Theoretical Studies on Molecular Structure and Vibrational Spectra of 2,4-Difluoro-1-Methoxy Benzene and 1-Chloro-3-Methoxy Benzene

R. Rajathi Subbulakshmi[1], E. Palanichamy[2] , M. Arivazhagan[3]*, S. Manivel[4]

[1,3]Department of Physics, Government Arts College, Trichy-022
[2]Department of Physics, Government Arts College, Karur-005
[4]Department of Physics, National College, Trichy-001

Available online at: www.isroset.org

Abstract: -In this paper, we have studied the numerical analysis of the effect of Grashof number , modified Grashof number and chemical reaction on the non-Darcy MHD flow of a Casson fluid over a nonlinearly stretching sheet in a porous medium. In the mathematical model, using similarity variables, the momentum , energy and concentration equations are transformed to non-dimensional ordinary differential equations.. And then these are solved numerically using bvp4c method, a Matlab in-built bvp4c-programm. A discussion for the effects of the parameters involved on the boundary layer regions and the magnitude of the velocity, temperature and concentration and Local skin friction , Local Nusselt Number and Local Sherwood Number have been done graphically and numerically using figures and tables.

Mathematics Subject Classification: 35A22, 35A35, 35A99, 35G20, 35G30*Abstract:* The FT-IR and FT-Raman spectra Of 2,4-Difluoro-1-Methoxybenzene (DFMB) and 1-Chloro-3-Methoxy Benzene (CMB) have been recorded in the region 4000-400 cm^{-1} and 3000-50 cm^{-1} respectively. The DFT computations were employed at the B3LYP methods with 6-311++G(d,p) basis set to determine the Molecular structure and vibrational frequencies of the molecule. The geometry of the molecules were fully optimized, the assignments of vibrational frequencies were done by Total energy distribution (TED) analysis. The theoretically computed vibrational frequencies of (DFMB) and (CMB) were compared with the reported experimental values.The complete data of these molecules provide the information for future development of substituted benzene. The calculated HOMO-LUMO energy gap reveals that the charge transfer occurs within the molecule.The thermodynamic properties like entropies and their correlations with temperatures were obtained. NLO properties related to polarizability and hyperpolarizability are also discussed.

I. INTRODUCTION

Molecular organic compounds with one or more aromatic systems in conjugated positions leading to charge transfer systems, are intensely studied for the past two decades. Now-a-days organic crystals are highly recognized as the materials of the future because of their molecular nature, combined with versatility of synthetic chemistry can be used to alter their structure in order to maximize the non-linear properties [1-3]. The substituted benzene derivatives with high optical non-linearities are very promising materials for future optoelectronic and non-linear optical applications. Particularly, the new non-linear optical crystal of chloro and nitro substituted benzene are grown by low temperature solution growth technique. The optical transparency of this crystal is quite good and hence it can be a potential material for frequency doubling of non-linear optics [4]. Moreover, benzene derivatives are widely used to manufacture therapeutic chemicals, dyes, artificial leather and detergent

products. Further, the fluoro benzene derivatives are used to control carbon content in steel manufacturing. They also act as an intermediate for pharmaceuticals, pesticides and other organic compounds. When substituted benzene molecules undergo electrophilic reactions, substituents on a benzene ring can influence the reactivity. The inclusion of substituents in benzene leads to the variation of charge distribution in the molecule, and consequently affects the structural, electronic and vibrational parameters. The main focus of the present investigation is the study of the molecular structure and vibrational spectra of 2,4-difluoro-1-methoxybenzene (DFMB) and 1-chloro-3-methoxy benzene (CMB) completely by density functional theory (DFT) levels using 6-311++G(d,p) basis set and to identify the various normal modes with greater wave number accuracy. It should be emphasized that in this calculations the p-polarization functions are included on the hydrogen atoms, which are known to be very important for reproducing the out-of-plane vibrations involving hydrogen atoms. The density functional theory calculations are reported [5] to provide accurate vibrational frequencies of organic compounds, if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation for basis set deficiencies and for the anharmonicity.

II. EXPERIMENTAL DETAILS

The fine samples of DFMB and CMB were purchased from Lancaster chemical company, UK and they were used as such without any further purification to record FT-IR and FT-Raman spectra. The FT-IR spectrum of DFMB and CMB has been recorded in the region 4000-400 cm^{-1} at a resolution of $\pm$ 1 cm^{-1} using BRUKER IFS 66V model FT-IR spectrometer equipped with an MCT detector, a KBr beam splitter and globar arc source.

The FT-Raman spectrum of DFMB and CMB has been recorded using 1064 nm line of Nd:YAG laser as excitation wavelength in the Stokes region 3500-50 cm^{-1}on a BRUKER IFS-66V model interferometer equipped with an FRA-106 FT-Raman accessory operating at 200 mW power. The calibrated wave numbers are expected to be accurate within $\pm$ 1 cm^{-1}.

III. COMPUTATIONAL DETAILS

In order to meet the requirements of both accuracy and computing economy, theoretical methods and basis sets should be considered. DFT has proved to be extremely useful in treating electronic structure of molecules. The DFT calculations were carried out for DFMB and CMB with GAUSSIAN 09W program package [6]. Initial geometry, generated from the standard geometrical parameters was minimized without any constraint on the potential energy surface at DFT level adopting the standard 6-311++G(d,p) basis set. All the parameters were allowed to relax and all the calculations converged to an optimized geometry, which corresponds to a true minimum, as revealed by the lack of imaginary values in the wavenumber calculations. The Cartesian representation of the theoretical force constants are computed at the fully optimized geometry. The multiple scaling of the force constants were performed according to the SQM procedure [7,8] using selective scaling in the natural internal coordinate representation [9,10]. The transformation of force field, the subsequent normal coordinate analysis including the least square refinement of the scale factors and calculation of the Total energy distribution (TED) were done on a PC with the MOLVIB program (version V7.0-G77) written by Sundius [11,12]. The systematic comparison of the results from DFT theory with results of experiments has shown that the method using B3LYP functional is the most promising in providing correct vibrational wave numbers.

IV. RESULTS AND DISCUSSION

4.1. Molecular Geometry
The optimized molecular structures of DFMB and CMB along with numbering of atoms are shown in Figs. 1 and 2 respectively. The optimized geometrical parameters calculated at B3LYP/6-311++G(d,p) levels for both the compounds are presented in Tables 1and 2 for DFMB and CMB respectively. The calculated geometric parameters can be used as a foundation to calculate the other parameters for the compounds. The optimized molecular structure of DFMB and CMB, the bonding properties of the molecules are influenced by the rearrangement of electrons during substitutions and addition reactions.
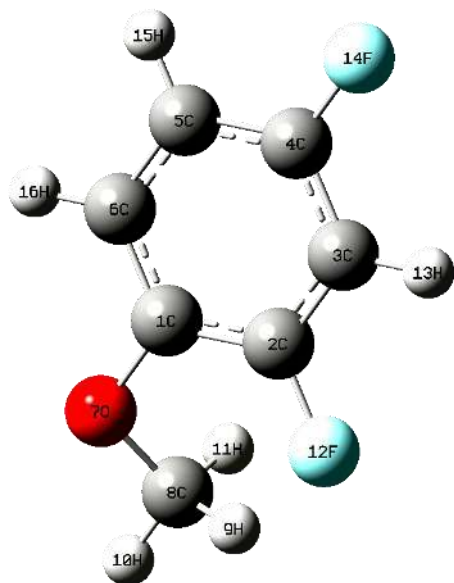
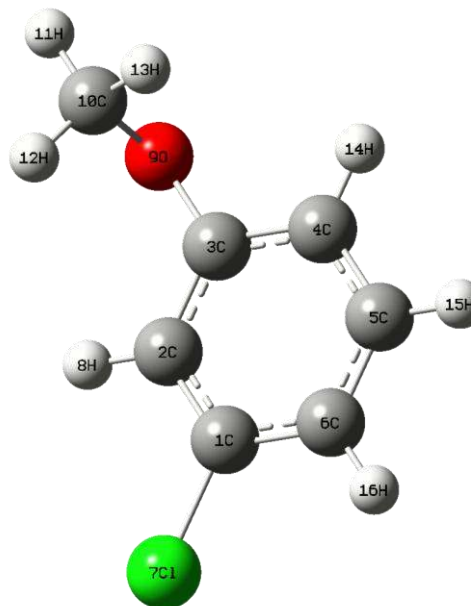Fig 1: Molecular structure of 2,4-difluro-1-methoxy benzene

Fig 2: Molecular Structure of 1-chloro -3-methoxy benzene

Normal coordinate analyses are carried out for DFMB and CMB to provide a complete assignment of fundamental frequencies. For this purpose, a full set of 55 standard internal coordinates (containing 13 redundancies) for both DFMB and CMB are defined as given in Tables.3 and 4 respectively. From these, a non-redundant set of local symmetry coordinates are constructed by suitable linear combinations of internal coordinates following the recommendations of Fogarasi *et al.* [10,13] and are summarized in Tables 5 and 6 for DFMB and CMB respectively. The theoretically calculated force fields are transformed to this set of vibrational coordinates and used in all subsequent calculations.

