Experimental and theoretical study of 3-methyl-4-nitrobenzoic acid using DFT and IVP methods

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Abstract. The Fourier Transform Infrared (FTIR) and FT-Raman spectra of 3-methyl-4-nitrobenzoic acid have been recorded in the range 4000-400 cm⁻¹ and 3500-50 cm⁻¹, respectively. The optimized geometry of the molecule, its vibrational frequencies have been computed using the Density Functional Theory (DFT) employing B3LYP/6-311++G basis set. The scaled values of harmonic vibrational frequencies so obtained have been compared with their experimental counter parts. The scaling factors have been refined to reproduce the frequencies with an RMS error of 9.26 cm⁻¹ between the experimental and computed frequencies. The theoretically predicted FTIR and FT-Raman spectra agree satisfactorily with those of experimental spectra. A 89-parameter modified valence force field was evaluated by solving inverse vibrational problem (IVP) using Wilson's GF matrix method. The force constants were refined using 44 experimental frequencies of this molecule in overlay least-squares technique. The average error between observed and computed frequencies was found 11.61 cm⁻¹. PED and eigen vectors computed in the process were used to make unambiguous vibrational assignments of all the fundamental vibrations of this molecule. The values of dipole moment and hyperpolarizability were determined to study the NLO behaviour of this molecule. The HOMO and LUMO energies were also evaluated for this molecule.

1. Introduction
Vibrational assignment for complex systems can be proposed based on frequency agreement between the computed and observed fundamental frequencies. The spectroscopists have been investigating to develop ‘a priori’ method of predicting vibrational frequencies of a given molecule for the past two and a half decades. In this process, two different and distinct methods, namely classical experimental approach [1] and theoretical quantum mechanics approach [2-13], have been evolved.

In experimental approach, Snyder and Schachtschneider [1] proposed the overlay least-square technique wherein a set of related molecules can be treated together to reduce the number of force constants. This method has been applied successfully to some representative molecular systems as reported in our earlier work on nitrotoluenes, dimethylanilines and some substituted methylbenzenes [14]; and on other molecules as mentioned therein.

Spectroscopic investigation has been carried out in theoretical approach in our earlier work on 3,6-dichloro-4-methylpyridazine and 3,6-dichloropyridazine-4-carboxylic acid by DFT method using B3LYP functional with 6-311++G(d,p) basis set [15]; and 4-methyl-3-nitrobenzoic acid employing DFT method employing B3LYP/6-311++G level of theory [16]. We have recently reported the results
of both theoretical (DFT) and experimental (inverse vibrational problem (IVP)) methods for some pyridine-dicarboxylic acids [17]. Now, we have taken up the task to test further in case of 3-methyl-4-nitrobenzoic acid (3M4NA) by DFT method and solving IVP using Wilson’s GF matrix method [18].

Benzoic acid occurs widely in plants and animal tissues. It is used in miticides, contrast media in urology, cholecystographic examinations and the manufacture of pharmaceuticals. The derivatives of benzoic acid are essential components of the Vitamin B-complex [19]. Further, the herbicidal activity of a molecule containing carboxylic acid group is mainly due to the presence of the acid moiety or a group that is easily convertible to this moiety [20]. The vibrational analysis of benzoic acid and $d_5$-deuterated benzoic acid was made by Furic and Durig using IR and Raman spectroscopy [21]. Normal coordinate analysis was carried out for urea meta nitrobenzoic acid for the assignment of vibrational frequencies using potential energy distribution by Gunasekaran et al [22]. Sundaraganesan et al reported vibrational analysis of 5-amino-2-chlorobenzoic acid [23]; p-chlorobenzoic acid [24]; 3,4-diaminobenzoic acid [25]; 5-amino-2-nitrobenzoic acid [26]; and 2-chlorobenzoic acid [27] employing ab initio HF and DFT methods using FTIR and FT-Raman spectra. Methylnitrobenzoic acid and its derivatives are also known for their local anaesthetic action [28]. Further, it has been demonstrated that 4-Methyl-3-nitrobenzoic acid is a potent inhibitor cancer cell chemotaxis and may be developed into a novel anti-metastasis drug [29]. Hence, we have taken up experimental and theoretical investigation of 4-Methyl-3-nitrobenzoic acid using its FTIR and FT-Raman spectra and suggested vibrational analysis by Density Functional Theory (DFT) [16]. From the above, it is clear that the experimental (infrared and Raman) and theoretical investigation of 3-methyl-4-nitrobenzoic (3M4NA) acid are by no means complete. Hence, a systematic investigation of vibrational spectra of this molecule employing experimental and theoretical methods is undertaken. The purpose of this investigation is:

