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Comparison of DFT methods for molecular structure and vibrational spectrum of pyrimidine molecule

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ABSTRACT

The effect of ten chosen Density Functional Theory (DFT) methods at various basis sets for predicting the molecular structure, vibrational frequencies and infrared intensities of pyrimidine molecule has been investigated. The exchange functionals DFT employed in this study include local (SVWN), Gradient corrected (BLYP, PW91PW91, mPWPW91, G96LYP, PBEPBE) and hybrid (B3LYP, B3PW91, mPW1LYP, mPW1PW91) and basis sets include Pople basis sets 6-311G(d,p), 6-311++G(d,p), 6-311G(2d,2p), 6-311++G(2d,2p), 6-311G(3d,3p) 6-311++G(3d,3p), 6-311G(2df,2pd) 6-311++G(2df,2pd), 6-311G(3df,3pd), 6-311++G(3df,3pd) and Dunning's correlation-consistent basis sets cc-pVDZ, aug-cc-pVDZ, cc-pVTZ and aug-cc-pVTZ. The results are compared with the available experimental data in the gas phase. Bond distances and bond angles computed at the PBEPBE/6-311G (3df, 3pd) level are in good agreement with the available experimental data. The results also indicate that for the vibrational spectrum of pyrimidine, B3LYP/6-311++G(d,p) result shows a good agreement with the experimental results than other DFT methods.

Keywords: DFT Methods, Vibrational Frequencies, Basis Sets, Molecular Structure, Pyrimidine.

INTRODUCTION

Pyrimidine (Pd) is the parent heterocyclic of a very important group of compounds that have been studied extensively because of their occurrence in living systems [1, 2]. Pyrimidine and its derivatives possess remarkable biological activity and they have been used widely in the fields ranging from medicinal to industrial applications. The pyrimidine ring system provides a potential binding site for metals and hence any information on their coordinating property is important for understanding the role of metal ions in biological systems, which are extremely vital for many life processes.

A large number of studies on the vibrational spectroscopy of pyrimidine reported after the publication of the papers by Ito et al [3] and Lord et al [4]. These reports describe investigations of the compound in the vapor phase [5], in the neat condensed phases and in solutions [6-9] as well as the results of theoretical predictions [10, 11]. The molecular structure of pyrimidine in the gas-phase was investigated using electron diffraction by Fernholt et al [12] and using rotational spectroscopy by Kisiel et al [13]. The crystal structure of the compound was solved much earlier by Wheatley [14].

Density functional theory (DFT) is a quantum mechanical modeling method used in physics and chemistry to investigate the electronic structure of many-body systems, in particular atoms, molecules, and the condensed phases [15]. With DFT, the properties of a many-electron system can be determined by using functional, i.e. functions of another function, which in this case are the spatially dependent electron densities. Hence the name density functional theory comes from the use of functional of the electron density. DFT is among the most popular and versatile methods available in condensed-matter physics, computational physics, and computational chemistry. DFT has been very popular for calculations in solid-state physics since the 1970s. However, DFT was not considered accurate enough for calculations in quantum chemistry until the 1990s, when the approximations used in the theory were greatly refined to improve the exchange and correlation interactions modeling. In many cases the results of DFT calculations for solid state systems agree quite satisfactorily with experimental data. Computational costs are relatively low when compared to traditional methods, such as Hartree–Fock theory and its descendants based on the complex many-electron wave function. Since there are a large variety of DFT methods, choosing appropriate method and basis set are of crucial importance especially when dealing with large biological molecules with hetero-aromatic rings. Previous studies show that select and use of appropriate methods, computational tasks and basis sets are related to the structure under investigation [16, 17]. Numerous reports have been made citing the successes of density functional theory (DFT) compared to conventional methods, in computing molecular and chemical properties such as geometries, harmonic frequencies, and energies [15–17]. Therefore, the DFT method was chosen as the basic method in the present paper for calculating the geometries and vibrational frequencies of Pyrimidine. Yue Yang et al [18,19] and M. Malekzadeh [20] studied the comparative study of various DFT methods for chosen molecules.

The aim of this work is the comparison of a series of different DFT methods and higher basis sets than above studied in order to find a more suitable method and basis set in predicting geometry and vibration spectra of Pyrimidine.

EXPERIMENTAL SECTION

DFT methods can be divided into three groups on the basis of their exchange functional including local, gradient-corrected and hybrid methods. Local exchange functional assumes that exchange-correlation energy at any point in space is only a function of the electron density at that point in space and can be given by the electron density of a homogeneous electron gas of the same density. The only local exchange functional available in *Gaussian* is the Slater exchange functional (S) [21] which utilizes local VWN [22] correlation functional. Gradient corrected exchange functional assumes that exchange and correlation energies dependent not only on the density but also on the gradient of the density. The gradient-corrected exchange functionals studied include Becke88 (B) [23], Perdew-Wang (PW91)[24] , Modified Perdew-Wang by Barone and Adamo (mPW)[25], Gill96 (G96) [26], Perdew-Burke-Ernzerhof (PBE) [27, 28] and the gradient-corrected correlation functionals include Lee, Yang, and Parr (LYP) [29], Perdew-Wang (PW91)[24], Perdew-Burke-Ernzerhof (PBE)[27, 28]. Aside from above "pure" DFT methods, another group of hybrid functionals exists, which include a mixture of Hartree-Fock exchange with DFT exchange-correlation. Hybrid-DFT is a very attractive alternative for the structural and thermo chemical applications due to the good performance and low cost. Becke Three Parameter Hybrid Functional (B3) [30], and one parameter hybrid modified Perdew-Wang (mPW1) exchange functionals of Adamo and Barone [25]. These functional have been proved to be a successful approach to obtain accurate molecular structures, vibrational frequencies and bond energies.

