CHAPTER – VI

VANILLIN AND ISOVANILLIN: COMPARATIVE VIBRATIONAL SPECTROSCOPIC STUDIES, CONFORMATIONAL STABILITY AND NLO PROPERTIES BY DENSITY FUNCTIONAL THEORY CALCULATIONS

ABSTRACT

This study is a comparative analysis of FT-IR and FT-Raman spectra of vanillin (3-methoxy-4-hydroxybenzaldehyde) and isovanillin (3-hydroxy-4-methoxybenzaldehyde). The molecular structure, vibrational wavenumbers, infrared intensities, Raman scattering activities were calculated for both molecules using the B3LYP density functional theory (DFT) with the standard 6-311++G(d,p) basis set. The computed values of frequencies are scaled using multiple scaling factors to yield good coherence with the observed values. The calculated harmonic vibrational frequencies are compared with experimental FT-IR and FT-Raman spectra. The geometrical parameters and total energies of vanillin and isovanillin were obtained for all the eight conformers (a, b, c, d, e, f, g and h) from DFT/B3LYP method with 6-311++G(d,p) basis set. The computational results identified the most stable conformer of vanillin and isovanillin as in the "a" form. Non-linear properties such as electric dipole moment (\(\mu\)), polarizability (\(\alpha\)) and hyperpolarizability (\(\beta\)) values of the investigated molecules have been computed using B3LYP quantum chemical calculation. The calculated HOMO and LUMO energies show that charge transfer occurs within the molecules.
CHAPTER – VI

VANILLIN AND ISOVANILLIN: COMPARATIVE VIBRATIONAL SPECTROSCOPIC STUDIES, CONFORMATIONAL STABILITY AND NLO PROPERTIES BY DENSITY FUNCTIONAL THEORY CALCULATIONS

6.1 INTRODUCTION

There are some organic crystalline solids that comprises of highly polar molecules and form non-centro symmetrical crystal structures that exhibit second-order non-linear optical (NLO) properties and lesser damage thresholds that are potentially superior to those of currently available inorganic systems. The compounds vanillin and isovanillin whose IUPAC names are 3-methoxy-4-hydroxybenzaldehyde and 3-hydroxy-4-methoxybenzaldehyde, respectively, exhibit good NLO properties. The properties such as optical transmission, refractive index, electro-optic effect and dielectric constant etc. of vanillin have been evaluated by Sreeramana Aithal and Mohan Rao [206]. Vanillin and isovanillin are trisubstituted benzene with –CHO, –OCH₃, and (–OH) groups. The vibrational spectra of the vanillin had already been interpreted by Gunasekaran and Ponnusamy [207] on the basis of normal coordinate analysis (NCA) based on p-substituted benzaldehyde such as vanillin, which is a p-hydroxybenzaldehyde, using Wilson-FG matrix method [208].

Chlorobenzaldehyde and anisaldehyde are used in the synthesis of biologically active polymers, for example, in chitosan derivatives, which are known for its application in cosmetics and tensile, as biomaterials and for its anti-microbial activities [209]. Benzaldehyde and acetophenone derivatives are treated with base to
form a substituted chalcone, which has been found to have anti-cancer properties [210]. Several workers have investigated vibrational spectroscopic properties, mutual influence of different types of substituents such as halogens, methyl, methoxy and hydroxyl through benzaldehyde and the interaction between the ring and substituents, using the joint experimental and theoretical methods [211−217]. Vibrational spectral data of isomeric benzaldehyde and dihydroxybenzaldehyde have been calculated based on NCA by Singh et al. [210, 211]. The vibrational assignments and force field calculation for a series of halo- and nitro-substituted benzaldehyde have been investigated by Ramana Rao et al. [211, 213]. Akai et al. [214] have investigated the existence of two rotational isomers between phenyl and formyl groups in 2-chlorobenzaldehyde.

To the best of our knowledge, there is no DFT based Becke3-Lee-Yang-Parr (B3LYP) functional with standard 6-311++G(d,p) basis set of vanillin and isovanillin has been reported so far. It has been felt that a thorough knowledge of different normal modes of vibrations could be of much help to understand such properties of these compounds. As vibrational spectroscopy is believed to be an effective experimental technique for such understanding, Raman and IR spectra of vanillin and isovanillin have been critically examined and special attention has also been paid to explain all the remarkable qualitative and quantitative differences in these spectra.

Vibrational spectroscopy has the potential to yield valuable structural and conformational information of organic compounds if used in conjugation with accurate quantum chemical calculations. The possible stable conformers of vanillin and isovanillin were searched. There are eight conformers for vanillin and isovanillin.
The optimized geometry and vibrational wavenumbers for conformers of vanillin and isovanillin were calculated at DFT/B3LYP level of theory with the 6-311++G(d,p) basis set. The “a” form is the more stable conformer than the others for the title molecules. The results of the theoretical and spectroscopic studies are reported herein. Detailed interpretations of the vibrational spectra of vanillin and isovanillin have been made on the basis of the calculated potential energy distribution (PED). So, atomic charges of vanillin and isovanillin were investigated using B3LYP method with 6-311++G(d,p) basis set. The calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies and hyperpolarizability analysis show that charge transfer occurs in vanillin and isovanillin.

6.2 EXPERIMENTAL DETAILS

The fine samples of vanillin and isovanillin were obtained from Lancaster Chemical Company, UK, with a stated purity of greater than 98% and they were used as such without further purification. The FT-IR spectra of vanillin and isovanillin were recorded at room temperature in the region 4000–400 cm\(^{-1}\) using Perkin-Elmer spectrum RX1 spectrophotometer equipped with KBr pellet technique. The signals were collected for 100 scans with a scan interval of 1 cm\(^{-1}\) and at optical resolution of 0.4 cm\(^{-1}\). The FT-Raman BRUKER FRA-106/IFS-100 spectrometer was used for the Raman spectral measurements at room temperature. The spectrometer consisted of a quartz beam splitter and a high sensitive germanium diode detector cooled to the liquid nitrogen temperature. The samples were packed in a glass tube of about 5 mm diameter and excited in the 180° geometry with 1064 nm laser line at 75 mW power from a diode pumped air cooled-cw Nd:YAG laser as excitation wavelength in the
region 3500–100 cm$^{-1}$. The signals were collected for 300 scans at the interval of 1 cm$^{-1}$ and optical resolution of 0.1 cm$^{-1}$.