V. FIRST HYPERPOLARIZABILITY

The potential application of DFMB and CMB in the field of nonlinear optics demands the investigation of its structural and bonding features contributing to the hyperpolarizability enhancement, by analyzing the vibrational modes using IR and Raman spectroscopies. Many organic molecules, containing conjugated π electrons are characterized by large values of molecular first hyperpolarizabilities, were analyzed by means of vibrational spectroscopy [14,15]. In most of the cases, even in the absence of inversion symmetry, the strongest band in the Raman spectrum is weak in the IR spectrum and vice-versa. But the intramolecular charge from the donor to acceptor group, through a π- bond conjugated path can induce large variations of both the molecular dipole moment and the molecular polarizability, making IR and Raman activity strong at the same time. The experimental spectroscopic behavior described above is well accounted for calculations in π conjugated systems that predict exceptionally infrared intensities for the same normal modes [15]. The first hyperpolarizabilities (β) of these novel molecular systems are calculated using *ab initio* quantum mechanical method, based on the finite-field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. The first hyperpolarizability is a third-rank tensor that can be described by a 3 × 3 × 3 matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [16].

The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the electric field is weak and homogeneous, this expansion becomes

$$E = E_0 - \sum_i \mu_i F^i - \frac{1}{2}\sum_{ij}\alpha_{ij}F^iF^j - \frac{1}{6}\sum_{ijk}\beta_{ijk}F^iF^jF^k - \frac{1}{24}\sum_{ijkl}\nu_{ijkl}F^iF^jF^kF^l + ... \qquad ... (1)$$

where E_0 is the energy of the unperturbed molecule; F^i is the field at the origin; and μ_i , α_{ij}, β_{ijk} and γ_{ijkl} are the components of dipole moment, polarizability, the first hyperpolarizabilities and second hyperpolarizibilites, respectively. The calculated total dipole moment (μ) and mean first hyperpolarizability (β) of DFMB are 1.8077 Debye and 0.6007 × 10^{-30} esu, respectively, which is comparable with the reported values of similar derivatives [4,17]. Similarly, the total dipole moment (μ) and mean first hyperpolarizability (β) of CMB are found to be 1.6071 Debye and 0.7848 × 10^{-30} esu, respectively. The large value of hyperpolarizability, β which is a measure of the non-linear optical activity of these molecular systems, are associated with the

intramolecular charge transfer, resulting from the electron cloud movement through π conjugated frame work from electron donor to electron acceptor groups. The physical properties of these conjugated molecules are governed by the high degree of electronic charge delocalization, along with the charge transfer axis and by the low band gaps. So, DFMB and CMB are an attractive objects for future studies of nonlinear optical properties.

VI. HOMO-LUMO ANALYSIS

The electronic absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The atomic orbital HOMO and LUMO compositions of the frontier molecular orbital for DFMB are shown in Figs.3. For CMB, the atomic orbital HOMO and LUMO compositions of the frontier molecular orbital are shown in Fig.4. The HOMO–LUMO energy gap of DFMB and CMB are calculated at B3LYP/6-311++G(d,p) levels and are shown in Table 7 and 8 respectively. It reveals that the energy gap reflects the chemical activity of the molecules. The LUMO, as an electron acceptor, represents the ability to obtain an electron, and HOMO represents the ability to donate an electron. Moreover, a lower HOMO–LUMO energy gap explains the fact that eventual charge transfer interaction is taking place within the molecules.
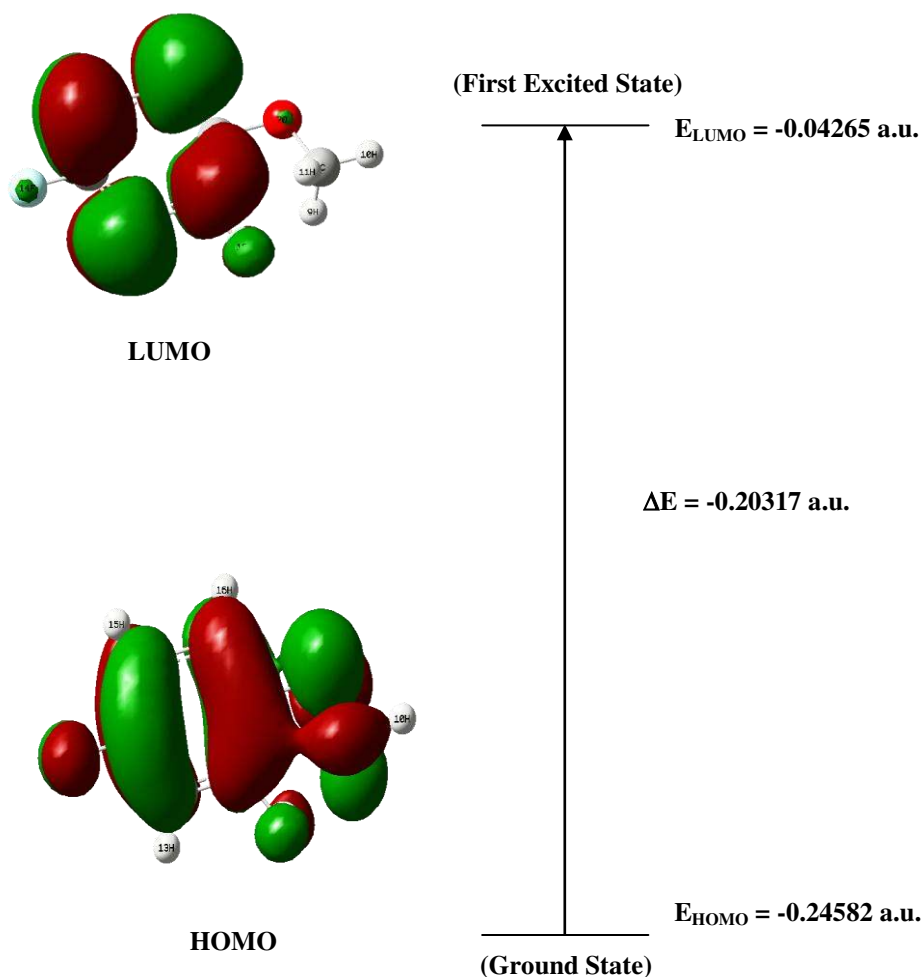

(First Excited State)

E_{LUMO} = -0.04265 a.u.

LUMO

ΔE = -0.20317 a.u.

E_{HOMO} = -0.24582 a.u.

HOMO

(Ground State)

Fig 3: HOMO – LUMO energy gap of 2,4-difluro-1-methoxy benzene

(First Excited State)

E_{LUMO} = **-0.03580 a.u**.