The molecular geometry optimization and frequency calculation of Pyrimidine were performed on the basis of the chosen ten density functional theory (DFT) methods with the program GAUSSIAN 09 [31]. For all computations the starting geometry of Pyrimidine was the same and all computations were carried out in gas phase. The geometries of Pyrimidine have been optimized through the application of ten chosen density functional theory methods including SVWN, BLYP, PW91PW91, mPWPW91, G96LYP, PBEPBE, B3LYP, B3PW91, mPW1LYP, mPW1PW91 with fourteen basis sets including 6-311G(d,p), 6-311++G(d,p), 6-311G(2d,2p), 6-311++G(2d,2p), 6-311G(3d,3p) 6-311++G(3d,3p), 6-311G(2df,2pd), 6-311++G(2df,2pd), 6-311G(3df,3pd), 6-311++G(3df,3pd), cc-pVDZ, aug-cc-pVDZ, cc-pVTZ and aug-cc-pVTZ. This was followed by harmonic frequency calculations at the same level of theory and compare the all the normal modes of pyrimidine e.g. υ_{16a}, υ_{16b}, υ_{6b}, υ_{6a}, υ_{4}, υ_{10b}, υ_{11}, υ_{17a}, υ_{5}, υ_{1}, υ_{18b}, υ_{12}, υ_{9a}, υ_{15}, υ_{3}, υ_{14}, υ_{19b}, υ_{19a}, υ_{8b}, υ_{8a}, υ_{13}, υ_{2}, υ_{20a}, and υ_{7b} in the notation of Lord et al [4]. The calculated vibration frequencies and infrared intensity of the vibration normal modes using Gaussian 09 are picked up by the GAUSSVIEW [32]. In order to better compare the calculated and experimental data of Pyrimidine and to determine which method give the best agreement, we also calculated the mean absolute deviations between the calculated and experimental data.

RESULTS AND DISCUSSION

The purpose of this calculation on pyrimidine molecule is to compare various DFT methods at 6-311 G(3df,3pd) basis set to calculate the exact level of optimized energy and dipole moment. The results are shown in Table 1. The pyrimidine molecule is found to be most stable at B3LYP level and least stable at SVWN level. Also the dipole moment is maximum at B3PW91 and mPW1PW91 which indicate that strongest intermolecular attraction in optimized structure is at B3PW91 and mPW1PW91.

Table:1 Parameters corresponding to optimized geometry calculated for Pyrimidine with various DFT Methods at 6-311G(3df,3pd) basis set

Sr. No.	DFT Method	Total Energy (Hartree)	Dipole Moment (Debye)
1.	SVWN	-262.93750959	2.200
2.	BLYP	-264.32125142	2.159
3.	PW91PW91	-264.30983452	2.151
4.	mPWPW91	-264.37571362	2.157
5.	G96LYP	-264.30327111	2.178
6.	PBEPBE	-264.08422447	2.148
7.	B3LYP	-264.40970033	2.206
8.	B3PW91	-264.30118360	2.207
9.	mPW1LYP	-264.27718279	2.205
10.	mPW1PW91	-264.33811607	2.207

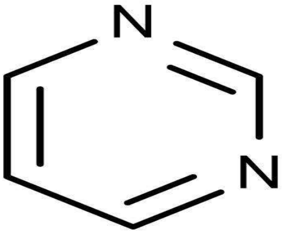

Fig.1. The chemical structure of pyrimidine

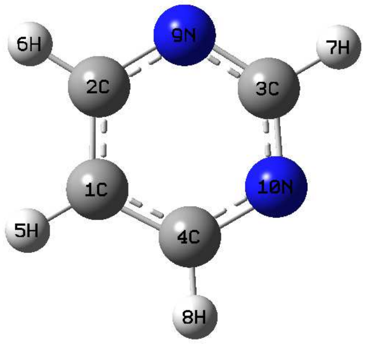

Fig.2. The optimized structure of Pyrimidine at B3LYP/6-311(3df,3pd) and number assigned for the atoms

3.1. Optimization parameters calculated with various methods at 6-311G(3df, 3pd) basis set

The chemical structure of Pyrimidine is shown in Figure 1. Figure 2 represents the optimized structure of pyrimidine at B3LYP/6-311G(3df, 3pd) level. The optimized structures of pyrimidine using other methods which investigated in this study are similar to ones of pyrimidine calculated at B3LYP/6-311G(3df, 3pd) level. The optimized geometrical parameters determined with SVWN, BLYP, PW91PW91, mPWPW91, G96LYP, PBEPBE, B3LYP, B3PW91, mPW1LYP, mPW1PW91 methods at 6-311G(3df, 3pd) basis set for molecule are shown in Table 2. The values are compared with experimental data obtained in Gas phase by the electron diffraction method [12]. To compare the bond lengths obtained from different DFT methods at 6-311G(3df, 3pd), the mean absolute deviations between the calculated and experimental value have been determined. It has been found that bond length calculated by SVWN, BLYP, PW91PW91, mPWPW91, G96LYP, PBEPBE, B3LYP, B3PW91, mPW1LYP and mPW1PW91 have mean absolute deviations of 0.0103 Å, 0.0062 Å, 0.0038 Å, 0.0032 Å, 0.0054 Å, 0.0027 Å, 0.0107 Å, 0.0114 Å, 0.0120 Å and 0.0132 Å respectively. Average absolute deviations for different DFT methods at 6-311G(3df, 3pd) have been shown in figure 3. We see that PBEPBE functional gives the best result in bond length calculation of pyrimidine. Figure 4 shows the correlation between the experimental [12] and calculated bond lenths with PBEPBE method at 6-311(3df,3pd) basis set.

Table 2 Comparison of bond lengths (in Å) and bond angles (in ^{0}) calculated for pyrimidine with various DFT Methods at 6-311G(3df,3pd) basis set

