Structure and vibrational spectroscopic studies of 1-Naphthol: Density functional theory calculations

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ABSTRACT

The molecular vibrations of 1-Naphthol were investigated in polycrystalline sample, at room temperature, by FT-IR and FT-Raman spectroscopy. In parallel, ab initio and various density functional (DFT) methods were used to determine the geometrical, energetic and vibrational characteristics of 1-Naphthol. On the basis of B3LYP/6-31G* and B3LYP/6-311+G** methods and basis set combinations, a normal mode analysis was performed to assign the various fundamental frequencies according to the total energy distribution (TED). The vibrational spectra were interpreted, with the aid of normal coordinate analysis based on a scaled quantum mechanical force field. The Infrared and Raman spectra were also predicted from the calculated intensities. Comparison of simulated spectra with the experimental spectra provides important information about the ability of the computational method to describe the vibrational modes. Simulation of Infrared and Raman spectra, utilizing the results of these calculations led to excellent overall agreement with observed spectral patterns. The investigation is performed using quantum chemical calculations conducted by means of the Gaussian 98W and Guassview set of programs. Further, density functional theory (DFT) combined with quantum chemical calculations to determine the first-order hyperpolarizability.

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and background. The FT-Raman spectra of 1-Naphthol were recorded on a BRUKER IFS-66V model interferometer equipped with an FRA106 and a FT-Raman accessory. The spectra were recorded in the 4000-100 cm⁻¹ stokes region using the 1064 nm line of a Nd:YAG laser for the excitation operating at 200mW power. The reported wave numbers are believed to be accurate within ±1 cm⁻¹.

Computational details

The calculation of the vibrational frequencies is essential and also useful for the vibrational assignments of the spectra. Quantum chemical calculations for 1-Naphthol was performed with the Gaussian 98W program [10] using the Becke 3-Lee-Yang-Parr (B3LYP) functional [11,12] supplemented with the standard B3LYP/6-31G* (small basis set) and B3LYP/6-311+G** (large basis set) for the Cartesian representation of the theoretical force constants have been computed at the fully optimized geometry by assuming C₂ point group symmetry. Scaling of the force field was performed according to the SQM procedure [13,14] using selective (multiple) scaling in the natural internal coordinate representation[15,16]. Transformations of the force field and the subsequent normal coordinate analysis including the least squares refinement of the scaling factors, calculation of total energy distribution (TED) and IR and Raman intensities were done on a PC with the PCAT (Program for Characterization of Atomic Transition) package. The TED elements provide a measure of each internal coordinate contribution to the normal coordinate. For the plots of simulated IR and Raman spectra, pure Lorentzian band shapes were used with a bandwidth of 10 cm⁻¹. The prediction of Raman intensities was carried out by following the procedure outlined below. The Raman activities calculated by the Gaussian 98W program and adjusted during scaling procedure with MOLVIB were converted to relative Raman intensities using the following relationship derived from the basic theory of Raman scattering [19-21],

\[ I_i = \frac{f(v - v_i)^4 S_i}{v_i[1 - \exp(-h\nu_i/kT)]} \]

where \( v_i \) is the excitation frequency (in cm⁻¹ units), \( v_i \) the vibrational wavenumber of the \( i^{th} \) normal mode, \( h, c \) and \( k \) are the universal constants and \( f \) is the suitably chosen common scaling factor for all the peak intensities.

Essentials of nonlinear optics related to \( \beta \)

The nonlinear response of an isolated molecule in an electric field \( E_0(t) \) can be represented as a Taylor expansion of the total dipole moment \( \mu \), induced by the field:

\[ \mu(t) = \mu_0 + \alpha_\mu E_0 + \beta_\mu E_0^2 + \ldots \]

Where \( \alpha \) is linear polarizability, \( \mu_0 \) the permanent dipole moment and \( \beta_\mu \) are the first-order hyperpolarizability tensor components.

