Vibrational Analysis and Inverse Vibatrional Problem (IVP) of 4-Methyl Picolinic acid

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ABSTRACT

The FTIR and FT-Raman spectra of 4-Methyl Picolinic acid (4MPA) was recorded in the range 4000-400 cm-1 and 4000-50 cm-1. A normal coordinate analysis was carried out for all the vibrations of this molecule by solving inverse vibrational problem (IVP) using a 74-parameter modified valence force field employing overlay technique. This reproduced 45 observed frequencies of this molecule with an error of 10.23 cm-1 in the zero-order calculations. PED and eigen vectors calculated in the process were used to make unambiguous vibrational assignments of all the fundamentals.

Keywords : 4MPA, IR, RAMAN, NCA

I.   INTRODUCTION

We have been investigating the molecular structure and vibrational analysis of 4-Methyl Picolinic acid (4MPA) by recording their infrared and Raman spectra; and subjecting them to normal coordinate analysis and solving inverse vibrational problem (IVP).   The vibrational frequencies of this molecule were reported by Varsanyi [1]. In our earlier paper, we reported the results of experimental and theoretical study of 2,3-, 2,4- and 3,4-pyridine-dicarboxylic acids; and evaluated their optimized geometries and valence force field [2]. Picolinic acid, an isomer of nicotinic acid, is one of the most important chelating agents present in the human body. Liver and kidneys biosynthesized picolinic acid during the catabolism of the essential amino acid tryptophan and transported to the pancreas [3]. It is also secreted during digestion in the intestine which is used as a complexing agent in the absorption of essential metals such as chromium, zinc, manganese, copper, iron and molybdenum [4, 5]. Picolinic acid and its isomers played roles as diverse as reaction partners in industrial processes [6] and as building blocks in photovoltaic devices [7].The purpose of this investigation is:

i) To record FTIR and FT-Raman spectra of 4MPA to get complete information on its vibrational frequencies.

ii) To solving inverse vibrational problem using optimized geometry by Wilson's GF-matrix method employing overlay least-squares technique.

iii) To make unambiguous vibrational assignment of all the fundamental vibrations of the molecule using PED and eigen vectors obtained in the results by IVP.

II. Experimental Details

The compound 4-Methyl Picolinic acid (4MPA) was obtained from TCI Chemical Company, Japan and used as such for the spectral measurements. The room temperature FTIR spectra is recorded using Bruker IFS 66V spectrometer employing KBr optics in the spectral range 4000-400 cm^{-1} with a scanning speed of 30 cm^{-1} min^{-1} with spectral width 2.0 cm^{-1}.   The FT-Raman spectra is recorded in the range 4000-50 cm^{-1} using FRA 106 Raman module equipped with Nd:YAG laser source operating at 200 mw power with spectral resolution of 2 cm^{-1}. The wavelength of the exciting radiation used was 1064 nm. The structure and experimental FTIR and FT-Raman spectra are presented in fig. 1and 2.
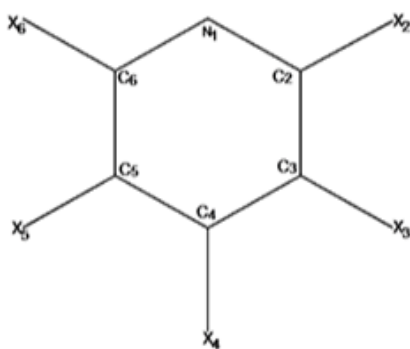
Figure 1. Structure of 4MPA

Where, 4MPA: $X_2 = R_1$ (COOH), $X_3 = X_5 = X_6 = H$, & $X_4 = R_3$ (CH$_3$)
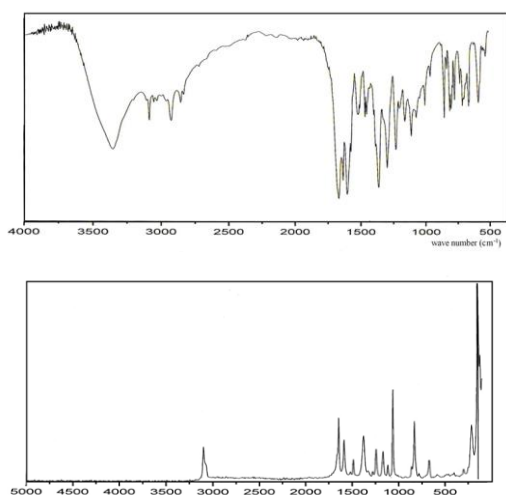
Figure 2. FT-IR &FT- Raman spectrum of 4MPA