Geometry	Expt. [12]	6-311G(3df,3pd)									
		SVWN	**BLYP**	**PW91PW91**	**mPWPW91**	**G96LYP**	**PBEPBE**	**B3LYP**	**B3PW91**	**mPW1LYP**	**mPW1PW91**
C1-C2	1.393	1.3805	1.3969	1.3921	1.3929	1.3955	1.3937	1.3867	1.3848	1.3855	1.3834
C1-C4	1.393	1.3805	1.3969	1.3921	1.3929	1.3955	1.3937	1.3867	1.3848	1.3855	1.3834
C1-H5	1.099	1.0909	1.0875	1.0882	1.0882	1.0869	1.09	1.0805	1.0816	1.0791	1.0804
C2-H6	1.099	1.0958	1.0912	1.0921	1.0924	1.0908	1.0942	1.0845	1.086	1.0831	1.0848
C2-N9	1.340	1.325	1.3449	1.3392	1.3403	1.3432	1.3408	1.3326	1.3303	1.3313	1.3276
C3-H7	1.099	1.096	1.0909	1.0918	1.0923	1.0905	1.0941	1.0842	1.0859	1.0828	1.0845
C3-N9	1.340	1.3246	1.3444	1.3386	1.3397	1.3427	1.3402	1.3315	1.329	1.33	1.3266
C3-N12	1.340	1.3246	1.3444	1.3386	1.3397	1.3427	1.3402	1.3315	1.329	1.33	1.3266
C4-H8	1.099	1.0958	1.0912	1.0921	1.0924	1.0908	1.0942	1.0845	1.086	1.0831	1.0848
C4-N12	1.340	1.325	1.3449	1.3392	1.3403	1.3432	1.3408	1.3326	1.3303	1.3313	1.3276
Mean absolute deviations		**0.0103**	**0.0062**	**0.0038**	**0.0032**	**0.0054**	**0.0027**	**0.0107**	**0.0114**	**0.0120**	**0.0132**
□C2C1C4	116.8	116.6	116.7	116.6	116.6	116.7	116.6	116.6	116.5	116.6	116.5
□C2C1H5	121.6	121.7	121.6	121.7	121.7	121.7	121.7	121.7	121.7	121.7	121.8
□C4C1H5	121.6	121.7	121.6	121.7	121.7	121.7	121.7	121.7	121.7	121.7	121.8
□C1C2H6	121.6	121.1	121.2	121.2	121.2	121.2	121.2	121.2	121.2	121.2	121.2
□C1C2N9	122.3	122.1	122.3	122.4	122.4	122.3	122.4	122.2	122.3	122.2	122.3
□H6C2N9	115.3	116.7	116.5	116.5	116.4	116.5	116.4	116.6	116.5	116.6	116.5
□H7C3N9	115.3	116.5	116.3	116.2	116.2	116.4	116.2	116.5	116.4	116.5	116.4
□H7C3N12	115.3	116.5	116.3	116.2	116.2	116.4	116.2	116.5	116.4	116.5	116.4
□N9C3N12	127.6	126.9	127.3	127.5	127.5	127.3	127.6	127.0	127.2	126.9	127.2
□C1C4H8	121.6	121.1	121.2	121.2	121.2	121.2	121.2	121.2	121.2	121.2	121.2
□C1C4N12	122.3	122.1	122.3	122.4	122.4	122.3	122.4	122.2	122.3	122.2	122.3
□H8C4N12	115.3	116.7	116.5	116.5	116.4	116.5	116.4	116.6	116.5	116.6	116.5
□C2N9C3	115.5	116.1	115.7	115.5	115.5	115.7	115.5	116.0	115.9	116.1	115.9
□C3N12C4	115.5	116.1	115.7	115.5	115.5	115.7	115.5	116.0	115.9	116.1	115.9
Mean absolute deviations		**0.640**	**0.429**	**0.407**	**0.393**	**0.457**	**0.386**	**0.571**	**0.507**	**0.593**	**0.521**

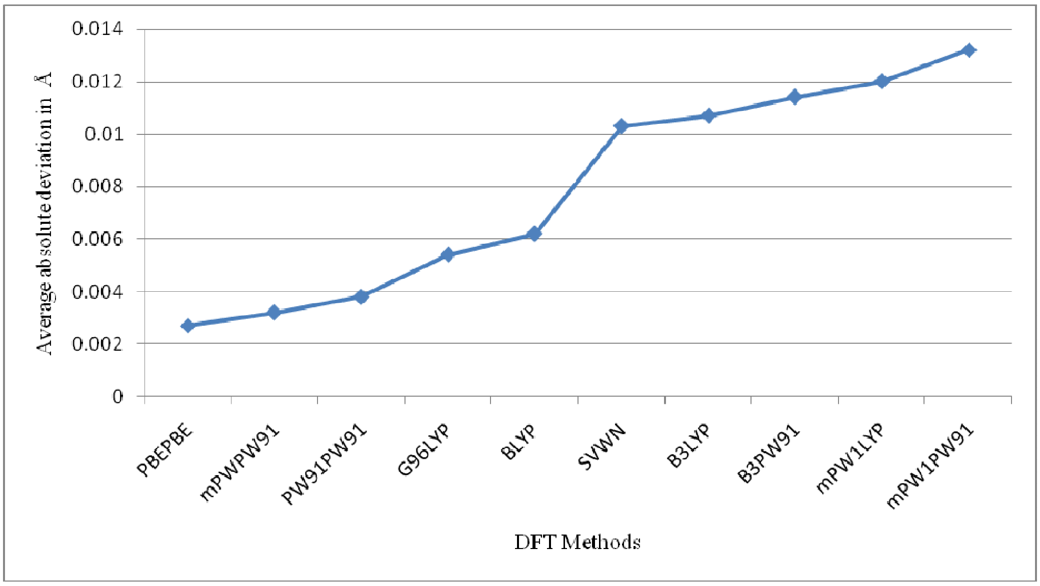

Fig.3: Average absolute deviation from experimental value[12] in bond lenths (Å) for different DFT Methods at 6-311G(3df,3pd) basis

The calculated bond angles with various DFT methods are very closer to their experimental data. To compare the bond angles obtained from different DFT methods at 6-311G(3df, 3pd), the mean absolute deviations between the calculated and experimental value have been determined. It has been found that bond angle calculated by SVWN, BLYP, PW91PW91, mPWPW91, G96LYP, PBEPBE, B3LYP, B3PW91, mPW1LYP and mPW1PW91 have mean absolute deviations of 0.636^0 , 0.429^0, 0.407^0 , 0.393^0, 0.457^0, 0.386^0, 0.571^0, 0.507^0 0.593^0 and 0.521^0 respectively. We again see that PBEPBE functional gives the best result in bond angle calculation of pyrimidine.

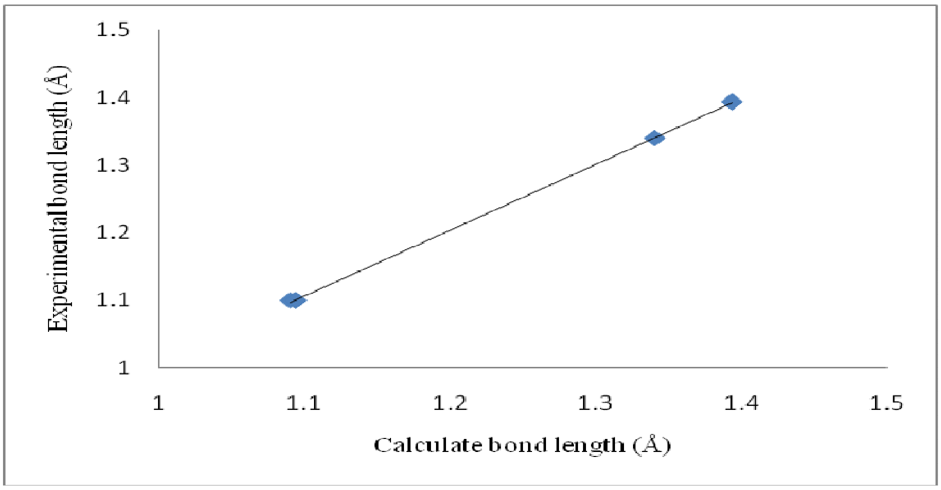

Fig.4. Correlation between experimental [12] and PBEPBE/6-311(3df,3pd) calculated bondlength for pyrimidine, Equation: r_{exp} =0.976 r_{cal}+0.032, R^2=0.999