The components of first-order hyperpolarizability can be determined using the relation

\[ \beta_i = \beta_{ii} + \frac{1}{3} \sum_{r<s,j} (\beta_{ijj} + \beta_{ji} + \beta_{jij}) \]

Using the \( x, y \) and \( z \) components the magnitude of the total static dipole moment (\( \mu \)), isotropic polarizability (\( \alpha_0 \)), first-order hyperpolarizability (\( \beta_{\text{iso}} \)) tensor, can be calculated by the following equations:

\[ \mu_0 = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \]

\[ \beta_{\text{iso}} = (\beta_{xx}^2 + \beta_{yy}^2 + \beta_{zz}^2)^{1/2} \]

The complete equation for calculating the first-order hyperpolarizability from Gaussian 98W output is given as follows [10]:

\[ \beta_i = (\beta_{xx} + \beta_{yy} + \beta_{zz} + \beta_{xy} + \beta_{yz} + \beta_{zx})^{1/2} \]

The \( \beta \) components of GAUSSIAN 98W output are reported in atomic units, the calculated values have to be converted into electrostatic units (1 a.u. = 8.3693 x 10⁻²⁵ esu).

Before calculating the hyperpolarizability for the investigated compound, the optimization has been carried out in the UHF (unrestricted open-shell Hartree-Fock) level. Molecular geometries were fully optimized by B3LYP's optimization algorithm using redundant internal coordinates. All optimized structures were confirmed to be minimum energy conformations. An optimization is complete when it has converged. i.e., when it has reached a minimum on the potential energy surface, thereby predicting the equilibrium structures of the molecules. This criterion is very important in geometry optimization. The inclusion of d polarization and double zeta function in the split valence basis set is expected to produce a marked improvement in the calculated geometry [22]. At the optimized structure, no imaginary frequency modes were obtained proving that a true minimum on the potential energy surface was found. The electric dipole moment and dispersion free first-order hyperpolarizibility were calculated using finite field method. The finite field method offers a straightforward approach to the calculation of hyperpolarizabilities [23]. All the calculations were carried out at the DFT level using the three-parameter hybrid density functional B3LYP and a 3-21 G (d, p) basis set.

Results and discussion

Molecular geometry

The optimized molecular structure of 1-Naphthol was shown in Fig.1. The global minimum energy obtained by the DFT structure optimization was presented in Table 1. The optimized geometrical parameters obtained by the large basis set calculation were presented in Table 2.

| Method | Energies (Hartrees) |
|--------|-------------------|
| B3LYP/6-31G* | -461.084753 |
| B3LYP/6-311+G** | -461.109185 |

Fig.1. The optimized molecular structure of 1-Naphthol

Detailed description of vibrational modes can be given only after normal coordinate analysis (NCA). For this purpose, the full set of 72 standard internal coordinates containing 21 redundancies were defined as given in Table 3. From these, a non-redundant set of local symmetry coordinates were constructed by suitable linear combinations of internal coordinates following the recommendations of Fogarasi et. al [15,16] are summarized in Table 4. The theoretically calculated DFT force fields were transformed in this later set of vibrational coordinates and used in all subsequent calculations.
Table 2. Optimized geometrical parameters of 1-Naphthol obtained by B3LYP/6-311+G** density functional calculations

