

VIBRATIONAL STUDIES AND MOLECULAR POLARIZABILITY OF 2,6-PYRIDINE DI METHANOL

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(Received: May 28, 2006; Accepted: June 21, 2006)

ABSTRACT

Vibrational (Infrared and Laser Raman) spectra and molecular polarizability of 2,6-pyridine di-methanol have been reported. Vibrational assignments have been made on the basis of related molecules and polarizability has been calculated by using Lippincott and Stutman model.

Key words: Infrared and Raman spectra, Molecular polarizability, 2,6-pyridine di methanol.

INTRODUCTION

Vibrational spectra of pyridine and its derivatives have been extensively investigated by earlier workers but so far no work appears to have been carried out on methanol substituted pyridines. In the present paper, Laser Raman and IR spectra of 2,6-pyridine dimethanol have been reported alongwith vibrational assignments. Molecular polarizability has been calculated by using Lippincott and Stutman¹ semi empirical delta function model of chemical binding.

EXPERIMENTAL

98% pure compound was purchased from M/s Sigma Aldrich Chemical Company, U.S.A. and was used as such. The infrared spectrum was recorded on Perkin-Elmer spectrophotometer in the region 400-4000 cm⁻¹. Laser Raman spectrum was recorded on "Spex Rama Lab" spectro photometer using 52 mg argon-krypton laser beam of wavelength 488 nm in the region 30-3500 cm⁻¹.

Theoretical considerations

Molecular polarizability is calculated by

using semi empirical delta function model suggested by Lippincott and Stutman. In this model the coulombic potentials in Schrodinger equation of the molecular system are replaced by the delta function potentials. The molecular wave functions are constructed from the linear combinations of atomic delta function wave functions².

Molecular polarizability is contributed by the parallel and perpendicular components of the constituent bond polarizabilities. Bond parallel component is taken to be sum of bonding electron contribution and the contribution from the valence shell non bonding electrons in each atom of the bond. The bonding electron contribution $\alpha_{//b}$ is calculated by using a linear combination of atomic delta – function wave functions representing the nuclei involved in the bond i.e. the expectation value of the electron position squared ($\bar{X}^2$) along the bond axis is calculated and this in turn is used to obtain the bond parallel component of the polarizability. $\alpha_{//b}$ is given by the equation :

$$\alpha_{//b} = 4nA_{12} [\bar{X}^2]^2 / a_0$$

Where $\bar{X}^2 = R^2/4 + 1/2C_{12}^2$, $A_{12} = (A_1A_2)^{1/2}$

n is the bond order, R is intermolecular distance at the equilibrium position and

$$C_{12} = (n_1 n_2 N_1 N_2)^{1/4} (A_1 A_2)^{1/2}$$

Here n_i and N_i ($i=1,2$) are the principal quantum number and number of electrons making contributions to the binding respectively. In case, the bond is of heteronuclear type, the bond parallel component of the polarizability must be corrected to account for the charge density introduced by the electronegativity difference of the bonding atoms. Here, the charge density in the bond region should be related to the percent covalent character, believed to exist in the form

$$\sigma = \exp [-(\chi_1 - \chi_2)^2/4]$$

where χ_1 and χ_2 are the electro negativities of atom 1 and 2 forming the bond on Pauling scale³. Taking into account the polarity correction, $\alpha_{//b}$ is given by

$$\alpha_{//p} = \sigma \alpha_{//b}$$

Contribution of the non-bonded region electrons, $\alpha_{//n}$, to the parallel component of the polarizability is given as

$$\alpha_{//n} = \sum_j f_j \alpha_j$$

where f_j is the fraction of valence electrons in the j^{th} atom not participating in bonding and α_j is the atomic polarizability of the j^{th} atom.

Following an empirical approach Lippincott and Stutman obtained a general expression for the evaluation of the perpendicular component of the polarizability which is expressed as

$$\sum 2\alpha_{\perp j} = n_{df} \sum_j \chi_j^2 \alpha_j / \chi_j^2$$

where $n_{df} = 3N - 2n_b$, the residual atomic polarizability degrees of freedom. This is obtained by taking into account the symmetry and geometry of the molecule. The average molecular polarizability thus can be expressed as

$$\alpha_M = 1/3[\alpha_{//p} + \sum_j f_j \alpha_j + n_{df} \sum_j \chi_j^2 \alpha_j / \chi_j^2]$$

RESULTS AND DISCUSSION

Molecular structure of 2,6-pyridine dimethanol is shown in figure 1. IR and Laser Raman spectra are shown in figure 2 & 3 respectively. Vibrational assignments for the observed frequencies are listed in table 1. For the atoms involved in the molecule, delta function strengths in atomic units, the atomic polarizability and electronegativities are listed in table 2. The molecular structural data are taken from literature⁴⁻⁷.

