

## VIBRATIONAL SPECTROSCOPIC STUDIES OF 4-CYANOBENZOIC ACID

**M.Fathima Beegum<sup>a</sup>, L.Usha Kumari<sup>a</sup>, B.Harikumar<sup>b</sup>, Hema Tresa Varghese<sup>c</sup>, C.Yohannan Panicker<sup>a\*</sup>**

<sup>a</sup>Department of Physics, TKM College of Arts and Science, Kollam, Kerala, India.

<sup>b</sup>Department of Chemistry, TKM College of Arts and Science, Kollam, Kerala, India.

<sup>c</sup>Department of Physics, Fatima Mata National College, Kollam, Kerala, India.

\*Email: [cyphyp@rediffmail.com](mailto:cyphyp@rediffmail.com)

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### ABSTRACT

*A complete vibrational spectral analyses of 4-cyanobenzoic acid is performed. The wavenumbers are calculated by Hartree-Fock/6-31G\* and B3LYP/6-31G\* basis sets. Comparison of the observed fundamental vibrational wavenumbers of 4-cyanobenzoic acid with calculated results is found in agreement with the experimental data. The predicted infrared intensities, Raman activities and force constants are reported.*

**Keywords:** 4-cyanobenzoic acid, Hartree-Fock, Infrared, Raman

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### INTRODUCTION

The development of photorefractive materials for modern optical signal processing applications such as image amplification, phase conjugate mirrors, and dynamic holography has recently generated wide interest<sup>1-7</sup>. Research on doped liquid crystals<sup>3-7</sup> seeks to optimize optical nonlinearity, charge generation, and charge trapping, while moving towards near infrared wavelengths of interest to optical communication. 4-cyano benzoic acid is a liquid crystal used for many industrial applications. Computational method is at present widely used for simulating IR spectrum. Such simulations are indispensable tools to perform normal coordinate analysis so that modern vibrational spectroscopy is unimaginable without involving them. In the present study the IR, Raman and theoretical calculations of the wavenumbers of the title compound are reported.

### EXPERIMENTAL (COMPUTATIONAL DETAILS)

Vibrational wavenumbers of 4-cyano benzoic acid are calculated by HF/6-31G\* and B3LYP/6-31G\* basis using Gaussian03 software on a personal computer<sup>8</sup>. The vibrational wavenumbers were calculated using analytic second derivatives to confirm the convergence to minima on the potential surface and to evaluate the zero point vibrational energies. The wavenumber values computed at the HF level contain known systematic errors due to the negligence of electron correlation<sup>9</sup>. Therefore, we have used the scaling factor value of 0.8929 for the HF/6-31G\* and 0.9613 for DFT basis sets. Parameters corresponding to optimized geometry of title compound (HF method) (Fig.1) are given in Table 1. The calculated vibrational spectrum has no imaginary wavenumbers, which helped to confirm that the structure of the title compound deduced following optimization corresponds to energy minimum. The optimum geometry was determined by minimizing the energy with respect to all geometric parameters without imposing molecular symmetry constraints. The assignments of the calculated wavenumbers are aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes<sup>10,11</sup>.