6.3 COMPUTATIONAL DETAILS

The quantum chemical computations of vanillin and isovanillin has been performed using Gaussian 09W program package [76] at the Becke3-Lee-Yang-Parr (B3LYP) functional [74, 75] with the standard 6-311++G(d,p) basis set. In order to obtain stable structures, the parameters of eight conformers of title molecules were optimized at B3LYP/6-311++G(d,p) level. The vibrational wavenumbers for the most stable conformers are calculated using our calculation. We tabulated “a” conformer calculations data because of most stable conformer for vanillin and isovanillin. All the calculations were performed using the Gaussian 09W program package on personal computer [76]. The Cartesian representation of the theoretical force constants have been computed at the fully optimized geometry, by assuming the molecules belongs to C$_s$ point group symmetry. Multiple scaling of the force field has been performed by the SQM procedure [120, 121] using selective scaling in the natural internal coordinate representation [122, 125]. Transformations of force field and the subsequent NCA including least square refinement of scaling factors, potential energy distribution (PED), IR and Raman activities were done on a PC with the MOLVIB program (version V7.0-G77) written by Sundius [98, 99].

In the presence of an applied electric field, the energy of a system is a function of the electric field. Polarizability and hyperpolarizability characterize the response of a system in an applied electric field [126]. They determine not only the strength of molecular interactions (long-range inter induction, dispersion force, etc.,) as well as
the cross sections of different scattering and collision processes but also the NLO properties of the system [127, 128]. 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 [129]. It can be given in the lower tetrahedral format. This is obviously shows that the lower part of the $3 \times 3 \times 3$ matrixes is a tetrahedral. The components of $\beta$ are defined as the co-efficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogeneous, this expansion becomes

$$E = E^0 - \mu_\alpha F_\alpha - \frac{1}{2} \alpha_{\alpha\beta} F_\alpha F_\beta - \frac{1}{6} \beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma + \cdots \quad (6.1)$$

where $E^0$ is the energy of the unperturbed molecules, $F_\alpha$ is field at the origin and $\mu_\alpha$, $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ are the components of dipole moment, polarizability and the first hyperpolarizability, respectively. The total static dipole moment ($\mu$), the mean polarizability ($\alpha$), the anisotropy of the polarizability ($\Delta\alpha$) and the mean first hyperpolarizability ($\beta_{ii}$) using the $x$, $y$ and $z$ components they are defined as

$$\mu = \left( \mu_x^2 + \mu_y^2 + \mu_z^2 \right)^{\frac{1}{2}} \quad (6.2)$$

$$\alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \quad (6.3)$$

$$\Delta\alpha = \left[ \frac{\left( \alpha_{xx} - \alpha_{yy} \right)^2 + \left( \alpha_{yy} - \alpha_{zz} \right)^2 + \left( \alpha_{zz} - \alpha_{xx} \right)^2}{2} \right]^{\frac{1}{2}} \quad (6.4)$$
\[ \beta_{ii} = \frac{1}{5} (\beta_{iiz} + \beta_{iz} + \beta_{zii}) \] 

(6.5)

where \( \alpha_{xx}, \alpha_{yy}, \) and \( \alpha_{zz} \) are tensor components of polarizability; \( \beta_{iiz}, \beta_{iz}, \) and \( \beta_{zii} \) (i from x to z) are tensor components of hyperpolarizability [127, 128].

The total static dipole moments, polarizabilities and hyperpolarizabilities of vanillin and isovanillin were calculated. Table 6.1 lists the values of the electric dipole moments in D (Debye) dipole moment components, polarizabilities and hyperpolarizabilities of the vanillin and isovanillin. In addition to the hyperpolarizabilities, the isotropic polarizabilities and polarizability anisotropic invariant are also calculated. The calculated isotropic polarizabilities of vanillin and isovanillin are \(-64.6359\) a.u and \(-65.6317\) a.u, respectively.

6.4 RESULTS AND DISCUSSION

6.4.1 Molecular Geometry

Optimized structures and numbering of the atoms of vanillin and isovanillin are shown in Figs. 6.1 and 6.2, respectively. There are eight possible conformers a–h and they are shown in Figs. 6.3 and 6.4, respectively. Total energies and energy difference [the relative energy of the other conformers was as: \( \Delta E = E(a-b) - E(a) \) the conformers “h” is the lowest energy as reference point] for all conformers of vanillin and isovanillin were calculated at B3LYP/6-311++G(d,p) level and they are given in Table 6.2. It is evident for the energy calculations that the conformer “a” for vanillin and isovanillin produces the global minimum energy and hence they are the most stable conformers were considered for further calculations. Additionally, the
Fig. 6.1 Atom numbering scheme adopted in this study for vanillin (3-methoxy-4-hydroxybenzaldehyde).

Fig. 6.2 Atom numbering scheme adopted in this study for isovanillin (3-hydroxy-4-methoxybenzaldehyde).
Fig. 6.3 Eight conformers of vanillin (3-methoxy-4-hydroxybenzaldehyde).
Fig. 6.4 Eight conformers of isovanillin (3-hydroxy-4-methoxybenzaldehyde).
calculations showed that the conformers “h” to be the least stable conformers as shown in Table 6.2. From the DFT calculations of conformers with 6-311++G(d,p) basis set, the conformer “a” is predicted more stable from 0.0333, 0.0094 to 0.1816 kJ/mol and from 0.0005 to 0.0049, 0.1179 kJ/mol than the other conformers of vanillin and isovanillin, respectively. The most optimized structural parameters were also calculated, and they are listed in Table 6.3 along with available experimental data.

In benzene, the C–C bonds in vanillin and isovanillin not of the same length. The bond lengths of C1–C2 and C1–C6 are equal to experimental value of 1.40 Å. The calculated bond lengths of C1–C2 (1.41 Å), C1–C6 (1.41 Å) and C3–C4 (1.41 Å) are slightly differed from bond C2–C3 (1.38 Å), C4–C5 (1.38 Å) and C5–C6 (1.39 Å). Among those bond lengths of C2–C3, C4–C5 and C5–C6 are equal to experimental value of 1.39 Å and C3–C4 is slightly greater than the experimental values [218]. This may be due to the substitution of OH and OCH₃. The bond length C1–C7 (1.47 Å) is good agreement with experimental value of 1.48 Å since C1–C7 out of the ring. The substitution of aldehyde group, bond lengths of C7–O8 (1.21 Å) and C7–H9 (1.11 Å) are good agreement with experimental value of 1.21, and 1.11 Å for the title molecules. The out of ring bonds C2–H10 (1.08 Å), C5–H18 (1.08 Å) and C6–H19 (1.08 Å) are approximately coincide with the experimental value of 1.09 Å. The ring angle C2–C1–C6 is 120.2 and 119.9° approximately coincide with the experimental value 119.9°. The benzene ring angles C1–C2–C3, C3–C4–C5, C4–C5–C6 and C1–C6–C5 of 119.6, 120.3, 119.5 and 120.5° for vanillin and 120.3,
120.4, 119.7 and 120.1° for isovanillin, respectively at the B3LYP/6-311++G(d,p) method approximately match with experimental values of 118.2, 121.2, 117.6 and 121.8°. Similarly, the benzene ring substitution of CH and CHO bond angles of DFT method agree with experimental values. The hetero aromatic ring is obvious from the dihedral angles are also discussed for vanillin and isovanillin.

