FT-IR, FT-RAMAN SPECTROSCOPIC VIBRATIONAL ANALYSIS OF 2 AMINO 3 BROMO PYRIDIN

R.SANGEETHA.

Assistant Professor, Department of Physics, Dhanalakshmi Srinivasan college of Arts and Science for women (Autonomous), Perambalur.

ABSTRACT

The optimized structure of 2 Amino 3 Bromo Pyridin (2A3BP) has been done by density functional theory (DFT) with B3LYP level and 6-311G++ (d,p) basis set. The fundamental vibrational frequencies of 2 Amino 3 Bromo Pyridin are calculated using density functional theory (DFT) methods at different levels of calculation. The HOMO-LUMO energies have been investigated which proposes that the probability of charge transfer to take place inside the molecule. Mulliken population study on atomic charges was also calculated.

Keyword: Optimization, FTIR, Raman, HOMO-LUMO, Mulliken analysis

INTRODUCTION

Organic crystals are increasingly being recognized as materials of the future because of their molecular nature combined with the versatility of synthetic chemistry can be used to alter and optimize their molecular structure in order to maximize nonlinear properties. Organic crystals were completely scrutinized due to their high nonlinearities, rapid response in electro-optic effect and tailor made flexibility [1–6]. These compounds need to form in a non-Centro symmetric crystal in view of applications with quadratic optically nonlinear effects. The organic NLO crystals performed well in second harmonic generation (SHG), frequency mixing, electro-optic modulation, optical parametric oscillation, optical bistability, etc. [7-8]. However, their practical applications are limited by poor chemical stability, poor phase matching properties caused by a large birefringence [9]and difficulties stiller main in crystal growth with sufficient quality and hardness for applications, such as optical and electro-optical (EO) sampling devices. The basic necessities for an NLO crystal to be effectively applied in frequency conversion are a nonzero NLO coefficient, transparency at all wavelengths involved, proficient transfer of energy between the optical waves scattering through the crystal, and noble physical (low vapor pressure, high thermo stability) and optical (high damage threshold, large birefringence, low dispersion) properties. Crystal growth from solution is a significant procedure that is utilized in numerous applications from laboratory to industrial scale. An innumerable number of organic and inorganic crystals are grown in this fashion [10].

In the present work, we have done the computational studies of (2A3BP) by density functional theory with B3LYP/6-311G++(d,p) basis set. The optimized structure of 2 Amino 3 Bromo Pyridin (2A3BP) has been calculated. FTIR and Raman studies reveal the functional group of the grown crystal. The Mulliken charge analysis was completed to survey the intra-molecular charge transfer interaction. The investigation from HOMO-LUMO orbital's explained the charge distribution among the molecules.

COMPUTATIONAL DETAILS

The DFT calculations of (2A3BP) have been performed by using the Gaussian 09 program kit [11]at the Becke3-Lee-Yang- Parr functional (B3LYP) [12,13] with 6-311G++(d,p) basis set to obtain energy minimization. The equation was solved by the method of self-consistent interactively to acquire all the optimized geometry. The optimization of (2A3BP) is shown in Fig. 1. From the full-featured Gauss View approach [14], the fact concerning molecular displacement vectors with vibrations was achieved.

Anisotropic scaling factor 0.9615 was used to obtain the molecular vibrations from B3LYP/6-311G++ (d,p) level of theory. The transformation of relative intensities of the Raman Spectrum (Ii) from the Raman activities (Si) was achieved by the Raman Scattering [15, 16]. The generated Infrared and Raman spectral peaks by the Gaussian 09 program were charted adopting pure spectral line shapes of full bandwidth at half maximum of 10 cm $^{-1}$.

MULLIKEN ANALYSIS

The atomic charge has been utilized to explain the process of electro negativity equalization and charge transfer in chemical reactions [17, 18]. Also, it has been used to model the electrostatic potential at outside molecular surfaces [19-22]. The Mulliken atomic charge was calculated through DFT at B3LYP/6-311G++(d,p) method and the graphical representation is shown in Fig. 2. The atom C1 has a maximum positive charge of 0.636521 and every hydrogen atom have exposed a positive charge. The magnitude of hydrogen atom changed between 0.324031 and 0.187395. The atoms N6 and N8 have the top value of negative charges -0.6013 and -0.78748 respectively. All the carbon atoms have exhibited a negative charges except C1 and C5.