| Bond length | Value (Å) | Bond angle | Value (Å) | Dihedral angle | Value(Å) |
|-------------|-----------|------------|-----------|----------------|----------|
| C2-C1       | 1.379     | C2-C3-C2   | 120.157   |                  | -0.013   |
| C3-C2       | 1.414     | C4-C3-C4   | 120.797   |                  | 0.022    |
| C4-C3       | 1.375     | C5-C4-C5   | 120.255   |                  | -179.976 |
| C5-C4       | 1.421     | C6-C5-C6   | 122.131   |                  | -179.955 |
| C6-C5       | 1.420     | C7-C6-C7   | 121.089   |                  | 0.048    |
| C7-C6       | 1.376     | C8-C7-C8   | 120.320   |                  | -0.092   |
| C8-C7       | 1.415     | C9-C8-C9   | 120.296   |                  | 0.054    |
| C9-C8       | 1.377     | C10-C9-C10 | 120.648   |                  | 179.945  |
| C10-C9      | 1.418     | O11-C10-C12| 122.792   |                  | 179.935  |
| O11-C12     | 1.368     | H12-C12-C3 | 119.938   |                  | -179.963 |
| H12-C3      | 1.088     | H13-C3-C4  | 120.253   |                  | 0.0186   |
| H13-C4      | 1.086     | H14-C4-C5  | 119.064   |                  | -179.981 |
| H14-C5      | 1.086     | H15-C5-C6  | 120.364   |                  | 179.952  |
| H15-C6      | 1.087     | H16-C6-C7  | 119.674   |                  | -179.985 |
| H16-C7      | 1.086     | H17-C7-C8  | 119.985   |                  | 0.086    |
| H17-C8      | 1.086     | H18-C8-C9  | 118.791   |                  | -0.096   |
| H18-C9      | 1.084     | H19-O11-C1   | 118.727  |               |
| H19-O11     | 0.969     |             |           |                |          |

Table 3. Definition of internal coordinates of 1-Naphthol

| Nodi(1) | symbol | Type | Definition |
|---------|--------|------|------------|
|         | v      |       |            |
| 1       | τ      | C-H  | C2-H11,C3-H13,C4-H14,C6-C8-H17,C9-H18 |
| 8       | q      | C-O  | C1-O11    |
| 9       | Ω      | O-H  | O11-H19   |
| 10-20   | R      | C-C  | C2-C1,C3-C2,C4-C4,C5-C6,C7-C8-C9,C9-C10-C10-C5-C2-C3 |
| 21-34   | β      | C-C-H| C2-C1,C3-C2,C4-C4,H14,C5-C6-H16,C8-C7-H16,C9-C8-H17,C8-H18,C10-H9,C10-H9 |
| 35-36   | θ      | C-C-O| C1-C2-C3,C2-C3-C4-C4,C5-C6-C7,C8-C9-C10-C10-C5-C2-C3 |
| 37      | φ      | C-O-H| C1-O11-H19 |
| 38-43   | α      |      | C1-C2-C3,C2-C3-C4,C4-C5,C5-C6-C7,C8-C9-C10-C10-C5-C2-C3 |
| 44-49   | α      |      | C5-C6-C7,C6-C7-C8,C7-C8-C9,C8-C9-C10-C10-C5-C2-C3 |
| Out-of-plane   |      |      | H12-C2-C1,C3-H3,C4-C2-C4,C4-H14-C5-H15,C6-C7-C8-C9,C8-C9-C10-C10-C5-C2-C3 |
| 50-56   | α      |      | H16-C7-C6-C8-H17-C8-C7-C9,C8-H18-C9-C10-C10-C5-C2-C3 |
| 57      | α      |      | O11-C1-C10-C2 |
| 58-63   | τ      |      | C1-C2-C3,C4-C4-C5,C5-C6-C7,C8-C9-C10-C10-C5-C2-C3 |
| 64-69   | τ      |      | C5-C6-C7,C6-C7-C8,C7-C8-C9,C9-C10-C10-C5-C2-C3 |
| 70      | τ      | τ-O-H | C1-C10-C11-H19 |
| 71-72   | τ      |      | C4-C5-C10-C9-C6-C5-C10-C1 |

Analysis of vibrations spectra

The 51 normal modes of 1-Naphthol are distributed among the symmetry species as \( \Gamma_{\text{ina}} = 35 A' \) (in-plane) + 16 A" (out-of-plane), and in agreement with C_{2v} symmetry. All the vibrations were active both in Raman scattering and infrared absorption. In the Raman spectrum the in-plane vibrations (A') give rise to polarized bands while the out-of-plane ones (A") to depolarized band. The TED were reported in Table 5. For visual comparison, the observed and simulated FT-IR and FT-Raman spectra of 1-Naphthol are produced in a common frequency scales in Fig. 2 & Fig. 3. Root mean square (RMS) values of frequencies were obtained in the study using the following expression,

\[
\text{RMS} = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} \left( \nu_i^{\text{calc}} - \nu_i^{\text{exp}} \right)^2}
\]

