

## Normal Coordinate Analysis and Vibrational Analysis of Pyridine-Dicarboxylic Acids

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### ABSTRACT

The FTIR and FT-Raman spectra of Pyridine-dicarboxylic acids (23, 24, 25, 26, 34, 35PDA) were recorded in the range 4000-450cm<sup>-1</sup> and 4000-50cm<sup>-1</sup>, respectively. A normal coordinate analysis was carried out for all the vibrations using 74-parameter modified valence force field by solving inverse vibrational problem (IVP) employing overlay least-squares technique. This reproduced 39 experimental frequencies of this molecule with an average error of 10.33 cm<sup>-1</sup> in zero order calculations. PED and eigen vectors calculated in the process were used to make unambiguous vibrational assignments of all the fundamentals.

**Keywords:** FT-IR, FT-Raman and Pyridine dicarboxylic acids.

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### I. INTRODUCTION

Pyridine-dicarboxylic acids find great importance in coordination chemistry, biochemistry, pharmaceuticals and medicine. In our earlier work [1], we reported the vibrational analysis of 2,3-pyridine-dicarboxylic acid; 2,4-pyridine-dicarboxylic acid and 3,4-pyridine-dicarboxylic acid using the DFT method at B3LYP/6-311++(d,p) level of theory and solving inverse vibrational problem using optimized geometries. In this paper we report the results of similar investigation for all 23, 24, 25, 26, 34, 35 pyridine-dicarboxylic acids using normal coordinate analysis. In pharmaceuticals and medicines, PDA is found to be suitable ligand to develop more effective HIV agents [2-4]. Hence, experimental and theoretical investigation of pyridine-dicarboxylic acids gained importance in recent years. Wasylina et al [5] reported NMR, UV, and IR absorption spectra of 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-pyridine-dicarboxylic acids. The tentative assignments were proposed for very few IR bands on the basis of qualitative considerations, leaving many other observed vibrational frequencies unassigned. McCann and Laane [6] investigated dipicolinic acid, dinicotinic acid and their dianions experimentally and theoretically, whereas, Alexandre et al [7] reported

its Raman spectra in microcrystalline form. Thermo-chemical and theoretical studies of 2,3-; 2,5-; and 2,6-pyridine-dicarboxylic acids are also available along with that of dimethyl pyridine-2,6-dicarboxylate [8].

The purpose of this investigation is:

1. To record FTIR and FT-Raman spectra to get complete information on its vibrational frequencies.
2. To solve inverse vibrational problem using optimized geometries and employing overlay least-squares technique.

### II. SPECTRAL MEASUREMENT

The molecule, PDAS, are obtained from TCI Chemical Company, Japan and used as such for the spectral measurements. The room temperature FTIR spectra of this compound is recorded using Bruker IFS 66V spectrometer employing KBr optics in the spectral range 4000-450 cm<sup>-1</sup> with a scanning speed of 30 cm<sup>-1</sup> min<sup>-1</sup> with spectral width 2.0 cm<sup>-1</sup>. The FT-Raman spectra of this molecules are recorded in the range 4000-50cm<sup>-1</sup> using FRA 106 Raman module equipped with Nd:YAG laser source operating at 200 mw power with spectral resolution of 2 cm<sup>-1</sup>. The wavelength of the exciting radiation used was 1064 nm.