Energy gap of HOMO-LUMO

To obtain the information about the molecular orbital (MO) structure, the energies of HOMO (π-donor) and LUMO (π- acceptor) of (2A3BP) molecule are investigated through the B3LYP level with the 6-311G++(d,p) level. The expansion of the word HOMO is the highest occupied molecular orbital. The expansion of the word LUMO is the lowest unoccupied molecular orbital. Orbital of HOMO and LUMO are displayed in Fig. 3. HOMO, LUMO energies and their band gap energy exhibit the actual molecular chemical reaction. Naturally, HOMO is called as an electron donor due to having the capability to contribute an electron. LUMO is called as an electron acceptor due to having the capacity to grab an electron. The energies of HOMO and LUMO are reckoned at **- 5.6933 eV** and **- 0.4070 eV** correspondingly. The band gap between HOMO and LUMO is observed as **5.2863 eV**. The computed energies of HOMO and LUMO have revealed that the charge transformation takes place in the molecule itself. The low value of energy gap declares that the appropriateness of the grown (2A3BP) in the field of NLO [23].

SPECTROSCOPIC ANALYSES

Raman spectra of (2A3BP) and structurally related molecules are examined and vibrational transitions assigned for the C-C, C-H stretching modes of these molecules. Particular emphasis is placed on the characteristics of the Raman spectra in the 3240-3240, 3184 and 552, 592 cm^{-1} regions. It is found transitions dominate the spectra at the expense of those of the phosphate and choline groups. The methyl and methylene C-H stretching assignments have been clarified for the Raman spectra of phospholipid systems.

Vibrations are depicted in the Table 1. The FTIR and Raman spectra are displayed in Fig. 4 and Fig. 5.

C-H Vibrations

In higher frequency region almost all vibrations belong to C-H stretching. In this region, the bands are not affected appreciably by the nature of the substituent. In the present study, the bands observed in 1088 cm^{-1} in FT-Raman spectrum have been assigned to C-H in plane bending vibrations. The C-H bending vibrations are expected to interact a little around 1088-1096 cm^{-1} with ring vibrations. Hence in the present study, the bands observed at 1192 cm^{-1} in FT-Raman and 1192 cm^{-1} in FT-IR spectrum have been assigned to C-H in-plane bending modes. The bands observed at 3184 cm^{-1} in FT-Raman and 3184 cm^{-1} in FT-IR spectrum have been assigned to C-H stretching modes.

C-C Vibrations

Medium strong FT-Raman bands at 1568 cm^{-1} are all assigned to C-C stretching vibrations. Similarly, a medium FT-Raman band at 1512 cm^{-1} are assigned to C-C symmetric stretching vibrations. Thus, we have found that the vibrational bands corresponding to vibrations practically remain the same in magnitude and intensity. Methyl rocking frequencies are mass sensitive and variable in position due to the interaction with stretching modes. Normally, these bands are observed weakly in the range 696-696 cm^{-1} out plane bending strong FT-IR band at 880 cm^{-1} combined with computed ones have been assigned, since the medium FT-Raman band at 904 cm^{-1} with significant contribution to which have been assigned to C-C in plane bending modes. These band observed in weekly FT-Raman the range 552, 592 cm^{-1}torsionCNCC torsion CCCC out of plane bending NCCC modes.

NH2 Vibrations

The ring C-C and stretching vibrations, known as semicircle stretching usually occur in the region 1616-1616 cm^{-1}. Hence in the present investigation, the FT- IR bands identified The band ascribed at in FT-IR and 1672-1672 cm^{-1} FT-Raman spectra has been designated NH2 in plane bendingHNH2, hence in present investigation the FT-IR has been designed NH2 torsion a .C-C stretching in-plane and out-of plane bending mode.