1. To record FTIR and FT-Raman spectra of this molecule to get complete information on its vibrational frequencies.
2. To make DFT (Density Functional Theory) calculations in order to identify the most stable rotational isomer in the ground state, calculate theoretical vibrational frequencies using scaling, obtain the values of first order hyperpolarizability and to evaluate HOMO-LUMO energies.
3. To solve inverse vibrational problem using optimized geometries and employing overlay least-squares technique.
4. To make unambiguous vibrational assignments of all the fundamentals of the molecule using PED and eigen vectors in conjunction with scaled DFT results.

2. Spectral measurements
The molecule 3M4NA was obtained from Aldrich Chemical Company, USA and used as such for the spectral measurements. The room temperature FTIR spectrum of the compound was recorded using Bruker IFS 66V spectrometer employing KBr optics in the spectral range 4000-400 cm$^{-1}$ with a scanning speed of 30cm$^{-1}$ min$^{-1}$ with spectral width 2.0cm$^{-1}$. The FT-Raman spectrum of this molecule was recorded in the 3500-50 cm$^{-1}$ spectral region using FRA 106 Raman module with a resolution of of ±2 cm$^{-1}$, using 1064 nm line of Nd:YAG laser operating at 200 mw power for excitation.

3. Methods of computations
3.1. Quantum chemical calculations
3.1.1. Molecular geometry
The starting point for calculations is to determine the most stable conformer for the molecule under investigation. The bonds around which rotation are permitted are the C-C$_{\alpha}$ and C=O of acid group. Hence, the molecule 3M4NA was subjected to a rigorous conformational analysis resulting from the rotation of these bonds using Gaussian 09w software package [30] implemented on Pentium-V (3.2GHz) workstation. The computations were established by employing the standard density functional triply-parameter hybrid model DFT/B3LYP [31, 32] using 6-311++G basis set. These computations yielded four stable rotational conformers as shown in figures 1(a), 1(b), 1(c) and 1(d),
respectively. The conformer in figure 1(a) has the lowest global minimum energy at -664.61788 Hartree. Hence, this is accepted as the most stable conformer for optimizing the geometry of this molecule. Subsequent calculations were performed with this optimized structure as shown in figure 2. The same figure contains numbering of atoms also.

![Figure 1. Conformers of 3M4NA (Energy, E in Hartree)](image)

(a) E = -664.61788  
(b) E = -664.57236  
(c) E = -664.55366  
(d) E = -664.548461

Figure 2. Optimized molecular structure

The experimental and simulated FTIR and FT-Raman spectra are presented in figures 3 and 4. For plotting simulated IR and Raman spectra, a pure Lorentzian band shape was used with a full width at half maximum (FWHM) of 10 cm$^{-1}$. The optimized structure parameters namely bond lengths, bond angles and dihedral angles of 3M4NA in its most stable conformation are presented in Table 1. Scaling of the force constants was made according to scaled quantum mechanical (SQM) procedure [33, 34] employing selective scaling in the natural coordinate representation [35, 36]. Transformation of the force field, normal coordinate analysis, least-square refinement of scale factors and calculation of potential energy distribution (PED) were established with the MOLVIB program (version 7.0) written by Suindius [37,38].
Table 1: Optimized geometrical parameters of 3M4NA