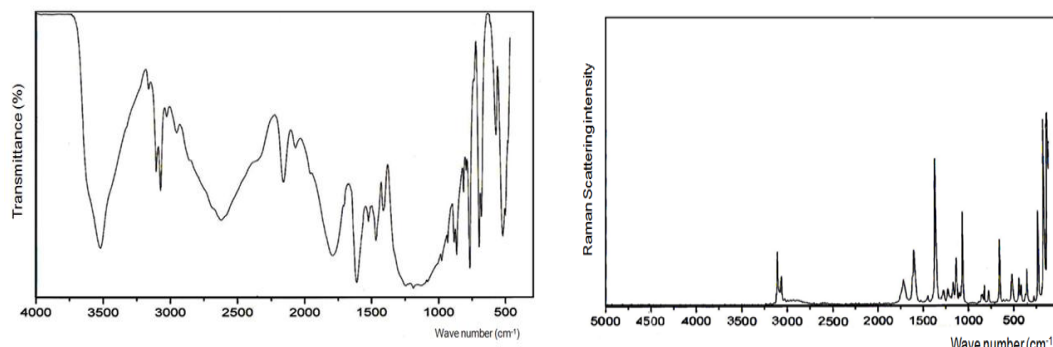


Fig. 1(a & b) represents the FTIR and FT-Raman spectra of Pyridine-2,3-dicarboxylic acid

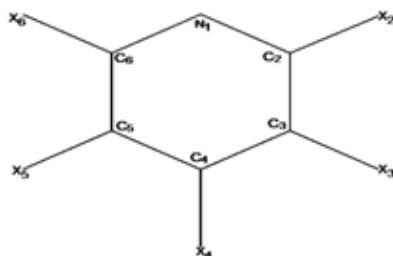
### III. NORMAL COORDINATES ANALYSIS OF PDAS

As emphasized in literature [9,10], it is very essential to carry out a rigorous mathematical treatment of vibrational spectra for complete understanding of the vibrational modes. Hence, we approach normal coordinate analysis methods of the six molecules namely,

- Pyridine-2,3-dicarboxylic acid (23PDA),
- Pyridine-2,4-dicarboxylic acid (24PDA),
- Pyridine-2,5-dicarboxylic acid (25PDA),

- Pyridine-2,6-dicarboxylic acid (26PDA),
  - Pyridine-3,4-dicarboxylic acid (34PDA), and
  - Pyridine-3,5-dicarboxylic acid (35PDA),
- for which the author has recorded the vibrational spectra, has been undertaken. The aim is to obtain a single force field for the six molecules using frequencies in overlay technique proposed by Synder and Schachtschneider [11] and to use the results in order to characterize the frequencies. The structure of Pyridine di-carboxylic acid is shown in the fig.2.

Fig.2. The structure of Pyridine dicarboxylic acid



where  $\begin{matrix} \text{O} \\ \parallel \\ \text{R}-\text{C} \\ | \\ \text{OH} \end{matrix}$  function represents acid group in the structure.

- 23PDA :  $X_2 = X_3 = \text{R}$  and  $X_4 = X_5 = X_6 = \text{H}$
- 24PDA :  $X_2 = X_4 = \text{R}$  and  $X_3 = X_5 = X_6 = \text{H}$
- 25PDA :  $X_2 = X_5 = \text{R}$  and  $X_3 = X_4 = X_6 = \text{H}$
- 26PDA :  $X_2 = X_6 = \text{R}$  and  $X_3 = X_4 = X_5 = \text{H}$
- 34PDA :  $X_3 = X_4 = \text{R}$  and  $X_2 = X_5 = X_6 = \text{H}$
- 35PDA :  $X_3 = X_5 = \text{R}$  and  $X_2 = X_4 = X_6 = \text{H}$

### IV. CHOICE OF FORCE CONSTANTS AND THEIR REFINEMENT

A comparison of the vibrational frequencies of the title compounds reveals close similarity in the magnitudes of the frequencies of similar modes in spite of the fact that the substituent's are different and occupy different

positions. Hence, force constants corresponding to common groups are expected to be transferable among these molecules. This indicates the possibility of obtaining a common force field for the molecules under investigation. Based on these considerations a valence force field is chosen for

making normal coordinate analysis of this set of molecules.

The reasons for using a valence force field rather than a Urey–Bradley force field are:

(a) In the present state of our knowledge, a dynamic model based solely on the forces acting through the bond system seems more readily interpretable in chemical terms, particularly for complex molecules of low symmetry (1).

(b) In a study on the planar vibrations of the chlorinated benzenes, Scherer concluded that a 26–parameter valence force field led to a significantly better frequency fit than a 38–parameter Urey–Bradley force field.