C-N Vibrations

In middle frequency region almost all vibrations belong to C-N stretching. In the present study, the bands observed in 1288 cm^{-1} FT-Raman spectrum have been assigned to C=N stretching vibrations. The bands at in 1288, 1288 cm^{-1} FT–IR are associated with C-N out plane bending. The bands at 312 cm^{-1} in FT–IR spectrum are associated with C-N out plane bending modes.

CONCLUSION

The optimization of the structure and the Vibrational spectral analysis of (2A3BP) were performed using DFT calculations. From the FT-IR analysis it is concluded that the major portion of the lattice force is largely derived from hydrogen bonding of the NH group of the heterocyclic ring. From the Raman analysis the ring breathing vibrations, which are observed at 1512 cm^{-1} in the IR spectrum are also observed in the Raman spectrum nearly at these wavenumbers. The collaborations of the charge between the molecules have been established by Mulliken charge investigation. The HOMO-LUMO showed the charge transfer interaction in cation and anion groups.

List of Figures:

Fig. 1 Optimized structure of 2A3BP
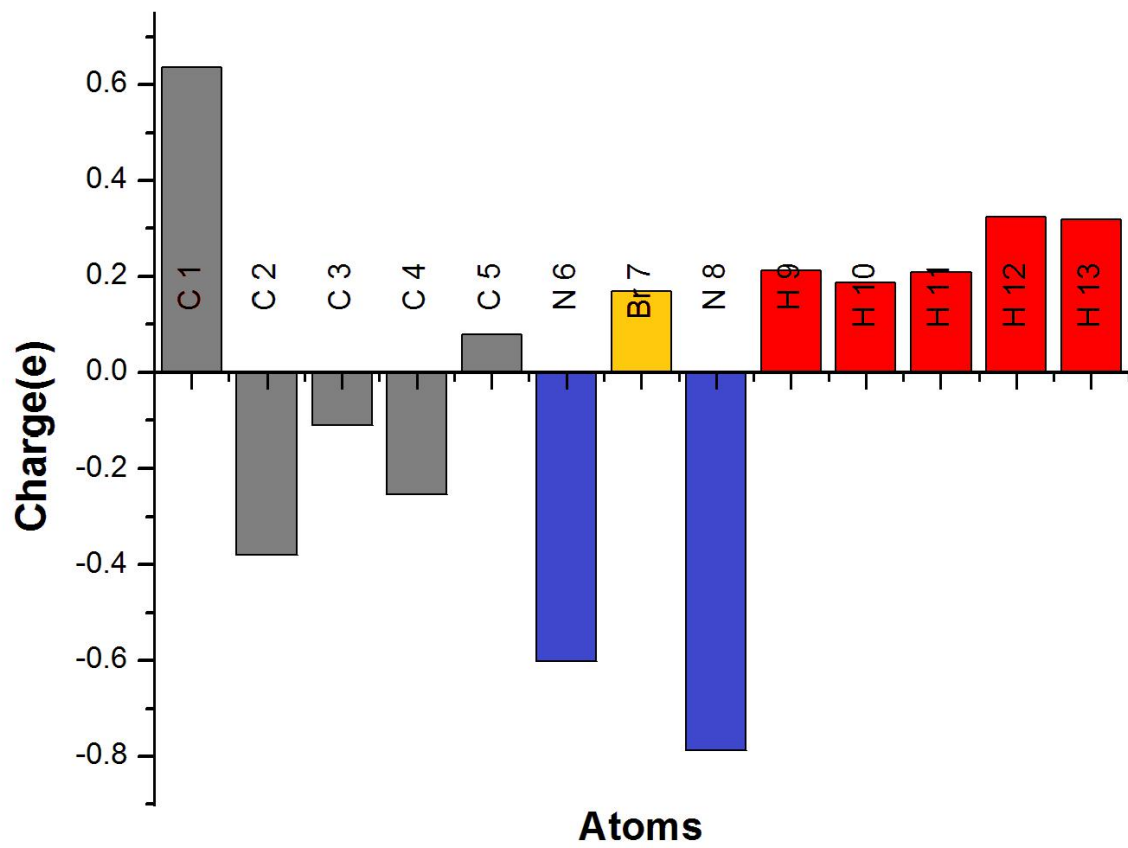
Fig. 2 Mulliken charge distribution of 2A3BP