III. Vibrational assignments of in-plane vibrations

3.1. C-C and C-N stretching vibrations:

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. In the molecules under investigation, vibrations 8a and 8b are expected around 1600 cm^{-1}. The higher frequency has 51 % of C–C stretching character in the molecule studied here. It is note–worthy that this mode mixes with $\widehat{CCC}$ bending vibration 12 and stretching vibration of 7b in 4MPA. The lower frequency is a C–C stretching mode to the extent of 48%. It mixes with mode 18b and 7b. Thus, the frequency around 1653 cm^{-1} is attributed to mode 8a, whereas, frequency around 1597cm^{-1} is ascribed to mode 8b in 4MPA. Modes 19a and 19b are expected in the spectral range 1400-1500

cm^{-1} in benzene and its derivatives. On the basis of calculations, the absorptions at 1516 cm^{-1} is assigned to mode 19a and around 1522 cm^{-1} is ascribed to mode 19b in 4MPA. Another important feature is that both the modes 19a and 19b mixes with C–H in–plane bending modes in the present molecule. C-C and C-N stretching vibrations of above molecules are good agreements in the literature of P. Koczon and his co-workers [8].

On the basis of the calculations, mode 14, called the Kekule mode has been assigned around 1214 cm^{-1} in 4MPA and exhibit strong mixing with mode 3.

3.2. 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 [9]. The frequencies and mixing of PED with others modes are given in the Table 1.

3.3. C – H Stretching vibrations

A detailed discussion of these modes is not necessary, as they are far removed from other vibrational frequencies and do not mix even among themselves. They are designated as modes 2, 20a and 20b in 4MPA, respectively. In tetrasubstituted benzenes the phase relations are +, + for mode 20a or 7b and +, – for vibration 20b. In trisubstituted benzenes, the phase relations are +, +, + for mode 2; +2, –1, –1 for mode 20a or 7a; and 0, +2, –2 for mode 20b. The C–H stretching vibrations identified in this manner are shown in Table 1.

3.4. C–H Bending vibrations

The C-H in-plane bending vibrations are designated as mode 3, 18a and 18b in 4MPA. In aromatic compounds, they generally appear in the spectral region 1000-1300 cm^{-1}. 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 cm^{-1} [10-13].The highest C–H bending vibration is mode 3. Its assignment is usually difficult, as mode 14 (Varsanyi

in 1,2,3-tri-substituted benzenes (see Ref. [14], pp 298)., in which alternate C–C bonds either increase or decrease, appears in its vicinity. According to the calculations, the bands around 1288 cm^{-1} are due to mode 3 in 4MPA. It is interesting to note that this vibration mixes with the Kekule mode 14 in 4MPA. On the basis of calculations, the absorptions near 1162 and 1141 cm^{-1} are due to modes18a and18b, respectively in present molecule. The mixing of PED with others modes are given in the Table 1.

IV. Substituent Vibrations

The in–plane and out–of–plane vibrations of substituent groups under consideration are discussed in this section for the sake of clarity and convenience.

a. Vibrations of the acid group

There are four in-plane vibrations for acid group in the molecules under study. These are, $\nu(C_\alpha=O)$, $\nu(C_\alpha-O)$, $\delta(OH)$, $\nu(O-H)$, $\delta(C_\alpha=O)$, $\gamma(C_\alpha-O)$.The band near 1791 cm^{-1} is assigned to $C_\alpha=O$ stretching vibration in 4MPA. It has 98% carbonyl stretching character and do not have mixing from any other vibration as is evident from Table 1. The stretching and in-plane bending vibrations, $\nu(C_\alpha-O)$ and $\delta(OH)$, of the acid group generally appear in the range 1200-1450 cm^{-1} depending on whether monomeric, dimeric or other hydrogen bonded species are present. Usually, $\delta(OH)$ appears at higher frequency than that of $\nu(C_\alpha-O)$. 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 calculations, the ir absorptions near 1330 cm^{-1} are found to have 73% PED from $\delta(OH)$ character in present molecule hence, it is attributed to $\delta(OH)$ vibration. The frequency near 1388 cm^{-1} having PED to the extent of 61% are assigned to mode $\nu(C_\alpha-O)$ in these molecules. These vibrations mix with other modes as can be seen from Table 1. All benzoic acids, being hydrogen bonded in the solid state, are characterised by a strong ir absorption in the region 2200-3500 cm^{-1}, attributable to $\nu(O-H)$ 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 3659 cm^{-1} are assigned to mode $\nu(O-H)$ in present molecule. Based on the calculations, as expected, this mode is pure as it has PED to the extent of 99% from $\nu(O-H)$ vibration. Vibrations of the acid groups like $\nu(C_\alpha=O)$, $\nu(C_\alpha-O)$, $\delta(OH)$, $\nu(O-H)$, $\delta(C_\alpha=O)$, $\gamma(C_\alpha-O)$, $\omega(OH)$, and $\omega(C_\alpha=O)$ are good agreements in the assignments of K. McCan, and J. Laane [16].

