# FT-Raman, FTIR Spectra and Normal Co-Ordinate Analysis of Isoquinoline

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## Abstract

The Fourier Transform Raman and Fourier Transform- Infrared spectra of Isoquinoline have been recorded. The observed frequencies were assigned to various modes of vibrations on the basis of normal co-ordinate analysis assuming Cs point group symmetry. The potential energy distribution associated with normal modes is also reported here. The assignment of fundamental vibrations agrees well with the calculated frequencies.

**Keywords:** Fourier Transform Raman, Fourier Transform − Infrared spectra, Isoquinoline, Normal co-ordinate analysis.

## Introduction

Isoquinoline is made up of two aromatic rings. One a benzene and the other a pyridine, like naphthalene both quinoline and isoquinoline undergo aromatic substitution at an ∝-position in all carbon ring. As the pyridine ring is strongly deactivated a substitution in the benzene half of the molecule is preferred. Isoquinoline is a colourless solid having an odour resembling that of benzaldehyde. Quinoline and isoquinoline derivatives are more anesthetics. Its anesthetic activity is similar to those of procaine or cocaine when injected. Isoquinoline is also used in the synthesis of drugs 2627. In the present investigation, a complete study of vibrational spectra of the title compound has been carried out. The normal co-ordinate analysis and potential energy distribution calculations have also been performed for the first time to understand the bonding properties of isoquinoline.

## Experimental Details

The spectroscopically pure compound in powder form was obtained from ACROS

ORGANICS. New jersey, USA and used as such without any further purification. The mid and far FTIR spectra were recorded on BRUKER IFS 66V model FTIR spectrometer, using $KB_r$ and polyethylene pellets in the region 4000-400 cm$^{-1}$ and 400 – 100 cm$^{-1}$ respectively. The FT Raman spectrum of isoquinoline was recorded on the same instrument with FRA 106 FT Raman attachments. The Nd:YAG laser with 1064 nm excitation was used as the laser source. The resolution of the recorded spectra is accurate 0.1 cm$^{-1}$

## Spectra, Structure and Symmetry

The molecular structure of isoquinoline as shown in figure 1. The mid FTIR far FTIR and FT Raman spectra are shown is fig 2, 3 and 4 respectively from the spectral point of view the molecule isoquinoline belongs to Cs point group symmetry. The 17 atoms of the molecule give rise to 45 normal molecules of vibrations and they are distributed into 31 in-planes (a′) and 14 out of plane (a″) vibrations respectively.
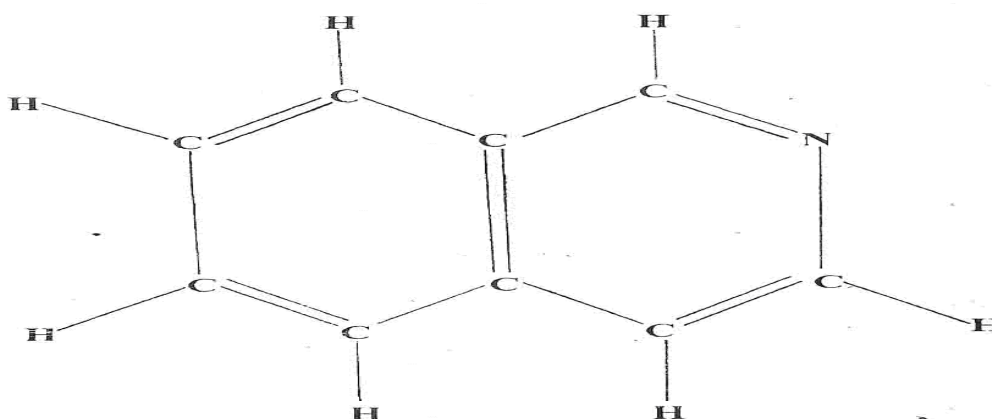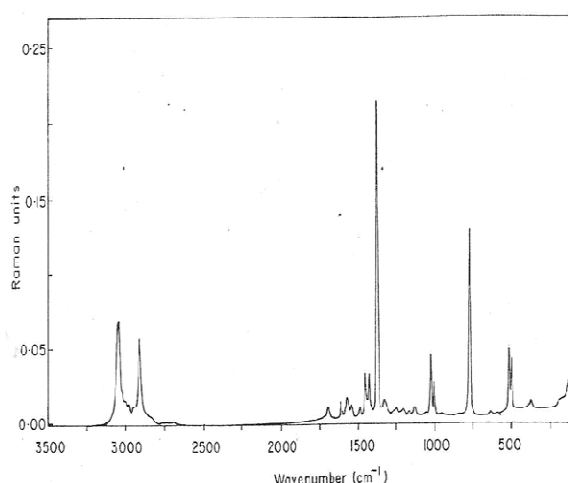