(c) The potential energy distribution (PED) obtained on the basis of valence force field shows remarkable stability for the variation of both diagonal and interaction valence type constants [12, 13]. Hence it can be used as a reliable means of quantifying the vibrational modes.

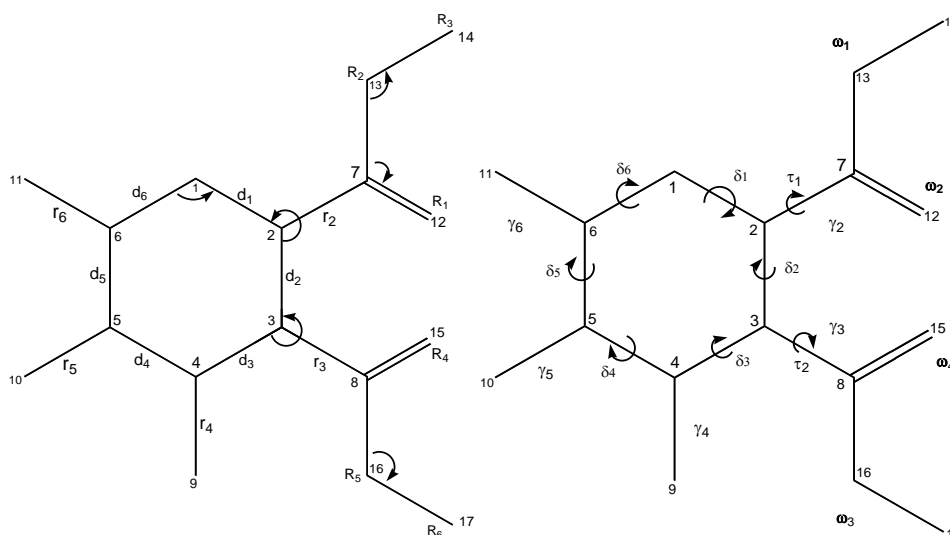
(d) It is in line with the attempts being made to find a few hundred constants that can explain the spectra of a few thousands molecules [14] and

(e) It affords easy comparison with similar studies on other substituted benzenes [15-17].

As such the C–C, C–N, C–H, C–C<sub>α</sub>, C<sub>α</sub>=O, C<sub>α</sub>-O, O–H, CCC, CNC, NCC, CCH, NCH, CC<sub>α</sub>-O, CC<sub>α</sub>=O, OC<sub>α</sub>=O, C<sub>α</sub>-OH, CCC<sub>α</sub> and NCC<sub>α</sub> diagonal force constants are chosen to be the same irrespective of position of substitution. The difference in positions is taken into account by suitable interaction constants. It is well known that significant interaction constants are obtained only for neighboring coordinates [18].

Therefore 74–element valence force field is employed for the normal coordinate analysis of in-plane and out-of-plane vibrational modes. This modified valence force field can be represented by the following equation for in-plane and out-of-plane vibration.

Fig.3: shows that Definition of in-plane out-of-plane internal coordinates in Pyridine-2,3-dicarboxylic acid where as fig.4- shows that Numbering of valence internal co-ordinates for Pyridine-2,3-dicarboxylic acid and numbering of redundant free internal co-ordinates (after removing redundancies around the ring carbon atom).



