SPECTROSCOPIC STUDY ON STRUCTURE OF 2-*CHLORO-6-TRIFLUOROMETHYLPHENYLISOCYANATE* AS STUDIED BY EXPERIMENTAL AND DFT METHODS

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Abstract

The vibrational spectra of substituted benzene such as 2-chloro-6-trifluoromethylphenylisocyanate show features rather similar to benzene. In the present work we report a systematic study and interpretation and vibrational band assignments for identify the type as well as functionality of the chemical functional, the experimental FTIR spectrum of 2-chloro-6-trifluoromethylphenylisocyanate with the aid of density functional theoretical electronic structure calculation at B3LYP/6-31G*level of theory. The electronic structure calculations have been performed using Gaussian 09W software, giving optimized structure, energies, harmonic vibrational frequencies. All the computed harmonic frequencies have been scaled with suitable scale factor 0.9614. Vibrational assignments for FTIR spectrum of 2-chloro-6-trifluoromethylphenylisocyanate has been proposed, aided by the hybrid density functional method: B3LYP level using 6-31G* basis set. Characteristic benzene as well as C-X vibrations is in the correlation range. The CF3 stretching vibrations are modified as compared to CH3 vibrations. We also note that the in-plane and out-of-plane C-X bending vibrations show dominance in the region below 650 cm-1. All the assignments are in agreement with the similar systems.

Keywords: *2-chloro-6-trifluoromethylphenylisocyanate*; Ab Initio; DFT; IR; Raman.

1. Introduction:

The vibrational spectra of substituted benzene such as 2-*chloro-6-trifluoromethylphenylisocyanate* show features rather similar to benzene. In the

present work we report a systematic study and interpretation and vibrational band assignments for identify the type as well as functionality of the chemical functional, the experimental FTIR spectrum of *2-chloro-6-trifluoromethylphenylisocyanate* with the aid of *density functional* theoretical electronic structure calculation at B3LYP/6-31G*level of theory. The electronic structure calculations have been performed using Gaussian 03W software [8], giving optimized structure, energies, harmonic vibrational frequencies. All the computed harmonic frequencies have been scaled with suitable scale factor 0.9614 [9].

Literature survey of isocyanate and phenylisocyanate derivatives:

The treatment of graphite oxide with organic isocyanates results in a new class of isocyanated- graphite oxide materials possessing reduced hydrophilic properties that can be exfoliated in polar aprotic solvents to yield derivatized graphene oxide nanoplatelets [10]. A detailed ab initio molecular orbital study using minimal and split-valence basis sets has been carried out for singlet isomers of R(CNO), R = Li, BH_2. CH_3. OH, F, CI, CN, C_6H_5, p-$SH_2C_2H_4$, and p-$NO_2C_6H_4$. Calculated structures are in reasonable agreement with available experimental data [11]. Isocyanates are useful compounds capable of participating in a variety of reactions, including nucleophilic addition reactions with alcohols and amines, to produce carbamates and ureas, cycloaddition reactions to generate heterocycles, and polymerization reactions to produce commodities, such as polyurethanes [12]. Thomson et al demonstrated the utility of mid-IR spectroscopy (using a fibre optic FTIR probe) as a tool for monitoring the reactions of isocyanates, both in solutions and in polymerization reactions as a semi-solid mass cures. The distinctive asymmetrical N=C=O stretch is a particularly convenient spectroscopic marker in these reactions, and can be used to determine the extent of reaction even when the detailed chemistry of the system is not understood [13]. Doddamani et al proposed a complete vibrational assignment, for isomeric, 3-ClMe, 4-ClMe, and 5-ClMe,[ClMe-Chloro-methylphenyl isocyanate],based on IR and Raman spectra, aided by electronic structure calculations (at RHF and B3LYP using 6-311G* basis set), and normal coordinate treatment. The electronic structure calculations showed C_s symmetry. The structure of the spectra is considerably different from their parent-phenyl isocyanate. The vibrational structure of 4-ClMe shows features different from the spectra of 3-ClMe and 5-

ClMe, with regard to the substituents position, and methyl, in-plane and out-of-plane vibrations [14].