$\sum 2\alpha_{\perp j}$ is 172.04, $\alpha_{//n}$ is 10.86 and $\alpha_{//b}$ is 259.24 for the molecule under consideration which gives α_M to be $147.38 \times 10^{-25} \text{ cm}^3$.

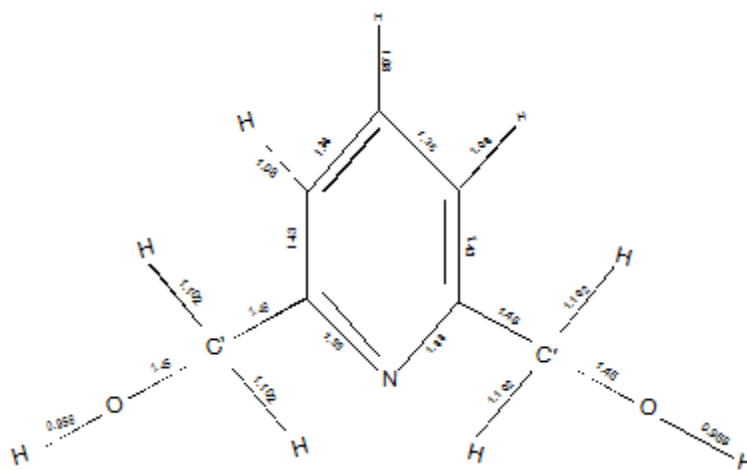


Fig. - 1: Molecular structure and bond lengths of 2,6-pyridine di-methanol

Table - 1: Vibrational assignments of 2,6-pyridine dimethanol

IR Freq (cm ⁻¹)	Raman freq (cm ⁻¹)	Mode assigned
450 (vs)	454 (w)	(C-C) γ
-	467 (s)	(C-C) γ
532 (vs)	534 (w)	(O-H) γ
-	568 (w)	(O-H) γ
617 (vs)	621 (w)	(C-C) β
634 (vvs)	648 (vw)	(C-C) β
658 (vs)	661 (vw)	(C'-OH)def
-	688 (s)	(C-C) γ
771 (vs)	749 (vs)	(C-H) γ
817 (vvs)	836(ms)	(C-H) γ
900 (s)	896 (s)	(C-H) γ
967 (vvs)	976 (ms)	(C-C) ν
1017 (vvs)	1010 (ms)	(C-C) β
-	1032 (vs)	(C'H ₂ -OH) ν
1087 (vvs)	1085 (w)	(C'H ₂ -OH) ν
-	1140 (vvs)	(C-H) β
1168 (vs)	1180 (ms)	(C-H) β
1230 (vs)	1233 (ms)	(C-H) β , (O-H) β
1258 (s)	1260 (s)	(O-H) b
-	1320(w)	(C'-H ₂) wag, (C-C) ν
1347 (s)	1327 (ms)	(C-N) ν
-	1367 (ms)	(C'-H) def
-	1387 (ms)	(C'-H) def
1415 (s)	1394 (w)	(-OH) def
1469 (vs)	1461 (w)	(C-C) ν , (C-N) ν
-	1488 (ms)	(C'-H) def, (C-C) ν
1558 (s)	1555 (ms)	(C-C) ν
-	2841 (ms)	(C'-H) ν
-	2868 (ms)	(C'-H) ν
2900 (s)	2888 (ms)	(C'-H) ν
2941 (s)	2921 (s)	(C'-H) ν
-	3049 (ms)	(C-H) ν
-	3096 (ms)	(C-H) ν
3109 (vw)	3122 (s)	(C-H) ν
3358 (s)	3357 (s)	(O-H) ν
-	3397 (ms)	(O-H) ν

Vs = very strong, ms = medium strong, s = strong, vw = very weak, mw = medium weak, w = weak, def = deformation, wag = wagging, n = stretching, b = in-plane bending, g = out-of-plane bending.

Table - 2: Delta function strengths (in atomic units), atomic polarizabilities (in 10^{-25} cm^3) and electronegativities of atoms constituting the molecule.