**Fig .3**

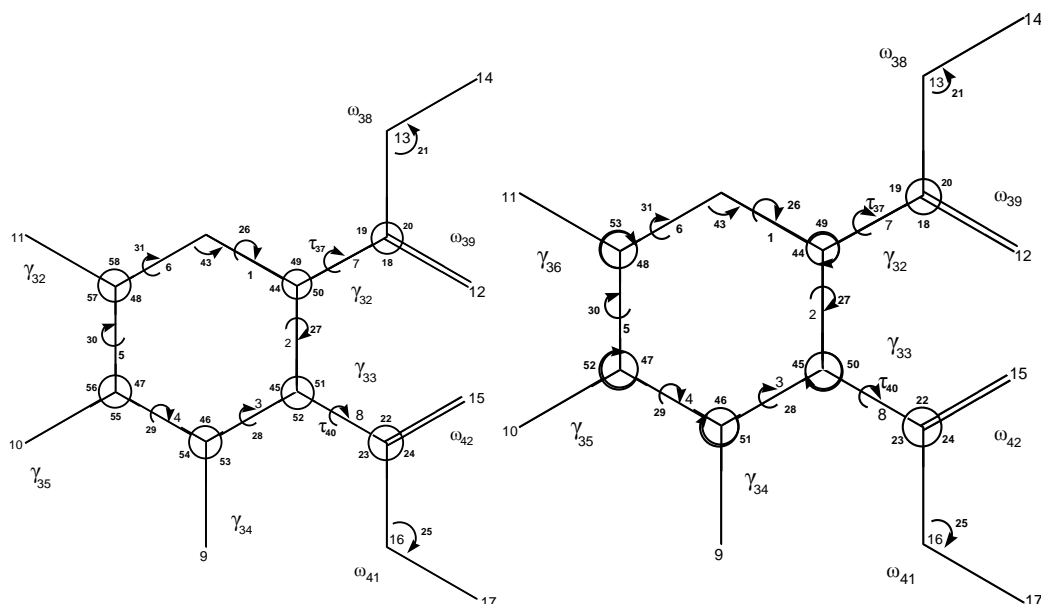


Fig.4

## V. VIBRATION ASSIGNMENTS

A better understanding of various groups involved in any particular mode corresponding to a given frequency can now be obtained by a study of the PED among the various force constants.

The observed and calculated (NCA and DFT) frequencies of 23PDA, 24PDA, 25PDA, 26PDA, 34PDA and 35PDA, are presented in the vibrational assignments. The frequencies are assigned to different vibrational modes using the potential energy distribution (PED) and eigen vectors obtained in the computations. The vibrations are represented in Wilson's notation [19] following the suggestions made by Varsanyi for 1,2,3-tri light and 1,2,4-tri light and 1,3,5-tri light substituted benzenes [See Ref. 20, pp. 298, 323 and 280], respectively. It can be understood from Tables from 4.13 to 4.17 that the calculated frequencies obtained by normal coordinate analysis method are in good agreement with experimental frequencies and DFT. PED shown in these tables is obtained from the results of NCA method. The assignments presented in these tables are self-explanatory and the discussion is confined to some of the important vibrational modes only.

### i) C-C and C-N stretching vibrations

The modes 1, 8a, 8b, 14, 19a and 19b (Wilson's notation is used for benzene ring modes, see Ref. 4) are known as C-C stretching vibrations in benzene and its derivatives. The molecules under investigation consist one nitrogen atom and five carbon atoms in aromatic nucleus. Hence, we get four C-C and one C-N stretching vibrations for the molecules under investigation. The modes 8a,

14, 19a and 19b designate the C-C stretching vibrations, whereas, the modes 1 and 8b represent C-N stretching vibrations in these molecules. Mode 1 is highly sensitive to the nature of the substituent and hence classified as ring vibration. Further, mode 14 is observed to have considerable mixing with C-H in-plane bending vibration 3. Hence, only the modes 8a, 19a, 19b and 8b are discussed in this section by deferring the discussion of modes 1 and 14 to appropriate sections to a later stage. For the molecules 23PDA, 24PDA, 25PDA, 26PDA, 34PDA and 35PDA, the modes 8a and 8b are expected around  $1600\text{ cm}^{-1}$ . The higher frequency has PED to the extent of 63%, 47%, 51%, 71%, 49% and 50% from C-C stretching character and the remaining PED comes from C-C $_{\alpha}$  stretching mode 7b and ring vibrations in 23PDA, 24PDA, 25PDA, 26PDA, 34PDA and 35PDA, respectively. The lower frequency is a C-N stretching mode to the extent of 55%, 33%, 34%, 56%, 46% and 41% in these molecules and mixes with C-C $_{\alpha}$  stretching vibration and C-H in-plane bending vibration. Hence, the absorptions near  $1603, 1638\text{R}, 1622\text{R}, 1642\text{R}, 1640$  and  $1610\text{ cm}^{-1}$ , are assigned to C-C stretching vibration 8a and bands near  $1583, 1609, 1609, 1574, 1592$  and  $1591\text{C cm}^{-1}$  are ascribed to C-N stretching vibration 8b in 23PDA, 24PDA, 25PDA, 26PDA, 34PDA and 35PDA, respectively. Modes 19a and 19b are expected in the spectral range  $1400\text{-}1500\text{ cm}^{-1}$  in benzene and its derivatives. The higher frequency is a C-C stretching mode to the extent of 71%, 31%, 35%, 70%, 32% and 36% and has a good amount of mixing from C-C $_{\alpha}$  stretching vibration, whereas, the lower frequency exhibits C-