| Bond     | Bond length (Å) | Bond angle (in °) | Torsional angle (in °) | Value (in °) |
|----------|-----------------|-------------------|------------------------|--------------|
| C1-C2    | 1.393           | C1-C2-C3 120.11   | C1-C2-C3-4 -1.0        |              |
| C2-C3    | 1.397           | C2-C3-C4 122.54   | C2-C3-C4-5 1.0         |              |
| C3-C4    | 1.410           | C3-C4-C5 115.78   | C3-C4-C5-6 1.0         |              |
| C4-C5    | 1.408           | C4-C5-C6 122.46   | C3-C2-C1-7 -178.0      |              |
| C5-C6    | 1.388           | C6-C1-C2 118.70   | O8-C7-C1-2 157.0       |              |
| C6-C1    | 1.406           | C2-C1-C7 122.95   | C2-C1-C7-09 -22.0      |              |
| C1-C7    | 1.490           | C1-C7-O8 123.19   | C1-C7-O9-H10 -10.0     |              |
| O7-C8    | 1.226           | C1-C7-O9 117.79   | C6-C1-C2-H11 178.0     |              |
| C7-O9    | 1.384           | C7-C9-H10 114.92  | C4-C5-C6-H20 178.0     |              |
| O9-H10   | 0.974           | C1-C2-H11 122.46  | C2-C3-N12-O13 20.0     |              |
| C2-H11   | 1.079           | C2-C3-N12 115.68  | C2-C3-N12-O14 -159.0   |              |
| C3-N12   | 1.466           | C3-N12-O13 117.94 | C2-C3-C4-C15 -179.0    |              |
| N12-O13  | 1.270           | C3-N12-O14 119.00 | C3-C4-C15-H16 -70.0    |              |
| N12-O14  | 1.266           | C3-C4-C15 125.24  | C3-C4-C15-H17 48.0     |              |
| C4-C15   | 1.507           | C4-C15-H16 111.27 | C3-C4-C15-H18 169.0    |              |
| C15-H16  | 1.090           | C4-C15-H17 112.22 | C3-C4-C5-H19 -179.0    |              |
| C15-H17  | 1.089           | C4-C15-H18 119.74 | C4-C5-C6-H20 179.0     |              |
| C15-H18  | 1.089           | C4-C5-H19 118.18  | C4-C3-C2-C1 -1.0       |              |
| C5-H19   | 1.081           | C5-C6-H20 120.86  | C5-C4-C3-2 1.0         |              |
| C6-H20   | 1.080           | O13-N12-O14 123.04| C6-C5-C4-C2 1.0        |              |
| H16-C15-H17 | 106.27 | H17-C15-H18 108.70 | | | |

Figure 3. FTIR spectrum of 3M4NA: a) Observed, b) Simulated with DFT

Figure 4. FT-Raman spectrum of 3M4NA: a) Observed, b) Simulated with DFT
### 3.1.2. Vibrational frequencies

The molecule consists of 20 atoms. Hence, it has 54 fundamentals, distributed as 36 in-plane vibrations of \( a' \)-species and 18 out-of-plane vibrations of \( a'' \)-species in \( C_3 \) point group symmetry for the molecule. The vibrational modes of the molecule were described using the geometrical parameters presented in Table 1. Experimental frequencies (both IR and Raman) and computed frequencies (both unscaled and scaled), as obtained from DFT/B3LYP/6-311++G level of theory, are reported in Table 2. The rms error between unscaled frequencies and observed frequencies was found to be 90.41 cm\(^{-1}\). On using the refined scale factors, this error was reduced to 9.23 cm\(^{-1}\) for this molecule.