b. Vibrations of the methyl group

The in–plane vibrations of the methyl moiety are $\upsilon_{as}(CH_3)$, $\upsilon_s(CH_3)$, $\delta_{as}(CH_3)$, $\delta_s(CH_3)$ and $\gamma(CH_3)$, while the out–of–plane vibrations are $\upsilon_{as}(CH_3)$, $\delta_{as}(CH_3)$, $\gamma(CH_3)$ and $\tau(CH_3)$. According to the calculations $\upsilon_{as}(CH_3)$, $\upsilon_s(CH_3)$, $\delta_{as}(CH_3)$, $\delta_s(CH_3)$ and $\gamma(CH_3)$ of the methyl group are assigned to the absorption near 2989, 2850, 1474, 1381 and 893 cm^{-1} in 4MPA. $\upsilon_{as}(CH_3)$ and $\upsilon_s(CH_3)$ are pure in these molecules and has a PED contribution of 100% and 99% respectively. Similarly, $\delta_s(CH_3)$ is almost a pure mode while $\delta_{as}(CH_3)$ mixes with some other modes.

The important results of this discussion of the methyl group are:

i) The frequency of symmetric stretching is less than that of asymmetric stretching frequency. The difference is about 21 to 54 cm^{-1}. Further, they are almost pure.
ii) The frequency of the asymmetric deformation comes in the range 1443–1457 cm^{-1}, whereas that of symmetric deformation falls in the region of 1375– 1383 cm^{-1}. Further, $\delta_{as}(CH_3)$ mixes with mode 19a or 19b in and but $\delta_s(CH_3)$ is almost pure in the present molecule.
iii) The rocking vibration mixes with C–C stretching mode 14 in 4MPA.

c. C–X [X= C$_\alpha$(acid) C'(methyl)] stretching and bending vibrations

The vibrations 13 and7b are designated as CC$_\alpha$ and C-C' stretching vibrations. The vibrations 15 and 9a are designated to designate as CC$_\alpha$ and C-C' bending vibrations.Vibrational assignements of CC$_\alpha$ and C-C' stretching and bending vibrations with PED are shown in the Table 1.

V. Vibrational assignments of out-of-plane vibrations

a. C – H Bending vibrations

In trisubstituted benzene compounds, the modes 5, 11 and 17b are the C–H bending vibrations in 4MPA. The phase relations are +2, −1, −1 for mode 5; +1, +1, +1 for mode 11; 0, +2, −2, for mode 17a or 17b. The bands at 998, 845 and 736 cm^{-1} are assigned to modes 5, 11 and 17b, respectively in present molecule.

b. Ring torsions

The ring torsions are designated with modes 4, 16a and 16b in benzene and its derivatives. According to the results of normal coordinate analysis, mode 4 comes near 600-700 cm^{-1} and it has 68% PED from ring torsion character and mixes with C-H out-of-plane bending vibrations in the molecule investigated here. Mode 16a is ascribed to the band at 422C cm^{-1}, the mode 16b is around 339C cm^{-1} in 4MPA. It should be noted that mode 4 is almost pure in the present molecule. The percentage of PED contributions to these modes and nature of mixing is clear from Table 1.

c. C – X Bending vibrations

The two out-of-plane bending vibrations associated with C-C$_\alpha$ and C-C′ bonds are designated as modes 10a and 10b in 4MPA. The frequencies near 131 and 99 cm^{-1} are assigned to the modes 10a and 10b in present molecule. It is evident from Table.1 that these modes mix with several other vibrations.

d. Vibration of Acid and Methyl Groups

The bands near 210C, 850, 1330, 96 cm^{-1} are assigned to the modes ω(OH), ω(C$_\alpha$=O), δ(OH), and τ(CC$_\alpha$), where as bands near 2961, 1484, 896, and 86 cm^{-1} are assigned to the modes υ_{as}(CH$_3$), δ$_{as}$(CH$_3$), γ(CH$_3$) and τ(CH$_3$) in the present molecule. The PED of above modes are given in the Table 1.