LUMO (First Excited State) E_{LUMO} = - 0.4070eV

ENERGY DIFFERENCE ΔE (HOMO-LUMO GAP) = 5.2863 eV

HOMO (Ground State) E_{HOMO} = -5.6933 eV

Fig. 3 HOMO –LUMO plot of 2A3BP
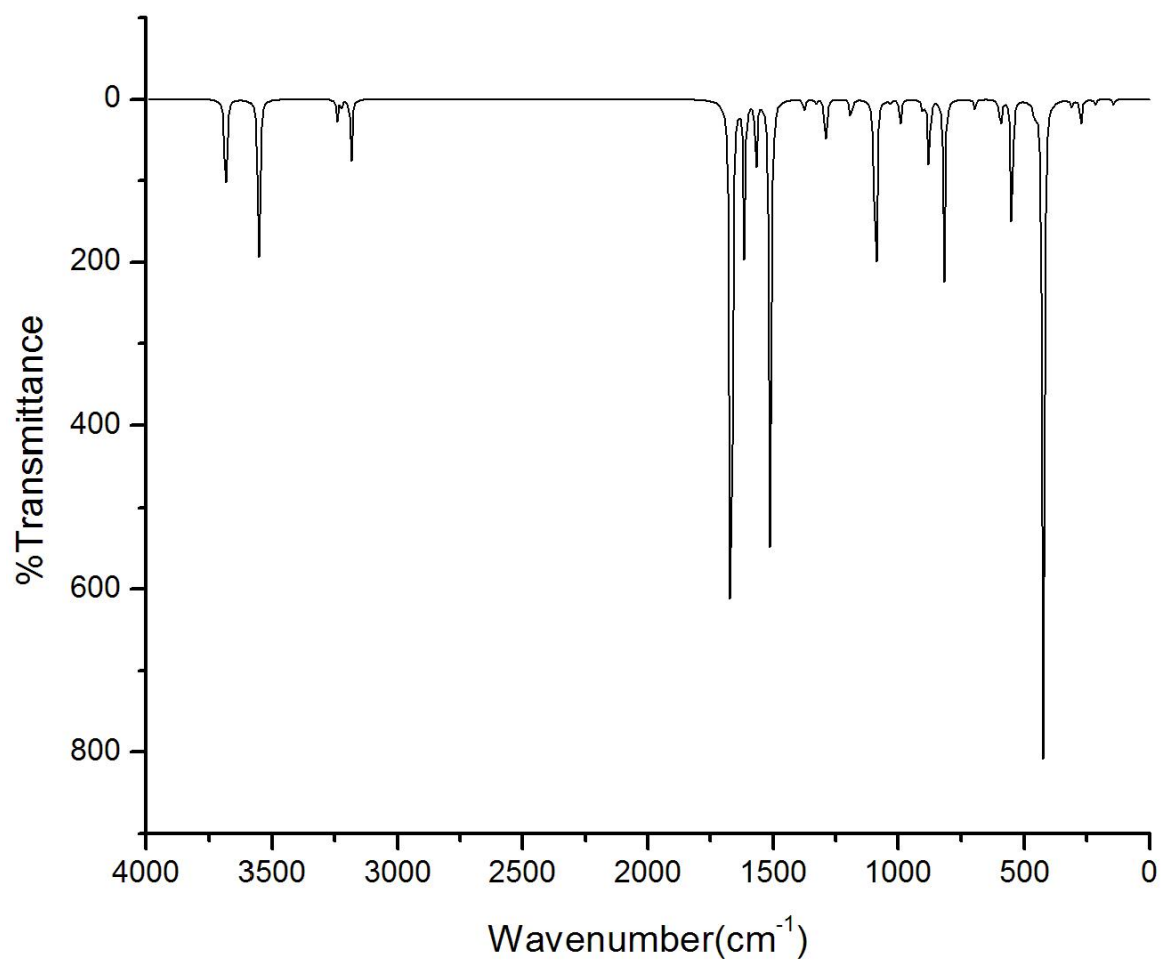
Fig. 4 FT-IR spectrum of 2A3BP
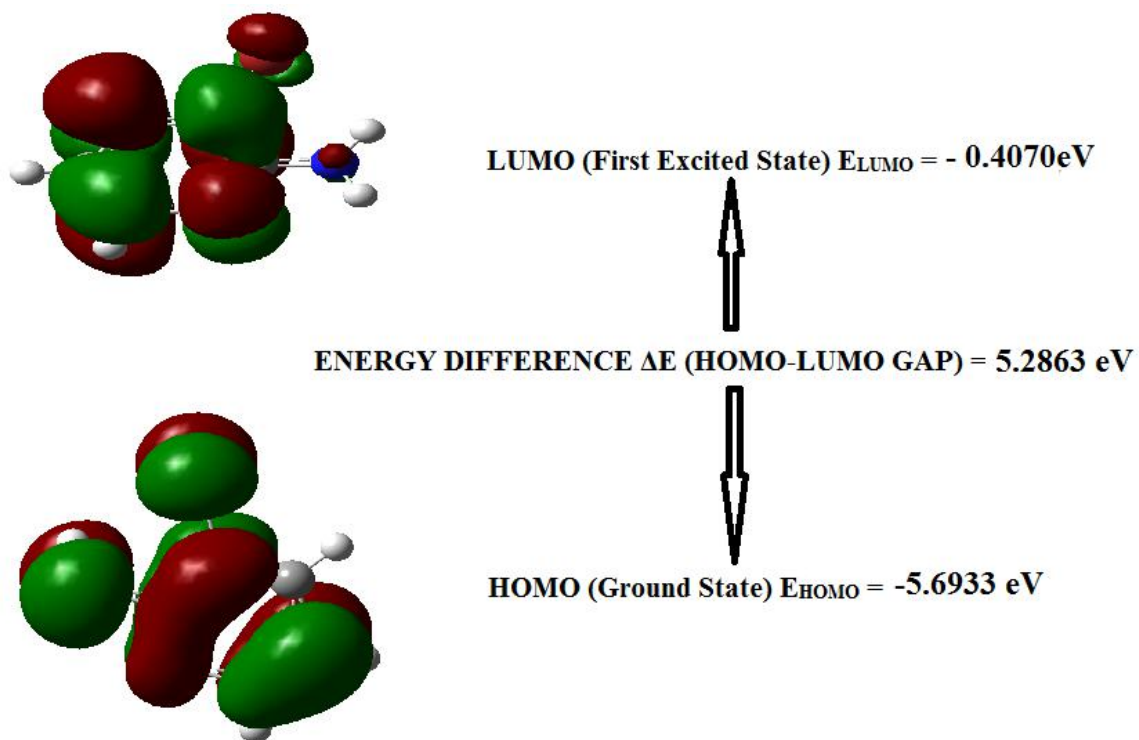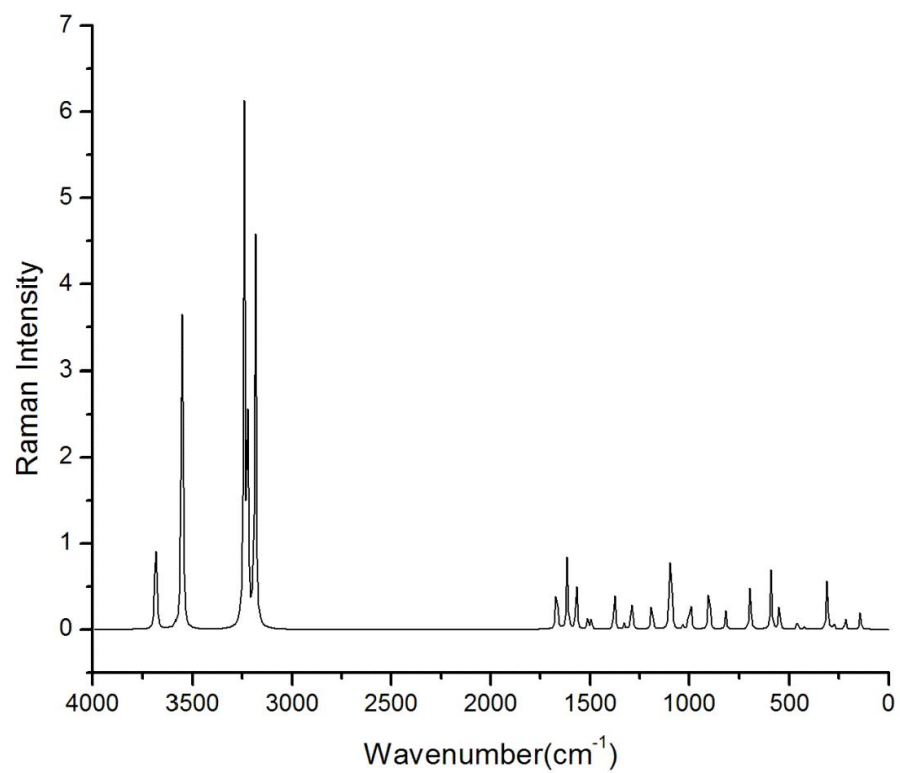
Fig. 5 FT-RAMAN spectrum of 2A3BP

