CHAPTER 5
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VIBRATIONAL SPECTRA AND NORMAL COORDINATE
ANALYSIS OF PICOLINES

INTRODUCTION

Molecular vibrational analysis of structurally related organic compounds have been reported from time to time by several workers. The picoline or methyl substituted pyridine is theoretically interesting because of their similarity to the methyl benzenes. Picolines are also important commercial chemicals; the α- form (boiling at 129°C) is used as solvent and chemical intermediate and is used to make 2-vinyl- pyridine, a component of nylon tyres (1)., β- picoline (boiling at 143.5°C) is oxidized to nicotinic acid, the antipellagra and blacktongue vitamin (1,2) and γ- picoline (boiling at 143.1°C) yields isonicotinic acid hydrazide, a drug used in the treatment of tuberculosis (2,3).

Works on methyl derivatives of pyridine and structurally similar molecules provided a good starting point for the vibrational analysis of Picolines. Yadav et al(4,5) reported the Raman and IR spectra of 3-fluoro-trifluoro methyl benzene and 1,3- bis (trifluoro methyl) benzene. The observed frequencies were assigned to the various modes of vibration in terms of the fundamentals.
overtones and combinations. An attempt was made by them to remove the ambiguity in the assignment of CF$_3$ symmetric deformation mode.

Kydd et al (6) reported the vapour phase infrared spectrum of N-methyl aniline. The absorption associated with the three large amplitude vibrations of this molecule were identified and the potential energy barriers were calculated. The results were found consistent with earlier microwave study and the error limits were improved. They also confirmed that N-methyl aniline is more planar than aniline itself. The barriers to torsion around the N-C (ring) bond were compared to those in similar molecules.

Goel et al (7) studied the near ultraviolet absorption spectra of di-substituted pyridines in vapour phase. The UV spectra of 2-amino-3-methyl, 2-amino-4-methyl and 3-amino-2-chloro-pyridines were recorded and used for the analysis of the bands. The bands observed at 34590, 33574 and 33634 cm$^{-1}$ in the three molecules respectively were attributed to 0,0 bands. Fundamentals determined in the ultraviolet study were correlated with those observed in infrared and Raman spectra. The red shift of 0,0 bands was also discussed. In case of 6-amino-2-methyl pyridine (8) Goel et al assigned 0,0 band at 34133cm$^{-1}$. They have also analysed the spectra in terms of
combinations and overtones of ground and excited state
fundamentals. The fundamentals were used to calculate
thermodynamical properties assuming hindered internal
rotation of NH$_2$ group about Z-axis.

Balfour et al (9) studied the Infrared and Raman
spectra of C$_6$H$_5$OCD$_3$, C$_6$D$_5$OCH$_3$ and C$_6$D$_5$OCD$_3$, in liquid
phase. The fundamentals were compared with that of C$_6$H$_5$OCH$_3$. They have also studied the near-ultraviolet vapour phase
absorption spectrum of anisole (methoxy benzene). The π*-π
electronic transition and its deuterated isotopes of the
compound were also studied. Based on this study, Progressions in a number of in-plane vibrations were
discussed.

Sharma (10) reported the Infrared and Laser Raman
spectra of m- and p- methyl anisole. The fundamentals of the
observed bands were assigned on the basis of C$_S$ point group
symmetry. Various modes of vibrations were discussed. The
ideal gas state thermodynamical functions were calculated
for these molecules in the range 100-2000 K.

Singh et al (11) recorded the infrared and Laser
Raman spectra of 2,5 and 2,6- dimethyl anilines . The
spectra were analysed assuming C$_S$ and C$_{2V}$ point groups
respectively for these two compounds. The assignments for
the fundamental vibrations, combinations, overtones, the internal modes of vibrations of methyl groups and amino groups were proposed.

Lamba et al(12) reported the liquid and vapour phase Infrared and Raman spectra of α-, β- and γ-picolines. The vapour phase infrared band (A-, B- and C- type) contours and depolarization ratios were measured for the observed bands and were used to revise some of the earlier assignments.