LUMO

ΔE = **-0.22215 a.u.**

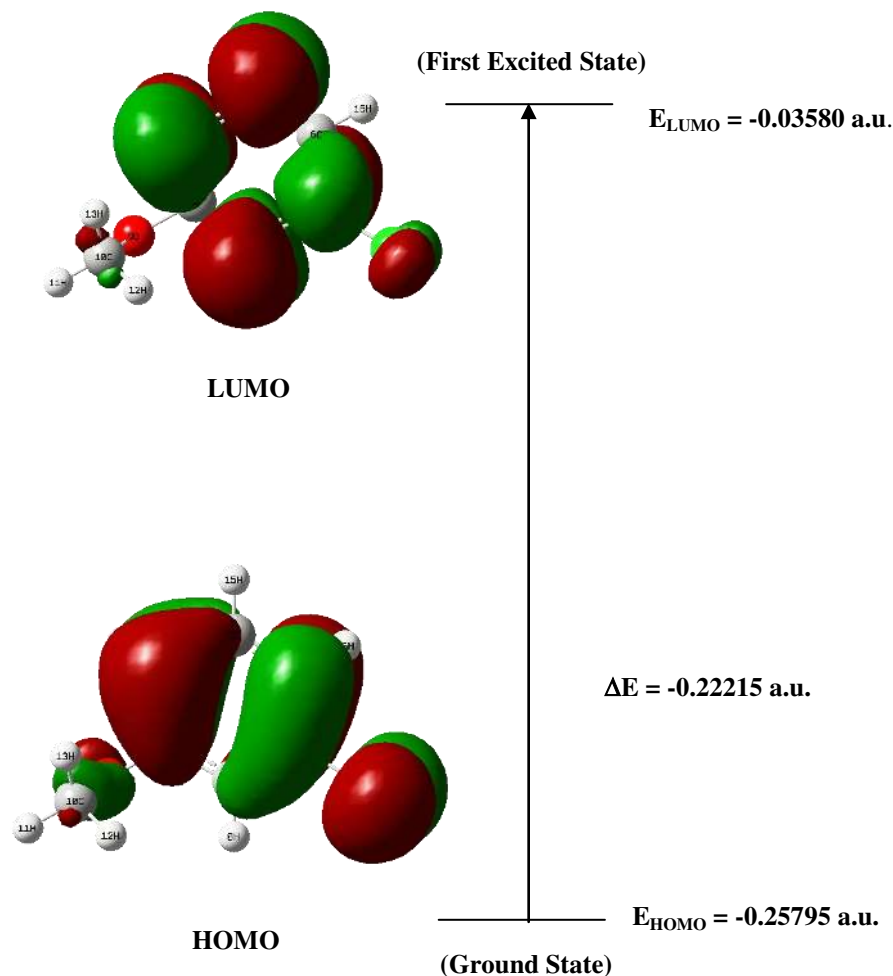E_{HOMO} = **-0.25795 a.u.**

HOMO

(Ground State)

Fig 4: HOMO – LUMO energy gap of 1-chloro -3-methoxy benzene

VII. OTHER MOLECULAR PROPERTIES

The thermodynamic properties like heat capacity, zero point energy, entropy along with the global minimum energy of DFMB and CMB are obtained by density functional method using 6-311++G(d,p) basis set calculations are presented in Tables 9 and 10 respectively. The difference in the values calculated by both the methods are marginal. Scale factors are recommended [17] for an accurate prediction in determining the zero-point vibration energy (ZPVE), and the entropy (S_{vib}). The variation in the ZPVE seems to be insignificant. The total energy and the change in the total entropy of the compounds at room temperature are also presented.

VIII. VIBRATIONAL SPECTRA

From the structural point of view, the molecules DFMB and CMB are assumed to have C_s and C_1 point group symmetries, respectively. The 42 fundamental modes of vibrations, arising for DFMB are classified into 29A' and 13A" species. The A' and A" species represent the in-plane and out-of-plane vibrations, respectively. From the structural point of view, the molecule CMB is assumed to have C_1 point group symmetry and hence all the calculated frequency transforming to the same symmetry species (A). The molecule CMB consists of 16 atoms and expected to have 42 normal modes of vibrations. These modes are found to be IR and Raman active suggesting that the molecule possesses a non-centrosymmetric structure, which recommends the compound for non-linear optical applications. The observed FT-IR and FT-Raman spectra of DFMB and CMB are shown in Figs. 5-8. The detailed Vibrational assignment of fundamental modes of DFMB and CMB along with the calculated IR and Raman frequencies and normal mode descriptions (characterized by TED) are reported in Tables.11 and 12 respectively.
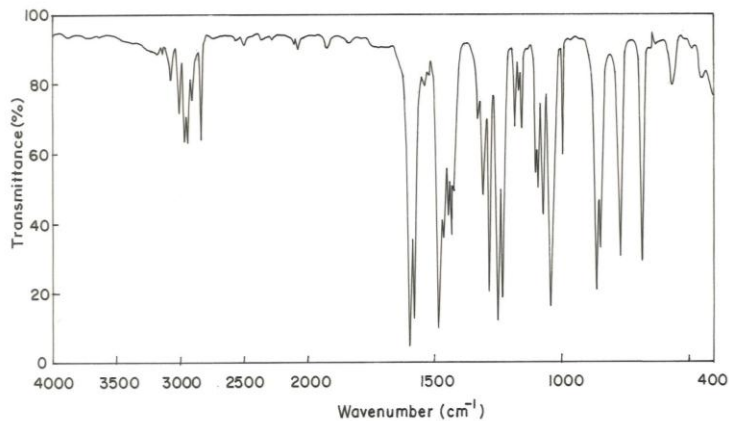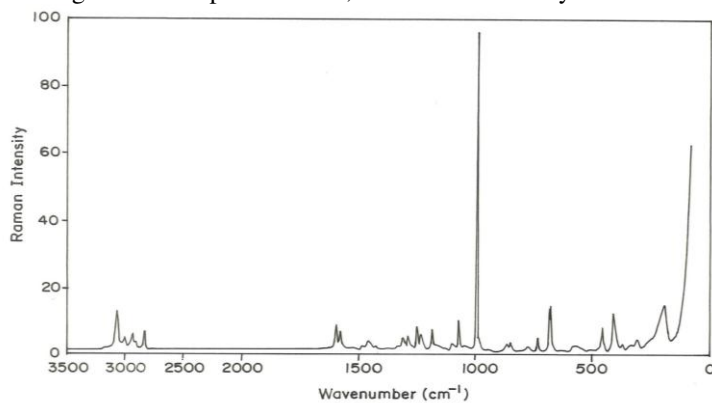
Fig. 5: FT-IR spectrum of 2,4-difluro-1-methoxy benzene

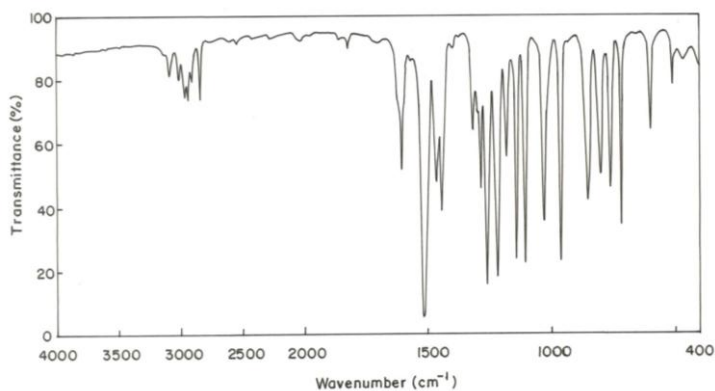
Fig. 6: FT-Raman spectrum of 2,4-difluro-1-methoxy benzene

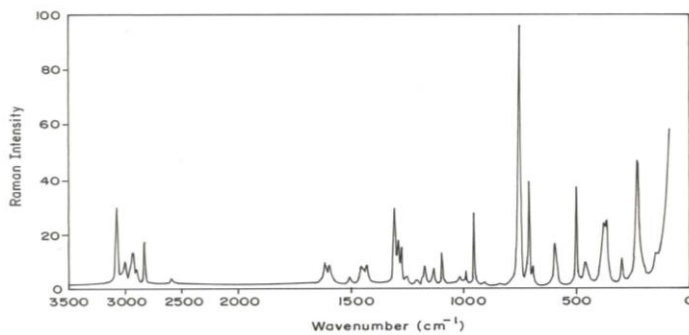Fig. 7: FT-IR spectrum of 1-chloro -3-methoxy benzene

Fig. 8: FT-Raman spectrum of 1-chloro -3-methoxy benzene

The vibrational analysis obtained for DFMB and CMB with the unscaled B3LYP/6-31+G(d,p) force field are generally greater than the experimental values due to neglect of anharmonicity in real system. These discrepancies can be corrected either by computing anharmonic corrections explicitly or by introducing a scaled field or directly scaling the calculated wave numbers with proper factor [18]. A tentative assignment is often made on the basis of the unscaled frequencies by assuming the observed frequencies, so that they are in the same order as the calculated ones. Then, for an easier comparison to the observed values, the calculated frequencies are scaled by the scale to less than 1, to minimize the overall deviation. A better agreement between the computed and experimental frequencies can be obtained by using different scale factors for different regions of vibrations. For that purpose, different scaling factors for all fundamental modes are utilized to obtain the scaled frequencies of the compounds. The resultant scaled frequencies are also listed in Table 11 and 12.