3.2. Optimization parameters calculated with PBEPBE methods at various basis sets

In an effort to better evaluate the limit performance and to determine basis set dependence, calculations for optimized geometries with PBEPBE functional using various basis sets have been carried out. The calculated geometry parameters with PBEPBE at different basis sets have been compared with the experimental parameters in Table 3. It is clear that the calculated bond lengths at 6-311G(3df,3pd) basis set are in better agreement with the experimental geometry. All of the calculated bond lengths yielded by the PBEPBE/6-311G(3df, 3pd) method are nearest to the experimental data. The mean absolute deviations are 0.0041 Å for 6-311G(d,p), 0.0042 Å for 6-311++G(d,p), 0.0037 Å for 6-311G(2d,2p), 0.0039 Å for 6-311++G(2d,2p), 0.0037 Å for 6-311G(3d,3p), 0.0040 Å for 6-311++G(3d,3p), 0.0029 Å for 6-311G(2df,2pd), 0.0032 Å for 6-311++G(2df,2pd), 0.0027 Å for 6-311G(3df,3pd), 0.0030 Å for 6-311++G(3df,3pd), 0.0062 Å for cc-pVDZ, 0.0053 Å for aug-cc-pVDZ, 0.0031 Å for cc-pVTZ, and 0.0032 Å for Aug-cc-pVTZ. Average absolute deviations at different basis sets for PBEPBE method have been shown in figure 5. Obviously, the 6-311G(3df, 3pd) gives the best results in the calculation for the bond lengths of pyrimidine. The bond angles calculated by the different basis sets are in a good agreement with the experimental value and are close to each other to within an average absolute deviation of half of a degree.

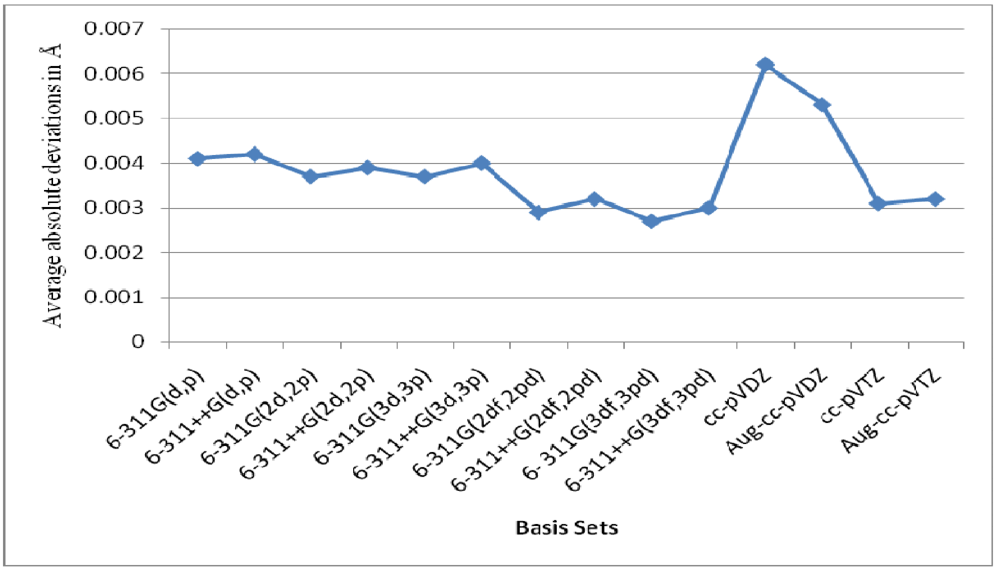

Fig.5: Average absolute deviation from experimental value[12] in bond lenths (Å) for different Basis sets for PBEPBE Method

Table 3 Comparison of bond lengths (in Å) and bond angles (^{0}) calculated for Pyrimidine with PBEPBE method at different basis sets

Geometry	Expt. [12]	**PBEPBE**													
		A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**	**K**	**L**	**M**	**N**
C1-C2	1.393	1.3972	1.3975	1.3945	1.3949	1.3955	1.3958	1.3938	1.3941	1.3937	1.394	1.4014	1.4014	1.3938	1.394
C1-C4	1.393	1.3972	1.3975	1.3945	1.3949	1.3955	1.3958	1.3938	1.3941	1.3937	1.394	1.4014	1.4014	1.3938	1.394
C1-H5	1.099	1.0917	1.0918	1.0898	1.0897	1.0902	1.0902	1.09	1.0898	1.09	1.0898	1.0994	1.0977	1.0898	1.0898
C2-H6	1.099	1.0956	1.0955	1.0939	1.0936	1.0944	1.094	1.0941	1.0937	1.0942	1.0938	1.104	1.1013	1.094	1.0938
C2-N9	1.340	1.3441	1.3442	1.3427	1.3428	1.3426	1.3429	1.3415	1.3416	1.3408	1.3411	1.3477	1.3477	1.3418	1.3418
C3-H7	1.099	1.0953	1.0952	1.0939	1.0934	1.0942	1.0938	1.0942	1.0936	1.0941	1.0936	1.104	1.1003	1.0939	1.0937
C3-N9	1.340	1.3434	1.3434	1.342	1.3420	1.342	1.3421	1.3406	1.3406	1.3402	1.3403	1.3473	1.347	1.3409	1.3409
C3-N12	1.340	1.3434	1.3434	1.342	1.3420	1.342	1.3421	1.3406	1.3406	1.3402	1.3403	1.3473	1.347	1.3409	1.3409
C4-H8	1.099	1.0956	1.0955	1.0939	1.0936	1.0944	1.094	1.0941	1.0937	1.0942	1.0938	1.104	1.1013	1.094	1.0938
C4-N12	1.340	1.3441	1.3442	1.3427	1.3428	1.3426	1.3429	1.3415	1.3416	1.3408	1.3411	1.3477	1.3477	1.3418	1.3418
Mean absolute deviations		**0.0041**	**0.0042**	**0.0037**	**0.0039**	**0.0037**	**0.0040**	**0.0029**	**0.0032**	**0.0027**	**0.0030**	**0.0062**	**0.0053**	**0.0031**	**0.0032**
□C2C1C4	116.8	116.5	116.6	116.6	116.7	116.6	116.6	116.6	116.7	116.6	116.6	116.4	116.6	116.6	116.7
□C2C1H5	121.6	121.7	121.7	121.7	121.7	121.7	121.7	121.7	121.7	121.7	121.7	121.8	121.7	121.7	121.7
□C4C1H5	121.6	121.7	121.7	121.7	121.7	121.7	121.7	121.7	121.7	121.7	121.7	121.8	121.7	121.7	121.7
□C1C2H6	121.6	121.2	121.2	121.1	121.2	121.2	121.2	121.1	121.2	121.2	121.2	121.1	121.2	121.2	121.2
□C1C2N9	122.3	122.5	122.4	122.5	122.4	122.5	122.4	122.5	122.3	122.4	122.3	122.7	122.4	122.4	122.4
□H6C2N9	115.3	116.3	116.3	116.4	116.4	116.4	116.4	116.4	116.5	116.4	116.5	116.3	116.4	116.4	116.5
□H7C3N9	115.3	116.1	116.2	116.1	116.3	116.1	116.3	116.2	116.3	116.2	116.3	115.9	116.2	116.2	116.3
□H7C3N12	115.3	116.1	116.2	116.1	116.3	116.1	116.3	116.2	116.3	116.2	116.3	115.9	116.2	116.2	116.3
□N9C3N12	127.6	127.8	127.6	127.8	127.5	127.7	127.5	127.7	127.4	127.6	127.4	128.2	127.6	127.6	127.4
□C1C4H8	121.6	121.2	121.2	121.1	121.2	121.2	121.2	121.1	121.2	121.2	121.2	121.1	121.2	121.2	121.2
□C1C4N12	122.3	122.5	122.4	122.5	122.4	122.5	122.4	122.5	122.3	122.4	122.3	122.7	122.4	122.4	122.3
□H8C4N12	115.3	116.3	116.3	116.4	116.4	116.4	116.4	116.4	116.5	116.4	116.5	116.3	116.4	116.4	116.5
□C2N9C3	115.5	115.3	115.5	115.3	115.6	115.4	115.6	115.4	115.7	115.5	115.7	115.0	115.5	115.5	115.6
□C3N12C4	115.5	115.3	115.5	115.3	115.6	115.4	115.6	115.4	115.7	115.5	115.7	115.0	115.5	115.5	115.6
Mean absolute deviations		**0.42**	**0.37**	**0.41**	**0.41**	**0.41**	**0.42**	**0.44**	**0.44**	**0.39**	**0.44**	**0.53**	**0.39**	**0.39**	**0.43**