Laha et al [15] reported the vibrational assignments of *p*-chlorophenylisocyanate. This was followed by work on three isomeric fluorophenylisocyanates and m- and o-chlophenylisocyanates by means of electronic absorption and infrared spectra, Tonannavar and Huralikoppi et al [16,17]. Motivations for these studies came from the sustained investigations on the structural aspects, and consequent vibrational assignments of the parent-phenyl isocyanates. Probably the first report on the assignment of phenylisocyanates is due to Ham and Willis [18]. In the infrared assignments of five monosubstituted benzenes, namely, nitrobenzene, phenyl isocyanate, thionylaniline and anisole, Stephenson et al [19] treated them all, following whiffen [20], as belonging to C_{2v} symmetry. Chantry et al. [21] reassigned the liquid vibrational spectra on the basis of C_S symmetry as established in the ground state microwave vapor spectrum by Bounchy and Roussy [22]. Some *ab initio* molecular orbital calculations also supported C_S structure [23,24]. It was finally established by Bouchy and Roussy, following their high-resolution microwave spectroscopic studies, that the linear NCO moiety makes an angle of ~140° to the C_2 phenyl axis [25]. Further corroboration in this direction came from a vibrational analysis of the 275 nm vapor absorption spectrum, aided by semi empirical calculations, by Balfour et al. [26].

It seems that study of experimental spectrum *2-chloro-6-triflouromethylphenylisocyanate* with the aid of theoretical electronic structure calculation has been not done. Therefore, in the present work we carried out the above study**.**

2. **Experimental details:**

The liquid sample of 2-chloro-6-trifluoromethyl phenylisocyanate was supplied by Aldrich Chemical Co. and used as received. *Nicolet's Impact 410 FT spectrometer* was used for the infrared spectral measurements at room temperature in the range of 4000-400 cm^{-1}. The instrument was provided with a Globar Mid IR source, a deuterated triglycine sulfate (DTGS) solid state detector and a KBr beam splitter. The solid

sample was grinded in KBr to form a pellet. The signals were collected for 100 scans with a resolution of $4cm^{-1}$.

3. Computational Detatils:

Electronic structure calculation methods:

The development of theoretical methods and in particularly quantum chemistry, allowed not only an interpretation of the experimental observations, but also made it possible to predict molecular properties. Computational chemistry is simply the application of quantum mechanical and computing skills to the solution of physical, chemical problems. Here, one uses computer softwares like GAUSSIAN and GAUSSVIEW to generate information such as properties of molecules or simulated experimental results. The Schrödinger equation is the basis for the computational methods. The Born-Oppenheimer approximation is the first of several approximations made while trying to solve Schrödinger's equation for more complex systems with more than one or two electrons. A few electronic structure computation methods are discussed in brief as follows.

In the *ab initio* Hartree-Fock self-consistent field (HF-SCF) method, the wave function is an antisymmetrized determinant product of one-electron orbitals (the "Slater" determinant). Schrödinger's equation is transformed into a set of Hartree-Fock equations. The wave function of each electron is optimized under the mean potential averaged over all the other electrons in the system, as well as the electrostatic potential generated by the fixed nuclei. In another words, during the Hartree-Fock calculation, the electron cannot 'see' other electrons, instead of averaged 'electron gas'. The primary deficiency of Hartree-Fock method is that the correlation of electron motion cannot be accounted adequately.

Density Functional Theory (DFT) method is one of the most popular approaches to quantum mechanical many-body electronic structure calculations of molecular and condensed matter systems. It has been proved that for molecules, the ground-state molecular energy is uniquely determined by the ground-state electron probability density. Therefore, all the ground-state molecular properties can be calculated from the electron density, without having to find the molecular wave function. In addition, according to the Hohenberg-Kohn variational theorem, the true ground-state electron density minimizes the energy functional [13]. The DFT method is variational. A number of density functional theoretical methods have been developed, one such method is B3-LYP (Becke's three parameter mixing of exchange functional with Lee Yang Parr correlation functional).

In order to model structures and vibrational spectral properties, we performed electronic calculations with the hybrid density functional theory's B3LYP/6-31G* level using the *Gaussian 03W* suite of programs [8]. Molecular electronic energies, equilibrium geometries, vibrational frequencies and IR intensities have been computed. All the computed harmonic frequencies have been scaled with scaling factor and 0.9614 (B3LYP) [9].