**Figure1:** Molecular Structure of Isoquinoline.
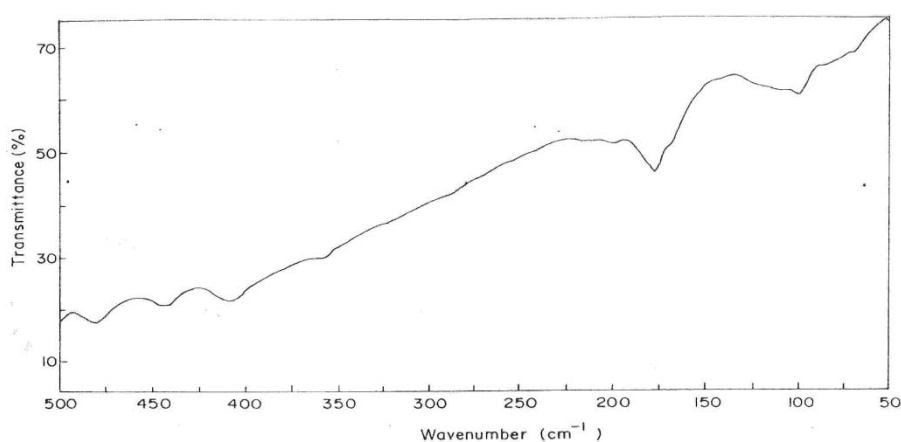


**Figure2:** For FTIR spectrum of isoquinoline.
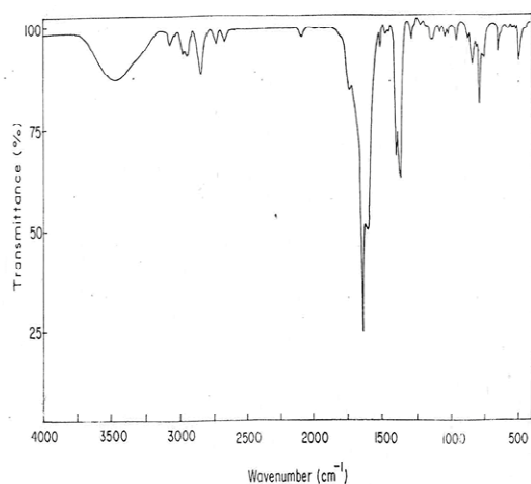
**Figure3:** FTIR spectrum of isoquinoline.



**Figure4:** FT raman spectrum of isoquinoline.

## Normal Co-Ordinate Analysis

The understanding of molecular structure requires good theoretical and high quality experimental approach in the study of poly atomic molecules. In order to obtain a complete description of molecular motions involved in the normal modes of the title compound. The normal co-ordinate analysis has been carried out utilizing the MOLVIB version 7.0 software [26]. The molecular parameters and the initial set of force constants required for performing the normal co-ordinate analysis are obtained from the literature [29]. The normal vibration calculations are performed on the both the in-plane and out-of-plane vibrations by setting up the secular equation described by Wilson. Because of the low symmetry and noticeable complexity of the molecular system, the number of independent force constants to be determined is exceedingly high and for this reason a simplified force field namely simple valence general force

field (SVGFF) was used. The force constants obtained in this study have also been refined by adopting a non-linear least square fit algorithm. In the refinement process, all the fundamental frequencies are used to refine 22 valence force constants. The refinement converged smoothly in four cycles. An average error of 12.8 cm$^{-1}$ was estimated between the calculated and observed frequencies.