### 6.4.2 Vibrational Analysis

Detailed description modes can be given by means of normal coordinate analysis (NCA). For this purpose, the set of 64 standard internal coordinates containing 13 redundancies are defined as given in Tables 6.4 and 6.5 for vanillin and isovanillin, respectively. From these, a non-redundant set of local symmetry coordinates was constructed by suitable linear combination of internal coordinates recommended by Fogarasi et al. [122, 125], which are summarized in Tables 6.6 and 6.7. The theoretically calculated DFT force fields were transformed to this latter set of vibrational coordinates and were used in all subsequent calculations.

The 3N–6=51 normal modes of both vanillin and isovanillin can be subdivided as $35 A'$ (in-plane modes) and $16 A''$ (out-of-plane modes) from the structural-point of view of the molecules vanillin and isovanillin, which have 19 stretching vibrations, 16 in-plane vibrations and 16 out-of-plane vibrations. In agreements with Cs symmetry all the vibrations are active in both infrared absorption and Raman scattering. In Raman spectrum, the $A'$ vibrations give rise to polarized bands, while $A''$ to depolarized bands. The observed frequencies, calculated vibrational frequencies, infrared intensities, Raman activities, reduced masses, force constants and
assignments of the fundamental modes of the most stable conformers of vanillin and isovanillin are listed in Tables 6.8 and 6.9, respectively. The vibrational frequencies obtained from our calculation were suitably scaled using the scale factors 0.983, 0.864, 0.984 and 0.989 for stretching, in-plane bending, out-of-plane bending and ring vibrations, respectively. The Figs. 6.5–6.8 show the observed and calculated FT-IR and FT-Raman spectra of vanillin and isovanillin.

### 6.4.3 C–H Vibrations

The hetero aromatic structure shows the presence of C–H stretching vibrations in the region 3100–3000 cm\(^{-1}\), which is the characteristic region for the ready identification of C–H stretching vibrations. In this region, the bands are not affected appreciably by the nature of the substituents. In the present investigation, the FT-IR and FT-Raman bands at 3093, 3037, 3000 cm\(^{-1}\) and 3078, 3047, 3000 cm\(^{-1}\), respectively, in vanillin and isovanillin has been assigned as C–H stretching vibrations. The theoretically computed frequencies by B3LYP/6-311++G(d,p), after scaling down, gives the frequency values at 3104, 3037, 3009 cm\(^{-1}\) and 3081, 3055, 3009 cm\(^{-1}\). In general the aromatic C–H vibrations calculated theoretically are in good agreement in the experimentally reported values \([2, 181, 219]\) for trisubstituted benzene in the region 3100–3000 cm\(^{-1}\).

In-plane aromatic C–H deformation vibrations occur in the region 1300–990 cm\(^{-1}\). The C–H in-plane bending vibrations computed at 1150, 1038, 962 cm\(^{-1}\) and 1248, 1177, 1150 cm\(^{-1}\) for vanillin and isovanillin by our work show excellent agreement with experimental values. The weak and very weak intensity band at 961 cm\(^{-1}\) and 1245 cm\(^{-1}\) in FT-IR spectra are assigned to in-plane C–H deformations.
Fig. 6.5 FT-IR spectrum of vanillin (3-methoxy-4-hydroxybenzaldehyde).
(a) Observed and (b) Calculated.
Fig. 6.6 FT-Raman spectrum of vanillin (3-methoxy-4-hydroxybenzaldehyde) (a) Observed and (b) Calculated.
Fig. 6.7 FT-IR spectrum of isovanillin (3-hydroxy-4-methoxybenzaldehyde). (a) Observed and (b) Calculated.
Fig. 6.8 FT-Raman spectrum of isovanillin (3-hydroxy-4-methoxybenzaldehyde).
(a) Observed and (b) Calculated.
for title molecules. The same vibrations appear in the FT-Raman spectra at 1031 cm\(^{-1}\) with medium strong intensity for vanillin and at 1249, 1172, 1149 cm\(^{-1}\) with medium and very weak intensity in FT-Raman bands for isovanillin.

The strong peaks below 960 cm\(^{-1}\), i.e., around 790 and 850 cm\(^{-1}\), clearly indicate aromatic nature. Substitution portions in the ring can be judged from the out-of-plane bending of the ring C–H bond in the region 960–675 cm\(^{-1}\) and these bands are highly informative [181]. C–H out-of-plane bending vibrations are strongly coupled vibrations and occur in the region 900–667 cm\(^{-1}\) [15]. Theoretically computed frequencies at 933, 910, 899 cm\(^{-1}\) and 1021, 968, 864 cm\(^{-1}\) for vanillin and isovanillin, respectively, by our calculation are assigned to C–H out-of-plane bending vibrations, which coincide with experimental values. In the present study, peaks at 934, 899 cm\(^{-1}\) and 1025 cm\(^{-1}\) in FT-IR and the band identified at 968, 865 cm\(^{-1}\) in FT-Raman counterpart confirms the C–H out-of-plane bending vibrations for vanillin and isovanillin, which agree with the literature values [15, 181].

**6.4.4 C–C Vibrations**

The bands 1650–1430 cm\(^{-1}\) were assigned to C–C stretching modes [7]. Socrates [220] mentioned that the presence of conjugate substituent such as C=C causes a heavy doublet formation around the region 1625–1575 cm\(^{-1}\). The six-ring carbon atoms undergo coupled vibrations called skeletal vibrations and give a maximum of four bands with region 1660–1420 cm\(^{-1}\) [221]. As predicted in the earlier studies, in these compounds also, there are prominent FT-IR and FT-Raman peaks at 1592, 1509, 1500 cm\(^{-1}\) for vanillin and at 1674, 1672, 1609, 1595 cm\(^{-1}\) for isovanillin designated to C–C stretching vibrations. The theoretically calculated values at 1598,
1514, 1501 cm\(^{-1}\) for vanillin and 1667, 1608, 1599 cm\(^{-1}\) for isovanillin, coincides with experimental results. The C–C in-plane bending vibrations are assigned to the FT-IR and FT-Raman bands at 750, 736, 599, 590, 567 cm\(^{-1}\) and at 765, 593 cm\(^{-1}\), respectively. These values are in good agreement with the literature values [222]. The FT-IR and FT-Raman bands observed at 533, 194 cm\(^{-1}\) and at 500, 485, 177 cm\(^{-1}\) of title compounds are identified as out-of-plane bending vibrations. In our case, weak band at 734 cm\(^{-1}\) in FT-Raman and 678 cm\(^{-1}\) is FT-IR spectrum, respectively, are assigned to ring breathing vibrations. The theoretically calculated values at 728 and 680 cm\(^{-1}\) by our work exactly correlate with experimental observations.