Table 1: Vibrational assignments of 2A3BP

IR	RAMAN	ASSIGNMENTS
…	144	lattice vibration
…	216	C-Br out-of-plane bending
…	312	C-N out-of-plane bending
424	…	NH2 torsion
552	592	torsionCNCC, torsionCCCC, out-of-plane bending NCCC
696	696	C-C out-of-plane bending
816	816	in-plane-bendingCNC, stretchingCC, stretchingNC, in-plane-bendingCCC
880	904	C-C in-plane- bending
992	992	stretchingNC, in-plane- bendingCCN, in-plane-bendingCNC
1088	1096	C-H in-plane-bending
1192	1192	C-H in-plane-bending
1288	1288	C-N stretching
1376	1376	C=N stretching
1512	1512	C-C stretching
1568	1568	C-C stretching
1616	1616	in-plane- bending HNH
1672	1672	in-plane-bending HNH, C-C stretching
3184	3184	C-H stretching
3240	3240	stretching asymmetric NH, stretching CH

REFERENCES

[1] N. Vijayan, R. Ramesh Babu, R. Gopalakrishnan, P. Ramasamy, W.T.A. Harrison, Journal of Crystal Growth 262 (2004)

[2] Received 20 July 2003; accepted 27 August 2003 [1] J. Williams (Ed.), Nonlinear optical properties of organic and polymeric materials, American Chemical Society Symposium Series 233, American chemical Society, Washington, DC, 1983.

[3] D.S. Chemla, J. Zyss (Eds.), Nonlinear Optical Properties of Organic Molecules and Crystals, Vols. 1 and 2,Academic Press, New York, 1987.

[4] P. Gunter, Ch. Bosshard, K. Sutter, H. Arend, G.Chapuis, R.J. Twieg, D. Dobrowolski, Appl. Phys. Lett.50 (1987) 486.

[5] K. Kagawa, M. Sagawa, A. Kakuta, M. Kaji, H.Nakayama, K. Ishii, J. Crystal Growth 139(1994) 309.

[6] Duorong Yuan, ZhenwuZhong, Mingguo Liu, Dong Xu,Qi Fang, Yonghong Bing, SuoyingSun, MinhuaJiang,J. Crystal Growth 186 (1998) 240.

[7] N. Vijayan, R. Ramesh Babu, M. Gunasekaran, R.Gopalakrishnan, P. Ramasamy, J. CrystalGrowth 256(2003) 174.