C-H Vibrations
The C-H Stretching vibrations of benzene derivatives generally occur in the range 3100-3000 cm^{-1}. The in-plane C-H bending vibrations appear in the range 1300-1000 cm^{-1} in the substituted benzenes and the out-of-plane bending vibrations in the range 1000-750 cm^{-1} [19]. The FT-IR vibrational frequencies obtained at 3087,3013, 2964 cm^{-1} are assigned to C–H Stretching vibrations of DFMB and show good agreement with the calculated results. The Raman counterparts of C-H Stretching vibrations are observed at 3020 cm^{-1}. The FT-Raman bands at 1150 cm^{-1} and infrared bands at 1183, 1143, 1106 cm^{-1} are assigned to C–H in-plane bending vibrations of DFMB. Accordingly, the C-H Stretching vibrations of CMB are observed at 3139, 3084, 3075, 3008 cm^{-1} in FT-IR and 3090, 3010cm^{-1} in the FT-Raman spectrum. The observed C–H out-of-plane bending modes of the compounds show consistent agreement with the computed B3LYP results and are listed in Tables 11 and 12.

C-C Vibrations
The C-C aromatic Stretching vibrations gives rise to characteristic bands in both the observed IR and Raman spectra, covering the spectral range from 1600 to 1400 cm^{-1}[19,20]. Therefore, the C-C Stretching vibrations of DFMB are found at 1606, 1516, 1460, 1445, 1401cm^{-1} in FT-IR spectrum and 1600, 1440 cm^{-1} in the FT-Raman spectrum. Further, the C-C Stretching vibrations of the CMB are found at 1596, 1579, 1541, 1484, 1465, 1446 cm^{-1} and 1600, 1580, 1450cm^{-1} in the FTIR and FT-Raman spectra respectively. These modes are confirmed by their TED values. Most of the ring vibrational modes are affected by the substitutions in the aromatic ring of DFMB and CMB. In the present investigation, the bands observed at 1051, 963, cm^{-1} in the FT-IR and 990 cm^{-1} in Raman spectrum are designated to ring in-plane bending modes of DFMB. The ring out-of-plane bending modes of DFMB are also listed in the Table 11. Further, the ring in-plane and out-of-plane bending vibrations are made for CMB by careful consideration of their qualitative descriptions and are reported in Table 12. The reductions in the frequencies of these modes are due to the change in force constant and the vibrations of the functional groups present in the molecules. The theoretically computed values for C-C vibrational modes of the compounds by B3LYP/6-311++G(d,p) method gives excellent agreement with experimental data.

C–F Vibrations
In the vibrational spectra of related compounds, the bands due to C-F Stretching vibrations [21] may be found over a wide frequency range 1360-1000 cm^{-1} since the vibration is easily affected by adjacent atoms or groups. In the present investigation, the FT-IR band observed at 1286, 1261 cm^{-1} is assigned to C-F Stretching mode of vibration for DFMB. The C-F in-plane vibrations of DFMB is found at 801 and 761 cm^{-1} in FT-IR and 810 cm^{-1} in Raman spectrum. The C-F out-of-plane deformation is also reported in the Table 11.

C-Cl Vibrations
The C–Cl Stretching vibrations generally yield strong bands in the region 760-505 cm^{-1} [22]. The FT-IR band observed at 768 cm^{-1} is assigned to C-Cl Stretching vibrations. Most of the aromatic chloro compounds have a band of strong-to-medium intensity in the region 385-265 cm^{-1} due to C–Cl in-plane bending vibrations. Accordingly, the FT-Raman band identified at 490 cm^{-1} is assigned to the C–Cl in-plane bending mode. The C–Cl out-of-plane deformation vibration is established at 410 cm^{-1} in FT-Raman spectrum.

C−O Vibrations
The interaction of the carbonyl group with a hydrogen donor group does not produce drastic and characteristic changes in the frequency of the C=O stretch as done by O–H stretch. A great deal of structural information can be derived from the exact position of the carbonyl Stretching absorption peak. Susi and Ard [23] identified the C=O Stretching mode at 1645 and 1614 cm^{-1}. On referring to the above findings and on the basis of the results of the normal coordinate analysis, the present investigation, the C–O Stretching vibrations are found at 1318, 1298 cm^{-1} in FT-IR and 1320, 1290 cm^{-1} in FT-Raman for DFMB and for CMB, the FT-IR peaks observed at 1432, 1424 cm^{-1} are assigned for C–O Stretching vibrations are confirmed by their TED

values. The C–O in-plane and out-of-plane bending vibrations level are also identified and presented in Tables 11 and 12 respectively for DFMB and CMB.

CH$_3$ group Vibrations

The investigated molecule under consideration possesses CH$_3$ groups in first position of DFMB and CMB third position of the ring. For the assignments of CH$_3$ group frequencies, one can expect that nine fundamentals can be associated to each CH$_3$ group, namely three Stretching, three bending, two rocking modes and a single torsional mode describe the motion of methyl group. The CH$_3$ symmetric Stretching frequency is identified at 2940 cm^{-1} in the FT-IR spectrum and 2935 cm^{-1} in the FT-Raman spectrum for DFMB and 2940 cm^{-1} in the FTIR spectrum for CMB. The CH$_3$ in-plane bending vibrations are identified at 2912 cm^{-1} in the FTIR spectrum for DFMB and 2960 cm^{-1} in FT-Raman spectrum and 2963cm^{-1} in the FT-IR spectrum for CMB. The CH$_3$ symmetric bending and CH$_3$ in-plane bending frequencies are attributed at 1205 cm^{-1} in FT-Raman and 1219 cm^{-1} in the FT-IR spectrum for DFMB respectively and 1183 cm^{-1} and 1232 cm^{-1} in the FT-IR spectrum and 1240 cm^{-1} FT-Raman spectrum for CMB respectively. These assignments are supported by literature [24]. The in-plane rocking and out-of-plane rocking modes of CH$_3$ group are found at 761 cm^{-1} and 718 cm^{-1} in the FTIR spectrum for DFMB respectively, and the peaks observed at 846cm^{-1} in the FTIR and 740 cm^{-1} in FT-Raman spectrum for CMB. The bands obtained at 2844 cm^{-1} and 2850 cm^{-1} in the FTIR and FT Raman spectrum and 1190 in FT-Raman spectrum for DFMB and at 2908 cm^{-1} and 1168 cm^{-1} in the FTIR for CMB are assigned to CH$_3$ out-of-plane stretching and CH$_3$ out-of-plane bending modes, respectively. The assignment of the bands at 250 cm^{-1} in the FT Raman spectrum for DFMB and 203 cm^{-1} FT-Raman spectrum for CMB are attributed to methyl twisting mode.