### 6.4.5 Aldehyde Group Vibrations

The C–H stretching vibrations of the aldehyde group [223] usually appear in the region 2871–2806 cm\(^{-1}\). Hence, in the present work, the C–H stretching vibrations computed by B3LYP/6-311++G(d,p) method at 2859 cm\(^{-1}\) for vanillin and at 2811 cm\(^{-1}\) for isovanillin, respectively, show a very good agreement with recorded values. The medium and very weak bands observed in FT-IR and FT-Raman spectra at 2840, 2859 cm\(^{-1}\) and 2805 cm\(^{-1}\) for our case, are assigned to C–H stretching vibrations of the aldehyde group. The in-plane C–H deformation mode of aldehyde group is observed at 957 and 1121cm\(^{-1}\) with weak and very strong intensities in the FT-Raman and FT-IR spectra for both vanillin and isovanillin. The carbonyl (C=O) stretching vibrations in the substituted benzaldehydes are reported near 1700 cm\(^{-1}\) [223]. The very strong bands at 1687 cm\(^{-1}\) in FT-IR and 1684 cm\(^{-1}\) in FT-Raman for vanillin and very weak band at 1734 cm\(^{-1}\) in FT-Raman for isovanillin are attributed to C=O stretching vibrations of the aldehyde group. Singh et al. [211] have assigned the C=O
in-plane bending vibrations for isomers of methoxybenzaldehydes to the region 585–620 cm$^{-1}$. Hence, in the present investigation, the medium strong, medium and very strong FT-IR and FT-Raman bands are observed at 641, 633 cm$^{-1}$ and 640 cm$^{-1}$ for vanillin and isovanillin, respectively, could be assigned to C=O in-plane bending vibrations. Hankin et al. [224] have assigned the band to 173 cm$^{-1}$ in the FT-Raman spectrum of chlorobenzaldehyde as aldehyde out-of-plane bending vibration. In vanillin and isovanillin, respectively, the very weak band at 108 cm$^{-1}$ and 130 cm$^{-1}$ in FT-Raman spectra could be assigned to C=O out-of-plane bending vibrations of aldehyde groups. A weak-to-medium intensity band due to the aldehyde group CHO deformation vibration [220] is found in the region 975–780 cm$^{-1}$. The medium and weak intensity FT-IR band at 804 cm$^{-1}$ and 788 cm$^{-1}$ could be assigned to CHO out-of-plane deformation for vanillin and isovanillin, respectively.

6.4.6 O–H Vibrations

The O–H group gives rise to three stretching vibrations, in-plane bending, and out-of-plane bending vibrations. The strong and broad band observed at 3396 cm$^{-1}$ in the solid-phase infrared spectrum and the sharp and strong band observed at 3528 cm$^{-1}$ in the solution spectrum are taken to represent the O–H stretching vibration [225]. In phenol [226], the free O–H group absorbs at 3615 cm$^{-1}$, while the associated group has a stretching frequency in the range 3250–3200 cm$^{-1}$. This is due to the O–H···O hydrogen bonding. The effect of the hydrogen bond increases the IR intensity lower of O–H stretching wavenumber. In vanillin and isovanillin, the O–H stretching vibrations are observed at 3212 and 3400 cm$^{-1}$ in FT-IR spectra. The DFT
computations give the wavenumber of these bands at 3220 cm\(^{-1}\) and at 3402 cm\(^{-1}\) for the O–H stretching vibrations for our title compounds.

The in-plane O–H deformation vibration usually [2, 150, 220] appears as a strong band in the region 1440–1260 cm\(^{-1}\). The O–H out-of-plane bending vibration gives rise to a broad band in the region 700–600 cm\(^{-1}\). The position of this band is dependent on the strength of the hydrogen bond. In the present work, the O–H in-plane bending vibrations computed by our calculation at 1273 cm\(^{-1}\) for vanillin and at 1382 cm\(^{-1}\) for isovanillin show very good agreement with recorded FT-IR band at 1383 cm\(^{-1}\). The counter-part of FT-Raman spectrum for vanillin is at 1278 cm\(^{-1}\). The FT-Raman bands observed at 813 cm\(^{-1}\) for vanillin and 795 cm\(^{-1}\) for isovanillin are assigned to O–H out-of-plane bending vibrations. The theoretically computed O–H out-of-plane bending vibration 819 cm\(^{-1}\) and 793 cm\(^{-1}\) shows good agreement with literature values [207, 150] as well as the experimental observations.

### 6.4.7 CH\(_3\) Vibrations

Both vanillin and isovanillin under consideration possesses one CH\(_3\) group. For the assignments of CH\(_3\) group frequencies one can expect that nine fundamentals can be associated to each CH\(_3\) group, namely the symmetrical stretching in CH\(_3\) (CH\(_3\) sym) and asymmetrical stretching (CH\(_3\) asym), in-plane stretching modes (i.e., in-plane hydrogen stretching mode); the symmetrical (CH\(_3\) sd) and asymmetrical (CH\(_3\) asym) deformation modes; the in-plane rocking (CH\(_3\) ipr), out-of-plane rocking (CH\(_3\) opr), and torsion (\(\tau\)CH\(_3\)) modes. Methyl groups are generally referred as electron-donating substituents in the aromatic ring system. The methyl hydrogen atoms in vanillin and isovanillin are subjected simultaneously to hyperconjugation and
backdonation, which causes the decrease of stretching wavenumbers and infrared intensities, as reported in literature [196] for similar molecular system. For the O–CH$_3$ group compounds [211], the stretching mode appear in the range 2870–2825 cm$^{-1}$, lower in magnitude compared to its value in CH$_3$ compounds (2860–2935 cm$^{-1}$), whereas two asymmetric stretching modes for both type of compounds lie in the same region 2985–2924 cm$^{-1}$. In case of vanillin and isovanillin, asymmetric and symmetric stretching vibrations of CH$_3$ group have been identified at 2969, 2937, 2915 cm$^{-1}$ and at 2985, 2969, 2937 cm$^{-1}$ by B3LYP/6-311++G(d,p) method. The recorded FT-Raman spectrum show one very weak band observed at 2969 cm$^{-1}$ and three very weak and weak bands observed at 2967, 2933 and 2933 in FT-IR spectra are assigned to C–H asymmetric and symmetric vibrations of CH$_3$ group for vanillin, while in the case of isovanillin, the same vibrational modes are identified at 2984, 2968, 2931 and 2985, 2925, 2933 cm$^{-1}$. The rocking vibrations for CH$_3$ group has been calculated at 1175, 1142 cm$^{-1}$ and at 1277, 1213 cm$^{-1}$ by DFT method also show good agreement with FT-IR and FT-Raman values at 1176, 1143 cm$^{-1}$ and at 1279, 1279, 1215, 1215 cm$^{-1}$ for vanillin and isovanillin, respectively.

