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Vibrational Spectral Characterization of 2-(Methylamino) Pyridine by Hybrid Functional Theory Calculations



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ABSTRACT

In the present work, the vibrational spectral analysis was carried out by FT-IR and FT-Raman spectra in the ranges 4000–400 cm^{-1} and 3500–100 cm^{-1} , respectively for 2-(Methylamino)pyridine (MAP). The molecular structure, fundamental vibrational frequencies and intensity of the vibrational bands were interpreted with the aid of structure optimizations based on Density Functional Theory (DFT) method with 6-31+G (d,p) basis set. The results of the calculations were applied to simulated vibrational spectra of the title compound, which show excellent agreement with observed spectra.

INTRODUCTION

Azo dyes are important class of pyridine derivatives that are extensively employed as color materials and used for their unusual electronic properties as well as their wide color range [1–3]. These dyes exhibit azo-hydrazo tautomerism that has been widely studied using IR and Raman [4], resonance Raman [5] and electron absorption and emission spectroscopies [6]. Pyridines including 2-methylpyridine are most crudely prepared by the reaction of acetylene and hydrogen cyanide. 2-methylpyridine was the first pyridine compound reported to be isolated in pure form. It was isolated from coal tar in 1846 by Anderson [7]. The derivatives of picoline have potent hypolipidemic effects, antineoplastic and anti-inflammatory activities and show good activity against leukemia and human glioma cell growth [8].

Many substituted pyridines are involved in bioactivities with applications in pharmaceutical drugs and agricultural products [6, 9]. Pyridine derivatives and prodrugs for treating neuronal damage caused by stroke to name a few. They also underpin analgesics for acute and chronic pain, treatment for tinnitus, depression and even diabetic neuropathy. The Picoline derivatives prepared from aminopyridine derivatives have been shown to have cholesterol lowering properties, anticancer and anti-inflammatory agents.

Aminopyridines are widely used in pharmacological and medical applications [10]. Some of them show anesthetic properties and have been used as drugs for certain brain diseases [10, 11]. 2-Aminopyridine tagged oligosaccharides have been widely used for sensitive qualitative and quantitative analysis by high performance liquid chromatography with fluorescence detection [10], in preparation of cytidine analogs [12] and it is also immensely used as a reagent in analytical chemistry the ring nitrogen of most pyridines undergoes reactions such as protonation, alkylation and acylation. The harmonic frequencies of pyridine derivatives were calculated by several authors [13, 14].

The FT-IR and FT-Raman spectra of 2-methylpyridine-1-oxide have been recorded. These spectra have been interpreted employing the Scaled Quantum Mechanical Force Field (SQMFF) methodology, by directly transferring the scale factors obtained for pyridine [5]. To the best of our knowledge, neither quantum chemical calculation nor the vibrational spectra of MAP have been reported. Therefore, in the present study, FT-IR and FT-Raman spectral investigation of MAP have been recorded and verified by DFT carried out by B3LYP/6-31+G(d,p) basis set.

EXPERIMENTAL DETAILS

The sample of the present compound 2-(Methylamino)pyridine (MAP) was purchased from Sigma-Aldrich Chemical Company with a stated purity of 98% and it was used as such without further purification. The sample was prepared using a KBr pellet technique because of solid state. The FT-IR spectrum of the sample was recorded in the region 4000–400 cm^{-1} on a Perkin Elmer FT-IR BX spectrometer calibrated using polystyrene bands. The FT-Raman spectrum of the sample was recorded using 1064 nm line of Nd: YAG laser as excitation operating at 200 mW power with wavelength in the region 3500–100 cm^{-1} on BRUKER IFS-66V model interferometer equipped with an FRA-106 FT-Raman accessory. The reported frequencies were accurate, $\pm 1 \text{ cm}^{-1}$ for FT-IR and FT-Raman.