Table 4. Definition of local symmetry coordinates and the value corresponding scale factors used to correct the force fields for 1-Naphthol

| No.(i) | Symbol | Definition |
|--------|--------|------------|
| 1-7    | C-H    | (\( \delta_{1,2,3,4,5,6,7} \)) |
| 8      | C-O    | q8         |
| 9      | O-H    | q9         |
| 10-20  | C-C-H  | (\( \beta_{21-34} \)) |
| 21-27  | C-C-H  | (\( \beta_{21-34} \)) |
| 28     | C-C-O  | (\( \alpha_{28-34} \)) |
| 29     | C-O-H  | q37        |
| 30     | τ      | (\( \tau_{30} \)) |
| 31     | τ      | (\( \tau_{31} \)) |
| 32     | τ      | (\( \tau_{32} \)) |
| 33     | τ      | (\( \tau_{33} \)) |
| 34     | τ      | (\( \tau_{34} \)) |
| 35     | τ      | (\( \tau_{35} \)) |
| 36-42  | τ      | (\( \tau_{36-42} \)) |
| 43     | τ      | (\( \tau_{43} \)) |
| 44     | τ      | (\( \tau_{44} \)) |
| 45     | τ      | (\( \tau_{45} \)) |
| 46     | τ      | (\( \tau_{46} \)) |
| 47     | τ      | (\( \tau_{47} \)) |
| 48     | τ      | (\( \tau_{48} \)) |
| 49     | τ      | (\( \tau_{49} \)) |
| 50     | τ      | (\( \tau_{50} \)) |
| 51     | τ      | (\( \tau_{51} \)) |
| 52     | τ      | (\( \tau_{52} \)) |

Fig. 2 FT-IR spectra of 1-Naphthol.

(a) Observed (b) Calculated with B3LYP/6-311+G**

The RMS error of the observed and calculated frequencies (unscaled / B3LYP/6-311+G**) of 1-Naphthol was found to be 107 cm^{-1}. This is quite obvious; since the frequencies calculated on the basis of quantum mechanical force fields usually differ appreciably from observed frequencies. This is partly due to the neglect of anharmonicity and partly due to the approximate nature of the quantum mechanical methods. In order to reduce the overall deviation between the unscaled and observed fundamental frequencies, scale factors were applied in the normal coordinate analysis and the subsequent least square fit refinement algorithm resulted into a very close agreement between the observed fundamentals and the scaled frequencies. Refinement of the scaling factors applied in this study achieved a weighted mean deviation of 9 cm^{-1} between the experimental and scaled frequencies of the title compound.

C-C vibration

The bands between 1407,1636 and 1658cm^{-1} are assigned to C-C stretching modes [24]. In the present study, the carbon stretching vibrations of the title compound have been observed at 1420,1652 cm^{-1} in the FT-IR and 1583 cm^{-1} in FT-Raman spectrum and are presented in Table 5. These assignments are in

\[
\text{RMS} = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} \left( \nu_i^{\text{calc}} - \nu_i^{\text{exp}} \right)^2}
\]
good agreement with literature [25,26]. In present investigation, the C-C mode mixes with C–H in-plane bending vibrations.

**C-H vibration**

The presence of hetero-aromatic-type structure is best recognized by the presence of C–H stretching vibrations [27] near 3200 cm⁻¹. Aromatic compounds commonly exhibit multiple weak bands in the region 3100–3000 cm⁻¹ due to aromatic C–H stretching vibrations. The bands due to C–H in-plane ring bending vibration interacting with C–C stretching vibration are observed as a number of m-w intensity sharp bands in the region 1300–1000 cm⁻¹. C–H out-of-plane bending vibrations are strongly coupled vibrations and occur in the region 900–667 cm⁻¹. Accordingly, in the present study the C–H vibrations of the title compounds are observed at 3227, 3206, 3204, 3191, 3187, 3178 and 3167 cm⁻¹ for 1-Naphthol.

