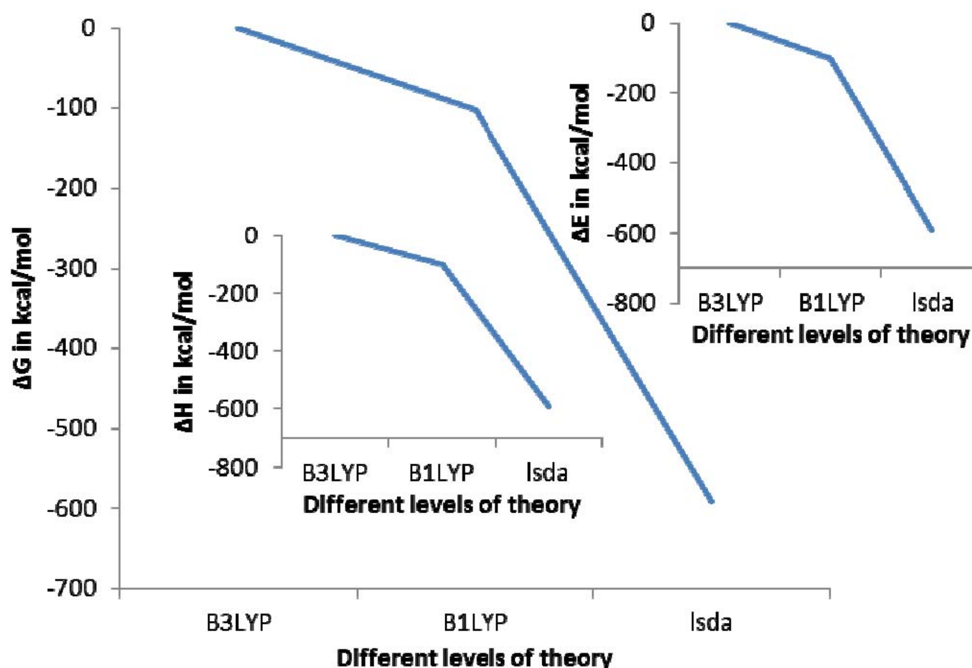

Fig. 2. Different levels of theory as a function of ΔG, ΔH, ΔE in kcal/mol.

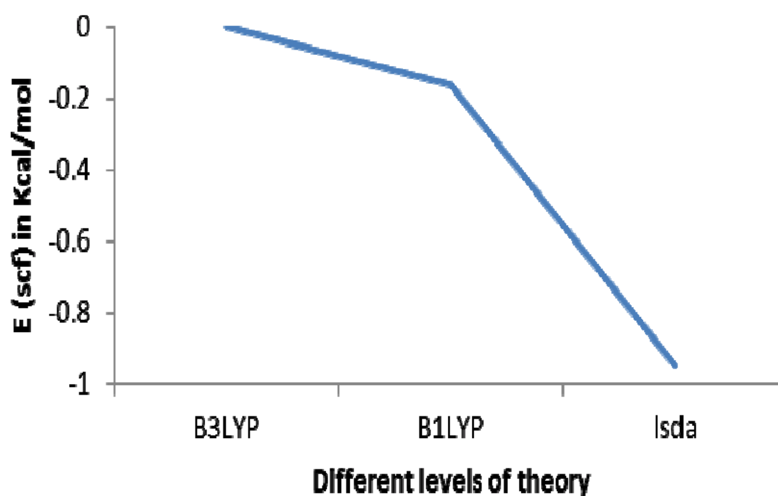

Fig. 3. Different levels of theory as a function of energy (scf) in kcal/mol.

Vibrational spectra

Frequency and IR intensities of $(GaN)_4$ nanosemiconductor cluster are calculated with B3LYP, B1LYP and LSDA methods using LANL2DZ basis sets and IR spectrum of this nanocluster shown in fig. 4, 5, 6 for B3LYP, B1LYP and LSDA methods of density functional theory (DFT), respectively. As can be seen the maximum intensity in B3LYP levels of theory is at frequencies of 486.812 $cm^{-1}$with 160.736 intensities, for B1LYP is at frequencies of 485.494 cm^{-1} with 162.834 intensities and for LSDA levels of theory is at frequencies of 492.57 cm^{-1} with 139.749 intensities. LSDA method has largest blue shift in

www.SID.ir

comparison of B3LYP and B1LYP levels of theory.