Element	Delta function Strength (A)	Atomic Polarizability (α)	Electro-negativities (c)
H	1.000	5.920	2.1
C	0.846	9.780	2.5
N	0.927	7.430	3.0
O	1.000	5.920	3.5

Table - 3: Bond parallel components of Polarizability (in 10^{-25} cm^3) for individual bonds

Bond	Bond Length ($^{\circ}\text{A}$)	$\alpha_{//b}$ (in 10^{-25} cm^3)
C-N	1.33	12.859
C-C	1.43	17.525
C-C	1.36	14.406
C-C	1.46	19.004
C-O	1.45	15.444
O-H	0.956	2.864
C-H	1.102	7.404
C-H	1.080	6.877

Bond and Molecular Polarizability

Bond parallel components of different bonds are listed in table 3. These values find good agreement with literature values⁵.

Vibrational Assignments

Ring vibrations

In benzene the bands between 1400 cm^{-1} and 1650 cm^{-1} are assigned to C-C stretching

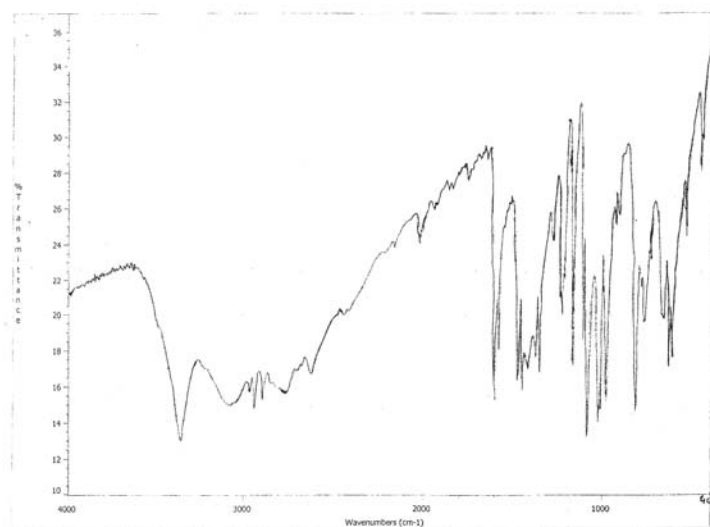


Fig. - 2: IR Spectrum of 2, 6 pyridine di methanol

modes⁸. It contains two doubly degenerate modes e_{2g} (1596 cm^{-1}) and e_{1u} (1485 cm^{-1}) and two non degenerate mode, b_{2u} (1310 cm^{-1}) and a_{1g} (995 cm^{-1}). The molecule under consideration exhibits a single peak at 1558 cm^{-1} (IR) / 1555 cm^{-1} (Raman) corresponding to e_{2g} mode. Corresponding to e_{1u} mode, peaks are obtained at 1469 cm^{-1} (IR) / 1461 cm^{-1} (Raman) and 1488 cm^{-1} (Raman). b_{2u} mode is exhibited only in Raman spectrum at 1320 cm^{-1} while a_{1g} mode appears at 967 cm^{-1} in IR spectrum

and at 976 cm^{-1} in the Raman spectrum. b_{1u} (1010 cm^{-1}) and e_{2g} (606 cm^{-1}) modes appear at 1017 cm^{-1} (IR) / 1010 cm^{-1} (Raman), 617 cm^{-1} (IR) / 621 cm^{-1} (Raman) and 634 cm^{-1} (IR) / 648 cm^{-1} (Raman) and represent in plane carbon bending vibrations. Carbon out-of-plane vibrations are represented by the non-degenerate b_{2g} (703 cm^{-1}) and degenerate e_{2u} (404 cm^{-1}) modes of benzene⁹. The non degenerate mode falls at 688 cm^{-1} in the present case while degenerate mode falls at 450 cm^{-1} in