![Fig. 3 FT-Raman spectra of 1-Naphthol.](image)

(a) Observed (b) Calculated with B3LYP/6-311+G**

Table 5. Detailed assignments of fundamental vibrations of 1-Naphthol by normal mode analysis based on SQM force field calculation

| No. | Symmetry species | Observed frequency (cm⁻¹) | Calculated frequency (cm⁻¹) with B3LYP/6-311+G** | TED (%) among type of internal coordinates |
|-----|-----------------|--------------------------|--------------------------------------------------|--------------------------------------------|
|     | C-H vibration   |                          |                                                  |                                            |
| 1   | A'              | 3781                     | 4129                                             | OH(100)                                    |
| 2   | A'              | 3258                     | 3549                                             | 3227                                        |
| 3   | A'              | 3526                     | 3206                                             | 20.078                                      |
| 4   | A'              | 3524                     | 3204                                             | 39.605                                      |
| 5   | A'              | 3222                     | 3510                                             | 20.519                                      |
| 6   | A'              | 3218                     | 3505                                             | 4.776                                       |
| 7   | A'              | 3495                     | 3178                                             | 1.212                                       |
| 8   | A'              | 3198                     | 3483                                             | 3.719                                       |
| 9   | A'              | 1705                     | 1681                                             | 34.219                                      |
| 10  | A'              | 1823                     | 1658                                             | 5.862                                       |
| 11  | A'              | 1652                     | 1799                                             | 3.297                                       |
| 12  | A'              | 1588                     | 1730                                             | 4.173                                       |
| 13  | A'              | 1529                     | 1519                                             | 4.373                                       |
| 14  | A'              | 1519                     | 1655                                             | 1.873                                       |
| 15  | A'              | 1462                     | 1461                                             | 2.173                                       |
| 16  | A'              | 1443                     | 1517                                             | 3.573                                       |
| 17  | A'              | 1420                     | 1407                                             | 3.713                                       |
| 18  | A'              | 1332                     | 1312                                             | 3.873                                       |
| 19  | A'              | 1294                     | 1281                                             | 3.973                                       |
| 20  | A'              | 1281                     | 1271                                             | 4.073                                       |
| 21  | A'              | 1245                     | 1242                                             | 4.173                                       |
| 22  | A'              | 1208                     | 1209                                             | 4.273                                       |
| 23  | A'              | 1198                     | 1305                                             | 4.373                                       |
| 24  | A'              | 1198                     | 1184                                             | 4.473                                       |
| 25  | A'              | 1121                     | 1124                                             | 4.573                                       |
| 26  | A'              | 1081                     | 1086                                             | 4.673                                       |
| 27  | A'              | 1059                     | 1045                                             | 4.773                                       |
| 28  | A'              | 1001                     | 1092                                             | 4.873                                       |
| 29  | A'              | 973                      | 1080                                             | 4.973                                       |
| 30  | A'              | 964                      | 960                                              | 5.073                                       |
| 31  | A'              | 899                      | 980                                              | 5.173                                       |
| 32  | A'              | 896                      | 877                                              | 5.273                                       |
| 33  | A'              | 862                      | 836                                              | 5.373                                       |
| 34  | A'              | 810                      | 883                                              | 5.473                                       |
| 35  | A'              | 808                      | 881                                              | 5.573                                       |
| 36  | A'              | 796                      | 876                                              | 5.673                                       |
| 37  | A'              | 752                      | 819                                              | 5.773                                       |
| 38  | A'              | 733                      | 716                                              | 5.873                                       |
| 39  | A'              | 652                      | 630                                              | 5.973                                       |
| 40  | A'              | 590                      | 580                                              | 6.073                                       |
| 41  | A'              | 590                      | 575                                              | 6.173                                       |
| 42  | A'              | 538                      | 540                                              | 6.273                                       |
| 43  | A'              | 491                      | 485                                              | 6.373                                       |
| 44  | A'              | 483                      | 526                                              | 6.473                                       |
| 45  | A'              | 474                      | 517                                              | 6.573                                       |
| 46  | A'              | 437                      | 476                                              | 6.673                                       |
| 47  | A'              | 371                      | 404                                              | 6.773                                       |
| 48  | A'              | 286                      | 283                                              | 6.873                                       |
| 49  | A'              | 267                      | 291                                              | 6.973                                       |
| 50  | A'              | 179                      | 171                                              | 7.073                                       |
| 51  | A'              | 144                      | 157                                              | 7.173                                       |