COMPUTATIONAL DETAILS

The entire calculations were performed at DFT level using Gaussian 09W [15] program package, invoking gradient geometry optimization [16]. We have utilized the gradient corrected density functional theory [17] with the three parameter hybrid functional (B3) [18] for the exchange part and the Lee-Yang-Parr (LYP) correlation function [19], accepted as a cost effective approach for the computation of molecular structure and vibrational frequencies of optimized structures. By combining the results of the Gauss view program [15] with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy. We have scaled the numbers with standard scaling factor 0.963.

The Raman activities (S_i) calculated by the Gaussian 09W program was converted to relative Raman intensities (I_i) using the following relationship derived from the intensity theory of Raman scattering [20, 21].

$$I_i = \frac{f(\nu_0 - \nu_i)^4 S_i}{\nu_i [1 - \exp(-hc\nu_i / KT)]} \quad (1)$$

where ν_0 is the laser exciting wavenumber in cm^{-1} (in this work, we have used the excitation wavenumber $\nu_0 = 9398.5 \text{ cm}^{-1}$, which corresponds to the wavelength of 1064 nm of a Nd: YAG laser), ν_i is the vibrational wavenumber of the i^{th} normal mode (cm^{-1}), while S_i is the Raman scattering activity of the normal mode ν_i , f (is a constant equal to 10^{-12}) is a suitably chosen common normalization factor for all peak intensities h , k , c and T are Planck and Boltzmann constants, speed of light and temperature in Kelvin, respectively.

RESULT AND DISCUSSION

VIBRATIONAL ASSIGNMENT

The optimized structure is shown in Figure 1. Transformation of force field, the subsequent normal coordinate analysis including the least square refinement of the scale factors and calculation of the Potential Energy Distribution (PED) were done on a PC with the MOLVIB program (version V7.0-G77) written by Sundius [22, 23]. For the graphs of simulated FT-IR and FT-Raman spectra, pure Lorentzian band shapes were used with a bandwidth of 10 cm^{-1} .

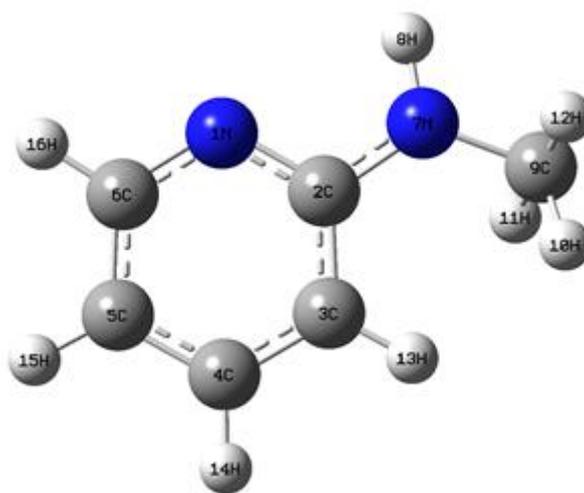


Figure 1. Molecular structure of MAP with numbering scheme.

The MAP consists of 16 atoms and belongs to $C1$ point group symmetry hence the number of normal modes of vibrations for this molecule has 42 normal modes of vibrations are active both in Raman scattering and in IR absorption. 29 Modes of vibrations are in-plane and remaining 13 is out-of-plane bending vibrations. The bands that belong to the in-plane modes are represented as A' while the out-of-plane modes A'' . The harmonic vibrational frequencies calculated for MAP at B3LYP levels using the triple split valence basis set along with the diffuse and polarization functions, 6-31+G(d,p) basis set. FT-IR and FT-Raman frequencies for various modes of vibrations are presented in Table 1. The experimental FT-IR and FT-Raman spectra in solid phase were shown in Figure 2 and Figure 3 along with calculated FT-IR and FT-Raman spectra by B3LYP/6-31+G(d,p) level.