IX. CONCLUSION

The optimized geometries, harmonic vibrational wave numbers and intensities of vibrational bands of 2,4-difluoro-1-methoxybenzene (DFMB) and 1-chloro-3-methoxy benzene (CMB) are determined using DFT/B3LYP method with 6-311++G(d,p) level calculations. The normal modes of the compounds have been studied by FT-IR and FT-Raman spectroscopies based on scaled quantum chemical calculations. The systematic comparison of the results from DFT theory with results of experiments has shown that the method using B3LYP functional is the most promising in providing correct vibrational wavenumbers. On the basis of the agreement between the calculated and experimental results, assignments of all the fundamental vibrational modes of DFMB and CMB are made in this investigation. The difference between the observed and scaled wave number values of most of the fundamentals are very small. The TED calculation regarding the normal modes of vibration provides a strong support for the frequency assignment. Furthermore, the thermodynamic, nonlinear optical, first-order hyperpolarizability and total dipole moment properties of the compounds are calculated in order to get insight into the compounds. These results will be of assistance in the quest of the experimental and theoretical evidence for DFMB and CMB in reaction intermediates, nonlinear optical and photoelectric materials.

Table 1: Optimized geometrical parameters of 2,4-difluoro -1-methoxybenzene in B3LYP/6-311++G(d,p) method

Atom	Bond Length (A^0)	Atom	Bond Angle (^{0})	Atom	Dihedral Angle (^{0})
C1-C2	1.3988	C2-C1-C6	117.66	C6-C1-C2-C3	-0.99
C1-C6	1.3952	C2-C1-O7	122.80	C6-C1-C2-F12	178.34
C1-O7	1.3674	C6-C1-O7	119.42	O7-C1-C2-C3	-176.99
C2-C3	1.3854	C1-C2-C3	122.46	O7-C1-C2-F12	2.34
C2-F12	1.3531	C1-C2-F12	119.14	C2-C1-C6-C5	0.31
C3-C4	1.3865	C3-C2-F12	118.39	C2-C1-C6-H16	-179.07
C3-H13	1.0819	C2-C3-C4	117.67	O7-C1-C6-C5	176.45
C4-C5	1.3851	C2-C3-H13	120.78	O7-C1-C6-H16	-2.94
C4-F14	1.3543	C4-C3-H13	121.54	C2-C1-O7-C8	-64.40
C5-C6	1.3932	C3-C4-C5	122.32	C6-C1-O7-C8	119.68
C5-H15	1.0822	C3-C4-F14	118.42	C1-C2-C3-C4	0.86
C6-H16	1.0831	C5-C4-F14	119.26	C1-C2-C3-H13	179.96
O7-C8	1.4356	C4-C5-C6	118.47	F12-C2-C3-C4	-178.48
C8-H9	1.0918	C4-C5-H15	120.00	F12-C2-C3-H13	0.62
C8-H10	1.0889	C6-C5-H15	121.53	C2-C3-C4-C5	-0.03

Atom	Bond Length	Atom	Bond Angle	Atom	Dihedral Angle
C8-H11	1.095	C1-C6-C5	121.41	C2-C3-C4-F14	179.71
H9-F12	2.3945	C1-C6-H16	117.89	H13-C3-C4-C5	-179.13
		C5-C6-H16	120.70	H13-C3-C4-F14	0.62
		C1-O7-C8	116.67	C3-C4-C5-C6	-0.60
		O7-C8-H9	111.52	C3-C4-C5-H15	179.61
		O7-C8-H10	105.81	F14-C4-C5-C6	179.65
		O7-C8-H11	110.40	F14-C4-C5-H15	-0.13
		H9-C8-H10	109.58	C4-C5-C6-C1	0.45
		H9-C8-H11	109.90	C4-C5-C6-H16	179.82
		H10-C8-H11	109.54	H15-C5-C6-C1	-179.77
				H15-C5-C6-H16	-0.40
				C1-O7-C8-H9	64.76
				C1-O7-C8-H10	-176.16
				C1-O7-C8-H11	-57.73

For numbering of atoms refer Fig. 1.

Table 2: Optimized geometrical parameters of 1-chloro-3-methoxybenzene in B3LYP/6-311++G(d,p) method

Atom	Bond Length (A^0)	Atom	Bond Angle(^{0})	Atom	Dihedral Angle(^{0})
C1-C2	1.3943	C2-C1-C6	122.34	C6-C1-C2-C3	0.0011
C1-C6	1.3865	C2-C1-Cl7	118.31	C6-C1-C2-H8	179.99
C1-Cl7	1.7621	C6-C1-Cl7	119.34	Cl7-C1-C2-C3	180.00
C2-C3	1.3976	C1-C2-C3	118.61	Cl7-C1-C2-H8	0.00
C2-H8	1.08	C1-C2-H8	119.47	C2-C1-C6-C5	0.00
C3-C4	1.4011	C3-C2-H8	121.91	C2-C1-C6-H16	-179.99
C3-O9	1.3616	C2-C3-C4	120.07	Cl7-C1-C6-C5	-180.00
C4-C5	1.3865	C2-C3-O9	123.97	Cl7-C1-C6-H16	0.00
C4-H14	1.0828	C4-C3-O9	115.96	C1-C2-C3-C4	0.00
C5-C6	1.3978	C3-C4-C5	119.76	C1-C2-C3-O9	179.98
C5-H15	1.084	C3-C4-H14	118.69	H8-C2-C3-C4	-179.99
C6-H16	1.0816	C5-C4-H14	121.54	H8-C2-C3-O9	-0.01
O9-C10	1.4226	C4-C5-C6	121.19	C2-C3-C4-C5	0.00
C10-H11	1.0885	C4-C5-H15	119.51	C2-C3-C4-H14	179.99
C10-H12	1.0952	C6-C5-H15	119.30	O9-C3-C4-C5	-179.98
C10-H13	1.0952	C1-C6-C5	118.02	O9-C3-C4-H14	0.01
		C1-C6-H16	120.60	C2-C3-O9-C10	0.02
		C5-C6-H16	121.38	C4-C3-O9-C10	180.00
		C3-O9-C10	118.79	C3-C4-C5-C6	0.00
		O9-C10-H11	105.78	C3-C4-C5-H15	180.00
		O9-C10-H12	111.36	H14-C4-C5-C6	-179.99
		O9-C10-H13	111.35	H14-C4-C5-H15	0.00
		H11-C10-H12	109.34	C4-C5-C6-C1	0.00
		H11-C10-H13	109.35	C4-C5-C6-H16	-180.01
		H12-C10-H13	109.58	H15-C5-C6-C1	180.01
				H15-C5-C6-H16	0.00
				C3-O9-C10-H11	-180.01
				C3-O9-C10-H12	-61.33
				C3-O9-C10-H13	61.30

For numbering of atoms refer Fig. 2.

Table 3: Definition of internal co-ordinates of 2,4-diflouro-1-methoxy benzene

No	Symbol	Type	Definition
Stretching			
1-6	r_i	C-C	C1-C2, C2-C3, C3-C4, C4-C5, C5-C6, C6-C1
7-8	R_i	C-O	C1-O7, C8-O7
9-10	δ_i	C-CF	C2-F12, C4-F14
11-13	T_i	C-H	C3-H13, C5-H15, C6-H16
14-16	ρ_i	C-H(Methyl)	C8-H9, C8-H10, C8-H11
Bending			
In plane Bending			
17-22	α_i	Ring	C1-C2-C3, C2-C3-C4, C3-C4-C5, C4-C5-C6, C5-C6-C1, C6-C1-C2
23-25	β_i	O-C-H	O7-C8-H9, O7-C8-H10, O7-C8-H11
26-28	γ_i	H-C-H	H9-C8-H10, H9-C8-H11, H10-C8-H11
29-34	ϕ_i	C-C-H	C2-C3-H13, C4-C3-H13, C4-C5-H15, C6-C5-H15, C5-C6-H16, C1-C2-H16, C1-C6-H16
35-38	Σ_i	C-C-F	C1-C2-F12, C3-C2-F12, C3-C4-F14, C5-C4-F14
39-40	σ_i	C-C-O	C2-C1-O7, C6-C1-O7
41	θ_i	C-O-C	C1-O7-C8
Out of plane Bending			
42-44	ω_i	C-H	H13-C3-C4-C2, H15-C5-C6-C4, H16-C6-C1-C5
45-46	$\prod_i$	C-CF	F12-C2-C3-C1, F14-C4-C5-C3
47	ρ_i	C-O	O7-C1-C2-C6
48	λ_i	C-O	C8-O7-C8-(C2, C6)
49-54	τ_i	τring	C1-C2-C3-C4, C2-C3-C4-C5, C3-C4-C5-C6, C4-C5-C6-C1, C5-C6-C1-C2, C6-C1-C2-C3
55	τ_i	t-OCH$_3$	C1-O7-C8-(H9, H10, H11)