In above table: **A** stands for 6-311G(d,p), **B** stands for 6-311++G(d,p), **C** stands for 6-311G(2d,2p), **D** stands for 6-311++G(2d,2p), **E** stands for 6-311G(3d,3p), **F** stands for 6-311++G(3d,3p), **G** stands for 6-311G(2df,2pd), **H** stands for 6-311++G(2df,2pd), **I** stands for 6- 311G(3df,3pd), **J** stands for 6-311++G(3df,3pd), **K** stands for cc-pVDZ, **L** stands for Aug-cc-pVDZ, **M** stands for cc-pVTZ and **N** stands for Aug-cc-pVTZ.

3.3 Vibrational spectra calculated with various methods at 6-311G(3df,3pd) basis set

The harmonic vibrational frequencies are calculated at the same level of theories used for the calculation of optimized geometries. The calculated frequencies were scaled down by the wave number linear scaling procedure (WLS) of Yoshida et al. [33, 34] using the following equation:

$$\upsilon_{scale}=(1.0087-0.0000163\ \upsilon_{cal})\ \upsilon_{cal}\ \text{cm}^{-1} \qquad (1)$$

The computed vibrational frequencies (scaled values) of the all normal modes of pyrimidine e.g. υ_{16a}, υ_{16b}, υ_{6b}, υ_{6a}, υ_{4}, υ_{10b}, υ_{11}, υ_{17a}, υ_{5}, υ_{1}, υ_{18b}, υ_{12}, υ_{9a}, υ_{15}, υ_{3}, υ_{14}, υ_{19b}, υ_{19a}, υ_{8b}, υ_{8a}, υ_{13}, υ_{2}, υ_{20a}, and υ_{7b} in the notation of Lord et al [4] of pyrimidine with various DFT methods using 6-311G(3df,3pd) basis set are listed in Table 4. It should be noted that the calculated frequencies are generally higher than the observed frequencies due to observed frequencies contain anharmonic contributions. The anharmonicity of the fundamental frequencies is most often taken into consideration by scaling the calculated harmonic frequencies, and this procedure has been found to work well since the overestimation of vibrational frequencies is fairly uniform. Various scaled vibrational mode for pyrimidine with SVWN, BLYP, PW91PW91, mPWPW91, G96LYP, PBEPBE, B_3LYP, B_3PW91, mPW1LYP and mPW1PW91 methods at 6-311G(3df,3pd) basis set are given in the table 4. In order to make a comparison between the experimental and theoretical wave numbers, we have calculated mean absolute deviation which is a frequently used measure of the differences between values predicted by a model and actually observed from the thing being modeled. The mean absolute deviation between the calculated harmonic and observed fundamental vibration frequencies for each method are also given in Table 3. The mean absolute deviation values with SVWN, BLYP, PW91PW91, mPWPW91, G96LYP, PBEPBE, B3LYP, B3PW91, mPW1LYP and mPW1PW91 methods at 6-311G(3df,3pd) basis set are 47 cm^{-1}, 50 cm^{-1}, 45 cm^{-1}, 46 cm^{-1}, 49 cm^{-1}, 47 cm^{-1}, 43 cm^{-1}, 44 cm^{-1}, 48 cm^{-1} and 49 cm^{-1} respectively. Average absolute deviations for different DFT methods at 6-311G(3df, 3pd) have been shown in figure 6. It is remarkable that the B3LYP method performs well for the calculation of vibrational frequencies with the mean absolute deviation less than those reported for the other DFT methods. Obviously, B3LYP functional give results in closest agreement with the observed frequencies over the other methods. Figure 7 shows the correlation between the experimental [12] and calculated frequencies with B3LYP method at 6-311++G(d,p) basis set.