## RESULTS AND DISCUSSION

The IR and Raman spectra (Figs. 2 and 3) are downloaded from the official website of Sigma Aldrich<sup>12</sup>. Carboxylic acids are best characterized by the OH stretch, the C=O stretch and the OH out-of-plane deformation. Corresponding to the C=O stretching vibration, the spectrum of carboxylic acids<sup>13</sup> gives rise to a band in the region  $1725 \pm 65 \text{ cm}^{-1}$ . In the present case, we have observed a strong band at  $1710 \text{ cm}^{-1}$  in the IR spectrum and  $1805 \text{ cm}^{-1}$  theoretically. The deviation of the calculated wavenumber for this mode can be attributed to the under estimation of the large degree of  $\pi$ -electron delocalization due to conjugation of the molecule<sup>14</sup>. Two bands arising from the C-O stretch and OH bending appear in the spectra of carboxylic acids near  $1330\text{-}1270$  and  $1440\text{-}1395 \text{ cm}^{-1}$ , respectively<sup>15</sup>. Both of these bands involve some interaction between C-O stretching and in-plane C-O-H bending. For the title compound, the band observed at  $1334 \text{ cm}^{-1}$  in the IR spectrum,  $1323 \text{ cm}^{-1}$  in the Raman spectrum and  $1358 \text{ cm}^{-1}$  by HF calculation is assigned as  $\nu\text{C-O}$  mode<sup>16</sup>. The  $\delta\text{CO}_2$  vibration is active in the region  $770 \pm 50 \text{ cm}^{-1}$  and the  $\text{CO}_2$  wagging vibration which gives rise to a band with variable intensity in the range  $660 \pm 55 \text{ cm}^{-1}$ <sup>13</sup>. The bands observed at  $773 \text{ cm}^{-1}$  in the IR spectrum and  $769 \text{ cm}^{-1}$  in the Raman spectrum are assigned as the  $\text{CO}_2$  deformation bands. The HF calculations give these bands at  $775$  and  $681 \text{ cm}^{-1}$ . The  $\text{CO}_2$  rocking vibration<sup>13</sup> is located in the region  $495\text{-}565 \text{ cm}^{-1}$  with a weak to medium intensity, well separated from the wagging mode. The  $\text{CO}_2$  torsional modes<sup>13</sup> are expected in the region  $195 \pm 50 \text{ cm}^{-1}$  and found in the low wavenumber region.

Nitrogen compounds featuring triple or cumulated double bonds, such as cyanides or nitriles ( $\text{-C}\equiv\text{N}$ ) and cyanates  $\text{-O-(C}\equiv\text{N)}$  all provide a unique spectrum, with a single, normally intense absorption at  $2280\text{-}2200 \text{ cm}^{-1}$  (for cyano groups) and  $2285\text{-}1990 \text{ cm}^{-1}$  (for cyanates, isocyanates and thiocyanates)<sup>13,17</sup>. In the present case the stretching mode  $\nu\text{C}\equiv\text{N}$  is found at  $2240 \text{ cm}^{-1}$  in the IR spectrum and at  $2239 \text{ cm}^{-1}$  in the Raman spectrum. The calculated value for this mode is  $2330 \text{ cm}^{-1}$ .

The aromatic CH stretching vibrations<sup>13</sup> absorb weakly to moderately between  $3120\text{-}3000 \text{ cm}^{-1}$ . The ab initio calculations give bands at  $3057, 3054, 3033, 3033 \text{ cm}^{-1}$ . Experimentally we have observed bands at  $3100, 3060 \text{ cm}^{-1}$  in the IR spectrum and  $3092, 3077 \text{ cm}^{-1}$  in the Raman spectrum. The benzene ring possess six ring stretching vibrations of which the four with the highest wavenumbers occurring near  $1600, 1580, 1490$  and  $1440 \text{ cm}^{-1}$  are good group vibrations<sup>13</sup>. With heavy substituents, the bands tend to shift to somewhat lower wavenumbers and the greater the number of substituents on the ring, the broader the adsorption regions<sup>13</sup>. In the case of C=O substitution, the band near  $1490 \text{ cm}^{-1}$  can be very weak<sup>13</sup>. The fifth ring stretching vibration is active near  $1315 \pm 65 \text{ cm}^{-1}$ , a region that overlaps strongly with that of the CH in-plane deformation<sup>13</sup>. The sixth ring stretching vibration, the ring breathing mode appears as a weak band near  $1000 \text{ cm}^{-1}$  in mono-, 1,3-di- and 1,3,5-trisubstituted benzenes. In the other wise substituted benzenes, however, this vibration is substituent sensitive and difficult to distinguish from the other modes. For the title compound, the  $\nu\text{Ph}$  modes are observed in the range  $1292 - 1618 \text{ cm}^{-1}$ .