The asymmetrical CH$_3$ deformation vibrations are computed by B3LYP method at 1458, 1431 cm$^{-1}$ for vanillin and at 1575, 1513 cm$^{-1}$ for isovanillin. Similarly, the symmetrical deformation vibrations of CH$_3$ group are computed at 1397 cm$^{-1}$ and 1454 cm$^{-1}$ for our case. These fundamental values show good agreement with the observed FT-IR and FT-Raman values 1456, 1442, 1426 and 1392 cm$^{-1}$ for vanillin and at 1576, 1508, 1508, 1452 and 1450 cm$^{-1}$ for isovanillin. The theoretically computed CH$_3$ torsional mode also shows good agreement with experimental observations.
6.4.8 O–CH₃ vibrations

The O–CH₃ mode is assigned to ~1040 cm⁻¹ for anisole [227] and in the region 1000–1100 cm⁻¹ for anisole and its derivatives [228–230]. This mode is assigned to 1036, 1012, and 1007 cm⁻¹ for A-4 prodrug [231]. In our case, the O–CH₃ stretching mode is assigned as a medium and weak band in FT-IR at 1025 cm⁻¹ for vanillin. While, in isovanillin O–CH₃ stretching band is absent here. Theoretically computed values show agreement with experimental observations.

The CO–CH₃ angle bending mode is assigned near 300 cm⁻¹ for anisole by Owen and Hester [232] and at 421 cm⁻¹ for p-methoxybenzaldehyde by Campagnaro and Wood [233]. Ramana Rao and co-workers [182, 227–230] have proposed assignment for this mode in the region 670–300 cm⁻¹ for anisole and its derivatives. As this mode lies in the region of the ring planar C–C–C angle bending modes, a strong mixing amongst these two modes and other planar modes is expected. Smith [196] assigned the CO–CH₃ angle bending mode at 430, 382 and 341 cm⁻¹. In accordance with above, we have assigned the theoretically calculated values by our calculation at 409 and 350 cm⁻¹ for the title compounds as CO–CH₃ angle bending mode, the value that coincides with 404 and 354 cm⁻¹ band is observed in FT-Raman spectrum.

The torsional mode of the O–CH₃ group was observed for anisole at 100 cm⁻¹ by some workers [145, 234]. Balfour [227] assigned this mode at 82 cm⁻¹, Lakshmaiah and Ramana Rao [228] calculated this mode to be at 58 cm⁻¹ for anisole. The computed values predicted at 71 cm⁻¹ and 72 cm⁻¹ do not correlate with
experimental observations for O–CH₃ torsion, maybe due to substituent and conjugation effects for vanillin and isovanillin, respectively.

6.4.9 HOMO and LUMO Analyses

Many organic molecules that containing conjugated π electrons are characterized by large values of molecular first hyperpolarizabilities were analyzed by means of vibrational spectroscopy [164, 165]. In most cases, even in the absence of inversion symmetry, the strongest bands in the Raman spectrum are weak in the IR spectrum and vice-versa. But the intermolecular charge transfer from the donor to acceptor group through a single-double bond-conjugated path can induce large variations of both the molecular dipole moment and the molecular polarizability, making FT-IR and FT-Raman activity strong at the same time. The experimental spectroscopic behavior described above is well accounted for by *ab initio* calculations in π-conjugated systems that predict exceptionally large Raman and infrared intensities for the same normal modes [165]. It is also observed in vanillin and isovanillin that the bands at 3644, 3406, 1670, 1597, 1154, 1117, 740 and 521 cm⁻¹ in FT-IR spectrum have their counterparts in FT-Raman bands at 2974, 2841, 1670, 1595, 1117, 760 and 503 cm⁻¹, which suggest that the relative intensities in FT-IR and FT-Raman spectra are comparable resulting from the electron cloud movement through π-conjugated frame-work from electron donor to electron accepter groups. The analysis of the wave function indicates that the electron 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 (LOMO). The LUMO of π nature (i.e., benzene ring) is
delocalized over the whole C–C bond. By contrast, the HOMO is located over methoxy and hydroxyl groups; consequently, the HOMO→LUMO transition implies an electron density transfer to aromatic part and propionic acid of π-conjugated system from methoxy to hydroxyl groups. So, we assigned green color to represent positive charge and red color to represent negative charge of the isosurface of vanillin and isovanillin. Moreover, these orbital significantly overlap in their position for vanillin and isovanillin. The atomic orbital compositions of the frontier molecular orbital are shown in Figs. 6.9 and 6.10 for vanillin and isovanillin, respectively.

Generally, the atom occupied by more densities of HOMO should have stronger ability for detaching electrons, whereas the atom with more occupation of LUMO should be easier to gain electron. For vanillin and isovanillin, HOMO lying at –0.0089 and –0.0091 a.u is a delocalized π orbital. The HOMO–1 lying –0.0097 and –0.0099 a.u below the HOMO is a delocalized π orbital over the both molecules, while the HOMO–2 and HOMO–3, lying –0.0099, –0.0100 a.u and –0.0124, –0.0123 a.u below the HOMO, respectively, are π orbitals that are localized in benzene ring. In contrast, LUMO lying at –0.0026 and –0.0027 a.u, is π* orbital that is localized for vanillin and isovanillin. The LUMO+1 lying about –0.0008 and –0.0012 a.u above the LUMO, is also a π* that is similar to that of LUMO. The HOMO-LUMO energy gap of vanillin and isovanillin was calculated at the B3LYP/6-311++G(d,p) level and is –0.0063 a.u and –0.0063 a.u, revealing that the energy gap reflects the chemical activity of the molecules. LUMO as an electron acceptor represents the ability to obtain an electron and HOMO represents the ability to donate an electron.
Fig. 6.9 Isodensity plots of the frontier orbitals of vanillin (3-methoxy-4-hydroxybenzaldehyde) and corresponding orbital energies (in a.u.).
Fig. 6.10 Isodensity plots of the frontier orbitals of isovanillin (3-hydroxy-4-methoxybenzaldehyde) and corresponding orbital energies (in a.u.).
The calculated self-consistent field (SCF) energy of vanillin is $-535.34$ a.u and that for isovanillin is $-535.46$ a.u. Moreover, the lower in the HOMO and LUMO energy gap explain the eventual charge transfer interactions taking place within the vanillin and isovanillin molecules.