Table 4 Comparison of frequencies (in cm^{-1}) calculated for Pyrimidine and infrared intensities^{a} (Km/mol) with various DFT Methods at 6-311G(3df,3pd) basis sets

Mode	Expt.^{a}	SVWN	BLYP	PW91PW91	mPWPW91	G96LYP	PBEPBE	B3LYP	B3PW91	mPW1LYP	mPW1PW91
υ_{16b}	344	313(3)	330(3)	321(3)	321(3)	328(3)	319(3)	355(3)	347(3)	361(3)	353(3)
υ_{16a}	394	386(0)	391(0)	385(0)	385(0)	390(0)	384(0)	412(0)	406(0)	417(0)	410(0)
υ_{6b}	567	614(12)	618(11)	613(11)	613(11)	618(11)	611(11)	636(12)	630(12)	640(12)	633(12)
υ_{6a}	624	681(4)	676(3)	675(3)	674(3)	677(3)	673(3)	697(3)	694(3)	701(3)	698(3)
υ_{4}	679	723(39)	722(34)	721(35)	721(35)	723(35)	720(35)	742(37)	740(38)	746(37)	744(39)
υ_{10b}	722	805(2)	797(4)	797(3)	797(4)	799(4)	795(4)	828(5)	827(5)	833(5)	833(5)
υ_{11}	806	952(0)	947(0)	947(0)	947(0)	949(0)	945(0)	986(0)	984(0)	993(0)	992(0)
υ_{17a}	870	962(0)	962(0)	963(0)	963(0)	965(0)	961(0)	1003(0)	1001(0)	1010(0)	1010(0)
υ_{5}	980	992(0)	965(3)	975(4)	973(4)	967(4)	973(4)	1005(4)	1009(5)	1012(4)	1016(5)
υ_{1}	991	994(6)	988(0)	988(0)	988(0)	990(0)	986(0)	1030(0)	1028(0)	1038(0)	1037(0)
υ_{18b}	1021	1056(3)	1042(1)	1048(1)	1048(1)	1044(1)	1046(1)	1075(1)	1077(1)	1081(2)	1083(1)
υ_{12}	1066	1062(1)	1050(3)	1054(3)	1053(3)	1053(3)	1052(3)	1086(2)	1085(2)	1092(2)	1092(2)
υ_{9a}	1141	1141(1)	1116(4)	1125(3)	1123(3)	1119(3)	1122(2)	1154(3)	1157(2)	1160(3)	1166(2)
υ_{15}	1161	1197(9)	1164(1)	1190(7)	1189(6)	1171(6)	1188(7)	1198(4)	1216(7)	1199(4)	1223(8)
υ_{3}	1227	1292(0)	1196(9)	1224(2)	1219(3)	1201(3)	1223(2)	1240(7)	1253(3)	1246(7)	1262(2)
υ_{14}	1371	1318(0)	1341(0)	1332(0)	1333(0)	1343(0)	1328(0)	1377(0)	1370(0)	1385(0)	1377(0)
υ_{19b}	1402	1394(46)	1367(55)	1377(50)	1375(51)	1370(51)	1373(50)	1418(59)	1422(56)	1427(60)	1432(56)
υ_{19a}	1467	1432(5)	1426(4)	1427(5)	1427(5)	1429(5)	1423(5)	1475(7)	1474(8)	1484(7)	1484(8)
υ_{8b}	1570	1571(77)	1512(68)	1535(71)	1533(70)	1517(70)	1533(70)	1582(80)	1596(81)	1594(83)	1611(84)
υ_{8a}	1570	1577(48)	1513(27)	1536(34)	1534(33)	1519(33)	1534(34)	1583(40)	1596(44)	1594(42)	1613(48)
υ_{13}	3001	2951(16)	2943(14)	2957(15)	2954(16)	2947(16)	2948(16)	3016(14)	3021(16)	3029(14)	3036(15)
υ_{2}	3048	2953(14)	2946(28)	2959(25)	2957(26)	2950(26)	2951(25)	3019(24)	3024(23)	3031(24)	3039(22)
υ_{20a}	3083	2960(8)	2956(19)	2969(18)	2965(17)	2960(17)	2959(16)	3028(16)	3032(15)	3041(16)	3048(15)
υ_{7b}	3095	3003(5)	2986(16)	3001(13)	3001(13)	2990(13)	2996(12)	3061(10)	3070(9)	3073(10)	3085(8)
Mean absolute deviation		**47**	**50**	**45**	**46**	**49**	**47**	**43**	**44**	**48**	**49**

^{a} *IR intensity: the value in parentheses*

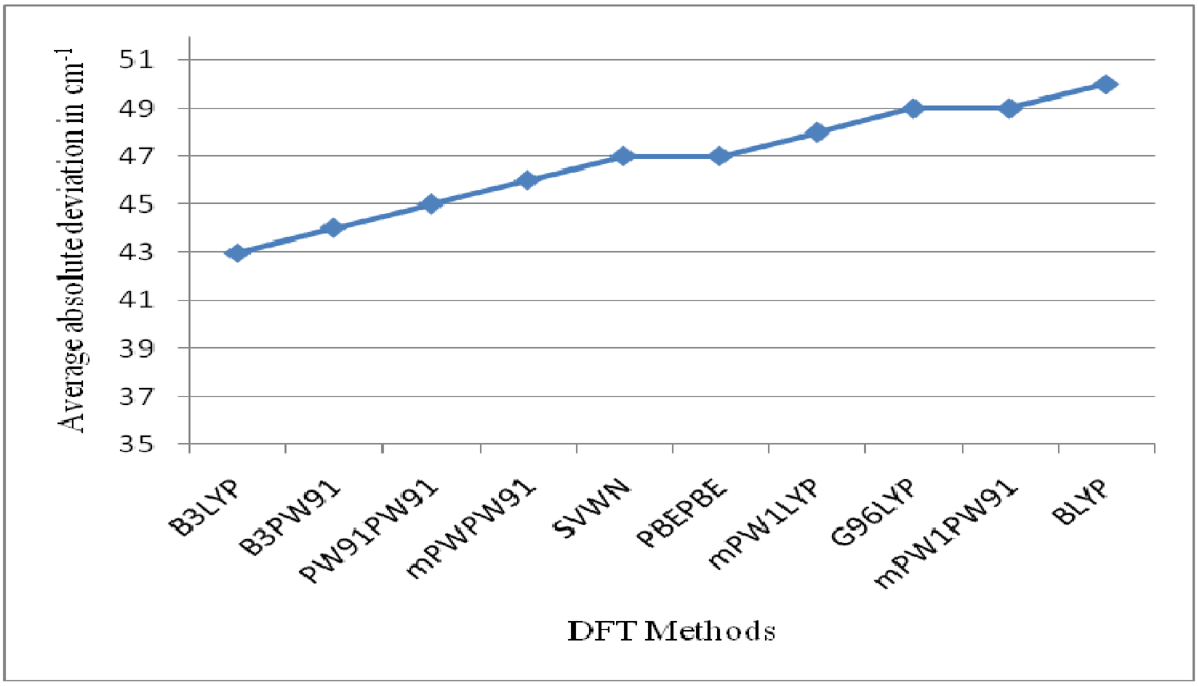

Fig. 6: Average absolute deviation from experimental value[12] in wavenumber (cm^{-1}) for different DFT Methods at 6-311G(3df,3pd) basis