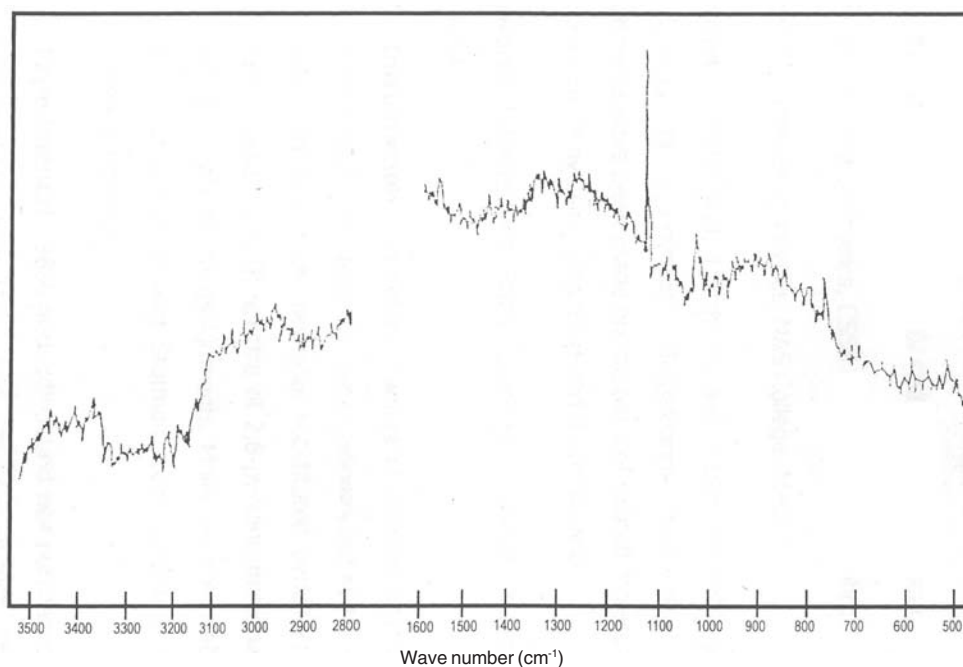


Fig. - 3: Laser Raman Spectrum of 2, 6 pyridine dimethanol

the IR spectrum and at 454 cm^{-1} and 467 cm^{-1} in the Raman spectrum. C-H stretching vibrations appear at 3049 cm^{-1} , 3096 cm^{-1} and 3122 cm^{-1} in the Raman spectrum with only one IR counterpart at 3109 cm^{-1} ¹⁰⁻¹². C-H out-of-plane bending mode has been assigned at 771 cm^{-1} (IR) / 749 cm^{-1} (Raman), 817 cm^{-1} (IR) / 836 cm^{-1} (Raman) and 900 cm^{-1} (IR) / 896 cm^{-1} (Raman) in accordance with Mohan and Ilangovan¹³ who obtained this mode around 790-880 in 2-amino pyrimidine. C-H in-plane bending has been assigned at 1140 cm^{-1} (Raman), 1168 cm^{-1} (IR) / 1180 cm^{-1} (Raman) and 1230 cm^{-1} (IR) / 1233 cm^{-1} (Raman) in analogy to Praveen and Sharma¹⁴ who obtained this mode at 1140 cm^{-1} and 1230 cm^{-1} in 2-hydroxy pyridine and at 1155 cm^{-1} and 1285 cm^{-1} in 2-chloropyridine.

Vibrations of $\text{-C'H}_2\text{OH}$ group

Symmetric stretching vibration of C'H_2 group is a pure mode around 2860 cm^{-1} and appears at 2841 cm^{-1} and 2868 cm^{-1} in the Raman spectra of the present molecule. Asymmetric stretch is obtained at 2900 cm^{-1} (IR) / 2888 cm^{-1} (Raman) and 2941 cm^{-1} (IR) / 2921 cm^{-1} (Raman). C'-H deformation is exhibited by medium strong peaks

at 1367 cm^{-1} , 1387 cm^{-1} and 1488 cm^{-1} in the Raman spectrum. Wagging mode of C'H_2 lies at 1320 cm^{-1} . For primary alcohols $\text{C'H}_2\text{-OH}$ stretching lies in the range $1000\text{-}1075\text{ cm}^{-1}$ ¹⁵. In view of this, bands at 1032 cm^{-1} and 1085 cm^{-1} have been designated as $\text{C'H}_2\text{-OH}$ stretching modes. Corresponding modes in IR spectrum occurs at 1087 cm^{-1} . C'-OH deformation is assigned at 658 cm^{-1} in the IR spectrum and at 661 cm^{-1} in Raman spectrum in accordance with Stuart and Sutherland¹⁶ who points out that out-of-plane C'-OH deformation in bound state absorbs very broadly and diffusely near 650 cm^{-1} . Due to the same, -OH deformation is assigned at 1415 cm^{-1} (IR) / 1394 cm^{-1} (Raman) in methanol. O-H stretching has been assigned at 3358 cm^{-1} (IR) / 3357 cm^{-1} (Raman) and 3397 cm^{-1} (Raman). Krishna Kumar and Xavier¹⁷ obtained O-H out-of-plane bending at 585 cm^{-1} and 528 cm^{-1} in 4,6-di hydroxy 2-mercapto pyrimidine in view of which 532 cm^{-1} (IR) / 534 cm^{-1} (Raman) and 568 cm^{-1} (Raman) are designated as O-H out-of-plane bending made. O-H in plane bending is obtained at 1230 cm^{-1} (IR) / 1233 cm^{-1} (Raman) and at 1258 cm^{-1} (IR) / 1260 cm^{-1} (Raman) in the present case which is supported by Yadavs and Vipin¹⁸.

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