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

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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.

Keywords: Casson fluid; magnetic parameter; darcy parameter; velocity slip parameter; forchheimer parameter; power index parameter.inclination Grashof number, modified Grashof number.

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.

Keywords: FT-IR; FT-Raman; DFMB; CMB; B3LYP; HOMO-LUMO; NLO

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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 \(\pm 1\ \text{cm}^{-1}\) 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 \(\pm 1\ \text{cm}^{-1}\).

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 1 and 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.
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 \textit{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 $3 \times 3 \times 3$ 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

$$E = E_0 - \sum_{i} \mu_i F_i - \frac{1}{2} \sum_{i,j} \alpha_{ij} F_i F_j - \frac{1}{6} \sum_{i,j,k} \beta_{ijk} F_i F_j F_k - \frac{1}{24} \sum_{i,j,k,l} \gamma_{ijkl} F_i F_j F_k F_l + ...$$

... (1)

where $E_0$ is the energy of the unperturbed molecule; $F_i$ is the field at the origin; and $\mu_i$, $\alpha_{ij}$, $\beta_{ijk}$ and $\gamma_{ijkl}$ are the components of dipole moment, polarizability, the first hyperpolarizabilities and second hyperpolarizabilities, respectively. The calculated total dipole moment ($\mu$) and mean first hyperpolarizability (β) of DFMB are 1.8077 Debye and 0.6007 $\times 10^{-30}$ esu, respectively, which is comparable with the reported values of similar derivatives [4,17]. Similarly, the total dipole moment ($\mu$) and mean first hyperpolarizability (β) of CMB are found to be 1.6071 Debye and 0.7848 $\times 10^{-30}$ 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.

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

Fig. 6: FT-Raman spectrum of 2,4-difluoro-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 give 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, 1401 cm\(^{-1}\) 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, 1466 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, 931 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 2963 cm$^{-1}$ 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 846 cm$^{-1}$ 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 (Å) | Atom   | Bond Angle (°) | Atom   | Dihedral Angle (°) |
|--------|-----------------|--------|----------------|--------|--------------------|
| 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 (Å) | Atom | Bond Angle(°) | Atom | Dihedral Angle(°) |
|------|----------------|------|--------------|------|------------------|
| C1-C2 | 1.3943         | C2-C1-C6 | 122.34       | C6-C1-C2-C3 | 0.0011          |
| C1-C6 | 1.3856         | C2-C1-C17 | 118.31       | C6-C1-C2-H8 | 179.99          |
| C1-C7 | 1.7621         | C3-C1-C17 | 119.34       | C7-C1-C2-C3 | 180.00          |
| C2-C3 | 1.3976         | C1-C2-C3 | 118.61       | C7-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       | C7-C1-C6-C5 | -180.00         |
| C4-C5 | 1.3865         | C2-C3-O9 | 123.97       | C7-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 | 180.00     |                  |                  |
| 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     |                  |                  |