C stretching character to the extent of 51%, 55%, 50%, 59%, 28%; and 58% mixes with C-H in-plane bending vibration. Hence, the frequencies near 1528C, 1519, 1519, 1455, 1478 and 1537C  $\text{cm}^{-1}$  are assigned to mode 19a and the absorptions around 1494, 1464, 1464, 1415, 1437 and 1466  $\text{cm}^{-1}$  are attributed to mode 19b in 23PDA, 24PDA, 25PDA, 26PDA, 34PDA and 35PDA, respectively. C-C and C-N stretching vibrations of above molecules are good agreements in the literature of P. Koczon and his co-workers [21].

### ii) Mode 14 and C-H in-plane bending vibrations

The assignment of mode 14 (the Kekule mode) in which alternate C-C bonds either increase or decrease, is usually difficult as the highest C-H in-plane bending vibration 3 appears in its vicinity around 1000-1300  $\text{cm}^{-1}$  [22-25]. According to the DFT and NCA calculations, the bands observed at 1277 and 1268C  $\text{cm}^{-1}$ ; 1248R and 1251C  $\text{cm}^{-1}$ ; 1270 and 1267C; 1264 and 1265C; 1263\* and 1276C; 1266 and 1267C  $\text{cm}^{-1}$ , in 23PDA, 24PDA, 25PDA, 26PDA, 34PDA and 35PDA, respectively exhibit strong mixing between the modes 14 and 3. Hence, it is difficult to make an unequivocal choice for their assignment. However, R indicates Raman shift, \* indicates DFT value, and C indicates calculated value in NCA considering the highest PED contribution, the bands near 1277, 1248R, 1270, 1264, 1276C and 1266  $\text{cm}^{-1}$ , which have 70%, 64%, 70%, 69%, 80% and 65% PED from C-C stretching character in these molecules can be attributed to mode 14. It seems reasonable as these frequencies fall in the range 1230-1330  $\text{cm}^{-1}$  proposed for mode 14 by Varsanyi in 1,2,3-tri-substituted benzenes [see Ref. [20] pp 298]. The C-H in-plane bending vibrations are designated as mode 3, 9b and 18a in 23PDA, 26PDA and modes 3, 18a and 18b in 24PDA, 25PDA, 34PDA and 35PDA. In aromatic compounds, they generally appear in the spectral region 1000-1300  $\text{cm}^{-1}$ .

Based on the calculations, the bands near 1232, 1232, 1228R, 1238C, 1250 and 1215  $\text{cm}^{-1}$ , which have 50%, 38%, 41%, 56%, 58% and 41% C-H in-plane bending character, are assigned as mode 3, respectively in these molecules. The absorptions near 1130 and 1173; 1162 and 1175  $\text{cm}^{-1}$ , are assigned to modes 9b and 18a in 23PDA, 26PDA, whereas the bands near 1118R and 1187  $\text{cm}^{-1}$ ; 1138R and 1187; 1117R and 1161; 1055 and 1162  $\text{cm}^{-1}$ , are ascribed to modes 18a and 18b in 24PDA, 25PDA, 34PDA and 35PDA, respectively. Both these vibrations mix with C-N stretching mode 1 in 23PDA, 26PDA; C-C stretching mode in 24PDA, 25PDA, 34PDA and 35PDA.