[8] N. Vijayan, R. Ramesh Babu, M. Gunasekaran, R.Gopalakrishnan, R. Kumaresan, P.Ramasamy, C.W.Lan, J. Crystal Growth 249 (2003) 309.

[9] HouWenbo, Yuan Duorong, Xu Dong, Zhang Nan, Yu Wentao, Liu Mingguo, Sun Suoying,Jiang Minhua,J. Crystal Growth 133 (1993) 71.

[10] S.A. deVries, P. Goedtkindt, W.J. Huisman, M.J. Zwanenburg, R. Feidenhans'l, S.L. Bennett, D.-M. Smilgies,A. Stierle, J.J. De Yoreo, W.J.P. van Enckevort, P.Bennema, E. Vlieg, J.Crystal Growth 205 (1999) 202.

[11] M.J. Frisch , G.W. Trucks , H.B. Schlegel , G.E. Scuseria , M.A. Robb , J.R. Cheeseman , G. Scalmani , V. Barone , B. Mennucci , G.A. Petersson , H. Nakat- suji, M. Caricato , X. Li , H.P. Hratchian , A.F. Izmaylov , J. Bloino , G. Zheng , J.L. Sonnenberg , M. Hada , M. Ehara , K. Toyota , R. Fukuda , J. Hasegawa , M. Ishida , T. Nakajima , Y. Hona , O. Kitao, H. Nakai , T. VrevenJr , J.A. Montgomery , J.E. Peralta , F. Ogliaro , M. Bearpark , J.J. Heyd , E. Brothers , K.N. Kudin , V.N. Staroverov , R. Kobayashi , J. Normand , K. Raghavachari , A. Rendell , J.C. Burant , S.S. Iyengar , J. Tomasi , M. Cossi , N. Rega , J.M. Millam , M. Klene , J.E. Knox , J.B. Cross , V. Bakken , C. Adamo , J. Jaramillo , R. Gomperts , R.E. Stratmann , O. Yazyev , A.J. Austin , R. Cammi, C. Pomelli , J.W. Ochterski, R.L. Mar- tin , K. Morokuma , V.G. Zakrzewski, G.A. Voth , P. Salvador , J.J. Dannenberg, S. Dapprich , A.D. Daniels , O. Farkas , J.B. Foresman, J.V. Ortiz , J. Cioslowski, D.J. Fox , Gaussian-09, Revision A.02, Guassian, Inc., Wallingford CT, 2009 .

[12] A.D. Becke , J. Chem. Phys. 98 (1993) 785–789 .

[13] C. Lee , W. Yang , R.G. Parr , Phys. Rev. B 37 (1993) 5648–5652 .

[14] A. Risch , A.B. Neilson , A.J. Holder , GUASSVIEW User Manual, Gaussian Inc, Pittsburgh, CT, 2009.

[15] G. Keresztury , S. Holly , J. Varga , J. Besenyei , A.Y. Wang , J.R. Durig , Spectrochim. Acta 49 A (1993) 2007–2026.

[16] G. Keresztury , J.M. Chalmers , P.R. Grifiths , Raman Spectroscopy: Theory in Handbook of Vibrational Spectroscopy, vol. 1, John Wiley & Sons Ltd, 2002 .

[17] K. Jug , Z.B. Maksic , Theoretical Model of Chemical Bonding, Part 3, Z.B. Maksic (Ed.),Springer, Berlin, 1991 .

[18] S. Fliszar, Charge Distributions and Chemical Effects, Springer, New York, 1983.

[19] P.E. Smith, J. Am. Chem. Soc. 113 (1991) 6029–6037.

[20] J. Gao, J. Chem. Phys. 98 (1993) 1975–1981.

[21] P. Cieplak, J. Comp. Chem. 12 (1991) 1232–1236.

[22] L. Xiao-Hong, L. Xiang-Ru, Z. Xian-Zhou, Comput. Theor. Chem. 969 (2011) 27–34.

[23] V. Charles Vincent, G. Bakiyaraj, K. Kirubavathi, K. Selvaraju, Chemical Data Collections22 (2019) 100247-1 – 100247-14.