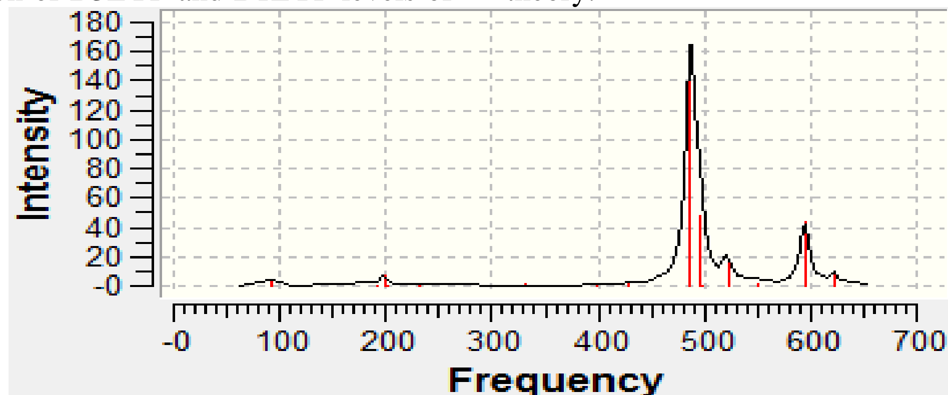

Fig. 4. IR spectrum of $(GaN)_4$ system obtained from B3LYP/LANL2DZ methods.

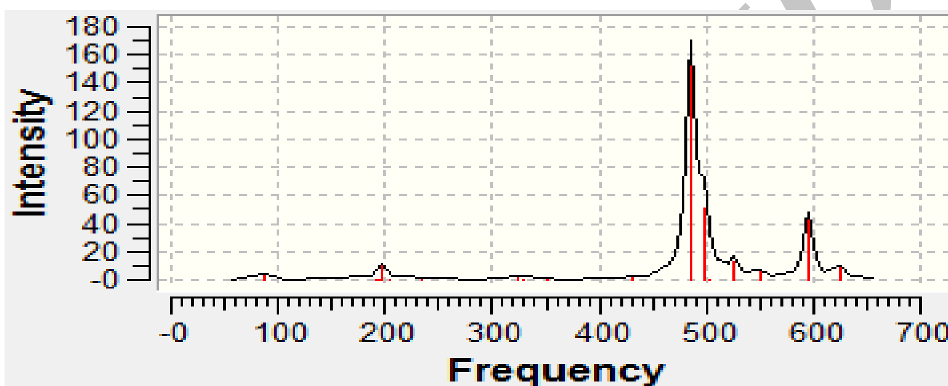

Fig. 5. IR spectrum of $(GaN)_4$ system obtained from B1LYP/LANL2DZ methods.

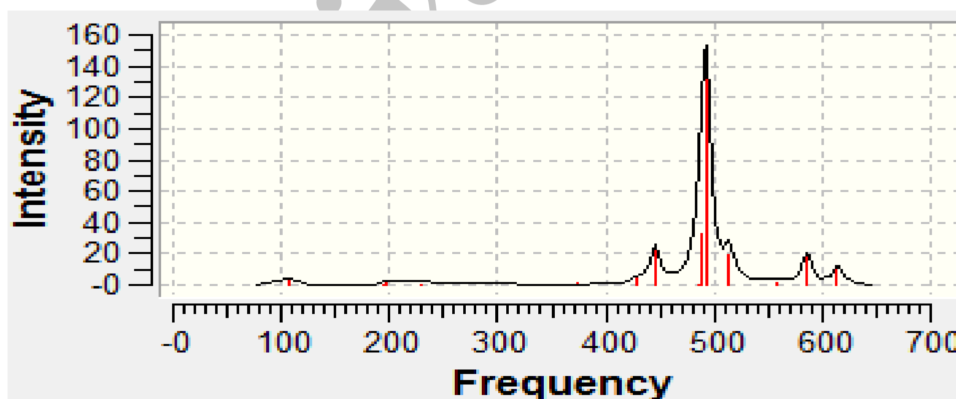

Fig. 6. IR spectrum of $(GaN)_4$ system obtained from LSDA/LANL2DZ methods.

REFERENCES

[1] J. T. Hu, T.W. Odom and C. M. Lieber, Acc. Chem. Res., 32 (1999) 435.