For para substituted benzenes, the  $\delta\text{CH}$  modes are seen in the range  $995\text{-}1315 \text{ cm}^{-1}$  and  $\gamma\text{CH}$  in the range  $700\text{-}1000 \text{ cm}^{-1}$ . The strong CH out-of-plane deformation band occurring at  $840 \pm 50 \text{ cm}^{-1}$  is typical for 1,4-di substituted benzenes<sup>13</sup>. For the title compound a strong band is observed at  $867 \text{ cm}^{-1}$  in the IR spectrum which is confirmed by computational results.

The linear regression equations are  $\nu_{(\text{Raman})} = -15.311 + 1.004 \nu_{(\text{HF})}$ , ( $R=0.999$ ),  $\nu_{(\text{IR})} = -5.723 + 0.996 \nu_{(\text{HF})}$ , ( $R=0.999$ ) for HF and  $\nu_{(\text{Raman})} = 1.667 + 0.991 \nu_{(\text{DFT})}$ , ( $R=0.999$ ),  $\nu_{(\text{IR})} = 19.427 + 0.982 \nu_{(\text{DFT})}$ , ( $R=0.999$ ) for DFT calculations.

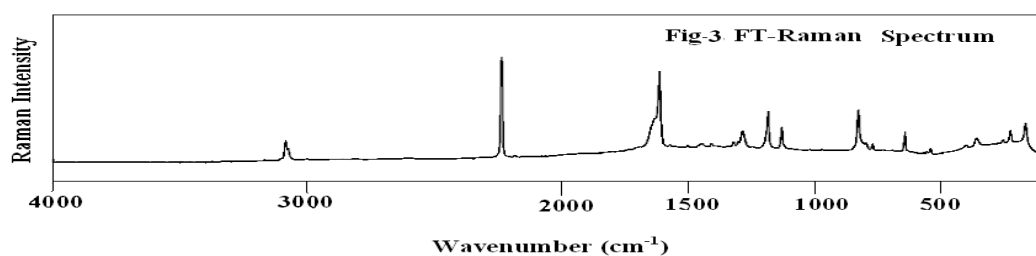
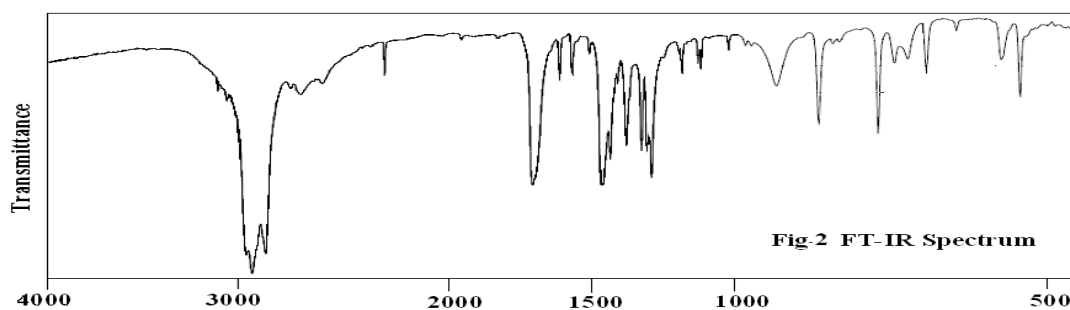
**Table 1: Optimized geometrical parameters of 4-cyanobenzoic acid (HF)**