Table 4: Definition of internal co-ordinates of 1-chloro -3-methoxy benzene

No	Symbol	Type	Definition
Stretching			
1-6	r_i	C-C	C1-C2, C2-C3, C3-C4, C4-C5, C5-C6, C6-C1
7-8	R_i	C-O	C3-O9, C10-O9
9	δ_i	C-Cl	C1-Cl7
10-13	T_i	C-H	C2-H8, C4-H14, C5-H15, C6-H16
14-16	ρ_i	C-H(Methyl)	C10-H11, C10-H12, C10-H13
Bending			
In plane Bending			
17-22	α_i	Ring	C1-C2-C3, C2-C3-C4, C3-C4-C5, C4-C5-C6, C5-C6-C1, C6-C1-C2
23-25	β_i	O-C-H	O9-C10-H11, O9-C10-H12, O9-C10-H13
26-28	γ_i	H-C-H	H12-C10-H13, H11-C10-H12, H13-C10-H12
29-36	ϕ_i	C-C-H	C1-C2-H8, C3-C2-H8, C3-C4-H14, C5-C4-H14, C4-C5-H15, C6-C5-H15, C5-C6-H16
37-38	Σ_i	C-C-Cl	C2-C1-Cl7, C6-C1-Cl7
39-40	σ_i	C-C-O	C2-C3-O9, C4-C2-O9
41	θ_i	C-O-C	C3-O9-C10
Out of plane Bending			
42-45	ω_i	C-H	H8-C2-C3-C1, H14-C4-C5-C3, H15-C5-C6-C4, H16-C6-C1-C5
46	$\prod_i$	C-Cl	Cl7-C1-C2-C6

47	ρ_i	C-O	O9-C3-C4-C2
48	λ_i	C-O	C3-O9-C10-(C4, C2)
49-54	τ_i	τring	C1-C2-C3-C4, C2-C3-C4-C5, C3-C4-C5-C6, C4-C5-C6-C1, C5-C6-C1-C2, C6-C1-C2-C3
55	τ_i	t-OCH$_3$	C3-O9-C10-(H12, H11, H13)

Table 5: Definition of local symmetry co-ordinates for 2,4-diflouro-1-methoxy benzene

NO	Symbol[a]	Definition[b]
1-6	C-C	$r_1, r_2, r_3, r_4, r_5, r_6$
7-8	C-O	$R_7 - R_8$
9-10	C-F	δ_9, δ_{10}
11-13	C-H	T_{11}, T_{12}, T_{13}
14	CH3ss	$(\rho_{14} + \rho_{15} + \rho_{16})/\sqrt{3}$
15	CH$_3$ips	$(2\rho_{14} + \rho_{15} + \rho_{16})/\sqrt{6}$
16	CH$_3$ops	$(\rho_{15} - \rho_{16})/\sqrt{2}$
17	Rtrigd	$(\alpha_{17} - \alpha_{18} + \alpha_{19} - \alpha_{20} + \alpha_{21} - \alpha_{22})/\sqrt{16}$
18	Rsymd	$(-\alpha_{17} - \alpha_{18} + 2\alpha_{19} - \alpha_{20} - \alpha_{21} + 2\alpha_{22})/\sqrt{12}$
19	Rasymd	$(\alpha_{17} - \alpha_{18} + \alpha_{20} - \alpha_{21})/\sqrt{2}$
20	CH$_3$sb	$(-\beta_{23} - \beta_{24} - \beta_{25} + \gamma_{26} + \gamma_{27} + \gamma_{28})/\sqrt{6}$
21	CH$_3$ipb	$(2\gamma_{26} - \gamma_{27} - \gamma_{28})/\sqrt{6}$
22	CH$_3$opb	$(\gamma_{27} - \gamma_{28})/\sqrt{2}$
23	CH$_3$ipr	$(2\beta_{23} - \beta_{24} - \beta_{25})/\sqrt{6}$
24	CH$_3$opr	$(\beta_{24} - \beta_{25})/\sqrt{2}$
25-27	bCH	$(\varphi_{29} - \varphi_{30})/\sqrt{2}$, $(\varphi_{31} - \varphi_{32})/\sqrt{2}$ $(\varphi_{33} - \varphi_{34})/\sqrt{2}$ $(\varphi_{35} - \varphi_{36})/\sqrt{2}$
28-29	bCF	$\varepsilon_{35} - \varepsilon_{36}/\sqrt{2}$, $(\varepsilon_{37} - \varepsilon_{38})/\sqrt{2}$
30	bCO	$(\sigma_{39} - \sigma_{40})/\sqrt{2}$
31	bOC	θ_{41}
32-34	ωCH	$\omega_{42}, \omega_{43}, \omega_{44}$
35-36	ωCF	$\prod_{45}, \prod_{46}$
37	ωCO	ρ_{47}
38	ωCO	λ_{48}
39	Tring	$(\tau_{49} - \tau_{50} + \tau_{51} - \tau_{52} + \tau_{53} - \tau_{54})/\sqrt{6}$
40	tRsymd	$(\tau_{49} - \tau_{51} + \tau_{52} - \tau_{53})/\sqrt{2}$
41	tRasymd	$(-\tau_{49} + 2\tau_{50} - \tau_{51} - \tau_{52} + 2\tau_{53} - \tau_{54})/\sqrt{12}$
42	τOCH$_3$	τ_{55}

[a]These symbols are used for description of normal modes by TED in Table 11
[b]The internal co-ordinate used here are defined in Table 3.

Table 6: Definition of local symmetry co-ordinates for 1-chloro-3-methoxy benzene

NO	Symbol[a]	Definition[b]
1-6	C-C	$r_1, r_2, r_3, r_4, r_5, r_6$
7-8	C-O	$R_7 - R_8$
9	C-Cl	δ_9
10-13	C-H	$T_{10}, T_{11}, T_{12}, T_{13}$
14	CH3ss	$(\rho_{14} + \rho_{15} + \rho_{16})/\sqrt{3}$
15	CH$_3$ips	$(2\rho_{14} + \rho_{15} + \rho_{16})/\sqrt{6}$
16	CH$_3$ops	$(\rho_{15} - \rho_{16})/\sqrt{2}$
17	Rtrigd	$(\alpha_{17} - \alpha_{18} + \alpha_{19} - \alpha_{20} + \alpha_{21} - \alpha_{22})/\sqrt{16}$
18	Rsymd	$(-\alpha_{17} - \alpha_{18} + \alpha_{19} - \alpha_{20} - \alpha_{21} + \alpha_{22})/\sqrt{12}$

19	Rasymd	$(\alpha_{17} - \alpha_{18} + \alpha_{20} - \alpha_{21})/\sqrt{2}$
20	CH$_3$sb	$(-\beta_{23} - \beta_{24} - \beta_{25} + \gamma_{26} + \gamma_{27} + \gamma_{28})/\sqrt{6}$
21	CH$_3$ipb	$(\gamma_{26} - \gamma_{27} - \gamma_{28})/\sqrt{6}$
22	CH$_3$opb	$(\gamma_{27} - \gamma_{28})/\sqrt{2}$
23	CH$_3$ipr	$(-\beta_{23} - \beta_{24} - \beta_{25})/\sqrt{6}$
24	CH$_3$opr	$(\beta_{24} - \beta_{25})/\sqrt{2}$
25-28	bCH	$(\varphi_{29} - \varphi_{30})/\sqrt{2}$, $(\varphi_{31} - \varphi_{32})/\sqrt{2}$, $(\varphi_{33} - \varphi_{34})/\sqrt{2}$, $(\varphi_{35} - \varphi_{36})/\sqrt{2}$
29	bCCl	$(\varepsilon_{37} - \varepsilon_{38})/\sqrt{2}$
30	bCO	θ_{41}
32-35	ΩCH	$\omega_{42}, \omega_{43}, \omega_{44}, \omega_{45}$
36	ωCl	$\prod_{46}$
37	ωCO	ρ_{47}
38	ωCO	λ_{48}
39	τring	$(\tau_{49} - \tau_{50} + \tau_{51} - \tau_{52} + \tau_{53} - \tau_{54})/\sqrt{6}$
40	tRsymd	$(\tau_{49} - \tau_{51} + \tau_{52} - \tau_{53})/\sqrt{2}$
41	tRasymd	$(-\tau_{49} + 2\tau_{50} - \tau_{51} - \tau_{52} + 2\tau_{53} - \tau_{54})/\sqrt{12}$
42	τOCH$_3$	τ_{55}

[a]These symbols are used for description of normal modes by TED in Table 12
[b]The internal co-ordinate used here are defined in Table 4.