Sanyal et al(13) studied the electronic and infrared absorption spectra of 3-amino-2-chloro pyridine. Electronic bands were analysed in terms of two ground state (386 and 562 cm\(^{-1}\)) and seven excited state (240, 345, 525, 576, 822, 864 and 1187 cm\(^{-1}\)) with 0,0 band at 3052.4 A\(^{-1}\). The vibrational spectra of the compound were analysed in terms of fundamentals, combinations and overtones. Assignments of the fundamentals in each spectrum were also proposed.

The Infrared and Raman spectra of 2,4,6- trimethyl aniline (mesidine) and 2,4,6- trimethyl phenol (mesitol) were recorded in solutions and also as solids by Faniran et al(14). The barrier to internal rotation of the NH\(_2\) group about C-N bond in mesidine and the OH group about the C-O bond in mesitol were found to be 18.6 and 15.6 kJ mol\(^{-1}\).
respectively. By comparison with unsubstituted aniline and phenol, they found that these values suggest an increase in double bond character of the C-N and C-D bonds, which mostly arises from an inductive interaction of the methyl groups with the aromatic ring. Further they have also assigned the frequencies to various normal modes.

The vibrational analysis of Pyridine-2-thione and Pyrimidine-2-thione were carried out by Sathyanarayana et al(15) for all the fundamentals employing the Uray-Bradley potential function supplemented with valence force function for the out-of-plane vibrations. The spectra of N-deutrated molecules were also utilized. The results of the vibrational analysis were discussed in relation to the assignments in structurally related molecules to note the consistency in assignments.

The vibrational frequencies of 2,4 and 2,5-dimethyl benzaldehyde was reported by Venkoji et al(16) from the study of IR and Raman spectra of these molecules recorded in liquid phase. The probable assignment for all the frequencies were presented in terms of fundamentals, overtones and combinations.

Yadav et al(17) reported the vibrational spectra and Normal coordinate analysis for o-, m- and p-
trifluoromethyl benzaldehydes. The polarised Raman and Infrared spectra of the three isomeric trifluoromethyl benzaldehydes were recorded in the region 50-4000 cm$^{-1}$ respectively. To check the vibrational assignments, Normal coordinate was performed for each molecule using general valence force field. It was found that the CF$_3$CHO group modes are strongly coupled with the ring modes and it was discussed in detail in their work. It was also confirmed that the force constants are transferable from one molecule to another to a good extent. In the same manner, they also studied (18) the vibrational spectra of p-trifluoromethyl aniline and performed Normal coordinate analysis.

Karthha (19) studied the vibrational spectra of 2,6-dichloro, 2,6-dimethyl and 2-methyl pyrazines. The IR and Raman spectra of the compound were recorded. Assignments of all fundamental modes were made with the help of vapour phase IR band contours and Raman depolarisation ratio measurements. Substantiation of the assignments was obtained from Normal coordinate analysis. The various modes of substituted pyrazines were correlated and the effect of substituents were discussed.

The IR and Raman spectra of 4,6- dichloro-2-methyl mercapto pyrimidine, with the assignment of fundamentals, overtones and combinations were reported by Gupta et al (20). The frequencies were discussed assuming $C_{2v}$ point group
symmetry for this molecule. Arenas et al (21) reported the vibrational spectra of 3-methyl pyridazine. On the basis of the experimental data a general assignment was proposed by him, which was consistent with $C_3$ symmetry. The molecular structure as well as the potential energy barrier for the internal rotation of the methyl group and the theoretical spectrum for that rotation was computed in the MINDO/3 approximation level.

Amatatsu et al (22) studied the gas phase Infrared spectrum of N-Chloromethylenimine, produced by the pyrolysis of N-chloroazetidine. The C=N double bond stretching band was observed to be weak whereas the N-Cl stretching was the strongest among all the observed absorption bands. Further they evaluated force constants by initio MO method, and the relative intensities of the bands of the in-plane modes were qualitatively reproduced.