| Bond lengths (Å)                 |        |                                  |        |                                  |        |                                  |        |                                 |        |                                 |        |
|----------------------------------|--------|----------------------------------|--------|----------------------------------|--------|----------------------------------|--------|---------------------------------|--------|---------------------------------|--------|
| C <sub>1</sub> -C <sub>2</sub>   | 1.3827 | C <sub>1</sub> -C <sub>6</sub>   | 1.3892 | C <sub>1</sub> -H <sub>7</sub>   | 1.0736 | C <sub>2</sub> -C <sub>3</sub>   | 1.3888 | C <sub>2</sub> -H <sub>8</sub>  | 1.0721 | C <sub>3</sub> -C <sub>4</sub>  | 1.3897 |
| C <sub>3</sub> -C <sub>12</sub>  | 1.4914 | C <sub>4</sub> -C <sub>5</sub>   | 1.3804 | C <sub>4</sub> -H <sub>9</sub>   | 1.0727 | C <sub>5</sub> -C <sub>6</sub>   | 1.3909 | C <sub>5</sub> -H <sub>10</sub> | 1.0736 | C <sub>6</sub> -C <sub>11</sub> | 1.446  |
| C <sub>11</sub> -N <sub>13</sub> | 1.1360 | C <sub>12</sub> -O <sub>14</sub> | 1.1885 | C <sub>12</sub> -O <sub>15</sub> | 1.3277 | O <sub>15</sub> -H <sub>16</sub> | 0.9525 |                                 |        |                                 |        |
| Bond angles (°)                  |        |                                  |        |                                  |        |                                  |        |                                 |        |                                 |        |
| A(2,1,6)                         | 119.6  | A(2,1,7)                         | 120.5  | A(6,1,7)                         | 120.0  | A(1,2,3)                         | 119.9  |                                 |        |                                 |        |
| A(1,2,8)                         | 120.0  | A(3,2,8)                         | 120.1  | A(2,3,4)                         | 120.3  | A(2,3,12)                        | 121.8  | A(4,3,12)                       | 117.9  |                                 |        |
| A(3,4,5)                         | 120.1  | A(3,4,9)                         | 119.2  | A(5,4,9)                         | 120.7  | A(4,5,6)                         | 119.5  | A(4,5,10)                       | 120.6  |                                 |        |
| A(6,5,10)                        | 120.0  | A(1,6,5)                         | 120.7  | A(1,6,11)                        | 119.6  | A(5,6,11)                        | 119.7  | A(6,11,13)                      | 180.0  |                                 |        |
| A(3,12,14)                       | 124.2  | A(3,12,15)                       | 113.3  | A(14,12,15)                      | 122.5  | A(12,15,16)                      | 108.1  |                                 |        |                                 |        |
| Dihedral angles (°)              |        |                                  |        |                                  |        |                                  |        |                                 |        |                                 |        |
| D(6,1,2,3)                       | -0.0   | D(6,1,2,8)                       | -180.0 | D(7,1,2,3)                       | 180.0  | D(7,1,2,8)                       | 0.0    | D(2,1,6,5)                      | -0.0   |                                 |        |
| D(2,1,6,11)                      | 180.0  | D(7,1,6,5)                       | -180.0 | D(7,1,6,11)                      | -0.0   | D(1,2,3,4)                       | 0.0    | D(1,2,3,12)                     | -180.0 |                                 |        |
| D(8,2,3,4)                       | 180.0  | D(8,2,3,12)                      | 0.0    | D(2,3,4,5)                       | -0.0   | D(2,3,4,9)                       | -180.0 | D(12,3,4,5)                     | 180.0  |                                 |        |
| D(12,3,4,9)                      | -0.0   | D(2,3,12,14)                     | 180.0  | D(2,3,12,15)                     | 0.0    | D(4,3,12,14)                     | 0.0    | D(4,3,12,15)                    | -180.0 |                                 |        |
| D(3,4,5,6)                       | -0.0   | D(3,4,5,10)                      | -180.0 | D(9,4,5,6)                       | 180.0  | D(9,4,5,10)                      | 0.0    | D(4,5,6,1)                      | 0.0    |                                 |        |
| D(4,5,6,11)                      | -180.0 | D(10,5,6,1)                      | 180.0  | D(10,5,6,11)                     | 0.0    | D(1,6,11,13)                     | -174.0 | D(5,6,11,13)                    | 6.0    |                                 |        |
| D(3,12,15,16)                    | 180.0  | D(14,12,15,16)                   | 0.0    |                                  |        |                                  |        |                                 |        |                                 |        |