### 6.4.10 Natural Charges

The natural atomic charges of vanillin and isovanillin obtained by Mulliken [110] population analysis with B3LYP/6-311++G(d,p) basis set are compared in Table 6.10. The results show that the substitution of the aromatic ring by CH$_3$, OH and CHO leads to a redistribution of electron density. The $\pi$-electron donating character of the CH$_3$ atom is demonstrated by the decrease of electron density on the C4 atom of vanillin and C3 in isovanillin. The C5 atom of vanillin can accommodate higher positive charge and become more acidic, in comparison to C1 atom of isovanillin. The charge on the C7 atom in isovanillin ($-0.086$ e) is less negative than H10 ($-0.090$ e) in vanillin. On the other hand, the positive charge on the C1 atom in vanillin is more positive (+0.946 e) than H12 atom in isovanillin (+0.275 e). Thus, H10=C1 bond becomes more polarized in vanillin than C7=H12 bond of isovanillin.

### 6.5 CONCLUSION

In the present work, we have performed proper frequency assignments for the compounds vanillin and isovanillin using FT-IR and FT-Raman spectra. The equilibrium geometries and harmonic frequencies of vanillin and isovanillin were determined and analyzed using B3LYP/6-311++G(d,p) basis set. The influences of C=O, C–H, O–H and CH$_3$, on the vibrational frequencies of the vanillin and isovanillin were also discussed. A satisfactory assignment for most of the
fundamentals was provided using the different scaling procedures. The calculated values agree with the experimental observations. The computational results reveal that the most stable conformer of vanillin and isovanillin is "a" form. The calculated isotropic polarizability is –64.6359 and –65.6317 a.u, anisotropy invariant is 9.9792 and 5.5295 a.u and hyperpolarizability is 0.3933 and 1.8562 (in a.u) for vanillin and isovanillin, respectively. The lowering of HOMO-LUMO energy gap value has substantial influence on intermolecular charge transfer of the molecules. The natural atomic charges calculated for vanillin and isovanillin using Mulliken population analysis in all cases are different from the values and results discussed. It could be concluded that population analysis is suitable for the estimation of the changes of the atomic charges.
Table 6.1
Calculated electric dipole moment $D$ (Debye), isotropic polarizability ($\alpha$ in a.u), anisotropy of the polarizability ($\Delta\alpha$ in a.u) and all hyperpolarizability ($\beta$) components (in a.u) values of vanillin and isovanillin.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Vanillin</th>
<th>Isovanillin</th>
<th>Parameters</th>
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<th>Isovanillin</th>
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<tr>
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Table 6.2
Calculated energies and energy difference for eight conformers of vanillin and isovanillin calculated by DFT-B3LYP/6–311++G(d,p) level.

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*Global minimum energy.

*aEnergies of the other seven conformers relative to the most stable “a” conformer.
Table 6.3
Optimized geometrical parameters (bond lengths (Å), bond angles (°) and dihedral angles (°)) of vanillin and isovanillin calculated by B3LYP/6-311++G(d,p) level.

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<th>Values (°)</th>
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<td>C1–C2–C3, C2–C3–C4, C3–C4–C5, C4–C5–C6, C5–C6–C1, C6–C1–C2</td>
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<tr>
<td>26–27</td>
<td>$\beta_i$</td>
<td>C–C–C</td>
<td>C2–C1–C7, C6–C1–C7</td>
</tr>
<tr>
<td>28–33</td>
<td>$\varphi_i$</td>
<td>C–C–H</td>
<td>C1–C2–H10, C3–C2–H10, C4–C5–H18, C6–C5–H18, C5–C6–H19, C1–C6–H19</td>
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<td>$\varphi_i$</td>
<td>C–C–H(OH)</td>
<td>C1–C7–H9</td>
</tr>
<tr>
<td>35–37</td>
<td>$\alpha_i$</td>
<td>O–C–H(OCH$_3$)</td>
<td>O11–C12–H13, O11–C12–H14, O11–C12–H15</td>
</tr>
<tr>
<td>38–40</td>
<td>$\lambda_i$</td>
<td>H–C–H(CH$_3$)</td>
<td>H13–C12–H14, H14–C12–H15, H13–C12–H15</td>
</tr>
<tr>
<td>41–44</td>
<td>$\theta_i$</td>
<td>C–C–O(CH$_3$)</td>
<td>C2–C3–O11, C4–C3–O11, C3–C4–O16, C5–C4–O16</td>
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<td>C–C–O</td>
<td>C1–C7–O8</td>
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<td>$\sigma_i$</td>
<td>C–O–H</td>
<td>C4–O16–H17</td>
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<td>$\gamma_i$</td>
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<td>Out–of–plane bending</td>
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</tr>
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<td>$\omega_i$</td>
<td>C–H</td>
<td>H10–C2–C1–C3, H18–C5–C4–C6, H19–C6–C1–C5</td>
</tr>
<tr>
<td>51</td>
<td>$\omega_i$</td>
<td>C–C</td>
<td>C7–C1–C2–C6</td>
</tr>
<tr>
<td>52–53</td>
<td>$\psi_i$</td>
<td>C–O</td>
<td>O11–C3–C2–C4, O16–C4–C3–C5</td>
</tr>
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<td>C–O–H</td>
<td>H17–O16–C4–C5(C3)</td>
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<td>C–O</td>
<td>C12–O11–C3–C4(C2)</td>
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<td>$\tau_i$</td>
<td>$\tau_{\text{Ring}}$</td>
<td>C1–C2–C3–C4, C2–C3–C4–C5, C3–C4–C5–C6, C4–C5–C6–C1, C5–C6–C1–C2, C6–C1–C2–C3</td>
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<tr>
<td>---------</td>
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<td>-----------------------------------------------------------------------------</td>
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<tr>
<td>56–61</td>
<td>$\tau_i$</td>
<td>C–OH</td>
<td>C1–C7–O8–H9</td>
</tr>
<tr>
<td>62</td>
<td>$\tau_i$</td>
<td>C–CO</td>
<td>O8–C7–C1–C2(C6)</td>
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<td>63</td>
<td>$\tau_i$</td>
<td>CO–CH(CH$_3$)</td>
<td>C3–O11–C12–(H13, H14, H15)</td>
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Table 6.5
Definition of internal coordinates of isovanillin.