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

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| $\delta_i$ | C-CF   | C2-F12, C4-F14                                 |
| 11-13| $T_i$  | C-H    | C3-H13, C5-H15, C6-H16                         |
| 14-16| $\rho_i$ | C-H(Methyl) | C8-H9, C8-H10, C8-H11 |
|     |        |        | **Bending**                                    |
|     |        |        | **In plane Bending**                           |
| 17-22| $\alpha_i$ | Ring  | C1-C2-C3, C2-C3-C4, C3-C4-C5, C4-C5-C6, C5-C6-C1, C6-C1-C2 |
| 23-25| $\beta_i$ | O-C-H  | O7-C8-H9, O7-C8-H10, O7-C8-H11                 |
| 26-28| $\gamma_i$ | H-C-H  | H9-C8-H10, H9-C8-H11, H10-C8-H11               |
| 29-34| $\phi_i$ | 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| $\Sigma_i$ | C-C-F  | C1-C2-F12, C3-C2-F12, C3-C4-F14, C5-C4-F14    |
| 39-40| $\sigma_i$ | C-C-O  | C2-C1-O7, C6-C1-O7                            |
| 41   | $\theta_i$ | C-O-C  | C1-O7-C8                                      |
|     |        |        | **Out of plane Bending**                       |
| 42-44| $\omega_i$ | C-H    | H13-C3-C4-C2, H15-C5-C6-C4, H16-C6-C1-C5       |
| 45-46| $\Pi_i$  | C-CF   | F12-C2-C3-C1, F14-C4-C5-C3                    |
| 47   | $\rho_i$  | C-O    | O7-C1-C2-C6                                   |
| 48   | $\lambda_i$ | C-O    | C8-O7-C8-(C2, C6)                             |
| 49-54| $\tau_i$  | t-Oring| 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   | $\tau_i$  | 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   | $\delta_i$ | C-Cl   | C1-C17                                         |
| 10-13| $T_i$  | C-H    | C2-H8, C4-H14, C5-H15, C6-H16                  |
| 14-16| $\rho_i$ | C-H(Methyl) | C10-H11, C10-H12, C10-H13 |
|     |        |        | **Bending**                                    |
|     |        |        | **In plane Bending**                           |
| 17-22| $\alpha_i$ | Ring  | C1-C2-C3, C2-C3-C4, C3-C4-C5, C4-C5-C6, C5-C6-C1, C6-C1-C2 |
| 23-25| $\beta_i$ | O-C-H  | O9-C10-H11, O9-C10-H12, O9-C10-H13             |
| 26-28| $\gamma_i$ | H-C-H  | H12-C10-H13, H11-C10-H12, H13-C10-H12          |
| 29-36| $\phi_i$ | 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| $\Sigma_i$ | C-C-Cl | C2-C1-C17, C6-C1-C17                           |
| 39-40| $\sigma_i$ | C-C-O  | C2-C3-O9, C4-C2-O9                            |
| 41   | $\theta_i$ | C-O-C  | C3-O9-C10                                     |
|     |        |        | **Out of plane Bending**                       |
| 42-45| $\omega_i$ | C-H    | H8-C2-C3-C1, H14-C4-C5-C3, H15-C5-C6-C4, H16-C6-C1-C5 |
| 46   | $\Pi_i$  | C-Cl   | C17-C1-C2-C6                                  |

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

| NO | Symbol* | Definition* |
|----|---------|-------------|
| 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 | \( \delta_9, \delta_{10} \) |
| 11-13 | C-H | \( T_{11}, T_{12}, T_{13} \) |
| 14 | CH3ss | \( (p_{14} + p_{15} + p_{16})/\sqrt{3} \) |
| 15 | CH3ips | \( (2p_{14} + p_{15} + p_{16})/\sqrt{6} \) |
| 16 | CHops | \( (p_{15} - p_{16})/\sqrt{2} \) |
| 17 | Rtrigd | \( (a_{17} - a_{18} + a_{19} - a_{20} + a_{21} - a_{22})/\sqrt{16} \) |
| 18 | Rsymd | \( (-a_{17} - a_{18} + 2a_{19} - a_{20} - a_{21} + 2a_{22})/\sqrt{12} \) |
| 19 | Rasymd | \( (a_{17} - a_{18} + a_{20} - a_{21})/\sqrt{2} \) |
| 20 | CH3sb | \( (-\beta_{23} - \beta_{24} - \beta_{25} + \gamma_{26} + \gamma_{27} + \gamma_{28})/\sqrt{6} \) |
| 21 | CH3ipb | \( (\gamma_{26} - \gamma_{27} - \gamma_{28})/\sqrt{6} \) |
| 22 | CH3opb | \( (\gamma_{27} - \gamma_{28})/\sqrt{2} \) |
| 23 | CH3ipr | \( (2\beta_{23} - \beta_{24} - \beta_{25})/\sqrt{6} \) |
| 24 | CH3opr | \( (p_{23} - p_{24})/\sqrt{2} \) |
| 25-29 | bCH | \( (\phi_{29} - \phi_{30})/\sqrt{5} \), \( (\phi_{31} - \phi_{32})/\sqrt{5} \), \( (\phi_{33} - \phi_{34})/\sqrt{5} \), \( (\phi_{35} - \phi_{36})/\sqrt{5} \) |
| 28-29 | bCF | \( (\epsilon_{35} - \epsilon_{36})/\sqrt{5} \), \( (\epsilon_{37} - \epsilon_{38})/\sqrt{5} \) |
| 30 | bCO | \( (\sigma_{39} - \sigma_{40})/\sqrt{2} \) |
| 31 | bOC | \( \theta_{41} \) |
| 32-34 | oCH | \( \omega_{42}, \omega_{43}, \omega_{44} \) |
| 35-36 | oCF | \( \bar{\pi}_{45}, \bar{\pi}_{46} \) |
| 37 | oCO | \( \rho_{47} \) |
| 38 | oCO | \( \lambda_{48} \) |
| 39 | Tring | \( (\tau_{49} - \tau_{50} + \tau_{51} - \tau_{52} + \tau_{53} - \tau_{54})/\sqrt{6} \) |
| 40 | tRsymd | \( (\tau_{49} - \tau_{50} + \tau_{52} - \tau_{53})/\sqrt{2} \) |
| 41 | tRasymd | \( (\tau_{49} + 2\tau_{50} - \tau_{51} - \tau_{52} + 2\tau_{53} - \tau_{54})/\sqrt{12} \) |
| 42 | tOCH3 | \( \tau_{55} \) |

