RAMAN AND INFRARED SPECTRA OF 4-CHLORO-BENZOPHENONE

R.SANGEETHA.

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

ABSTRACT

The optimized structure of 4-Chloro-Benzophenone (4CBZPE) has been done by density functional theory (DFT) with B3LYP level and 6-311G++ (d,p) basis set. The fundamental vibrational frequencies of 4CBZPE 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 crystalsperformedwell 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 significantprocedure 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 4CBZPE by density functional theory with B3LYP/6-311G++(d,p) basis set. The optimized structure of 4-Chloro-Benzophenone (4CBZPE) 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 (4CBZPE) 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 (4CBZPE) 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 0.396592 and every hydrogen atom and chlorine atom have exposed positive charges. The magnitude of hydrogen atom changed between 0.225979 and 0.195603. The atom O8 has the top value of negative charge -0.45747. All the carbon atoms have exhibited a negative charges except C1.

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 (4CBZPE) 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 **- 6.8773 eV** and **-2.0165 eV** correspondingly. The band gap between HOMO and LUMO is observed as **4.8588 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 (4CBZPE) in the field of NLO [23].

SPECTROSCOPIC ANALYSES

The various fundamental vibrational modes of 4-Chloro-Benzophenone (stretching, in-plane and out-of-plane) such as C-H vibrations, C-N vibrations and N-H vibrations are depicted in the Table 1. The FTIR and Raman spectra are displayed in Fig. 4 and Fig. 5.

C–H vibrations

The hetroaromatic structure shows the presence of C–H stretching vibrations in the region 3184 - 3179 cm^{-1} which is the region for ready identification of C–H stretching vibrations. The band appeared at 3100 and 3000 cm^{-1} in the 4-chloro benzophenone have been assigned to C–H stretching vibrations. In the present case, C–H in-plane bending vibrations of the present compounds are identified at 1461 cm^{-1} for 4-chloro benzophenone. The calculated frequencies of HF for C–H in-plane bending vibrations showed in Table1. The C–H out-of-plane bending vibrations are normally observed in the region 1359 cm^{-1}. The C–H out-of-plane bending vibrations are observed at 877 cm^{-1} for 4-chlorobenzophenone. These in-plane and out-of-plane vibrational frequencies are found to be well within their characteristic region.

5.2.4 C–C vibrations

The aromatic carbon–carbon stretching vibrations of the title compound are observed at 1625 and 1400 cm^{-1} and 1380 – 1280 cm^{-1} in IR spectrum. C-C stretching are observed at 1617 cm^{-1} and 807 cm^{-1}. Several ring modes were affected by the substitution to the aromatic ring of the title compound. In the present study, the IR bands for 4-chloro benzophenone compound have been assigned to ring in-plane modes and the out-of-plane deformation modes, are considered carefully by their quantitative descriptions. These assignments are shown in Table1.

5.2.5 C−N vibration

The identification of C − N vibrations is difficult tasks since the mixing of vibrations are possible in this region. However, with the help of force field calculations the C−N vibrations are identified and assigned in this study. The calculated band at 1782 and 1537 cm^{-1} by HF method was designated to C – N stretching vibrations. The assignments of C−N in-plane and out-of-plane bending vibrations are at 955 and 617 cm^{-1} made in this study were also supported by the literature.

N-H Vibrations

In plane vibrational modes N-H stretching. These modes have been observed and located within the IR- spectral range 3200 and 100-1700cm^{-1}.The values of 456-1136cm^{-1}.benzimidazole compound have been bending ,asymmetric stretching of vibrations.

CONCLUSION

The optimized structure has been derived by density functional theory. The FTIR spectrum reveals that the functional groups of The Vibrational spectral analysis of 4CBZPE was 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 CH group of the heterocyclic ring. 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:

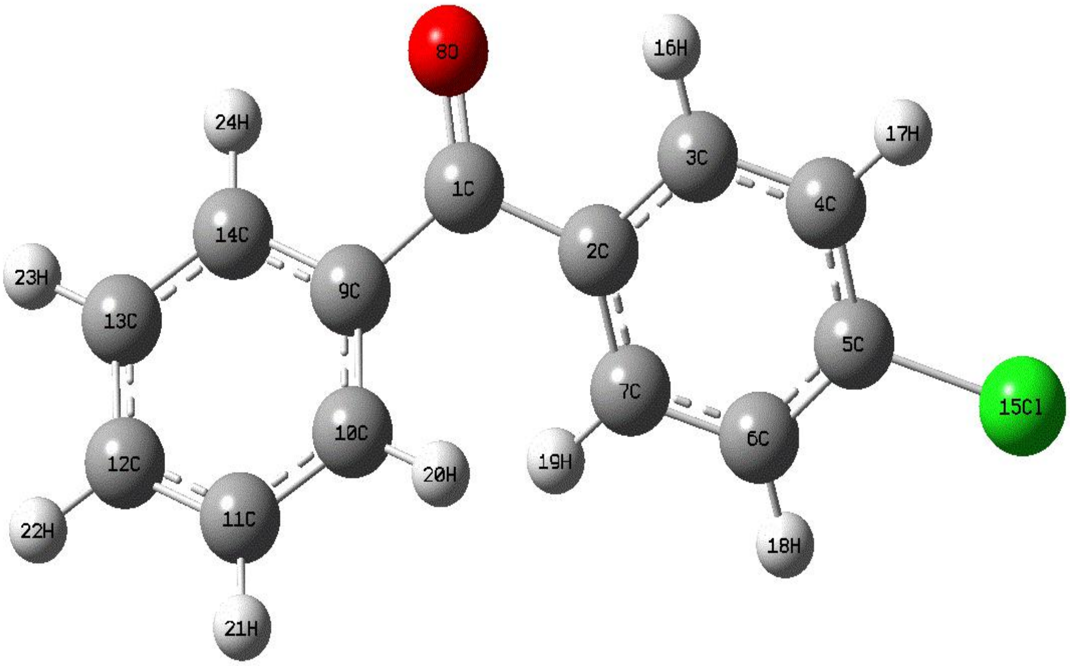

Fig. 1 Optimized structure of 4CBZPE

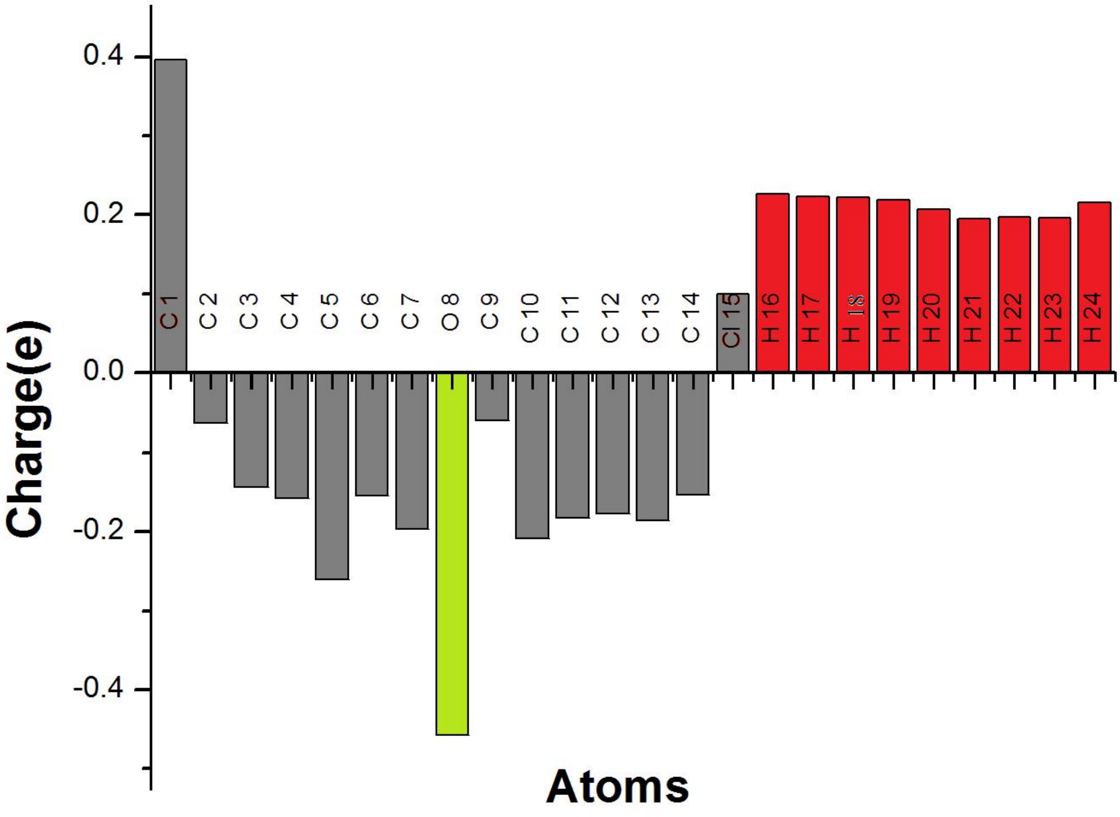

Fig. 2 Mulliken charge distribution of 4CBZPE

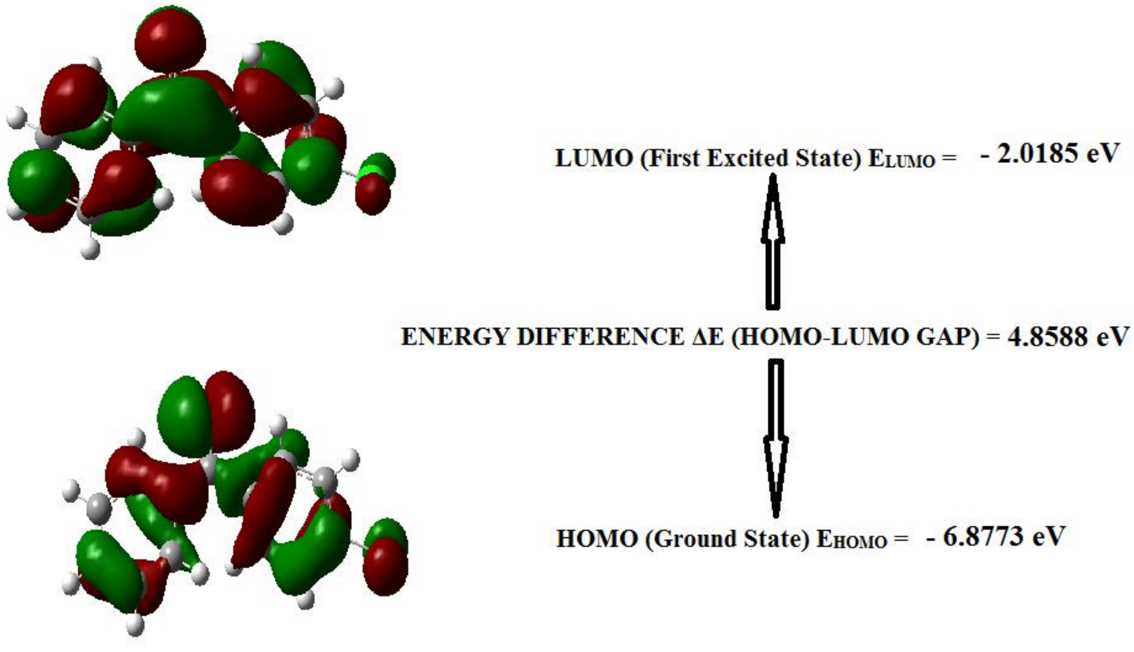

Fig. 3 HOMO –LUMO plot of 4CBZPE

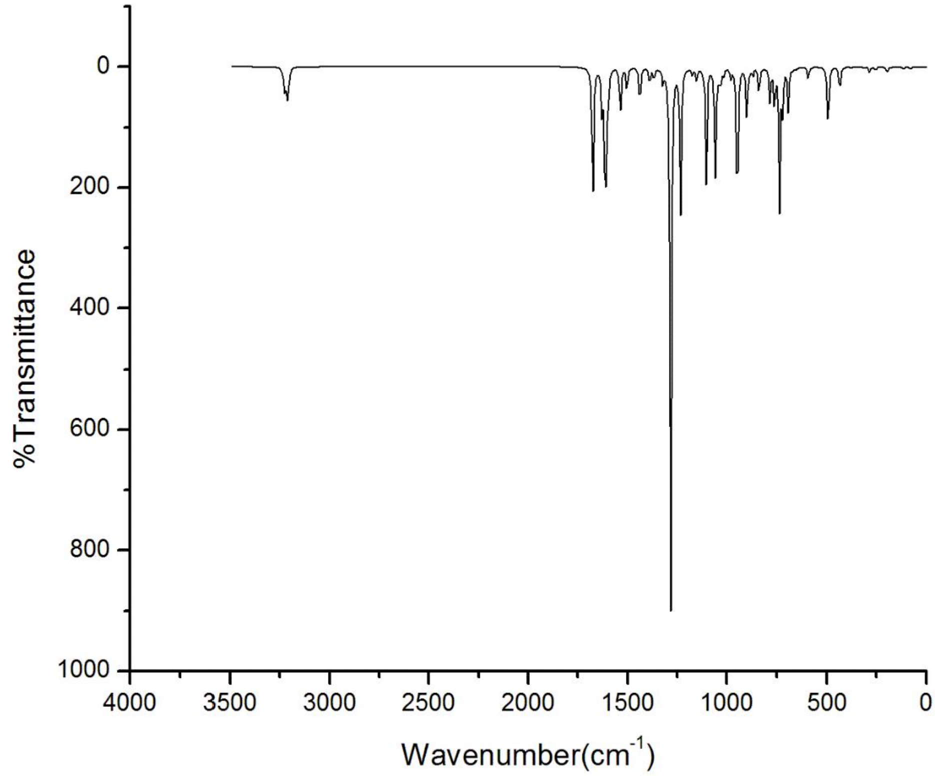

Fig. 4 FT-IR spectrum of 4CBZPE

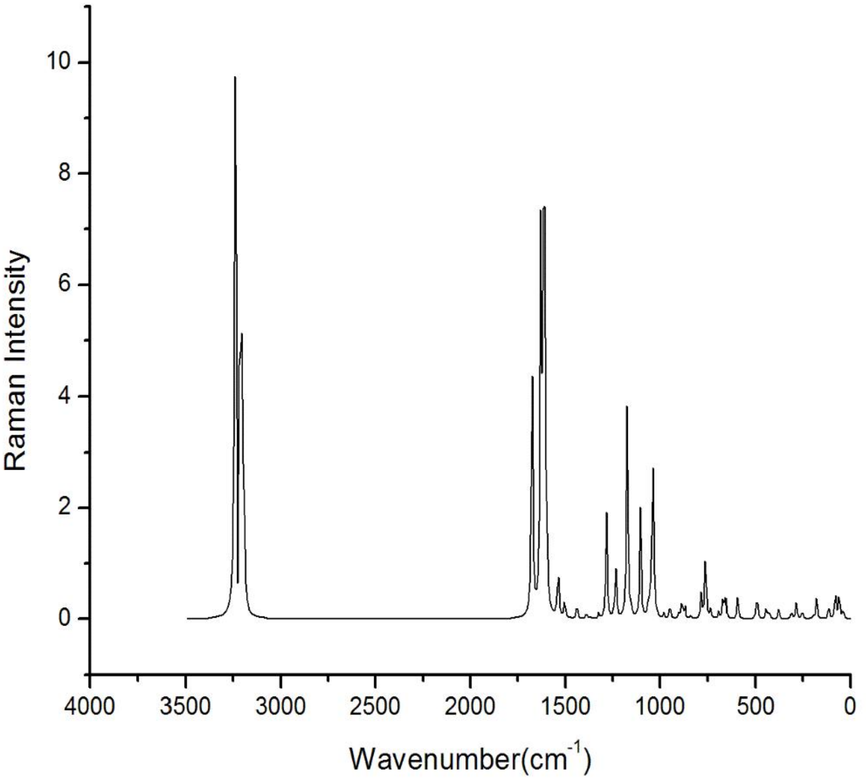

Fig. 5 FT-RAMAN spectrum of 4CBZPE

List of Table :

Table 1: Vibrational assignments of **4CBZPE**

Table 1: Vibrational assignments of 4CBZPE

IR	RAMAN	ASSIGNMENTS
434	448	C-C OUT-PLANE BENDING
497	497	C-C BENDING
595	595	C-N IN PLANE DEFORMATION
721	658	C-C-C OUT PLANE BENDING
735	….	C-N OUT PLANE BENDING
784	763	RING REATHING
840	….	C-C STRETCHING
903	889	C-H DEFORMATION
952	952	C-C-C IN PLANE BENDING
1057	1036	C-H IN PLANE BENDING
1106	1106	C-N STRETCHING
1232	1232	STRETCHING AROMATIC AMINES
1281	1281	CH_2 OUT PLANE BENDING
1393	….	CH OUT PLANE BENDING
1442	1442	CH IN PLANE BENDING
1533	1533	C-O-O ASYMMETRIC STRETCHING
1610	1610	C-C STRETCHING
1673	1673	C=N STRETCHING
3213	3206	CH_2 ASYMMETRIC STRETCHING

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 Propertiesof 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.