<table>
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<th>No (i)</th>
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<td>Stretching</td>
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<td>$P_i$</td>
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<td>$q_i$</td>
<td>C–H</td>
<td>C2–H10, C5–H18, C6–H16, C7–H9</td>
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<td>12–14</td>
<td>$q_i$</td>
<td>C–H(CH$_3$)</td>
<td>C14–H15, C14–H16, C14–H17</td>
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<tr>
<td>15–17</td>
<td>$r_i$</td>
<td>C–O</td>
<td>C3–O11, C4–O13, C14–O13</td>
</tr>
<tr>
<td>18</td>
<td>$r_i$</td>
<td>C=O</td>
<td>C7–O8</td>
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<td>$R_i$</td>
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<td>Bending</td>
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<td>$\beta_i$</td>
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</tr>
<tr>
<td>28–33</td>
<td>$\varphi_i$</td>
<td>C–C–H</td>
<td>C1–C2–H10, C3–C2–H10, C4–C5–H18, C6–C5–H18, C5–C6–H19, C1–C6–H19</td>
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<td>$\varphi_i$</td>
<td>C–C–H(OH)</td>
<td>C1–C7–H9</td>
</tr>
<tr>
<td>35–37</td>
<td>$\alpha_i$</td>
<td>O–C–H(OCH$_3$)</td>
<td>O13–C14–H15, O13–C14–H16, O13–C14–H17</td>
</tr>
<tr>
<td>38–40</td>
<td>$\lambda_i$</td>
<td>H–C–H(CH$_3$)</td>
<td>H15–C14–H16, H16–C14–H17, H15–C14–H17</td>
</tr>
<tr>
<td>41–44</td>
<td>$\theta_i$</td>
<td>C–C–O(CH$_3$)</td>
<td>C2–C3–O11, C4–C3–O11, C3–C4–O13, C5–C4–C6</td>
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<td>$\theta_i$</td>
<td>C–C–O</td>
<td>C1–C7–O8</td>
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<td>$\sigma_i$</td>
<td>C–O–H</td>
<td>C3–O11–H12</td>
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<td>$\nu_i$</td>
<td>C–O–C</td>
<td>C4–O13–C14</td>
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<tr>
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<td></td>
<td>Out–of–plane bending</td>
</tr>
<tr>
<td>48–50</td>
<td>$\omega_i$</td>
<td>C–H</td>
<td>H10–C2–C1–C3, H18–C5–C4–C6, H19–C6–C1–C5</td>
</tr>
<tr>
<td>51</td>
<td>$\omega_i$</td>
<td>C–C</td>
<td>C7–C1–C2–C6</td>
</tr>
<tr>
<td>52–53</td>
<td>$\psi_i$</td>
<td>C–O</td>
<td>O13–C4–C3–C5, O11–C3–C2–C4</td>
</tr>
<tr>
<td>54</td>
<td>$\psi_i$</td>
<td>C–OH</td>
<td>H12–O11–C3–C2(C4)</td>
</tr>
<tr>
<td>55</td>
<td>$\psi_i$</td>
<td>C–O</td>
<td>C14–O13–C4–C3(C5)</td>
</tr>
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<td></td>
<td>Torsion</td>
</tr>
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<td>56–61</td>
<td>$\tau_i$</td>
<td>tRing</td>
<td>C1–C2–C3–C4, C2–C3–C4–C5, C3–C4–C5–C6, C4–C5–C6–C1, C5–C6–C1–C2, C6–C1–C2–C3</td>
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<tr>
<td>62</td>
<td>$\tau_i$</td>
<td>C–OH</td>
<td>C1–C7–O8–H9</td>
</tr>
<tr>
<td>63</td>
<td>$\tau_i$</td>
<td>C–CO</td>
<td>O8–C7–C1–C2(C6)</td>
</tr>
<tr>
<td>64</td>
<td>$\tau_i$</td>
<td>CO–CH(OCH$_3$)</td>
<td>C4–O13–C14–(H15, H16, H17)</td>
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Table 6.6
Definition of local symmetry coordinates of vanillin.

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<tr>
<th>No(i)</th>
<th>Symbol</th>
<th>Definition</th>
<th>Scale factors</th>
</tr>
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<tr>
<td>1–7</td>
<td>νCC</td>
<td>P1, P2, P3, P4, P5, P6, P7</td>
<td>0.983</td>
</tr>
<tr>
<td>8–11</td>
<td>νCH</td>
<td>q8, q9, q10, q11</td>
<td>0.983</td>
</tr>
<tr>
<td>12</td>
<td>CH₃sym</td>
<td>(q12 + q13 + q14)/√3</td>
<td>0.983</td>
</tr>
<tr>
<td>13</td>
<td>CH₃asym</td>
<td>(2q13 – q12 – q14)/√6</td>
<td>0.983</td>
</tr>
<tr>
<td>14</td>
<td>CH₃asym</td>
<td>(q12 – q14)/√2</td>
<td>0.983</td>
</tr>
<tr>
<td>15–17</td>
<td>νCO</td>
<td>r15, r16, r17</td>
<td>0.983</td>
</tr>
<tr>
<td>18</td>
<td>νC=O</td>
<td>r18</td>
<td>0.983</td>
</tr>
<tr>
<td>19</td>
<td>νOH</td>
<td>R19</td>
<td>0.983</td>
</tr>
<tr>
<td>20</td>
<td>Rtrigd</td>
<td>(a20 – a21 + a22 – a23 + a24 – a25)/√6</td>
<td>0.989</td>
</tr>
<tr>
<td>21</td>
<td>Rsymd</td>
<td>(–a20 – a21 + 2a22 – a23 – 2a24 + 2a25)/√12</td>
<td>0.989</td>
</tr>
<tr>
<td>22</td>
<td>Rsymd</td>
<td>(a20 – a21 + a23 – a24)/2</td>
<td>0.989</td>
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<tr>
<td>23</td>
<td>βCC</td>
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<tr>
<td>24–26</td>
<td>βCH</td>
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<tr>
<td>27</td>
<td>βCH(OH)</td>
<td>φ34</td>
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<tr>
<td>28</td>
<td>CH₃sd</td>
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<td>0.864</td>
</tr>
<tr>
<td>29</td>
<td>CH₃ipd</td>
<td>(–λ38 – λ39 – 2λ40)/√6</td>
<td>0.864</td>
</tr>
<tr>
<td>30</td>
<td>CH₃opd</td>
<td>(λ38 – λ40)/√6</td>
<td>0.864</td>
</tr>
<tr>
<td>31</td>
<td>CH₃ipr</td>
<td>(–a35 + 2a36 – a37)/√6</td>
<td>0.864</td>
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<tr>
<td>32</td>
<td>CH₃opr</td>
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<tr>
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<td>βCCO(CH₃)</td>
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<td>βCCO(OCCH₃)</td>
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<td>βCOC</td>
<td>γ47</td>
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<td>38–40</td>
<td>γCH</td>
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<td>γCC</td>
<td>ω51</td>
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<td>42–44</td>
<td>γCO</td>
<td>ψ52, ψ53, ψ54(C2)</td>
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<td>γCOH</td>
<td>ψ55 (C3)</td>
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<tr>
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<td>tRtrigd</td>
<td>(τ56 – τ57 + τ58 – τ59 + τ60 – τ61)/√6</td>
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</tr>
<tr>
<td>47</td>
<td>tRsymd</td>
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<td>τ63</td>
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<td>τCH₃</td>
<td>τ64</td>
<td>0.984</td>
</tr>
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<td>No(i)</td>
<td>Symbol</td>
<td>Definition</td>
<td>Scale factors</td>
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<td>--------------</td>
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</tr>
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</tr>
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</tr>
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<td>φ₃₄</td>
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<td>CH₁₃ipd</td>
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</tr>
<tr>
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<td>CH₁₃opd</td>
<td>(λ₃₈ – λ₄₀)/√6</td>
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<tr>
<td>31</td>
<td>CH₁₃ipr</td>
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</tr>
<tr>
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<tr>
<td>37</td>
<td>bCOC</td>
<td>γ₄₇</td>
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<td>38–40</td>
<td>ωCH</td>
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<td>ωCC</td>
<td>ω₅₁</td>
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<td>ψ₅₅(C₅)</td>
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Table 6.8
Experimental and calculated B3LYP/6–311++G(d,p) level vibrational frequencies (cm\(^{-1}\)), IR intensities (km/mol) and Raman activities (Å\(^4\)/amu) of vanillin.