4. **Result and Discussion:**

The structure of the 2-*chloro-6-trifluoromethyl phenylisocyanate* is shown in Fig-5 belongs to C_1 symmetry with 45 normal modes of vibration. The experimental FTIR spectrum is presented in Fig-6. The molecular electronic energy is -1196.3583708 hartrees at B3LYP/6-31G*level. We present the optimized geometrical parameters in Table-4. Table-5 presents experimental FTIR and theoretical fundamental vibrational frequencies with assignments. The observed vibrational frequencies were analyzed and assigned to different normal modes of the molecule. The error obtained between experimental and theoretical frequencies is in general very low. Other general conclusions have also been deduced. There is good agreement between theory and experiment.
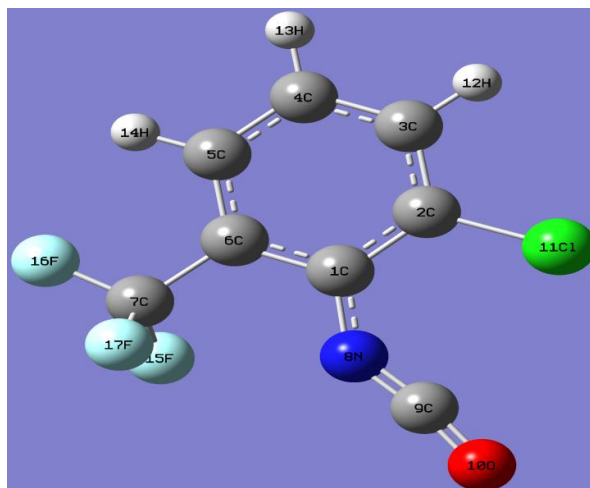

Fig-5: Molecular structure of *2-chloro-6-trifluoromethylphenylisocyanate*

Table-4: Optimized Geometrical Parameters: Bond lengths

Name	Definition	Value
R1	C1–C2	1.409
R2	C1–C6	1.411
R3	C1–N8	1.380
R4	C2–C3	1.393
R5	C2–Cl11	1.749
R6	C3–C4	1.392
R7	C3–H12	1.084
R8	C4–C5	1.394
R9	C4–H13	1.085
R10	C5–C6	1.393
R11	C5–H14	1.083
R12	C6–C7	1.512
R13	C7–F15	1.349
R14	C7–F16	1.352
R15	C7–F17	1.349
R16	N8–C9	1.213
R17	C9–O10	1.174