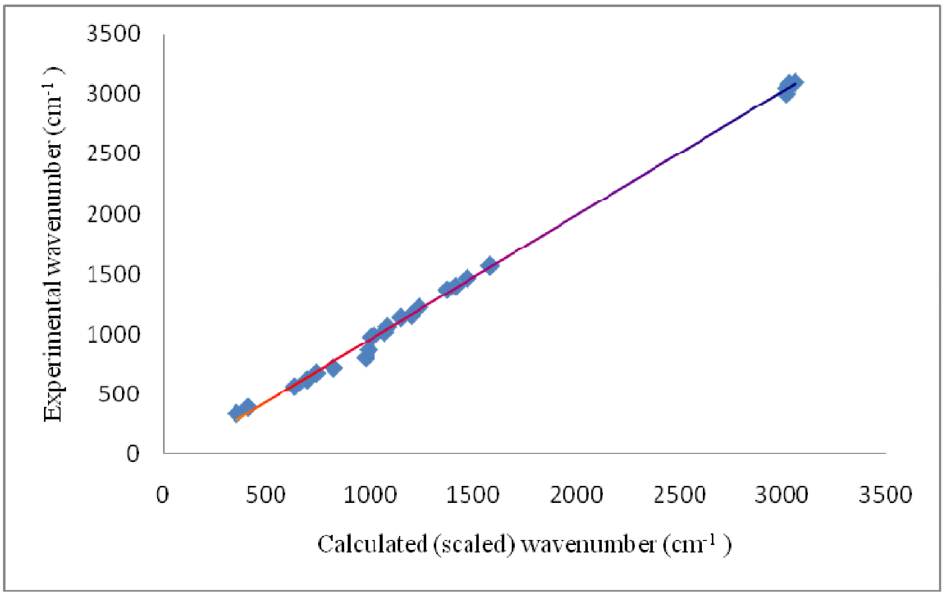

Fig.7. Correlation between experimental [12] and B3LYP/6-311++G(d,p) calculated (scaled) wavenumber for pyrimidine, Equation: υ_{exp}=1.035 υ_{scale}-79.64, R^2=0.997

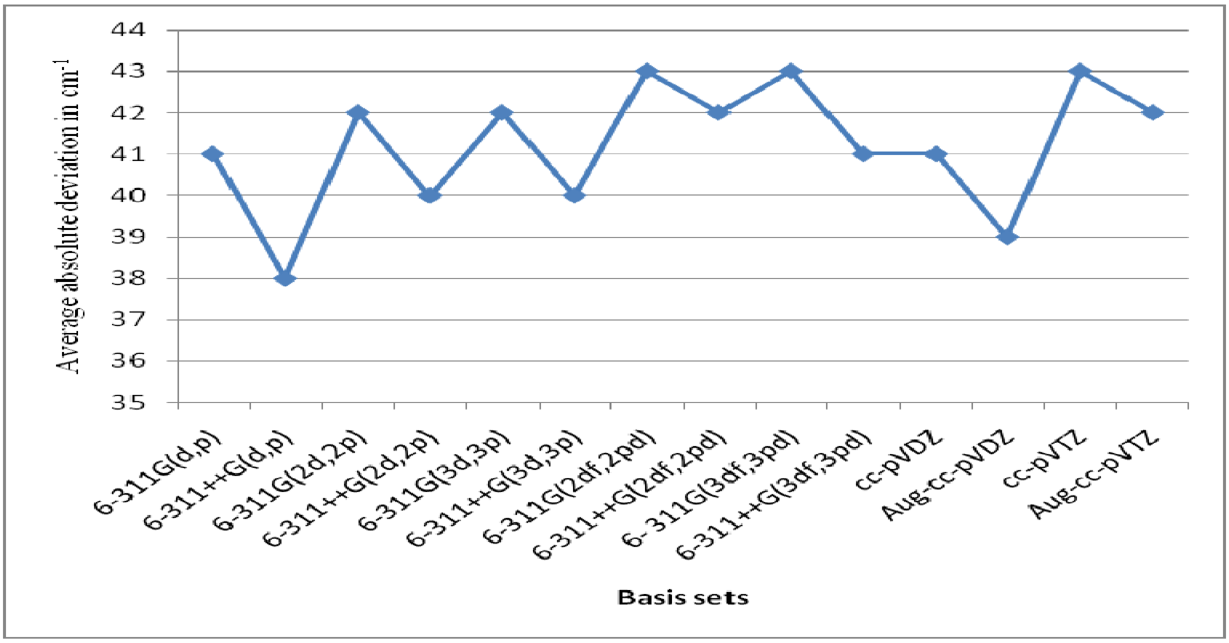

Fig. 8: Average absolute deviation from experimental value[12] in wavenumber (cm^{-1}) for B3LYP Method at basis sets

Table:5: Comparison of frequencies (in cm^{-1}) calculated for Pyrimidine and infrared intensities[a] (Km/mol) with B3LYP method at different basis sets