Table 1 : Vibrational assignement of 4MPA

Mode*	Obs.freq IR	Raman	Calc. freq /IVP	Vibrationalassignment/PED
υ(CH)2	-	-	3051	2(98)
υ(CH)20a	-	3111	3104	20a(100)
υ(CH)20b	3091	-	3084	20b(99)
υ(C-C$_\alpha$)13	842	-	832	13(46)+19a(27)+6a(10)
υ(C-C')7b	1242	-	1274	7b(48)+19b(15)+υ(C$_\alpha$-O)'(13)
υ(CN)1	1039	-	1085	1(74)+12(28)
υ(CC)8a	1677	-	1653	8a (51)+12(20)+7b(13)
υ(CN)8b	-	1560	1597	8b(39)+18b(24)+13(13)
υ(CC)14	-	-	1214	14(68)+3(31)
υ(CC)19a	-	-	1516	19a(33)+18b(25)+7b(10)
υ(CC)19b	1522	-	1518	19b(58)+18b(30)
β(CH)3	1300	1289	1288	3(48)+14(28)
β(CH)18a	1168	-	1162	18a(45)+19a(27)
β(CH)18b	1121	1133	1141	18b(51)+13(30)
β(C-C$_\alpha$)15	-		201	15(65)+γ (Cα-O)(33)
β(C-C')9a	-	220	232	9a(74)+γ(C$_\alpha$-O)(12)
β(CCC)6a	-	480	453	6a(41)+γ(C$_\alpha$O)(30)
β(CCC)6b	561	-	569	6b(38)+13(21)
β(CCC)12	-	684	701	12(56)+18a(15)
υ(C$_\alpha$=O)	1761	-	1791	υ(C$_\alpha$=O)(98)
υ(C$_\alpha$-O)	1352	-	1388	υ(C$_\alpha$-O)(61)+18a(13)
υ(OH)	3348	-	3659	υ(O-H)(99)
δ(C$_\alpha$=O)	-	-	771	δ(C$_\alpha$=O)(41)+υ(C$_\alpha$-O)(11)
γ(C$_\alpha$-O)	739	-	363	γ(C$_\alpha$-O)(49)+19a(10)
υ_{as}(CH$_3$)	-	-	2989	υ_{as}(100)
υ_s(CH$_3$)	2955	-	2850	υ_s(99)
δ$_{as}$(CH$_3$)	2851	2859	1474	δ$_{as}$(85)
δ$_s$(CH$_3$)	1462	-	1381	δ$_s$(100)
γ(CH$_3$)	-	-	893	γ(85)+8b(10)
π(CH)5	-	-	998	5(99)
π(CH)11	991	-	845	11(99)
π(CH)17b	-	-	736	17b(81)+4(12)
π(C-C$_\alpha$)10a	-	123	131	10a(45)+ω(C$_\alpha$=O)(20)
π(C-C')10b	-		99	10b(42)+ω(C$_\alpha$=O)(20)
τ(CCCC) 4	610	-	639	4(68)+11(10)
τ(CCCC)16a	-		422	16a(45)+17b(20)+10b(11)
τ(CCCC) 16b	-	-	339	16b(55)+ω(OH)(19)+5(12)
τ(CC$_\alpha$)	-	-	96	τ(CC$_\alpha$)(69)+10b(12)+17b(10)
τ(CC')	-	-	86	τ(CC')(77)+11(20)
ω(OH)	-	-	210	ω(OH)(39)+10b(20)+τ(CC$_\alpha$)(17)
ω(C$_\alpha$=O)	-	-	850	ω(C$_\alpha$=O)(44)+5(20)+4(18)
υ_{as}(CH$_3$)	2961	-	2997	υ_{as}(99)
δ$_{as}$(CH$_3$)	-	-	1484	δ$_{as}$(100)
γ(CH$_3$)	-	-	896	γ(98)
δ(OH)	-	-	1330	δ(OH)(73)+ υ(C$_\alpha$=O)(10)

VI. CONCLUSION

A complete vibrational analysis of 4MPA is performed using the solving IVP using optimized geometries of the molecule. NCA study has given that the calculated frequencies are in good agreement with the corresponding experimental values. A 74-element modified valence force filed is evaluated for these molecules. All the fundamental

frequencies of the molecule are assigned unambiguously based on the PED and eigenvectors obtained from NCA.

VII. REFERENCES

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