*These symbols are used for description of normal modes by TED in Table 11
*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* | Definition* |
|----|---------|-------------|
| 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 | \( \delta_9 \) |
| 10-13 | C-H | \( T_{10}, T_{11}, T_{12}, T_{13} \) |
| 14 | CH3ss | \( (p_{14} + p_{15} + p_{16})/\sqrt{3} \) |
| 15 | CH3ips | \( (2p_{14} + p_{15} + p_{16})/\sqrt{6} \) |
| 16 | CH3ops | \( (p_{15} - p_{16})/\sqrt{2} \) |
| 17 | Rtrigd | \( (a_{17} - a_{18} + a_{19} - a_{20} + a_{21} - a_{22})/\sqrt{16} \) |
| 18 | Rsymd | \( (-a_{17} - a_{18} + 2a_{19} - a_{20} - a_{21} + 2a_{22})/\sqrt{12} \) |
These symbols are used for description of normal modes by TED in Table 12.

The internal co-ordinate used here are defined in Table 4.

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

| Parameters                        | Method / Basis set |
|------------------------------------|---------------------|
| Optimized global minimum Energy,(Hartrees) | B3LYP/ 6-311++G(d,p) |
| 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 in B3LYP/6-311++G(d,p) method

| Parameters                        | Method / Basis set |
|------------------------------------|---------------------|
|                                    | B3LYP/ 6-311++G(d,p) |
Table 11: Vibrational assignments of Fundamental modes of **2,4-difluoro-1-methoxy benzene** along with calculated IR intensity (Km mol\(^{-1}\)), Raman activity (A\(^2\) 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 |
|--------|-----------------|---------------------------------|---------------------------------|----------------------------------------------------------|
|        |                 | FTIR & FT-Raman | B3LYP/6-311++G(d,p) |                                           |
|        |                 |                  | Frequencies | IR Intensity | Raman Activity |
|        |                 |                  | Unscaled | Scalled |               |
| 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 | 10.8193 | 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  | Rsymd(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\(_{3}\) op(76) |
| 32.    | A'              | 610              | -        | 521  | 618  | 2.4223  | 3.5857  | αCH(65) |
| 33.    | A'              | 606              | -        | 492  | 613  | 2.6666  | 0.8772  | αCH(63) |
| S. No. | Species | Observed fundamentals (cm\(^{-1}\)) | Calculated values (cm\(^{-1}\)) | Assignments with TED (%) among types of internal coordinates |
|--------|---------|-------------------------------------|----------------------------------|-------------------------------------------------------------|
|        |         | FTIR | FT-Raman | B3LYP/6-31++G(d,p) | FTIR | FT-Raman | B3LYP/6-31++G(d,p) | FTIR | FT-Raman | B3LYP/6-31++G(d,p) | FTIR | FT-Raman | B3LYP/6-31++G(d,p) |
| 1.     | A'      | 3139 | -        | 3224              | 3146 | 0.8801 | 53.3595 | CH (99)            |
| 2.     | A'      | 3084 | 3090     | 3211              | 3092 | 1.3935 | 134.1082 | CH (96)            |
| 3.     | A'      | 3075 | -        | 3199              | 3082 | 3.5372 | 117.9424 | CH (98)            |
| 4.     | A'      | 3008 | 3010     | 3177              | 3016 | 7.2725 | 82.4804 | CH (97)            |
| 5.     | A'      | 2963 | 2960     | 3138              | 2970 | 19.1201 | 123.7926 | CH, ips (91)       |
| 6.     | A'      | 2940 | -        | 3068              | 2950 | 34.4016 | 51.2635 | CH, ss (92)        |
| 7.     | A'      | 2908 | -        | 3008              | 2916 | 47.1817 | 156.6249 | CH, ops (90)       |
| 8.     | A'      | 1596 | 1600     | 1636              | 1602 | 121.3460 | 17.6193 | CH (87)            |
| 9.     | A'      | 1579 | 1580     | 1610              | 1586 | 89.0219 | 19.1209 | CH (85)            |
| 10.    | A'      | 1541 | -        | 1515              | 1550 | 61.2683 | 2.4738  | CH (82)            |