Table-4: Optimized Geometrical Parameters: Bond angles

| Name	Definition	Value
A1	C2–C1–C6	118.0
A2	C2–C1–N8	123.3
A3	C6–C1–N8	118.7
A4	C1–C2–C3	121.2
A5	C1–C2–Cl11	119.7
A6	C3–C2–Cl11	119.1
A7	C2–C3–C4	119.9
A8	C2–C3–H12	119.1
A9	C4–C3–H12	121.0
A10	C3–C4–C5	119.9
A11	C3–C4–H13	119.9
A12	C5–C4–H13	120.2
A13	C4–C5–C6	120.5
A14	C4–C5–H14	120.3
A15	C6–C5–H14	119.1
A16	C1–C6–C5	120.5
A17	C1–C6–C7	119.6
A18	C5–C6–C7	119.9
A19	C6–N7–F15	111.8
A20	C6–C7–F16	111.3
A21	C6–C7–F17	111.8
A22	F15–C7–F16	107.1
A23	F15–C7–F17	107.4
A24	F16–C7–F17	107.1
A25	F1–N8–O9	141.1
A26	F1–N8–O9 –C1	188.6
A27	F1–N8–O9 –C2	188.0
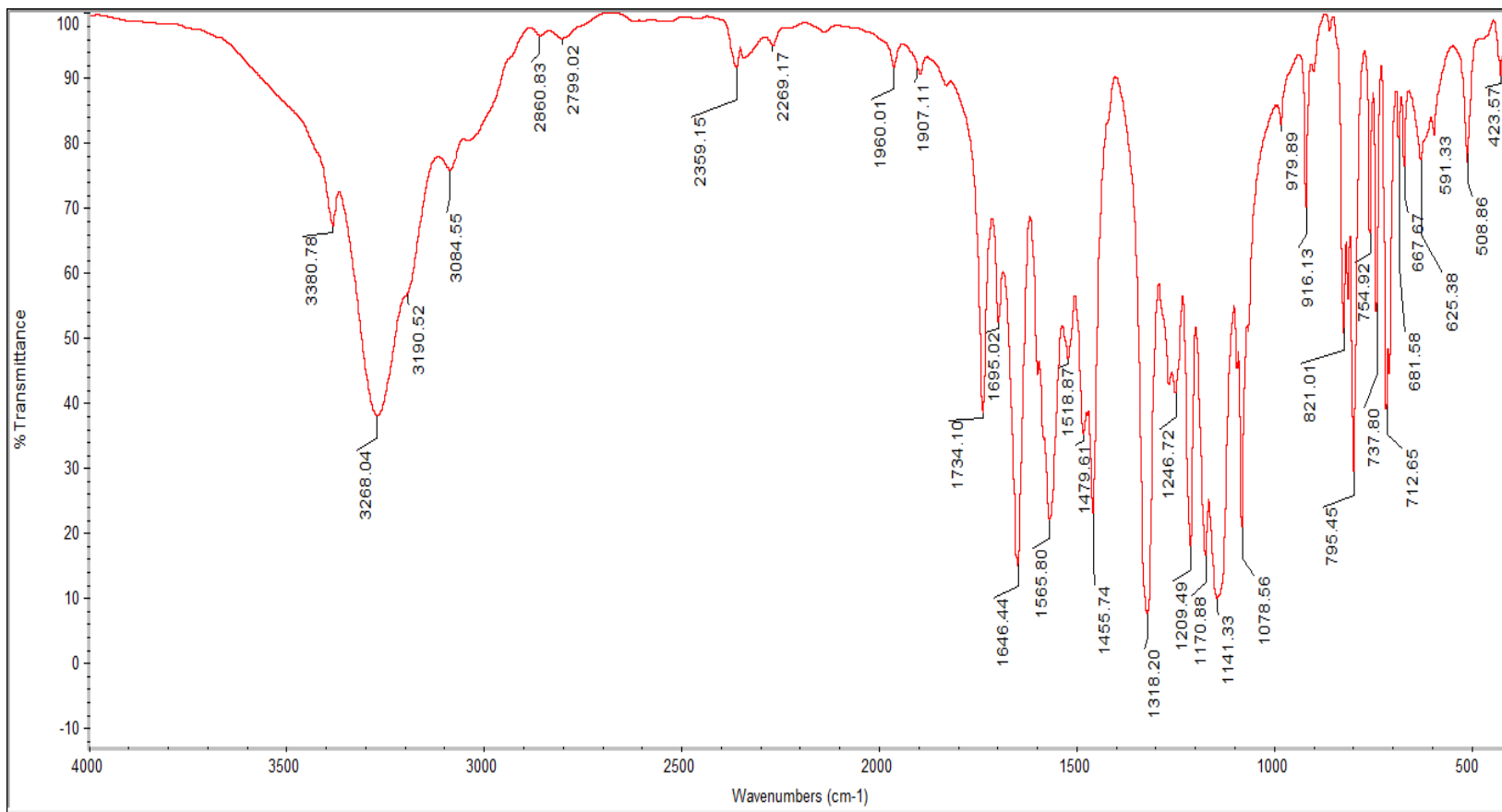
Fig.6:   FTIR Spectrum of 2-chloro-6-trifluoromethylphenylisocynate