**Table 2: Observed, calculated frequencies (in cm\(^{-1}\)) with DFT/B3LYP/6-311++G and IVP; and vibrational assignment of 3M4NA**

| S.No | Mode\(^a\) | Obs. freq.(cm\(^{-1}\)) | Cal. freq.(cm\(^{-1}\)) | Vibrational assignment\(^b\) |
|------|-------------|--------------------------|--------------------------|-----------------------------|
|      |             | IR Raman                 | DFT Unscaled Scaled      |                             |
| a'-species |     |                          |                          |                             |
| 1    | \( \nu(C-C)1 \) | - 675                    | 699 679 673              | 18va(32)+1(23)+7b(18)        |
| 2    | \( \nu(C-C)8a \) | 1587 - 1590              | 1626 1603 1589           | 8a(65)+3(12)+6a(10)          |
| 3    | \( \nu(C-C)8b \) | 1612 - 1618              | 1648 1623 1620           | 8b(76)+6b(10)                |
| 4    | \( \nu(C-C)14 \) | 1269 - 1269              | 1240 1250 1265           | 14(78)+18a(12)               |
| 5    | \( \nu(C-C)19a \) | - 1484                   | 1496 1473 1498           | 19a(67)+7b(24)               |
| 6    | \( \nu(C-C)19b \) | - -                      | 1510 1498 1525           | 19b(51)+3(49)                |
| 7    | \( \nu(CH)2 \)  | 3102 -                    | 3221 3102 3100           | 2(100)                      |
| 8    | \( \nu(CH)20a \) | - 3082                   | 3207 3082 3089           | 20a(97)                      |
| 9    | \( \nu(CH)20b \) | - 3002                   | 3206 3002 3002           | 20b(95)                      |
| 10   | \( \nu(C-C)13 \) | 1200 - 1204              | 1172 1207 1195           | 14(46)+13(24)+\nu(C-C=OH)(13)+18a(10) |
| 11   | \( \nu(C-C)7a \) | - -                      | 1093 1094 1075           | 7a(48)+6a(20)+8a(13)+19a(11) |
| 12   | \( \nu(C-C)7b \) | 1161 - 1160              | 1163 1166 1171           | 7b(40)+13(2)+12b(11)+18a(11) |
| 13   | \( \beta(CH)3 \) | 1297 - 1288              | 1234 1279 1265           | 3(73)+14(15)                 |
| 14   | \( \beta(CH)18a \) | 1127 -                    | 1112 1122 1118           | 1(43)+18a(25)+\nu(C=C=OH)(11) |
| 15   | \( \beta(CH)18b \) | - 1078                   | 1061 1085 1090           | 18b(65)+19b(17)              |
| 16   | \( \beta(CC)15 \) | - 256                    | 251 258 237              | 15(68)+9a(18)                |
| 17   | \( \beta(CN)9b \) | 304 -                     | 300 294 314              | 9b(50)+\gamma(NO2)(16)       |
| 18   | \( \beta(CC)9a \) | 338 -                     | 370 380 364              | 9a(43)+9b(22)+\gamma(NO2)(19) |
| 19   | \( \beta(CC)6a \) | 534 -                     | 505 490 502              | 6a(35)+13(25)+\delta(C=C)(19) |
| 20   | \( \beta(CC)6b \) | - 372                    | 425 395 390             | 6b(32)+1(23)+7b(16)         |
| 21   | \( \beta(CCC)12 \) | 836 837                   | 850 852 833            | 12(29)+\delta(C=O)(24)+1(22) |
| a''-species |     |                          |                          |                             |
| 22   | \( \pi(CH)5 \) | 853 -                     | 873 890 870             | 5(78)                        |
| 23   | \( \pi(CH)11 \) | 789 785                   | 800 783 794            | 11(75)+10b(10)               |
| 24   | \( \pi(CH)17b \) | - -                      | 935 945 936            | 17b(85)                      |
| 25   | \( \pi(CC)10b \) | - 201                     | 192 196 188          | 10b(29)+10a(21)+\delta(OH)(19) |
| 26   | \( \pi(CN)17a \) | - -                      | 180 182 169            | 17a(75)+4+(23)               |
| 27   | \( \pi(CCC)10a \) | 270 -                     | 257 264 262          | 10a(31)+\tau(CC)(22)+\tau(NO2)(18) |
| 28   | \( \pi(CCC)4 \) | 736 -                     | 733 733 740          | 4(55)+\delta(C=C)(23)+5(13) |
| 29   | \( \pi(CCC)16a \) | 586 -                     | 574 573 572          | 16a(81)+\delta(OH)(14)       |
| 30   | \( \pi(CCC)16b \) | - 496                    | 482 510 517          | 16b(81)+5(10)               |