Table 7: HOMO-LUMO energy values of 2,4-difluro-1-methoxy benzene in B3LYP/6-311++G(d,p) method

Parameters	B3LYP/6-311++G(d,p)
HOMO energy	-0.24582 a.u
LUMO energy	-0.04265 a.u
HOMO - LUMO energy gap	-0.20317 a.u

Table 8: HOMO-LUMO energy values 1-Chloro -3-methoxy benzene in B3LYP/6-311++G(d,p) method

Parameters	B3LYP/6-311++G(d,p)
HOMO energy	-0.25795(a.u)
LUMO energy	-0.03580(a.u)
HOMO - LUMO energy gap	-0.22215(a.u)

Table 9: Thermodynamic parameters of calculated at 2,4-difluro-1-methoxy benzene B3LYP/6-311++G(d,p) method

Parameters	Method / Basis set B3LYP/ 6-311++G(d,p)
Optimized global minimum Energy,(Hartrees)	-545.394952925
Total energy(thermal) (kcal mol^{-1})	78.097
Heat capacity (cal mol^{-1} k^{-1})	32.592
Entropy (cal mol^{-1} k^{-1})	
Total	92.878
Translational	40.806
Rotational	29.566
Vibrational	22.506
Zero point vibrational energy (Kcal mol^{-1})	72.56188
Rotational constants (GHZ)	
A	2.78412
B	0.91107
C	0.71183
Dipole moment	1.8077

Table 10: Thermodynamic parameters of calculated of 1-chloro-3-methoxy benzene inB3LYP/6-311++G(d,p) method

Parameters	Method / Basis set B3LYP/ 6-311++G(d,p)

Optimized global minimum Energy, (Hartrees)	-806.490759222
Total energy(thermal) (kcal mol^{-1})	82.197
Heat capacity (cal mol^{-1} k^{-1})	30.351
Entropy (cal mol^{-1} k^{-1})	
Total	89.117
Translational	40.764
Rotational	29.774
Vibrational	18.579
Zero point vibrational energy (Kcal mol^{-1})	77.12368
Rotational constants (GHZ)	
A	2.26771
B	0.95636
C	0.67558
Dipole moment	1.6071

Table 11: Vibrational assignments of Fundamental modes of **2,4-difluro-1-methoxy benzene** along with calculated IR intensity (Km mol^{-1}), Raman activity (A° amu^{-1}) and normal mode descriptions (characterized by TED) based on quantum mechanical force field calculations using B3LYP/6-311++G(d,p) method and basis set.

S. No.	Species C$_s$	Observed fundamentals (cm^{-1})		Calculated values (cm^{-1})				Assignments with TED (%) among types of internal coordinates
				B3LYP/6-311++G(d,p)				
		FTIR	FT-Raman	Frequencies		IR Intensity	Raman Activity	
				Unscaled	Scaled			
1.	A′	3087	-	3215	3093	0.7993	114.8780	γCH(99)
2.	A′	3013	3020	3210	3017	0.5222	145.9710	γCH(99)
3.	A′	2964	-	3194	2968	2.0333	54.3555	γCH(97)
4.	A′	2940	2936	3137	2947	18.3316	110.9096	CH$_3$ss(91)
5.	A′	2912	-	3095	2917	25.9056	52.3267	CH$_3$ips(92)
6.	A′	2844	2850	3020	2850	57.3530	142.4741	CH$_3$ops(89)
7.	A′	-	1715	1653	720	14.5068	21.5554	γCC (83)
8.	A′	1606	1600	1634	1616	34.5857	5.4452	γCC (84)
9.	A′	1516	-	1534	1522	305.7562	2.1375	γCC (85)
10.	A′	1460	-	1507	1471	13.0705	8.4784	γCC (85)
11.	A′	1445	1440	1491	1450	5.3745	10.9110	γCC (87)
12.	A′	1401	-	1474	1408	19.2933	2.5608	γCC (87)
13.	A′	1318	1320	1450	1326	14.3769	0.9407	γCO (81)
14.	A′	1298	1290	1324	1305	36.7490	10.8139	γCO (80)
15.	A′	1286	-	1309	1296	26.8406	25.7286	γCF (85)
16.	A′	1261	-	1268	1270	92.8360	2.5543	γCF (86)
17.	A′	1219	-	1232	1228	71.0005	3.1403	γCH$_3$ips (83)
18.	A′	-	1205	1194	1216	35.1802	1.2943	γCH$_3$sb (84)
19.	A′	-	1190	1169	1201	1.5668	2.8788	γCH$_3$ops (83)
20.	A′	1183	-	1151	1195	67.4051	0.6291	bCH (75)
21.	A′	1143	1150	1110	1156	31.9685	3.1192	bCH (75)
22.	A′	1106	-	1027	1115	81.5425	6.5996	bCH (75)
23.	A′	1051	-	973	1062	70.1312	7.8343	Rtrigd (72)
24.	A′	-	990	951	998	2.6407	0.1753	Rsymd (72)
25.	A′	963	-	864	973	49.0832	0.0894	Rasymd (71)
26.	A′	-	880	834	890	15.8140	0.1130	bCO (69)
27.	A′	862	870	766	879	25.0642	17.9073	bCO (66)
28.	A′	801	810	736	819	18.6019	8.9184	bCF (68)
29.	A″	761	-	715	772	7.6477	0.6647	bCF (69)
30.	A″	718	-	618	726	10.1423	1.0538	CH$_3$ ipr(75)
31.	A″	698	-	592	706	5.7665	6.8282	CH$_3$ opr(76)
32.	A″	610	-	521	618	2.4223	3.5857	ωCH (65)
33.	A″	606	-	492	613	2.6666	0.8772	ωCH (63)

34.	A″	-	590	454	597	3.8289	0.8963	ωCH (62)
35.	A″	-	506	404	509	2.4018	3.5441	ωCC (63)
36.	A″	498	-	339	502	4.3054	0.2274	ωCC (65)
37.	A″	493	-	305	498	0.1380	1.0798	ωCC (65)
38.	A″	466	-	238	471	3.1614	1.9648	ωCO (64)
39.	A″	-	450	234	455	1.9122	1.5567	ωCO (66)
40.	A″	-	380	163	387	2.1146	0.4959	ωCF (60)
41.	A″	-	301	112	309	0.5855	0.9887	ωCF (59)
42.	A″	-	250	51	259	3.7615	0.9820	tCH₃ (49)

Abbreviations: γ – stretching; ss – symmetric stretching; ass – asymmetric stretching; b – bending; ω – out-of-plane bending; R – ring; trigd – trigonal deformation; symd – symmetric deformation; asymd – antisymmetric deformation.

Table 12:   Vibrational assignments of Fundamental modes of **1-chloro -3-methoxy benzene** along with calculated IR intensity (Km mol^{-1}), Raman activity (A° amu^{-1}) and normal mode descriptions (characterized by TED) based on quantum mechanical force field calculations using B3LYP/ 6-311++G(d,p) method and basis set.