Table-5: Experimental and Theoretical frequencies (cm^{-1}) with assignments

S.No.	FTIR	B3LYP	Assignments
ν_1	3268(62)	3120 (0.1)	νCH
ν_2	3190(44)	3105 (0.2)	νCH
ν_3	3085(26)	3089 (0.2)	νCH
ν_4	2269(8)	2291 (100)	ν_{as}NCO
ν_5	1595(48)	1587(2.1)	νCC
ν_6	1566(78)	1561(1.1)	νCC
ν_7	1519(53)	1525(6)	ν_sNCO
ν_8	1456(77)	1446(0.1)	νCC
ν_9	---	1394(3.8)	νCC
ν_{10}	1318(93)	1287(12)	νC-CF$_3$
ν_{11}	1247(59)	1275(9)	νCC
ν_{12}	1209(82)	1192(6)	βCH
ν_{13}	1171(82)	1169(7)	ν_{as}CF$_3$
ν_{14}	1141(90)	1156(17)	ν_{as}CF$_3$
ν_{15}	---	1134(1.4)	βCH
ν_{16}	---	1130(3.3)	βCH
ν_{17}	1080(79)	1062(3)	ν_sCF$_3$
ν_{18}	---	1043(0.5)	νC-Cl
ν_{19}	916(30)	945(0.1)	γCH
ν_{20}	---	897(0)	γCH
ν_{21}	795(72)	795(3)	βCC
ν_{22}	---	772(2.3)	γCH
ν_{23}	755 (35)	768(1.4)	νC-NCO
ν_{24}	713(63)	713(1)	γCC
ν_{25}	682(20)	673(2.4)	νCC
ν_{26}	625(29)	602(1.7)	βC-NCO
ν_{27}	591(20)	592(0)	γCC
ν_{28}	---	578(0.5)	δ_{as}CF$_3$
ν_{29}	---	533(1)	γC-NCO
ν_{30}	---	519(0.5)	δ_{as}CF$_3$
ν_{31}	509(23)	506(0.1)	δ_sCF$_3$
ν_{32}	---	484(0.1)	γCC
ν_{33}	---	483(0.6)	βCC
ν_{34}	---	379(0.2)	ρCF$_3$
ν_{35}	---	346(0)	ρCF$_3$
ν_{36}	---	312(0.2)	βNCO
ν_{37}	---	294(0.2)	βCC

ν_{38}	---	267(0.1)	βC-Cl
ν_{39}	---	244(0)	γC-Cl
ν_{40}	---	176(0)	γNCO

ν_{41}	---	152(0)	βC-CF$_3$
ν_{42}	---	91(0)	$\beta\omega$NCO
ν_{43}	---	84(0.1)	γC-CF$_3$
ν_{44}	---	54(0)	$\gamma\omega$NCO
ν_{45}	---	39(0)	τCF$_3$

The numbers inside bracket are relative intensities in case of frequencies. ν–stretching, β–in-plane-bending, γ–out-of-plane bending, ρ–rocking, as–asymmetric , s–symmetric, δ–deformation, ω–wagging, τ–torsion

5. Vibrational Band Assignments:

In the present work, vibrational assignments have been made based on "Spectra-Structure Correlations", aided by the electronic structure calculations that is, the scaled theoretical vibrational fundamental frequencies. In Table-5, assignments of vibrational frequencies are presented. Assignments are discussed with experimental frequencies and calculated B3LYP/6-31G* frequencies. Vibrations are visualized with the aid of GaussView, that is output of Gaussian is analyzed through GaussView and assignments are made.

1: C-H vibrations.
C-H stretching vibrations:

These vibrations show characteristic medium bands, as in the benzene derivatives, in the region 3100-3000 cm^{-1} [3-7]. Three, weak to medium IR bands at 3268, 3190 and 3085 cm^{-1} are assigned to these vibrations. These bands are predicted as weak at B3LYP.

C-H in-plane vibrations:

The CH in-plane bending vibrations are substitution sensitive, normally showing the bands in the region 1300-1000 cm^{-1} [3-7]. A strong IR band at 1209 cm^{-1} and computed weak bands at 1134, 1130 cm^{-1} are assigned to the CH in-plane bending vibrations.

C-H out-of-plane vibrations:

Bands involving the out-of-plane C-H vibrations appear in the range 1000-675 cm^{-1} [2-7]. Medium IR band at 916 cm^{-1} with weak computed bands at 897,772 cm^{-1} are assigned C-H out-of plane bending vibrations. The computed bands are with weak intensity.

2: C-C vibrations:

C-C stretching vibrations:

The C-C stretching vibrations occur in a wider spectral range covering 1650-650 cm^{-1} [6]. The five, weak medium to strong IR bands at 1595, 1566, 1456, 1247, and 682 cm^{-1} and a weak computed band at 1394 cm^{-1} are assigned to the C-C stretching vibrations. The computed bands are with weak intensity.