### iii) Vibrations of C-C<sub>α</sub> (bond between pyridine and acid groups)

Modes 7b and 20a in 23PDA and 26PDA; and 7b and 13 in 24PDA, 25PDA, 34PDA and 35PDA, designate the two C-C<sub>α</sub> stretching vibrations, whereas the modes 9a and 18b in 23PDA and 26PDA; and 9a and 15 in 24PDA, 25PDA, 34PDA and 35PDA, represent the corresponding in-plane bending vibrations. The pair of frequencies near 1037 and 1307  $\text{cm}^{-1}$ ; 1006R and 1301C  $\text{cm}^{-1}$ ; 1020R and 1304C  $\text{cm}^{-1}$ ; 996 and 1299  $\text{cm}^{-1}$ ; 1072 and 1305C  $\text{cm}^{-1}$ ; 1034R and 1305R are assigned to C-C<sub>α</sub> stretching vibrations in 23PDA, 24PDA, 25PDA, 26PDA, 34PDA and 35PDA, respectively based on the results of DFT and NCA calculations. The lower frequency has PED to the extent of 46%, 42%, 40%, 49%, 37% and 40% whereas, the higher frequency has 48%, 45%, 46%, 51%, 41% and 43%, PED from C-C<sub>α</sub> stretching character. Both these modes mix with C-C and C<sub>α</sub>-O stretching vibrations in these molecules. The pair of frequencies near 101R and 227R  $\text{cm}^{-1}$ ; 110C and 226R  $\text{cm}^{-1}$ ; 110R and 263R  $\text{cm}^{-1}$ ; 210R and 310R  $\text{cm}^{-1}$ ; 101R and 211R  $\text{cm}^{-1}$ ; 201R and 330R  $\text{cm}^{-1}$ , are assigned to C-C<sub>α</sub> in-plane bending modes, respectively in 23PDA, 24PDA, 25PDA, 26PDA, 34PDA and 35PDA.

The two out-of-plane bending vibrations associated with C-C<sub>α</sub> bonds are designated as modes 10b and 17b in 23PDA and 26PDA; and 10b and 17a in 24PDA, 25PDA, 34PDA and 35PDA. The frequencies near 160R and 122R  $\text{cm}^{-1}$ ; 187R and 135R  $\text{cm}^{-1}$  are assigned to the modes 10b and 17b in 23PDA and 26PDA. The frequencies near 178R and 130C; 163C and 128R; 185 and 142R; 189R and 137R are assigned to the modes 10b and 17a in 24PDA, 25PDA, 34PDA and 35PDA, respectively. It is evident from assignment that these modes mix with several other vibrations.

### iv) Ring vibrations

The four ring vibrations 1, 6a, 6b and 12 are sensitive to the position and the nature of the substituent, which makes their correlation with corresponding benzene modes very difficult. Hence, they were identified and assigned from careful consideration of their characteristic eigen vector distribution following Patel et al [27].

According to normal coordinate analysis, the absorptions near 353R and 460  $\text{cm}^{-1}$ ; 346R and 422R  $\text{cm}^{-1}$ ; 360R and 496; 395R and 441; 330R and 422R; and 330R and 532 and 476  $\text{cm}^{-1}$  are assigned to modes 6a and 6b, in 23PDA, 24PDA, 25PDA, 26PDA, 34PDA and 35PDA, respectively. As evident from Tables 4.14 to 4.19, they mix with several other modes. In spite of this mixing, these

vibrations retain their essential CCC bending character in the appropriate ratio for these modes. According to the calculations, the ir absorptions near 768, 728, 693, 752, 771 and 752  $\text{cm}^{-1}$  are assigned to mode 12 in these molecules. These frequencies retain the essential CCC bending nature despite their mixing with several other vibrational frequencies. In benzene, mode 1 at 990  $\text{cm}^{-1}$  is a pure C-C stretching vibration as it is totally symmetric and widely separated from C-H stretching modes. Hence, the band near 823, 807, 807, 800R, 1033 and 801  $\text{cm}^{-1}$ , which have PED to the extent of 63%, 75%, 75%, 60%, 68% and 71%, from C-N stretching character, are ascribed to mode 1 in 23PDA, 24PDA, 25PDA, 26PDA, 34PDA and 35PDA, respectively. They mix with mode 12 in three molecules under investigation.