**Vibrations of methyl group**

|     |     |                          |                          |                             |
| 31   | \( \nu(CH)3 \)  | - 2943                   | 3043 2943 2915           | \( \nu(CH)=O \) (99)          |
| 32   | \( \nu(CH)3 \)  | 2984 - 2981              | 3108 2984 2987           | \( \nu(CH)3 \) (99)           |
| 33   | \( \delta(CH)3 \) | - -                      | 1378 1360 1371          | \( \delta(CH)3 \) (99)        |
| 34   | \( \delta(CH)3 \) | 1399 - 1393              | 1423 1408 1397          | \( \delta(CH)=\delta(\text{CH})=\delta(\text{CH})=\delta(\text{CH}) \) (16) |
| 35   | \( \gamma(CH)3 \) | 1035 -                    | 997 1028 1046           | \( \gamma(CH)=\delta(CH)=\delta(CH)=\delta(CH) \) (30) |
| 36   | \( \nu(CH)3 \)  | - -                      | 3121 2961 2977          | \( \nu(CH)3 \) (92a)         |
| 37   | \( \delta(CH)3 \) | - 1443                   | 1514 1447 1453          | \( \delta(CH)=\delta(CH)=\delta(CH)=\delta(CH) \) (86) |
| 38   | \( \gamma(CH)3 \) | - -                      | 1026 1040 1019         | \( \gamma(CH)=\delta(CH)=\delta(CH)=\delta(CH) \) (19) |
| 39   | \( \pi(CH)3 \)  | - 83                     | 78 79 72               | \( \pi(CC)=\pi(CC)=\pi(CC)=\pi(CC) \) (13) |

*Cont’d on next page*
Vibrations of nitro group

| Mode | Frequency | Ref. | PED % |
|------|-----------|------|-------|
| $\nu$ (NO$_2$) | 1348 | 39 | 10 |
| $\delta$ (NO$_2$) | 1525 | 39 | 5 |
| $\gamma$ (NO$_2$) | 764 | 39 | 1 |
| $\omega$ (NO$_2$) | 665 | 39 | 6 |

Vibrations of acid group

| Mode | Frequency | Ref. | PED % |
|------|-----------|------|-------|
| $\nu$ (C$_6$=O) | 1689 | 39 | 10 |
| $\delta$ (C$_6$=O) | 1429 | 39 | 5 |
| $\gamma$ (C$_6$-OH) | 604 | 39 | 1 |
| $\omega$ (C$_6$-OH) | 468 | 39 | 10 |

3.2. Computations based on classical mechanics

This section deals with the solution of inverse vibrational problem, wherein Wilson’s GF-matrix method was employed for the normal coordinate analysis [39]. The computations were carried out using the structure parameters (Table 1) obtained from DFT computations, whereas the internal coordinates and the symmetry coordinates were similar to those used in our earlier work on 4-methyl-3-nitrobenzoic acid [16], which were derived following the suggestions made by Brooks and Cyvin for benzene [40] and the modifications mentioned in our earlier paper [41].

The initial force constants were transferred from our earlier work on nitrotoluenes and methylbenzenes [41] for methyl nitrobenzene part, whereas those of acid group were taken from the literature [42, 43]. The initial set of 89 force constants was subsequently refined with a damping factor of 0.10 employing overlay least-squares method using Schachtschneider program [44]. The refinement converged in four cycles with an average error of 11.61 cm$^{-1}$ between the observed and calculated frequencies. The PED obtained with final set of force constants, vibrational assignments along with calculated frequencies and mixing of modes are presented in Table 2 for 3M4NA.