C-C in-plane bending vibrations:

A strong IR band at 795 cm^{-1} and two weak computed bands at 483,294 cm^{-1} are assigned to C-C in-plane bending vibrations. The above bands are in the expected range, as in similar systems [2-7]. The three predicted bands are weak.

C-C out-of-plane bending vibrations:

In the substituted benzenes, CC out-of-plane vibrations are expected in the range 730-425 cm^{-1} [2-7]. Two, strong to medium IR bands at 713, 591cm^{-1} with a weak computed band at 484 cm^{-1} are assigned to C-C out-of-plane bending vibrations. The three respective predicted bands are weak.

3: C-X vibrations.

C-NCO vibrations.

In chloro-substituted methylphenylisocyanates, C-NCO stretching vibrations are assigned in the range 1108-1071 cm^{-1} [14]. We assigned this vibration to a medium strong IR band at 755 cm^{-1}. The C-NCO in-plane bending vibration is assigned to a medium strong IR band at 625 and a weak computed band at 602 cm^{-1} . The C-NCO out-of-plane bending vibration is assigned to a very weak computed band at 533 cm^{-1}.

C-Cl vibrations.

The X-sensitive C-Cl stretching band is expected around 1105-395 cm^{-1} [2-7]. A very weak computed band at 1043 cm^{-1} is assigned to C-Cl stretching vibration. A very weak computed band at 267 cm^{-1} is assigned to C-Cl in-plane bending vibration. A very weak computed band 244 cm^{-1} is assigned to C-Cl out-of-plane bending vibration.

C-CF_3 vibrations:

Aromatic fluorine compounds give stretching bands in the region 1270-1100 cm^{-1} [2-7]. We have observed that when hydrogen in methyl group is replaced by fluorine, IR and Raman spectrum gets modified [7]. Very strong IR band at 1318 cm^{-1} is assigned to C-CF$_3$ stretching vibration. C-F in-plane bending vibration is expected in the general range 501-375 cm^{-1} [2-7]. A very weak computed band at 152 cm^{-1} is assigned to C-CF$_3$ in-plane bending vibration. A very weak computed band at 84 cm^{-1} is assigned to C-CF$_3$ out-of-plane bending vibration.

4: Group vibrations.

NCO vibrations.

There are six vibrations for NCO moiety: asymmetric, symmetric stretching, in-plane bend, in-plane wag, out-of-plane bend and out-of-plane wag. In chloro-substituted methyl-phenyl isocyanates, NCO asymmetric stretching vibrations are assigned in the range 2289-2264 cm^{-1} [14]. In our work, a weak IR band at 2269 cm^{-1} with a very strong computed band at 2291 cm^{-1} is assigned to NCO asymmetric stretching vibration. A strong IR band at 1519 cm^{-1} is assigned to NCO symmetric stretching vibration. The NCO in-plane and out-of-plane bend vibrations are assigned to weak computed bands at 312, 176 cm^{-1} respectively. Similarly, the NCO in-plane and out-of-plane wagging vibrations are assigned to a very weak computed bands at 91 and 54 cm^{-1} respectively.

CF_3 vibrations.

Aromatic fluorine compounds give stretching bands in the region 1270-1100 cm^{-1} [2-7]. We have observed that when hydrogen in methyl group is replaced by fluorine, IR and Raman spectra get modified which is seen in theoretical spectrum as well [7]. A strong IR band at 1171, 1141 cm^{-1} are assigned to CF$_3$ asymmetric stretching vibrations; and strong IR band at 1080 cm^{-1} is assigned to CF$_3$ symmetric stretching vibration. Weak computed bands at 578,519 cm^{-1} are assigned to CF$_3$ asymmetric deformation vibrations; and a medium IR band at 509 cm^{-1} is assigned to CF$_3$ symmetric deformation vibration. Two weak computed bands at 379, 346 cm^{-1} are assigned to CF$_3$ rocking vibrations. A low frequency weak computed band at 39 cm^{-1} is assigned to CF$_3$ torsional vibration.

Conclusions

Vibrational assignments for FTIR spectrum of *2-chloro-6-trifluoromethylphenylisocyanate* has been proposed, aided by the hybrid density functional method: B3LYP level using 6-31G* basis set. Characteristic benzene as well as C-X vibrations is in the correlation range. The CF_3 stretching vibrations are modified as compared to CH_3 vibrations. We also note that the in-plane and out-of-plane C-X bending vibrations show dominance in the region below 650 cm^{-1}. All the assignments are in agreement with the similar systems [1-7,14].