In the present work, a complete vibrational analysis is carried out for all the three picolines using the observed spectra. The liquid phase Fourier Transform Infra-red and Laser Raman Spectra of picolines are recorded. The observed frequencies are assigned to different modes of vibrations. The potential energy associated with each vibrational type is reported. Some of the earlier vibrational assignments are modified in the present work.
EXPERIMENTAL

The pure picolines were obtained from Ms. British Drug House and used as such. The FTIR spectra of $\alpha$-, $\beta$- and $\gamma$- picolines in liquid phase were recorded on Nicolet 20 DxB spectrometer in the region 400-4000 cm$^{-1}$ at CLRI, Madras. The Laser Raman spectra of picolines were also recorded in the region 4000-100 cm$^{-1}$ on a Dilor Z24 Raman spectrometer equipped with a spectra physics Model 165 argon-ion laser source operating on 488nm line with 200 mw power. The spectra were recorded with scanning speed of 30 cm$^{-1}$ min$^{-1}$ with a spectral width 2.0 cm$^{-1}$. The frequencies for all sharp bands were accurate to $\pm$2cm$^{-1}$. The observed FTIR and laser Raman spectra of picoline are shown in Figs 1 to 6.

NORMAL COORDINATE ANALYSIS

The structure of $\alpha$, $\beta$ and $\gamma$ picolines are shown in figures 7 to 9 along with the structural parameters employed in the present work. It is assumed that two of the hydrogens of methyl group lie out of the plane of the molecular symmetry, one below and the other above the plane. The pyridine geometry was determined by Bak et al (23) and was assumed to remain unaffected by methyl substitution.

The $\alpha$ and $\beta$ picoline, belonging to Cs symmetry, posses 36 fundamental vibrations which are active in both IR
FIG-1 FTIR SPECTRUM OF \( \alpha \)-PICOLINE
FIG. 2. FTIR SPECTRUM OF β-PICOLINE
FIG-3. FTIR SPECTRUM OF γ-PICOLINE
FIG. 5. LASER RAMAN SPECTRUM OF β-PICOLINE
FIG. 6. LASER RAMAN SPECTRUM OF Y-PICOLINE
FIG. 7. STRUCTURE OF \textit{\textalpha{-picoline}}
FIG. 8. STRUCTURE OF β-PICOLINE
FIG. 9. STRUCTURE OF R-PICOLINE
and Raman. Of these, 24 are in-plane vibrations and 12 are out of plane vibrations. The observed frequencies, the assignments for the observed bands and PEDs are presented in Table 1 and 2. The \( y \) picoline belongs to \( C_{2v} \) symmetry which leads to four types of vibrations distributed as

\[
\Gamma_{\text{vib}} = 12 A_1 + 4 A_2 + 8 B_1 + 12 B_2
\]

Out of these 36 vibrations, there are 32 vibrations that are active in both Raman and IR. The vibrations belonging to symmetry species \( A_2 \) are only Raman active. The method of Wilson (24) was used to perform a normal coordinate calculations of picolines with the aid of Mink's computer program (25) after a suitable modification. The SGVFF has been shown to be very effective in the normal coordinate analysis (26) and also, the valence force constants can be transferred between the related molecules which is found to be very useful in the normal Coordinate analysis of polyatomic molecules. Hence in the present work SGVFF has been employed to express the potential energy. The force constants used in the case of pyridine (27) were transferred and slight alterations were made in few constants to obtain a close fit between the observed and calculated frequencies of picolines. This set of force constants is subsequently refined by damped least square technique, keeping few interaction constants fixed throughout the refinement process. The initial and final set of force constants are presented in Table-1. The observed frequencies of \( x, \beta \) and
γ- picolines and the probable assignment for the observed bands are present in the Table 2-4 along with the potential energy distribution.