S. No.	Species C$_s$	Observed fundamentals (cm^{-1})		Calculated values (cm^{-1})				Assignments with TED (%) among types of internal coordinates
				B3LYP/6-311++G(d,p)				
		FTIR	FT-Raman	Frequencies		IR Intensity	Raman Activity	
				Unscaled	Scaled			
1.	A′	3139	-	3224	3146	0.8801	53.3595	γCH (99)
2.	A′	3084	3090	3211	3092	1.3935	134.1082	γCH (96)
3.	A′	3075	-	3199	3082	3.5372	117.9424	γCH (98)
4.	A′	3008	3010	3177	3016	7.2725	82.4804	γCH (97)
5.	A′	2963	2960	3138	2970	19.1201	123.7296	CH₃ ips (91)
6.	A′	2940	-	3068	2950	34.4016	51.2635	CH₃ ss (92)
7.	A′	2908	-	3008	2916	47.1817	156.6249	CH₃ ops (90)
8.	A′	1596	1600	1636	1602	121.3460	17.6193	γCC (87)
9.	A′	1579	1580	1610	1586	89.0219	19.1209	γCC (85)
10.	A′	1541	-	1515	1550	61.2683	2.4738	γCC (82)
11.	A′	1484	-	1504	1490	73.5994	4.0124	γCC (87)
12.	A′	1465	-	1494	1471	9.7879	12.9615	γCC (85)
13.	A′	1446	1450	1478	1458	28.2688	2.0051	γCC (85)
14.	A′	1432	-	1450	1442	13.9664	3.9356	γCO (89)
15.	A′	1424	-	1350	1438	47.5497	7.7151	γCO (90)
16.	A′	1329	1322	1303	1338	3.1406	1.0291	bCH (73)
17.	A′	1309	-	1272	1318	184.5574	9.4353	bCH (75)
18.	A′	1284	1290	1203	1300	6.8720	4.2073	bCH (75)
19.	A′	1250	1260	1181	1262	10.0291	0.6140	bCH (73)
20.	A′	1232	1240	1169	1241	0.6033	2.7647	CH₃ipb (83)
21.	A′	1183	-	1116	1192	16.3913	3.3488	CH₃sb (84)
22.	A′	1168	-	1089	1179	19.3567	8.6715	CH₃opb (83)
23.	A′	1156	-	1058	1166	52.8151	1.4012	Rtrigd (72)
24.	A′	1100	-	1006	1109	7.6831	43.7441	Rsymd (70)
25.	A′	1092	-	979	1100	0.1493	0.1148	Rasymd (71)
26.	A′	1073	-	889	1085	0.9879	0.1280	bCO (69)
27.	A′	1042	-	868	1048	90.8615	2.2369	bCO (70)
28.	A′	-	1008	848	1015	26.5724	0.2794	ωCH (65)
29.	A″	994	-	784	1000	41.1347	0.3703	ωCH (64)
30.	A″	-	950	696	955	18.4687	0.1248	ωCH (63)
31.	A″	862	-	688	868	5.2394	8.4050	ωCH (64)
32.	A″	846	-	585	850	0.0392	0.0445	CH₃ ipr (75)
33.	A″	768	-	562	773	5.5015	1.6378	γCcl (73)
34.	A″	-	740	459	748	0.3611	6.1701	CH₃ opr (76)
35.	A″	682	690	453	698	3.7731	0.2606	tRtrigd (62)
36.	A″	-	580	406	585	4.7280	6.9885	tRsymd (61)

37.	A″	566	-	335	570	2.1405	1.5774	tRasymd (63)
38.	A″	-	490	270	496	0.5078	0.2410	bC-Cl (66)
39.	A″	449	-	216	453	0.4269	1.7288	ωC-O (64)
40.	A″	-	410	182	418	1.8989	2.3658	ωCCl (61)
41.	A″	-	305	174	312	0.0078	0.7079	ωCO (64)
42.	A″	-	203	95	207	5.3682	0.6869	tCH$_3$(58)

Abbreviations: γ – stretching; ss – symmetric stretching; ass – asymmetric stretching; b – bending; ω – out-of-plane bending; R – ring; trigd –trigonal deformation; symd – symmetric deformation; asymd – antisymmetric deformation.

REFERENCES

[1] J. Williams (Ed.), Nonlinear Optical Properties of Organic and Polymeric Materials, American Chemical Society Symposium Series, Vol.233, American Chemical Society, Washington, DC, 1983.

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

[3] N. Vijayan, R. Ramesh Babu, R. Gopalakrishnan, P. Ramasamy, W.T.A. Harrison, J. Cryst. Growth. 262 (2004) 490.

[4] Y. Goto, A. Hyashi, Y. Kimura, S.M. Nakayama, J. Cryst. Growth. 108 (1991) 688.

[5] M. Ramalingam, M. Jaccob, J. Swaminathan, P. Venuvanalingam, N. Sundaraganesan, Spectrochim. Acta 71A (2008) 996.

[6] M.J. Frisch, G.W. Trucks, H.B. Schlegal, G.E. Scuseria, M.A. Robb, J.R. Cheesman, V.G. Zakrzewski, J.A. Montgomerg, 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, N. Rega, P. Salvador, J.J. Dannenberg, D.K. Malich, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stetanov, 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, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN 09, Revision A 11.4, *Gaussian, Inc,* Pittsburgh PA, 2009.

[7] P. Pulay, G. Fogarasi, G. Pongor, J.E. Boggs, A. Vargha, *J. Am. Chem. Soc*. 105 (1983) 7037.

[8] G. Rauhut, P. Pulay, J. Phys. Chem. 99 (1995) 3093.

[9] W.B. Tzeng, K. Narayan, J.L. Lin, C.C. Tung, Spectrochim. Acta 55A (1999) 153.

[10] G. Fogarasi, P. Pulay, in: J.R. Durig (Ed.), Vibrational Spectra and Structure, vol.14, Elsevier, Amsterdam, 1985, p.125 (Chapter 3).

[11] (a) T. Sundius, *J. Mol. Struct.*, 218 (1990) 321. (b) MOLVIB (V.7.0): *Calculation of Hormonic Force Fields and Vibrational Modes of Molecules*, QCPE program No.807 (2002).

[12] T. Sundius, J.Mol. Struct, 218 (1990) 321 (MOLVIB (V.7.0): Calculation of Hormonic Force Fields and Vibrational Modes of Molecules, QCPE program No.807 (2002).

[13] G. Fogarasi, X. Zhou, P.W. Taylor, P. Pulay, J. Am. Chem. Soc. 114 (1992) 8191.

[14] T. Vijayakumar, Hubert. Joe, C.P.R. Nair, V.S. Jayakumar, Chem. Phys. 343(2008) 83.

[15] J. Karpagam, N. Sundaraganessan, S. Sebastian, S. Manoharan, M. Kurt, J. Raman Spectrosc. 41 (2010) 53.

[16] D.A. Kleinman, Phys. Rev. 126 (1962) 1977.

[17] V.B. Jothy, T. Vijayakumar, V.S. Jayakumar, K. Udayalekshmi, K. Ramamoorthy, I. Hubert Joe, J. Raman Spectrosc. 38 (2007) 1148.

[18] Virendra Kumar, Y. Panikar, M.A. Palafox, J.K. Vats, I. Kostova, K. Lang, V.K. Rastogi, Indian J. Pure Appl. Phys. 48 (2010) 85.

[19] Vennila.P, Govindaraju M, Venkatesh G, Kamal C, Armaković SJ, A complete computational and spectroscopic study of 2-bromo-1, 4dichlorobenzene – A frequently used benzene derivative, J. Mol. Struct., 1151 (2018) 245– 255

[20] S. Jeyavijayan, B. Vijitha, I. Vigneshwari Int. J. Pharm. Sci. Rev. Res., 48 (2018) 103-110

[21] R.Rajathi subbulakshmi, M.Arivazhagan International Journal of Research and Analytical Reviews Vol. 5 (2018) 4 957-971.

[22] S. Jeyavijayan, M. Arivazhagan, Spectrochim. Acta 81A (2011) 466.

[23] Arivazhagan M & Jeyavijayan S, *Indian J. Pure Appl. Phys*., 49 (2011) 516.

[24] Jag Mohsan, *Organic Spectroscopy - Principles and Applications*, second ed., Narosa, Publishing House, New Delhi, 2001.