**Table 2: Comparison of the calculated and observed vibrational spectra of 4-cyanobenzoic acid**

| $\nu_{\text{(HF)}}$ | $\nu_{\text{(DFT)}}$ | $\nu_{\text{(IR)}}$ | $\nu_{\text{(Raman)}}$ | Infrared intensity | Raman activity | Force constants | Assignments                           |
|---------------------|----------------------|---------------------|------------------------|--------------------|----------------|-----------------|---------------------------------------|
| 3621                | 3553                 |                     |                        | 178.02             | 120.26         | 10.32           | $\nu_{\text{OH}}$                     |
| 3057                | 3116                 | 3100 w              | 3092 w                 | 0.85               | 111.88         | 7.56            | $\nu_{\text{CH}}$                     |
| 3054                | 3111                 | 3060 w              | 3077 w                 | 0.86               | 72.95          | 7.55            | $\nu_{\text{CH}}$                     |
| 3033                | 3096                 |                     |                        | 2.50               | 67.78          | 7.43            | $\nu_{\text{CH}}$                     |
| 3033                | 3095                 |                     |                        | 1.90               | 46.01          | 7.42            | $\nu_{\text{CH}}$                     |
| 2330                | 2258                 | 2240 m              | 2239 s                 | 34.63              | 342.26         | 50.94           | $\nu_{\text{C}\equiv\text{N}}$        |
| 1805                | 1754                 | 1710 s              |                        | 479.26             | 44.77          | 25.0            | $\nu_{\text{C}=\text{O}}$             |
| 1627                | 1603                 | 1618 m              | 1615 s                 | 16.66              | 206.97         | 10.64           | $\nu_{\text{Ph}}$                     |
| 1574                | 1552                 | 1573 m              | 1569 w                 | 7.38               | 0.10           | 12.13           | $\nu_{\text{Ph}}$                     |
| 1506                | 1492                 | 1507 w              | 1500 w                 | 3.09               | 0.73           | 4.09            | $\nu_{\text{Ph}}$                     |
| 1396                | 1394                 | 1387 s              | 1400 w                 | 57.07              | 2.64           | 4.03            | $\nu_{\text{Ph}}, \delta_{\text{OH}}$ |
| 1358                | 1344                 | 1334 s              | 1323 w                 | 184.80             | 10.12          | 3.79            | $\nu_{\text{C}-\text{O}}$             |
| 1301                | 1301                 | 1293 s              | 1292 m                 | 3.76               | 1.79           | 1.62            | $\nu_{\text{Ph}}$                     |
| 1203                | 1288                 | 1195 w              | 1185 m                 | 249.13             | 14.84          | 1.99            | $\delta_{\text{CH}}$                  |
| 1170                | 1182                 |                     |                        | 7.60               | 1.66           | 1.72            | $\nu_{\text{CX}}(\text{X})$           |
| 1163                | 1176                 |                     |                        | 23.41              | 16.12          | 3.03            | $\nu_{\text{CX}}(\text{X})$           |
| 1157                | 1157                 | 1139 w              | 1138 m                 | 81.94              | 41.82          | 1.94            | $\delta_{\text{CH}}$                  |
| 1091                | 1100                 |                     |                        | 58.40              | 13.34          | 4.61            | $\delta_{\text{CH}}$                  |
| 1067                | 1080                 |                     |                        | 5.02               | 0.15           | 1.60            | $\nu_{\text{Ph}}$                     |
| 1005                | 1000                 | 1020 w              |                        | 0.01               | 0.73           | 1.02            | $\delta_{\text{CH}}$                  |
| 999                 | 961                  | 988 w               |                        | 6.10               | 0.05           | 2.27            | $\gamma_{\text{CH}}$                  |