* TED (%) among type of internal coordinates: A: Infrared, I: Raman, S: Scaling, TED: Torsion Energy Density, CC: Carbon–Carbon, bCH: Bonding Carbon–Hydrogen, CO: Carbon–Oxygen, bring: In-plane Bending, tring: Out-of-plane Bending.

**Notes:**

1. The observed frequencies are given in Table 5.
2. The calculated frequencies are given in Table 5.
3. The TED values are given in Table 5.
4. The IR and Raman data are given in Table 5.
5. The scaling factors are given in Table 5.
6. The type of internal coordinates are given in Table 5.
C-O vibration

The non-linearity of hydrogen bond in 1-Naphthol have an impact over the carbonyl group frequency. The interaction of carbonyl group with the other group present in the system does not produce such a drastic and characteristic changes in the frequency of O-C stretch. The carbonyl stretching frequency is very sensitive to the factors that disturb the nature of the type of the carbonyl compound being studied. Particularly detailed correlations have been made for the carbonyl bond stretching frequency. The carbonyl stretching frequency has been most extensively studied by infrared spectroscopy. This multiply bonded group is highly polar (\(>C=O\)) and therefore gives rise to an intense infrared absorption band. The carbon-oxygen double bond is formed by the p\(_{\pi}\)-p\(_{\pi}\) bonding between carbon and oxygen. Because of the different electro-negativities of carbon and oxygen atoms, the bonding electrons are not equally distributed between the two atoms. The following two resonance forms contribute to the bonding of the carbonyl group: C=O \(\leftrightarrow\) C\(^{-}\).O. The lone pair of electrons on oxygen also determines the nature of the carbonyl group. The position of the C=O stretching vibration is very sensitive to various factors such as the physical state, electronic effects by substituents, ring strains, etc. [24]. Consideration of these factors provides further information about the environment of the C=O group. The carbonyl stretching generally occurs as a strong absorption in the region from 1448, 1319,1282,1111, 1071, 891 cm\(^{-1}\). This portion of the infrared spectrum is most useful because the position of the carbonyl absorption is quite sensitive to substitution effects and the geometry of the molecule.

O-H vibrations

The precise positions of O-H band are dependent on the strength of hydrogen bond. The O-H stretching appears at 3800–3500 cm\(^{-1}\) in the inter-molecular hydrogen bonded systems. The observed peaks in this region are sharp and strong. The title compounds in this study showed a very strong absorption peak at 3754 cm\(^{-1}\) which are due to the O-H stretching vibrations.

C-O stretching and O-H bending vibrations

Two bands arising from C-O stretching and O-H bending appear in the spectra of carboxylic acids near 1210–1320 and 1400–1440 cm\(^{-1}\), respectively. Both these bands involve some interaction between C=O stretching and in-plane C-O-H bending. The more intense band near 1280–1315 cm\(^{-1}\) for dimers is generally referred to as C-O stretching band and it usually occurs as a doublet in the spectra of long-chain fatty acids. One of the characteristic bands in the spectra of dimeric carboxylic acid arises from the out-of-plane bending of the hydrogen bonded O-H. It appears near 1071 cm\(^{-1}\) and is characteristically broad with medium intensity [24].

Ring vibrations

Several ring modes are affected by the substitution in the aromatic ring. In the present study, the bands absorbed at 1689,1636, 1448, 1319, 1282 cm\(^{-1}\) and 891,801, 585, 487 cm\(^{-1}\) have been designated to ring in-plane and out-of-plane bending modes, respectively. For most of the remaining ring vibrations, the overall agreement is satisfactory. Small changes in frequencies observed for these modes are due to the changes in force constants/reduced mass ratio resulting mainly due to the extent of mixing between ring and substituent group.