| 11.    | A'      | 1484 | -        | 1504              | 1490 | 73.5994 | 4.0124  | CH (87)            |
| 12.    | A'      | 1465 | -        | 1494              | 1471 | 9.7879  | 12.9615 | CH (85)            |
| 13.    | A'      | 1446 | 1450     | 1478              | 1458 | 28.2688 | 2.0051  | CH (85)            |
| 14.    | A'      | 1432 | -        | 1450              | 1442 | 13.9664 | 3.9356  | CH (89)            |
| 15.    | A'      | 1424 | -        | 1350              | 1438 | 47.5497 | 7.7151  | CH (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 | 0.6303  | 2.7647  | CH, pb (83)        |
| 21.    | A'      | 1183 | -        | 1116              | 1192 | 16.3913 | 3.3488 | CH, sb (84)        |
| 22.    | A'      | 1168 | -        | 1089              | 1179 | 19.3567 | 8.6715  | CH, opb (83)       |
| 23.    | A'      | 1156 | -        | 1058              | 1166 | 52.8151 | 1.4012  | Rтрпд (72)         |
| 24.    | A'      | 1100 | -        | 1006              | 1109 | 7.6831  | 43.7441 | Rsymd (70)         |
| 25.    | A'      | 1092 | -        | 979               | 1100 | 0.1493  | 0.1148  | Rsymd (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  | bCO (65)           |
| 29.    | A'      | 994  | -        | 784               | 1000 | 41.1347 | 0.3703  | bCO (64)           |
| 30.    | A'      | -    | 950      | 696               | 955  | 18.4687 | 0.1248  | bCO (63)           |
| 31.    | A'      | 862  | -        | 688               | 868  | 5.2394  | 8.4050  | bCO (64)           |
| 32.    | A'      | 846  | -        | 585               | 850  | 0.0392  | 0.0445  | CH, irp (75)       |
| 33.    | A'      | 768  | -        | 562               | 773  | 5.5015  | 1.6378  | CH (73)            |
| 34.    | A'      | -    | 740      | 459               | 748  | 0.3611  | 6.1701  | CH, op (76)        |
| 35.    | A'      | 682  | 690      | 453               | 698  | 3.7731  | 0.2606  | tRтрпд (62)        |
| 36.    | A'      | -    | 580      | 406               | 585  | 4.7280  | 6.9885  | tRsymd (61)        |

Abbreviations:  
- γ – stretching; ss – symmetric stretching; ass – asymmetric stretching; b – bending; α – 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\(^2\) 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.
Abbreviations:
γ – stretching; ss – symmetric stretching; as – asymmetric stretching; b – bending; o – 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. Vijayaraghavan, 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. Jacob, J. Swaminathan, P. Venanavalingam, N. Sundaranagesan, Spectrochim. Acta 71A (2008) 996.
[6] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, 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. Stefanov, 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. Fogerarasi, G. Pongor, J.E. Boggs, A. Varga, 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. Fogerarasi, 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 Harmonic 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 Harmonic Force Fields and Vibrational Modes of Molecules, QCPE program No.807 (2002).
[13] G. Fogerarasi, 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. Sundaranagesan, S. Sebastian, S. Manoharan, M. Kurt, J. Raman Spectrosc. 41 (2010) 53.
[16] D.A. Kleinman, Phys. Rev. 126 (1962) 1977.
[17] V.B. Jothi, T. Vijayakumar, V.S. Jayakumar, K. Udayalekshmi, K. Ramamorthy, I. Hubert Joe, J. Raman Spectrosc. 38 (2007) 1148.
[18] Virendra Kumar, Y. Panikar, M.A. Palafox, I.K. Vats, I. Kostova, K. Land, V.K. Rastogi, Indian J. Pure Appl. Phys. 48 (2010) 85.
[19] Vennila.P, Govindaraju M, Venkatesh G, Kamal C, Armakovic SJ, A complete computational and spectroscopic study of 4dichlorobenzene – A frequently used benzene derivative, J. Mol. Struct., 1151 (2018) 245–255 2-bromo-1-
[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 Mohan, Organic Spectroscopy - Principles and Applications, second ed., Narosa, Publishing House, New Delhi, 2001.