|     |     |       |       |       |       |      |                        |
|-----|-----|-------|-------|-------|-------|------|------------------------|
| 995 | 948 | 933 m |       | 0.02  | 3.14  | 1.01 | $\gamma$ CH            |
| 875 | 846 | 867 s |       | 20.56 | 0.20  | 1.0  | $\gamma$ CH            |
| 860 | 830 | 848 w | 838 m | 0.35  | 2.15  | 0.69 | $\gamma$ OH            |
| 787 | 791 |       |       | 15.66 | 24.33 | 2.64 | $\gamma$ CH            |
| 775 | 751 | 773 s | 769 w | 81.71 | 3.98  | 1.77 | $\delta$ C=O           |
| 697 | 688 | 691 m |       | 63.55 | 1.64  | 1.19 | $\gamma$ Ph            |
| 681 | 676 |       |       | 52.61 | 0.63  | 1.46 | $\gamma$ C=O           |
| 631 | 632 | 639 w | 640 m | 1.67  | 4.03  | 2.21 | $\delta$ Ph            |
| 580 | 595 | 578 m |       | 33.23 | 0.44  | 0.37 | $\delta$ Ph(X)         |
| 558 | 549 |       | 550 w | 1.92  | 4.72  | 1.57 | $\gamma$ Ph(X)         |
| 543 | 518 | 546 m |       | 77.07 | 12.52 | 0.55 | $\gamma$ Ph            |
| 533 | 534 |       |       | 32.01 | 1.07  | 1.50 | $\rho$ CO <sub>2</sub> |
| 468 | 467 |       |       | 3.80  | 1.94  | 1.29 | $\delta$ Ph            |
| 405 | 398 |       | 405 w | 0.26  | 0.76  | 0.41 | $\gamma$ Ph            |
| 403 | 396 |       | 389 w | 1.78  | 1.19  | 0.45 | $\delta$ CX(X)         |
| 312 | 315 |       |       | 2.02  | 4.22  | 0.80 | $\delta$ CX(X)         |
| 223 | 219 |       | 228 w | 3.85  | 0.45  | 0.22 | $\gamma$ CX(X)         |
| 211 | 207 |       | 175 m | 4.07  | 0.13  | 0.22 | $\gamma$ CX(X)         |
| 110 | 127 |       |       | 6.68  | 2.68  | 0.12 | tCO <sub>2</sub>       |
| 79  | 77  |       |       | 3.95  | 0.56  | 0.04 | $\gamma$ C≡N           |
| 62  | 67  |       |       | 1.06  | 1.13  | 0.02 | tPh                    |



Wavenumbers in  $\text{cm}^{-1}$ , Infrared intensities (HF) in  $\text{KM}/\text{Mole}$ , Raman activities (HF) in  $\text{\AA}^4/\text{AMU}$ , force constants (HF) in  $\text{mDyne}/\text{\AA}$ ;  $\nu$ , stretching;  $\delta$ , in-plane deformation;  $\gamma$ , out-of-plane deformation;  $\rho$ , rocking; t, torsion; Ph phenyl; X substituent sensitive; v, very; m, medium; s strong; w, weak;

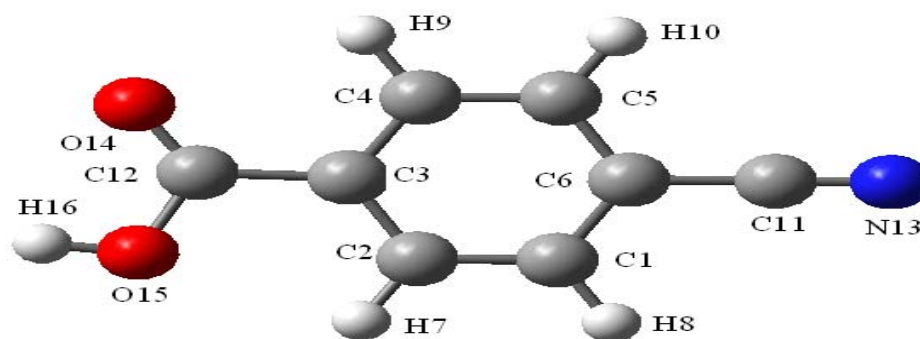


Fig-1 Optimized geometry of 4-cyanobenzoic acid

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