RESULT AND DISCUSSION

Issac et al (27) studied several mono substituted solid as liquid phase spectra of pyridines. According to him, pyridines substituted in two or three positions are usually identified by their strong bands in 600-400 cm$^{-1}$. His conclusions were taken as a guide to assign the spectra of α-, β- and γ picolines.

Ring Breathing Mode

The Raman spectra of normal pyridine and substituted pyridine give a strongest band for ring breathing vibration. As the band at 995 cm$^{-1}$ is stronger in γ picoline, it is assigned to the ring breathing vibration. This observation agrees well with Long et al (29). Green (30) proposed 1025 and 994 cm$^{-1}$ as ring breathing modes for α and β picolines respectively. But the present work suggest the bands at 1047 and 1040 cm$^{-1}$ belong to ring breathing mode of α- and β picolines

β CH Modes

The four CH in-plane bending modes of picoline are usually observed in 1000 to 1300 cm$^{-1}$ range. Accordingly
CH in-plane bending modes are assigned in \( \alpha \), \( \beta \) and \( \gamma \) picolines as 1095, 1145, 1242 and 1291 \( \text{cm}^{-1} \), 1101, 1123, 1188 and 1297 \( \text{cm}^{-1} \) and 1110, 1160, 1208 and 1286 \( \text{cm}^{-1} \) respectively.

\( \gamma \text{CC-CN Modes} \)

Long et al (28) assigned 1378 cm\(^{-1}\) band for \( \delta \text{HCH} \) mode of CH\(_3\) group for \( \gamma \) picoline. The relative Raman intensity of this band does not suggest that the mode is totally symmetric. From the potential energy distribution, the band at 1381 cm\(^{-1}\) is assigned to \( \gamma \text{CC-CN} \) mode rather than \( \delta \text{HCH} \) mode.

\( \gamma \text{CH Mode} \)

It is expected that the picoline ring should give four CH stretching modes. Among these four modes, the mode in which all hydrogen atom move in phase is expected to appear weakly in IR and strong in Raman spectra. This is true for \( \gamma \) picoline as it gives one strongest Raman band, while the corresponding band is not at all present in IR spectra, eventhough it is active. The spectra recorded in the present work is used to identify all the four bands produced due to the four CH stretching modes and the corresponding frequencies are given in Table III.

Green et al (30) have assigned a single frequency for the two of the \( \gamma \) picoline four modes. Long et al (28) assignment considerably vary with Green et al (30) values.
From the selection rules and potential energy distributions, the band at 781, 873 and 980 cm\(^{-1}\) are assigned to \(\gamma\)-picoline. Based on these assignments, we propose the bands at 751, 787, 919 and 992 cm\(^{-1}\) and 751, 768, 882 and 977 cm\(^{-1}\) to \(\gamma CH\) modes of \(\beta\)- and \(\alpha\) picolines.

CH\(_3\) Group Vibrations

From the established facts, it is easy to assign the CH\(_3\) group vibrations particularly \(\delta CH_3\), \(\delta CH\), \(\gamma CH\) and \(\gamma CH\) from the characteristics frequencies. They are listed as methyl group modes for \(\alpha\)-, \(\beta\)- and \(\gamma\) picolines in Table I, II and III respectively.

To check whether chosen set of assignments contributes maximum to the potential energy associated with normal coordinate of the molecules, the potential energy distribution (PED) has been calculated using the relation:

\[
PED = \frac{F_{ii} L_{ik}^2}{\lambda_k}
\]

Where \(F_{ii}\) are the force constants refined by the damped least square technique. The highest PED contribution corresponding to each of the observed frequencies are alone listed in the present work. The close assignment between the observed and calculated frequencies confirms the validity of the present assignment.
CONCLUSION

A complete vibrational assignment is proposed for $\alpha$-, $\beta$- and $\gamma$- picolines in the present work on the basis of normal coordinate calculations using IR and Raman spectra.