4. Results and discussion

4.1. Vibrational assignments

Assignments of both in-plane and out-of-plane vibrations were made by DFT and IVP methods by referring to potential energy distribution (PED) and eigen vectors obtained in the computations. A considerable help from Gauss View program was derived in DFT. There are no significant differences between the PED and hence the vibrational assignments in the two methods. Hence, the vibrational assignment that arrived based on IVP is presented in Table 2. The results presented in Table 2 are self-explanatory. Hence, the discussion is unwarranted.

4.2. First order hyperpolarizability

The total molecular dipole moment ($\mu_t$) and its components; total molecular polarizability ($\alpha_t$) and its components; and first order hyperpolarizability ($\beta_t$) and its components were computed using DFT/B3LYP/6-311++G level of theory. The first order hyperpolarizability is a measure of non-linear optical (NLO) effects. Urea is a prototypical molecule used in the NLO properties of molecular systems. Hence, it was used frequently as a threshold value for the purpose of comparison. Based on

Vibrational assignment for 3-nitrobenzoic acid [16], which were derived following the suggestions made by Brooks and Cyvin for benzene [40] and the modifications mentioned in our earlier paper [41].

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DFT computations, the calculated values of dipole moment and first order hyperpolarizability of 3M4NA are 4.0731 Debye and 1.982 \times 10^{-30} \text{ cm}^5/\text{esu}, whereas the corresponding values for Urea are 1.3732 Debye and 0.3728 \times 10^{-30} \text{ cm}^5/\text{esu}, respectively. Thus, we find that the value of \( \mu \) and \( \beta \) for 3M4NBA is greater than the corresponding threshold values of Urea. Hence, it can be concluded, on the basis of the magnitude of the first order hyperpolarizability, that 3M4NA may be a potential applicant in the development of NLO materials.

4.3. Frontier molecular orbitals

As presented in our earlier paper [17] and references cited therein, the frontier molecular orbitals (HOMO and LUMO) and their properties such as energy are very useful for Physicists and Chemists and are very important parameters for quantum chemistry. The HOMO and LUMO computed energies at B3LYP/6-311++G level are illustrated in figure 5. The energy values of HOMO, LUMO and difference between them are found -0.34510 eV, -0.21580 eV and 0.1293 eV for 3M4NA, respectively. It is seen from the HOMO and LUMO energy values that the chemical potential of the molecule under investigation is negative and hence, the compound is stable.

生产总最稳定的结构是具有C\text{\textsubscript{s}}点群对称性的结构。该论文中涉及的分子参数在研究中与文献报道值一致。DFT和IVP方法均表明计算的振动频率与相应的实验值一致。根据DFT和IVP结果，振动谱的分配在DFT和IVP结果中一致。还观察到没有在平面振动与那些在离平面的振动分子中，尽管这种混合是不配点群允许的。99-元素修改的价力常数表对于该分子是评估的。还证明了目标分子具有NLO特性。HOMO-LUMO能级也确定了该分子。

Conclusion

The most stable conformer with the minimum energy having C\text{\textsubscript{s}} point group symmetry has been suggested for 3-methyl-4-nitrobenzoic acid. The structure parameters evaluated in the study for nitrobenzoic acid are in agreement with the available literature values. Both DFT and IVP methods have demonstrated that the calculated frequencies are in good agreement with the corresponding experimental values. The vibrational assignments arrived at on the basis of DFT and IVP results are in good agreement. It is also observed that there is no mixing of in-plane vibrations with those of the out-of-plane vibrations in the molecule even though such mixing is not symmetry-forbidden. A 89-element modified valence force field is evaluated for this molecule. It is also demonstrated that title compound exhibits NLO property. HOMO-LUMO energies are also determined for the molecule.

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