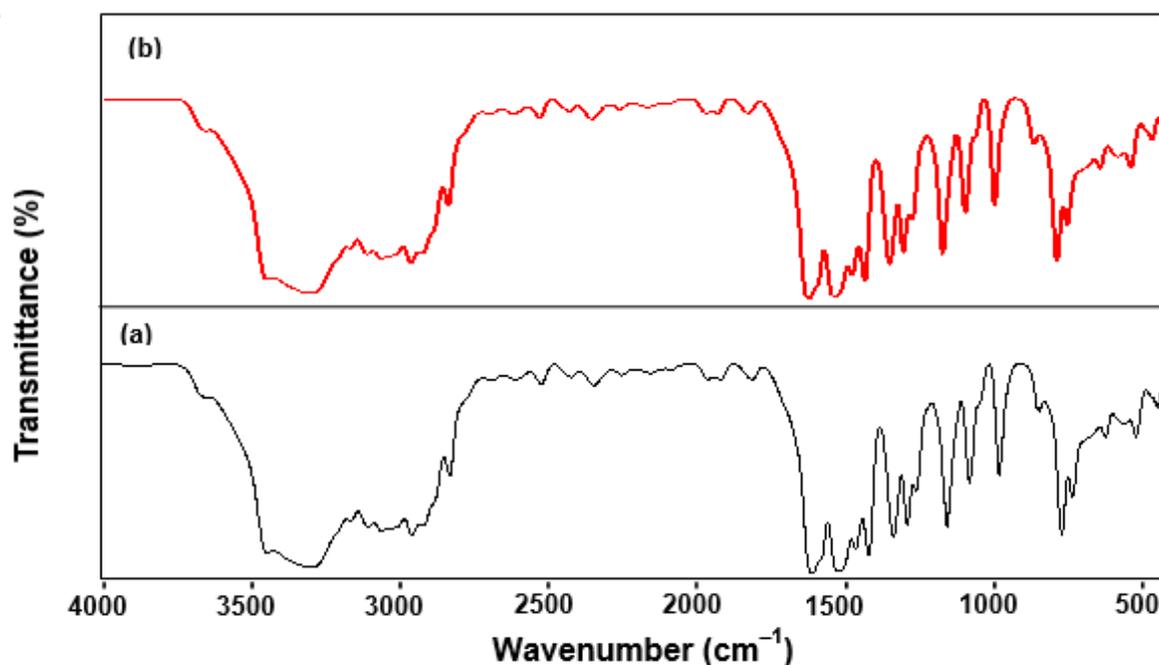


Figure. 2. Comparison of observed and calculated FT-IR spectra of MAP: (a) observed and (b) calculated with B3LYP/6-31+G(d,p).