#### a) Ring torsions

The ring torsions are designated with modes 4, 16a and 16b in benzene and its derivatives. In mode 4, alternate CCCC torsion angles either increase or decrease. In mode 16a, these angles change in the ratio +2, -1, -1, +2, -1, -1, whereas in mode 16b, they change in the ratio 0, +2, -2, 0, +2, -2. Thus, according to the calculations, the frequencies near 741C, 764, 764, 701, 808 and 771C  $\text{cm}^{-1}$ , are assigned as mode 4 in 23PDA, 24PDA, 25PDA, 26PDA, 34PDA and 35PDA, respectively. It has 37%, 51%, 63%, 35%, 44% and 35% PED from ring torsion character and mixes with C-H out-of-plane bending vibrations in three molecules investigated here. The ir absorptions near 612, 693, 563, 647, 677 and 677R  $\text{cm}^{-1}$  having 34%, 36%, 39%, 31%, 73% and 24% ring torsion character are attributed mode 16a, whereas, the frequencies around 414R, 467, 440R, 480R, 417C, and 496  $\text{cm}^{-1}$ , which have 71%, 41%, 51%, 64%, 70% and 68%, PED from ring torsion character are assigned to mode 16b in 23PDA, 24PDA, 25PDA, 26PDA, 34PDA and 35PDA, respectively. These modes mix with several other vibrations as is evident from vibrational assignment. It is seen that mode 4 is the highest ring torsion in the molecules under investigation.

#### v) Vibrations of the acid groups

There are six in-plane and three out-of-plane vibrations for each of two acid groups in the molecules under study. These are,  $\nu(\text{C}_\alpha=\text{O})$ ,  $\nu(\text{C}_\alpha-\text{O})$ ,  $\delta(\text{OH})$ ,  $\nu(\text{O}-\text{H})$ ,  $\delta(\text{C}_\alpha=\text{O})$ ,  $\gamma(\text{C}_\alpha-\text{O})$ ,  $\omega(\text{OH})$ ,  $\omega(\text{C}_\alpha=\text{O})$  and  $\tau(\text{CC}_\alpha)$ .

#### a) In-plane acid vibrations

The ir absorptions near 1714R, 1699, 1790, 1695, 1714 and 1719  $\text{cm}^{-1}$  are assigned to  $\nu(\text{C}_\alpha=\text{O})$  stretching vibration in 23PDA, 24PDA,