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Abbreviations: w-weak, vw-very weak, ms-medium strong, m-medium, s-strong, vs-very strong, v-stretching, β-in-plane bending, γ-out-of-plane bending, R-Ring, d-deformation, t-twisting, sym-symmetric stretching, asym-asymmetric stretching, trigd-trigonal deformation, symd-symmetric deformation, asymd-asymmetric deformation, ipd-in-plane deformation, opd-out-of-plane deformation, sd-symmetric deformation, ipr-in-plane rocking, opr-out-of-plane rocking, τ-torsion. PED, Potential energy distribution, only contribution larger than 10% were given.
Table 6.9
Experimental and Calculated B3LYP/6–311++G(d,p) level vibrational frequencies (cm\(^{-1}\)), IR intensities (km/mol) and Raman activities (Å\(^4\)/amu) of isovanillin.

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<tr>
<td>A''</td>
<td>500m</td>
<td>512</td>
<td>506</td>
<td>3.43</td>
<td>5.91</td>
<td>tRsymd (56) + βCH (18)</td>
</tr>
<tr>
<td>A''</td>
<td>485ms</td>
<td>502</td>
<td>493</td>
<td>2.31</td>
<td>1.35</td>
<td>tRsymd (57) + νCO (16) + tRtrigd (15)</td>
</tr>
<tr>
<td>A'</td>
<td>419m</td>
<td>452</td>
<td>425</td>
<td>2.78</td>
<td>6.02</td>
<td>βCO (38) + γOH (29)</td>
</tr>
<tr>
<td>A''</td>
<td>400ms</td>
<td>423</td>
<td>405</td>
<td>6.89</td>
<td>0.18</td>
<td>τCH₃ (75)</td>
</tr>
<tr>
<td>A'</td>
<td>354ms</td>
<td>361</td>
<td>350</td>
<td>0.66</td>
<td>0.12</td>
<td>βCO–CH₃ (37) + γOH (29)</td>
</tr>
<tr>
<td>A''</td>
<td>223w</td>
<td>228</td>
<td>226</td>
<td>0.14</td>
<td>0.42</td>
<td>γCO (67) + γCH₃ (27)</td>
</tr>
<tr>
<td>A''</td>
<td>208v</td>
<td>202</td>
<td>211</td>
<td>7.63</td>
<td>0.80</td>
<td>γCO (63) + γOH (24)</td>
</tr>
<tr>
<td>A''</td>
<td>177v</td>
<td>173</td>
<td>168</td>
<td>0.87</td>
<td>2.49</td>
<td>tRsymd (50) + γCC (12)</td>
</tr>
<tr>
<td>A''</td>
<td>130v</td>
<td>139</td>
<td>131</td>
<td>9.69</td>
<td>0.78</td>
<td>γC=O (32) + γOH (29)</td>
</tr>
<tr>
<td>A''</td>
<td>81</td>
<td>72</td>
<td>94</td>
<td>0.94</td>
<td>0.59</td>
<td>γCO–CH₃ (37) + γOH (23)</td>
</tr>
</tbody>
</table>

Abbreviations: w-weak, vw-very weak, ms-medium strong, m-medium, s-strong, vs-very strong, v-stretching, β-in-plane bending, γ-out-of-plane bending, R-Ring, d-deformation, t-twisting, sym-symmetric stretching, asym-asymmetric stretching, trigd-trigonal deformation, symd-symmetric deformation, asymd-asymmetric deformation, ipd-in-plane deformation, opd-out-of-plane deformation, sd-symmetric deformation, ipr-in-plane rocking, opr-out-of-plane rocking, τ-torsion. PED, Potential energy distribution, only contribution larger than 10% were given.
Table 6.10

Mulliken atomic charges (e) of vanillin and isovanillin performed at B3LYP level with 6-311++G(d,p) basis set.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Natural charges</th>
<th>Atoms</th>
<th>Natural charges</th>
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<tbody>
<tr>
<td></td>
<td>Vanillin</td>
<td></td>
<td>Isovanillin</td>
</tr>
<tr>
<td>C1</td>
<td>0.946</td>
<td>1.019</td>
<td>O11</td>
</tr>
<tr>
<td>C2</td>
<td>0.170</td>
<td>−0.510</td>
<td>C12(H12)</td>
</tr>
<tr>
<td>C3</td>
<td>0.615</td>
<td>−0.858</td>
<td>H13(O13)</td>
</tr>
<tr>
<td>C4</td>
<td>−0.909</td>
<td>−0.016</td>
<td>H14(C14)</td>
</tr>
<tr>
<td>C5</td>
<td>1.054</td>
<td>0.248</td>
<td>H15</td>
</tr>
<tr>
<td>C6</td>
<td>−0.248</td>
<td>−0.224</td>
<td>O16(H16)</td>
</tr>
<tr>
<td>C7</td>
<td>0.270</td>
<td>−0.086</td>
<td>H17</td>
</tr>
<tr>
<td>O8</td>
<td>−0.348</td>
<td>−0.231</td>
<td>H18</td>
</tr>
<tr>
<td>H9</td>
<td>0.153</td>
<td>0.145</td>
<td>H19</td>
</tr>
<tr>
<td>H10</td>
<td>−0.090</td>
<td>0.178</td>
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</table>