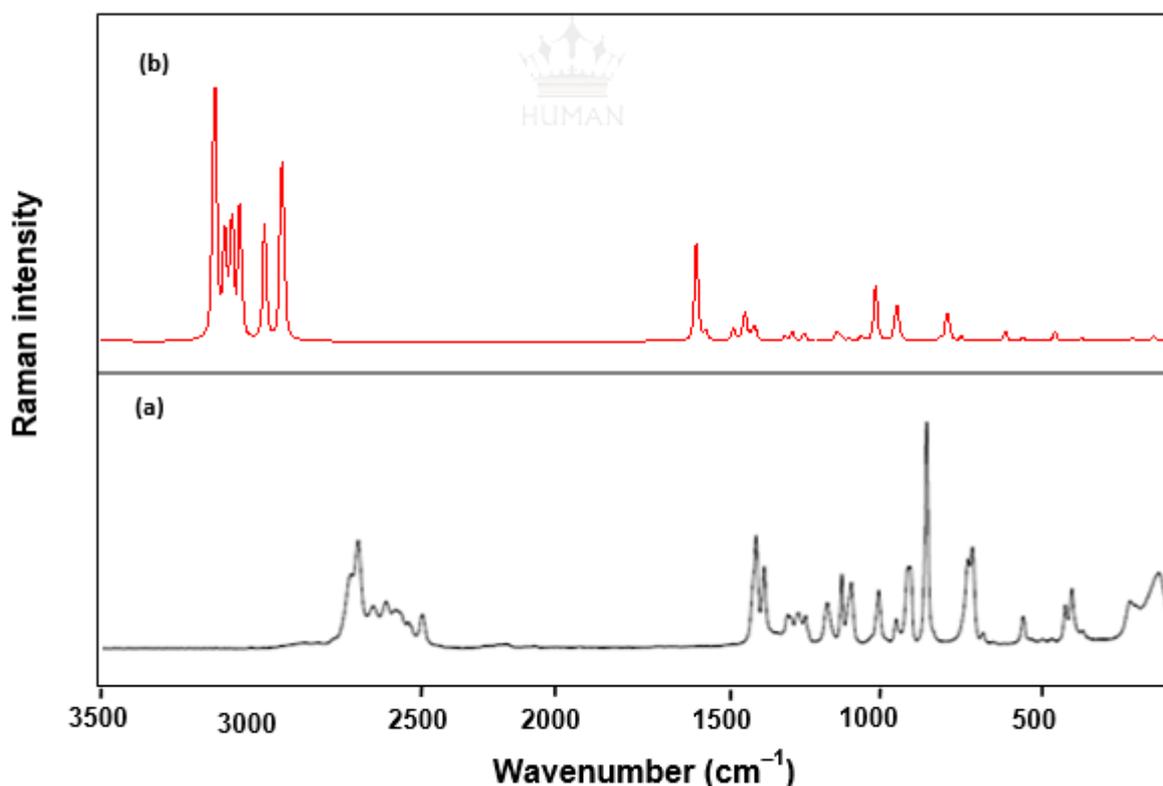


Figure. 3. Comparison of observed and calculated FT-Raman spectra of MAP: (a) observed and (b) calculated with B3LYP/6-31+G(d,p).

Table 1. Vibrational assignments of FT-IR and FT-Raman frequencies along with the theoretically computed (B3LYP/6-31+G(d,p)) wavenumbers and the percentage of potential energy distribution, IR intensities (Km mol^{-1}) and Raman intensities ($\text{\AA}^4 \text{amu}^{-1}$) are obtained for MAP.