25PDA, 26PDA, 34PDA and 35PDA, respectively. They have 82%, 85%, 99%, 92%, 91% and 90% carbonyl stretching character and do not have mixing from any other vibration as is evident from vibrational assignment. The stretching and in-plane bending vibrations,  $\nu(\text{C}_\alpha-\text{O})$  and  $\delta(\text{OH})$ , of the acid group generally appear in the range 1200-1450  $\text{cm}^{-1}$  depending on whether monomeric, dimeric or other hydrogen bonded species are present. Usually,  $\delta(\text{OH})$  appears at higher frequency than that of  $\nu(\text{C}_\alpha-\text{O})$ . Moreover, these bands overlap with other bands that are due to aromatic nucleus or aliphatic chain vibrations making unambiguous assignment difficult. Based on the results of computations, the ir absorptions near 1363, 1407, 1372R, 1378R, 1364 and 1389R  $\text{cm}^{-1}$  are found to have 71%, 80%, 78, 70, 77, 71% PED from  $\delta(\text{OH})$  character in 23PDA, 24PDA, 25PDA, 26PDA, 34PDA and 35PDA, respectively and hence, they are attributed to  $\delta(\text{OH})$  vibration. The frequencies near 1329C, 1326R, 1328R, 1328, 1337 and 1368  $\text{cm}^{-1}$ , having PED to the extent of 28%, 47%, 49%, 48%, 47% and 24%, are assigned to mode  $\nu(\text{C}_\alpha-\text{O})$  in these molecules. These vibrations mix with several other modes as can be seen from vibrational assignment. All benzoic acids, being hydrogen bonded in the solid state, are characterised by a strong ir absorption in the region 2200-3500  $\text{cm}^{-1}$ , attributable to  $\nu(\text{O}-\text{H})$  with a few superimposed maxima that have their origin in C-H stretching vibrations. The molecules under investigation are no exception. Thus, the ir absorptions identified near 3453, 3521, 3521, 3568, 3453 and 3436  $\text{cm}^{-1}$  are assigned to mode  $\nu(\text{O}-\text{H})$  in 23PDA, 24PDA, 25PDA, 26PDA, 34PDA and 35PDA, respectively. Based on the calculations, as expected, these modes are pure as they have PED to the extent of 99% from  $\nu(\text{O}-\text{H})$  vibration. Assignment of other vibrations of this group and mixing among them can be seen in vibrational assignment. The band near 651, 676, 676, 681R, 659, 626  $\text{cm}^{-1}$ , are assigned to  $\delta(\text{C}_\alpha=\text{O})$  in-plane bending vibration in 23PDA, 24PDA, 25PDA, 26PDA, 34PDA and 35PDA, respectively. Vibrations of the acid groups like  $\nu(\text{C}_\alpha=\text{O})$ ,  $\nu(\text{C}_\alpha-\text{O})$ ,  $\delta(\text{OH})$ ,  $\nu(\text{O}-\text{H})$ ,  $\delta(\text{C}_\alpha=\text{O})$ , and  $\gamma(\text{C}_\alpha-\text{O})$ , are good agreements in the assignments of K. McCan, and J. Laane [28].

#### v) Out-of-plane acid vibrations

The pair frequencies near 515 and 438R  $\text{cm}^{-1}$ ; 516 and 346  $\text{cm}^{-1}$ ; 516 and 424C  $\text{cm}^{-1}$ ; 515 and 431C  $\text{cm}^{-1}$ ; 518C and 438C  $\text{cm}^{-1}$ ; and, 525C and 468C  $\text{cm}^{-1}$ ; are assigned to the  $\omega(\text{OH})_1$  and  $\omega(\text{OH})_2$  out-plane acid vibrations. These vibrations having PED to the extent of 56%, 37%, 36%, 61%, 58% and 55% for  $\omega(\text{OH})_1$ , whereas extent of

29%, 40%, 41%, 31%, 44% and 44% for  $\omega(\text{OH})_2$  out-plane acid vibration. The ir absorption near 852, 882, 857R, 854, 845, and, 798R and are assigned to the  $\omega(\text{C}_\alpha=\text{O})$ , out-of-plane acid vibrations. These modes mix with several other vibrations as is evident from Tables 4.14 to 4.19. The pair bands near 114R and 75R  $\text{cm}^{-1}$ ; 99R and 68C  $\text{cm}^{-1}$ ; 75R and 81C  $\text{cm}^{-1}$ ; 74R and 113R  $\text{cm}^{-1}$ ; 82R and 121R  $\text{cm}^{-1}$ ; and 81R and 110R  $\text{cm}^{-1}$ ; are assigned to the  $\tau(\text{CC}_\alpha)_1$  and  $\tau(\text{CC}_\alpha)_2$ , out-of-plane vibrations presented in table.

## VI. RESULTS

Vibrational assignments were made by using solving classical inverse vibrational problem. PED and eigen vectors were used to make vibrational assignments in inverse vibrational.

## VII. CONCLUSION

A complete vibrational analysis of 23-, 24-, 25-, 26-, 34-, and 35- pyridine-dicarboxylic acids are performed using the solving inverse vibrational problem using optimized molecular geometry. All the fundamental frequencies of the molecule are assigned unambiguously based on the PED and eigen vectors obtained from normal coordinate analysis.

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