References
1. G. Herzberg, *Molecular Spectra and Molecular Structure Infrared and Raman Spectra of Polyatomic Molecules* ; V. N. Reinhold Co, NY (1995).
2. N. B. Colthup, L. H. Daly and S. E. Wiberley. *Introduction to Infrared and Raman Spectroscopy* Academic Press, London (1954).
3. G. Varsanyi, *Assignments for vibrational spectra of Seven Hundred Benzene Derivaties,* Vol.-1. Adam Hilger, London (1974).
4. L.J. Bellamy, *The Infrared Spectra of Complex Molecules* Vol-1. (3rd edition) Chapman and Hall, London (1975).
5. E. B. Wilson, Jr, J.C. Decius and P.C. Cross, *Molecular Vibrations ; The Theory of Infrared and Raman Vibrational Spectra* Dover Pub. Inc, NY (1955).
6. G. Varsanyi, *Vibrational Spectra of Benzene Derivatives*   Academic press, New York, 1969.
7. G. Socrates*, Infrared Characteristic Group Frequencies*, John Wiley, GB, 1980.
8. Gaussian 03, Revision D.01, GaussView 4.1
9. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria,
10. M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven,
11. K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi,
12. V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega,
13. G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota,
14. R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, 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, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Mrtin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004
15. A. P. Scott and L. Radom, *J. Phys. Chem.* **100** (1996) 16502.

19

16. Sasha Stankovich, Richard D. Piner, SonBinh T. Nguyen, Rodney S. Ruo. Carbon 44(2006) 3342

17. Dieter Poppinger and Leo Radom, *J. Am. Chem. Soc.* **100(12)** *June 7 , 1978*

18. Batool AKHLAGHINIA., Sima SAMIEI ,Turk J Chem**31**(2007), 35

19. 13. *Mary A. Thomson, Peter J. Melling, and Anne M. Slepski Polymer Preprints* 2001, *42*(1), 311

20. S.B. Doddamani, Anuradha Ramoji, Jayashree Yenagi, J. Tonannavar, Spectrochimica Acta Part A xxx (2006) xxx–xxx

21. S. Laha, S. Chakravarti, P.K. Mallick, S.B. Banerjee, Ind. J. Phys. 56B(1982) 104

22. J.R. Tonannavar, R. Rao, A.M. Joshi, K. Suryanarayan Rao, M.A. Shashidhar, Ind. J. Pure Appl. Phys. 26 (1988) 395.

23. A.M. Huralikoppi, Investigation on the spectra of some substituted aromatic molecules, Ph.D Thesis, Department of Physics, Karnataka University, Dharwad, 1985

24. N.S. Ham, J.S. Willis, Spectrochim. Acta 16 (1960) 279.

25. C.V. Stephenson, W.C. Coburn, W.S. Wilcox, Spectrochim. Acta 17 (1961) 933.

26. 20 D.H. Whiffen, J. Chem.Soc. 1350 (1956).

27. G.W. Chantry, E.A. Nicol, D.J. Harrison, A. Bouchy, G. Roussy, Spectrochim. Acta 30A (1974) 1717.

28. A. Bouchy, G. Roussy, C.R. Hebd Seances Acad Sci. 227 (1973) 143.

29. B.J. Haggins, L.L. Cooms, T.B. Mallory, R.L.Cook, J. Mol. Struct. 28 (1975) 121.

30. D.Poppinger, L. Radom. J. Am. Chem. Soc. 100 (1978) 3674.

31. A. Bouchy, G. Roussy, J. Mol. Spectrosc. 65 (1977) 395.

32. W.J Balfour. T.W. Dingle, R.S. Ram, J. Mol. Spectrosc. 96(1982) 306.

33. John. M. Chalmers and Peter R Griffiths Vol – 3. *Handbook of Vibrational Spectroscopy sample characterization and spectral data*. H.F. Shurvell. *Spectra-Structure Correlations in the MIR and FIR*; John Wiley and Sons Ltd 2002.