| Sr. No. | Observed wavenumbers (cm^{-1}) | | Calculated wavenumbers (cm^{-1}) | | IR intensities | ^a Raman intensities | Assignments with % of PED ^b |
|---------|---|----------|---|--------|----------------|--------------------------------|--|
| | FT-IR | FT-Raman | Unscaled | Scaled | | | |
| 1 | 3460(vw) | | 3446 | 3343 | 48.087 | 100.584 | vCH(99) |
| 2 | 3200(vw) | | 3218 | 3197 | 5.299 | 98.832 | vCH(99) |
| 3 | | | 3203 | 3175 | 21.538 | 71.568 | vCH(98) |
| 4 | | | 3185 | 3125 | 10.822 | 89.907 | vCH(97) |
| 5 | | | 3162 | 3102 | 25.938 | 84.467 | CH ₃ asym(98) |
| 6 | 3100(vw) | | 3135 | 3082 | 19.349 | 75.266 | CH ₃ asym(95) |
| 7 | | | 3054 | 3011 | 41.182 | 97.561 | CH ₃ sym(91) |
| 8 | 2900(vw) | | 2997 | 2953 | 82.975 | 86.601 | vCC(72), vCH(63) |
| 9 | 1620(s) | | 1648 | 1613 | 303.347 | 57.335 | vCC(78), vNH(48), vCN(18) |
| 10 | | | 1617 | 1592 | 44.552 | 6.476 | vCN(67), βCC(45), vCH(28) |
| 11 | 1550(s) | | 1558 | 1527 | 226.467 | 0.255 | vCN(69), βCH(37), vCC(17) |
| 12 | | | 1526 | 1509 | 6.952 | 7.654 | vNH(63), CH ₃ sym(43), βNH(19) |
| 13 | 1490(vw) | | 1494 | 1463 | 33.986 | 3.632 | vCC(62), βCH(31), vCN(29) |
| 14 | | | 1489 | 1456 | 11.215 | 15.167 | vCN(59), CH ₃ asym(35) |
| 15 | | | 1466 | 1438 | 25.772 | 5.424 | vNC(82), vCH(33), vCC(15) |
| 16 | 1450(m) | 1450(s) | 1456 | 1426 | 56.102 | 6.044 | vCC(65), βCN(47), βCH(25) |
| 17 | 1350(s) | | 1358 | 1332 | 53.650 | 3.052 | βCH(66), vCC(24), βNC(21) |
| 18 | | | 1336 | 1318 | 33.457 | 4.763 | βCH(63), vCC(22), vNH(19) |
| 19 | | 1270(vw) | 1296 | 1276 | 2.411 | 4.097 | CH ₃ ipb(71), βCN(26), βCH(16) |
| 20 | | 1190(m) | 1193 | 1183 | 12.776 | 4.337 | CH ₃ opb(75), CH ₃ sym(22) |
| 21 | 1160(vs) | 1170(m) | 1179 | 1136 | 12.104 | 3.924 | βCH(59), vCC(22), vCN(16) |
| 22 | | | 1153 | 1121 | 4.106 | 1.176 | CH ₃ sb(58), βCH(31), CH ₃ ipb(26) |
| 23 | 1100(vs) | | 1111 | 1093 | 3.448 | 2.314 | βCH(43), vCC(22), βCN(16) |
| 24 | | | 1099 | 1083 | 5.560 | 0.932 | CH ₃ ipr(68), βNC(21) |
| 25 | | 1020(m) | 1064 | 1045 | 7.099 | 27.564 | γCH(57), tRsymd(42), vCC(22) |
| 26 | 1000(vs) | 990(vw) | 995 | 972 | 8.474 | 25.288 | CH ₃ opr(58), vCN(32), βCH(17) |
| 27 | | | 983 | 965 | 0.012 | 0.567 | γCH(56), Rtrigd(45), βNH(11) |
| 28 | | 970(s) | 975 | 952 | 0.428 | 0.299 | γCH(51), tRtrigd(34), Rsymd(19) |
| 29 | | 840(vs) | 853 | 841 | 1.502 | 1.842 | γCH(47), CH ₃ ipr(22), γCN(13) |
| 30 | | | 828 | 912 | 3.050 | 18.193 | βNH(51), γCN(23), |

| | | | | | | | |
|----|---------|---------|-----|-----|--------|-------|--|
| 31 | | | 783 | 771 | 52.895 | 2.212 | CH ₃ opr(18) Rtrigd(43), vCC(39), vNH(17) |
| 32 | 750(s) | 750(s) | 746 | 732 | 18.018 | 0.145 | Rasymd(49), γ NC(38), CH ₃ ipb(11) |
| 33 | 700(vw) | | 641 | 627 | 0.978 | 4.451 | β NC(32), γ CN(23), CH ₃ asym(17) |
| 34 | | 550(w) | 584 | 573 | 8.322 | 1.629 | Rsymd(49), β CN(23), γ CH (18) |
| 35 | 540(vw) | 500(vw) | 531 | 518 | 0.311 | 0.171 | γ CN(35), Rsymd(29), Rasymd(19) |
| 36 | 490(vw) | 490(vw) | 499 | 476 | 12.134 | 4.038 | tRtrigd(31), γ CN(26), γ CH(18) |
| 37 | | 430(m) | 428 | 409 | 26.768 | 0.519 | β CN(37), β NC(26), β NH(12) |
| 38 | | 350(vw) | 391 | 385 | 72.271 | 1.160 | tRsymd(30), β CH(24), Rsymd(17) |
| 39 | | | 233 | 221 | 1.208 | 0.291 | tRasymd(25), tCH ₃ (13), γ NC(11) |
| 40 | | | 225 | 207 | 2.607 | 1.447 | γ NC(30), Rsymd(17), γ NH(13) |
| 41 | | | 158 | 142 | 0.839 | 2.144 | γ NH(36), tRasymd(18), γ CH(11) |
| 42 | | | 72 | 65 | 12.397 | 0.793 | tCH ₃ (44) |