Hyperpolarizability calculation

The first-order hyperpolarizability (\(\beta_{\mathrm{hk}}\)) of the novel molecular system of 1-Naphthol is calculated using 3-21G(d,p) basis set based on finite field approach. Hyperpolarizability is a third rank tensor that can be described by a 3 x 3 x 3 matrix. It strongly depends on the method and basis set used. The 27 components of 3D matrix can be reduced to 10 components due to Kleinman symmetry [28]. The calculated first-order hyperpolarizability (\(\beta_{\mathrm{tot}}\)) of 1-Naphthol is 1.1070x10\(^{-30}\) esu, which is nearly six times that of urea (0.1947 x 10\(^{-30}\) esu). The calculated dipole moment (\(\mu\)) and first-order hyperpolarizability (\(\beta\)) are shown in Table 6. The theoretical calculation seems to be more helpful in determination of particular components of \(\beta\) tensor than in establishing the real values of \(\beta\). Dominant of particular components indicates on a substantial delocalization of charges in those directions. It is noticed that in \(\beta_{\mathrm{yy}}\) (which is the principal dipole moment axis and it is parallel to the charge transfer axis) direction, the biggest values of hyperpolarizability are noticed and subsequently delocalization of electron cloud is more in that direction. The higher dipole moment values are associated, in general, with even larger projection of \(\beta_{\mathrm{tot}}\) quantities. The electric dipoles may enhance, oppose or at least bring the dipoles out of the required net alignment necessary for NLO properties such as \(\beta_{\mathrm{tot}}\) values. The connection between the electric dipole moments of an organic molecule having donor–acceptor substituent and first hyperpolarizability is widely recognized in the literature [29].

Table 6. The dipole moment (\(\mu\)) and first-order hyperpolarizability (\(\beta\)) of 1-Naphthol derived from DFT calculations

| \(\beta_{\mathrm{xx}}\) | -30.036823 |
| \(\beta_{\mathrm{yy}}\) | 30.0437602 |
| \(\beta_{\mathrm{zz}}\) | -13.7476317 |
| \(\beta_{\mathrm{xy}}\) | -1.618470719 |
| \(\beta_{\mathrm{xz}}\) | 0.0800745 |
| \(\beta_{\mathrm{yz}}\) | 0.1220257 |
| \(\beta_{\mathrm{ty}}\) | 0.6719205 |
| \(\beta_{\mathrm{tx}}\) | 0.4894769 |
| \(\beta_{\mathrm{tz}}\) | 0.0155964 |
| \(\beta_{\mathrm{ty}}\) | -0.0025623 |
| \(\beta_{\mathrm{total}}\) | 1.1070 |
| \(\mu_{\mathrm{x}}\) | 0.4960665 |
| \(\mu_{\mathrm{y}}\) | 0.1145269 |
| \(\mu_{\mathrm{z}}\) | 0.0019529 |
| \(\mu\) | 0.5091 |

Conclusion

In this work, the SQM force field method based on DFT calculations at the B3LYP/6-311+G** level have been carried out to analyze the vibrational frequencies of 1-Naphthol. Refinement of the scaling factors applied in this study achieved a weighted RMS deviation of 9 cm\(^{-1}\) between the experimental and scaled frequencies. This close agreement established between the experimental and scaled frequencies obtained using large basis set (6-311+G**) calculations has proved to be more reliable and accurate than the calculations using lower basis sets. The first-order hyperpolarizability (\(\beta_{\mathrm{hk}}\)) of the novel molecular system of 1-Naphthol is calculated using 3-21 G (d,p) basis set based on finite field approach. The calculated first-order hyperpolarizability (\(\beta_{\mathrm{tot}}\)) of 1-Naphthol is 1.1070x10\(^{-30}\) esu, which is nearly six times that of urea (0.1947 x 10\(^{-30}\) esu).

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