Mode	Expt.	A	B	C	D	E	F	G	H	I	J	K	L	M	N
υ_{16b}	**344**	354(3)	348(3)	355(3)	353(4)	354(3)	352(3)	356(3)	355(4)	355(3)	353(4)	355(3)	352(3)	355(3)	354(3)
υ_{16a}	**394**	410(0)	408(0)	411(0)	410(0)	410(0)	408(0)	412(0)	412(0)	412(0)	410(0)	408(0)	409(0)	412(0)	411(0)
υ_{6b}	**567**	635(11)	635(10)	638(12)	637(11)	636(12)	635(11)	635(13)	635(11)	636(12)	635(11)	630(12)	631(11)	635(12)	634(11)
υ_{6a}	**624**	695(4)	694(3)	697(3)	695(3)	696(3)	694(3)	696(3)	694(3)	697(3)	695(3)	690(4)	689(3)	694(3)	694(3)
υ_{4}	**679**	738(43)	731(44)	738(38)	736(42)	740(37)	736(41)	741(39)	738(41)	742(37)	738(40)	737(32)	734(42)	739(41)	739(40)
υ_{10b}	**722**	824(5)	817(7)	823(3)	819(5)	824(5)	818(5)	827(3)	825(5)	828(5)	823(5)	820(3)	814(5)	826(4)	825(5)
υ_{11}	**806**	979(0)	969(0)	981(0)	978(0)	982(0)	975(0)	987(0)	985(0)	986(0)	981(0)	973(0)	973(0)	984(0)	985(0)
υ_{17a}	**870**	994(0)	986(0)	998(0)	995(0)	999(0)	990(0)	1003(0)	1000(0)	1002(0)	995(0)	991(0)	992(0)	999(0)	1001(0)
υ_{5}	**980**	1003(5)	1003(0)	1003(4)	1002(4)	1004(4)	1003(4)	1005(5)	1003(4)	1005(4)	1004(4)	1003(5)	1000(4)	1003(4)	1002(4)
υ_{1}	**991**	1019(0)	1003(4)	1024(0)	1020(0)	1025(0)	1017(0)	1029(0)	1027(0)	1029(0)	1023(0)	1017(0)	1018(0)	1027(0)	1028(0)
υ_{18b}	**1021**	1070(2)	1069(1)	1075(2)	1073(1)	1072(2)	1070(1)	1074(1)	1072(1)	1074(1)	1073(1)	1071(1)	1068(1)	1074(1)	1073(1)
υ_{12}	**1066**	1085(4)	1084(4)	1085(3)	1085(3)	1084(2)	1083(3)	1086(3)	1085(3)	1086(2)	1085(3)	1080(3)	1079(3)	1086(3)	1085(3)
υ_{9a}	**1141**	1149(2)	1148(1)	1153(3)	1151(1)	1150(3)	1149(2)	1153(3)	1151(1)	1154(3)	1152(2)	1147(2)	1144(1)	1152(2)	1151(2)
υ_{15}	**1161**	1200(4)	1202(5)	1191(3)	1193(4)	1195(4)	1196(5)	1198(4)	1198(5)	1199(4)	1200(5)	1212(7)	1208(9)	1200(4)	1198(5)
υ_{3}	**1227**	1238(9)	1238(10)	1238(9)	1236(10)	1238(7)	1237(9)	1239(8)	1237(9)	1239(7)	1238(9)	1248(3)	1244(3)	1239(8)	1237(9)
υ_{14}	**1371**	1373(0)	1373(0)	1381(0)	1380(0)	1377(0)	1377(0)	1377(0)	1378(0)	1377(0)	1376(0)	1360(0)	1364(0)	1378(0)	1377(0)
υ_{19b}	**1402**	1414(61)	1414(59)	1417(61)	1416(61)	1416(59)	1415(59)	1419(60)	1418(60)	1419(59)	1418(59)	1408(54)	1409(54)	1417(61)	1417(59)
υ_{19a}	**1467**	1470(8)	1469(6)	1477(8)	1475(6)	1474(7)	1472(7)	1475(7)	1473(5)	1474(7)	1473(6)	1465(7)	1462(5)	1475(7)	1473(6)
υ_{8b}	**1570**	1581(42)	1580(85)	1580(79)	1578(83)	1580(80)	1578(44)	1582(81)	1579(85)	1583(80)	1580(45)	1590(43)	1583(45)	1582(42)	1580(84)
υ_{8a}	**1570**	1581(82)	1580(46)	1581(38)	1579(42)	1581(39)	1579(83)	1583(41)	1580(45)	1583(40)	1580(84)	1591(79)	1583(83)	1582(83)	1580(44)
υ_{13}	**3001**	3014(14)	3017(14)	3017(14)	3022(13)	3006(14)	3010(13)	3015(15)	3019(15)	3016(14)	3019(14)	3017(14)	3025(13)	3015(15)	3016(14)
υ_{2}	**3048**	3017(25)	3020(18)	3020(25)	3025(17)	3008(24)	3014(17)	3017(25)	3022(18)	3018(24)	3022(18)	3019(26)	3027(18)	3017(23)	3018(18)
υ_{20a}	**3083**	3027(18)	3031(14)	3031(18)	3036(13)	3019(17)	3025(13)	3027(17)	3032(12)	3028(16)	3034(13)	3027(18)	3039(14)	3027(16)	3028(13)
υ_{7b}	**3095**	3058(10)	3058(9)	3061(11)	3064(9)	3052(10)	3053(9)	3062(11)	3064(9)	3061(10)	3063(9)	3065(9)	3066(9)	3061(10)	3060(9)
Mean absolute deviation		**41**	**38**	**42**	**40**	**42**	**40**	**43**	**42**	**43**	**41**	**41**	**39**	**43**	**42**

In above table: **A** stands for 6-311G(d,p), **B** stands for 6-311++G(d,p), **C** stands for 6-311G(2d,2p), **D** stands for 6-311++G(2d,2p), **E** stands for 6-311G(3d,3p), **F** stands for 6-311++G(3d,3p), **G** stands for 6-311G(2df,2pd), **H** stands for 6-311++G(2df,2pd), **I** stands for 6- 311G(3df,3pd), **J** stands for 6-311++G(3df,3pd), **K** stands for cc-pVDZ, **L** stands for Aug-cc-pVDZ, **M** stands for cc-pVTZ and **N** stands for Aug-cc-pVTZ.

[a] IR intensity: the value in parentheses

3.4 Vibrational spectra calculated with B3LYP method at various basis sets

The calculated frequencies (scaled with WLS method) together with their intensities and the experimental frequencies given Table 5. It can be seen from Table 5 that the calculated frequencies yielded by B3LYP method at 6-311G(p,d) basis set are significantly overestimated whereas those calculated at 6-311G(3pd,3df) basis sets are closer to the experimental data. The mean absolute deviations between the calculated frequencies and experimental frequencies are 41 cm^{-1} for 6-311G(d,p), 38 cm^{-1} for 6-311++G(d,p), 42 cm^{-1} for 6-311G(2d,2p), 40 cm^{-1} for 6-311++G(2d,2p), 42 cm^{-1} for 6-311G(3d,3p), 40 cm^{-1} for 6-311++G(3d,3p), 43 cm^{-1} for 6-311G(2df,2pd), 42 cm^{-1} for 6-311++G(2df,2pd), 43 cm^{-1} for 6-311G(3df,3pd), 41 cm^{-1} for 6-311++G(3df,3pd), 41 cm^{-1} for cc-pVDZ, 39 cm^{-1} for Aug-cc-pVDZ, 43 cm^{-1} for cc-pVTZ and 42 cm^{-1} for Aug-cc-pVTZ. Average absolute deviations at different basis sets for B3LYP method have been shown in figure 8. It is remarkable that the B3LYP/6-311++G(d, p) level afforded the best quality to predict the vibration spectra of Pyrimidine.

CONCLUSION

In this paper, we have carried out DFT calculations on the molecular structure and vibration spectra of pyrimidine. Comparison between the calculated and experimental structural parameters indicates that the PBEPBE/6-311G(3df,3pd) level is clearly superior to all of the remaining DFT levels in predicting the structure of pyrimidine. Comparison between the calculated and experimental fundamental vibrational frequencies of pyrimidine indicate that the B3LYP/6-311G(3df,3pd) level shows better performance in the vibration spectra prediction of pyrimidine.

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