[2] P. N. Favennec, H. L'Haridon, M. Salvi, D. Moutonnet and Y. Le Guillou, J.Electron. Lett., 25 (1989) 718.

[3] T. P. Chow, R. Tyagi and IEEE Trans. Electron. Devices, J. 41 (1994) 1481.

[4] Y. F. Wu, B. P. Keller, S. Keller, D. Kapolnek, P. Kozodoy, S. Denbaars and U.K. Mishra, J. Appl. Phys. Lett., J. 69 (1996) 1438.

[5] R. J. Trew, M.W. Shin, V. Gatto, J. Solid-State Electron, 41 (1997) 1561.

www.SID.ir

[6] R. Gaska, M. S. Shur, A. D. Bykhovski, A.O. Oriov, G.L. Srider, J.Appl. Phys. Lett., 74 (1999) 287.

[7] (a) G. P. Pomrenke, P. B. Klein, D. W. Lange (Eds.), Mater. Res. Soc. Symp. Proc. MRS, Pittsburgh, PA., 301(1993). (b) S. Cotta, A. Polman, R.N. Schwartz (Eds.), Mater. Res. Soc. Symp. Proc. MRS, Pittsburgh, PA., 422 (1996).

[8] See for example GaN and Related Materials, ed. S.J. Pearton (Gordon and Breach, NY, (1997) and GaN, ed. J.I. Pankove and T. D. Moustakas (Academic Press, San Diego 1988), and references therein.

[9] SJ. Pearton, J.C. Zolper, RJ. Shul and F.Ren " GaN: DEFECT AND DEVICE ISSUES ".

[10] Ve´zian, S.; Le Louarn, A and Massies, J. J. Cryst. Growth., 303 (2007) 419.

[11] Meng, G.; Liu, X.; Xie, S. and Peng, D. J. Cryst. Growth., 232 (1996) 163.

[12] Yang, Y.-G.; Ma, H.-L.; Xue, C.-S; Hao, X.-T.; Zhuang, H.-Z and Ma, J. Physica, B325 (2003) 230.

[13] Xue, C.; Yang, L.; Wang, C.; Zhuang, H. and Wei, Q. J.Appl. Surf. Sci.153 (2003) 210.

[14] Dadgar, A.; Schulze, F.; Wienecke, M.; Gadanecz, A.; Bla¨sing, J;. Veit, P.; Hempel, T.; Diez, A.; Christen, J.and Krost, A. New J. Phys., 389 (2007) 9.

[15] Takemoto, K.; Murakami, H.; Iwamoto, T.; Matsuo, Y.; Kangawa, Y.; Kumagai and Y.; Koukitu and A. Jpn, J. Appl. Phys. 45 (2006) L478.

[16] Naritsuka, S.; Kondo, T.; Otsubo, H.; Saitoh, K.; Yamamoto, Y and Maruyama, T. J, Cryst. Growth, 300 (2007) 118.

[17] Ishikawa, H.; Yamamoto, K.; Egawa, T.; Soga, T.; Jimbo, T;. Umeno and M. J, Cryst. Growth 189/190 (1998) 178.

[18] Wu, Y.; Xue, C.; Zhuang, H.; Tian, D.; Liu, Y.; He, J.; Wang, F;. Sun, L. and Ai, Y. Mater, J. Lett, 60 (2006) 3076.

[19] Ji, X. H.; Lau, S. P.; Yang, H. J. and Zhang, Q. Y, J. Thin Solid Films.515, (2007)4619.

[20] Chang, K. J.; Chang, J. Y.; Chen, M. C.; Lahn, S. M.; Kao, C. J;. Li, Z. Y.; Uen, W. Y.; Chi, G. C, J. Vac. Sci. Technol. 25 (2007) 701.

[21] Yodo, T.; Shimada, T.; Tagawa, S.; Harada, Y, J. Cryst. Growth. 301-302, (2007), 504.

[22] Gaussian 98, Revision A.7, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr,.R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi,V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi ,R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.

[23] Check C. E., Faust T. O., Bailey J. M., Wright B. J., Gilbert T. M. and Sunderlin L. S., J. Physical Chemistry A, 105 (34), (2001) 8111.

[24] Parlak C, J. Molecular Structure, 966 (1-3) (2010) 1.

[25] Hay P.J. and Wadt W.R., J. Chem. Phys 82 (1) (1985) 270.

Archive of SID

www.SID.ir