Experimental relative intensities are abbreviated as follows: vs-very strong, s-strong, m-medium, w-weak, vw-very weak. Abbreviations; v-stretching, R-ring, sym-symmetric stretching, asym-antisymmetric stretching, b-bending, ipb-in-plane bending, opb-out-of-plane bending, sb-symmetric bending, ipr-in-plan rocking, opr-out-of-plane rocking, d-deformation, t-torsion, trig-trigonal. ^aRaman intensities normalized to 100. ^bOnly contributions larger than 10% are given.

C–H vibrations

For all the aromatic compounds the C–H stretching vibrations are observed in the region 3100–3000 cm⁻¹ [24]. In the present study four adjacent hydrogen atom left around the ring and give rise to four C–H stretching modes, four in-plane bending and four out-of-plane bending vibrations which correspond to modes C–H for the title molecule stretching vibrational bands are observed at 3460 and 3200 cm⁻¹ in FT-IR spectrum. The C–H in-plane bending and C–H out-of-plane bending vibrations are normally found in the range 1000–1300 cm⁻¹ and 750–100 cm⁻¹, respectively in aromatic compounds [25, 26]. The vibrational frequencies are assigned at 1350, 1160, 1170 and 1100 cm⁻¹ for in-plane bending in FT-IR and FT-Raman spectra as very strong and strong intensities. The C–H out-of-plane bending

vibrations are observed as medium, strong and very strong bands at 1020, 970 and 840 cm^{-1} in FT-Raman spectrum. The calculated wavenumbers supported the assignments at 1045, 965, 952 and 841 cm^{-1} .

CH₃ group vibrations

The title molecules MAP possess a CH₃ group in 2-positions, for the assignments of CH₃ group frequencies, nine fundamentals can be associated to each CH₃ group namely the symmetric stretching, asymmetric stretching (in-plane and out-of plane hydrogen stretching modes), in-plane bending, out-of-plane bending, symmetric deformation, in-plane rocking, out-of-plane rocking and twisting modes. The C–H stretching in CH₃ occurs at lower frequencies than those of aromatic ring (3100–3000 cm^{-1}). The asymmetric C–H stretching mode of CH₃ group is expected around 2980 cm^{-1} and the symmetric one is expected in the region 2870 cm^{-1} [27, 28]. The asymmetric deformation of CH₃ group is usually observed at around 1450 cm^{-1} for methyl substituted aromatic rings [29]. This is true for the title compound. CH₃ asymmetric vibration contributes to the bands observed at 3100 cm^{-1} in FT-IR spectrum as very weak band. The CH₃ symmetric vibration is also calculated at 3011 cm^{-1} . As predicted in the literature [30], very weak band at 1270 cm^{-1} is assigned to CH₃ in-plane bending vibration while the medium band at 1190 cm^{-1} is assigned to CH₃ out-of-plane bending vibration in FT-Raman spectrum. The out-of-plane rocking vibration appears at 1000 cm^{-1} and 990 cm^{-1} in FT-IR and FT-Raman spectra with very strong and very weak intensities.

C–C vibrations

The bands between 1650 and 1480 cm^{-1} are within the C–C stretching modes [31]. In the present study, the C–C stretching vibrations of the title compound was observed at 2900, 1620, 1490 and 1450 cm^{-1} in the FT-IR spectrum and 1450 cm^{-1} in FT-Raman spectrum. The in-plane and out-of-plane bending vibrations of C–C group are presented in Table 4. These assignments are in good agreement with literature [32].

CONCLUSION

MAP has been characterized by FT-IR, FT-Raman spectra using B3LYP method 6-31+G(d,p) basis set. The assignments of the fundamental frequencies are confirmed by the qualitative agreement between the calculated and observed frequencies.

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