## Results and Discussion
## Force Constants
The best fit force constants obtained in this study are presented in table 1.

As expected the values of the principal force constants for C-H, C-C and C-N obtained in this study are quite comparable to the characteristic values. The interaction force constants listed in table 1 suggest that the stretch – stretch interactions are stronger than stretch – bend and bend – bend interactions.

## Vibrational Analysis
### C-H Vibrations
The vibrational assignments of fundamental frequencies of isoquinoline are reported in Table 2. The aromatic and hetero aromatic structure shows the presence of C-H stretching vibrations in the region 3000 – 3100 cm$^{-1}$ C-H in-plane bending in the region 1000 -1100 cm$^{-1}$and C-H out-of-plane bending in the region 800 - 900 cm$^{-1}$, in this region the bands are not appreciably affected by the nature of the substituent's. The frequencies observed between 3102 – 2881 cm$^{-1}$in FTIR and Raman counter parts identified at 3057, 2931 and 2911 cm$^{-1}$are assigned to C-H stretching vibrations. The frequencies at 1070, 1066, 1035 and 1013 cm$^{-1}$are assigned for C-H in plane bending and they are in favorable agreement with the values given in the iterative. The frequencies found at 799, 775 and 717 cm$^{-1}$ are assigned to C-H out-of-plane bending and these assignments are also in good agreement with the literature values.

### C-N Vibrations
The assignment of bands in the region 1600 -1400 cm$^{-1}$are very difficult since the mixing of bands are taking place in this region, further the group frequency concept does not work out very precisely and accurately in this region. Hence in this study, based on the normal co-ordinate analysis and potential energy distribution calculation the strong and medium FT.IR bands found at 1631 and 1600 cm$^{-1}$are assigned to C-N stretching vibrations. The in-plane and out-of-plane bending vibrations of C-N bonds area found in their characteristic regions and they are listed in table 2.

## Carbon Vibrations
The title compound isoquinoline is a fused ring system in which one of the rings is benzene. Benzene has two doubly degenerate modes of $e_{2g}$ (1596 cm$^{-1}$) and $e_{12}$ (1485 cm$^{-1}$) and two non-degenerate modes $b_{2u}$ (1310 cm$^{-1}$) and $a_{12}$ (995 cm$^{-1}$) due to

skeletal stretching mode of C-C bonds[10]. In this study, the FTIR bands observed between 1590 and 1124 cm^{-1}are assigned to C-C stretching vibrations. The in-plane and out-of-plane bending of carbon vibrations are found in their characteristic regions. Further the predominant potential energy distribution values obtained for this group is also supporting the assignments proposed in this study.

Apart from these vibrations the N-C-C, C-N-C, N-C-H in-plane and out-of-plane bending, C-N-C-H and C-C-C-H torsion modes of vibration are assigned based on the PED calculations obtained from the find set of force constants using the relations

$$PED = \frac{F_{ij}L_{jk}^2}{\lambda_k}$$ Here PED is the combination of the $i^{th}$ symmetry co-ordinate to

the potential energy of the vibrations whose frequency is $V_k$, $F_{ij}$ is the potential constant. $L_{jk}$ is the $L$ matrix element and $\lambda_k = 4\pi^2 C^2 V^2 K$

**Table1:** Potential Energy Constants Of Isoquinoline. (In the units of m.dyne A[-1] , m.dyne rad[-1]and m.dyne A[0-1] rad[-2]).

| Types of constants | Parameter | Co-ordinates involved | Value |
|---|---|---|---|
| Diagonal constant stretching | $f_D$ | C-H | 5.1507 |
| | $f_d$ | C-C | 4.2619 |
| | $f_r$ | C-N | 5.3231 |
| Bending | $f_\infty$ | C C C | 1.3625 |
| | $f_\beta$ | C N C | 1.1037 |
| | $f_\gamma$ | N C C | 0.8911 |
| | $f_\delta$ | C C H | 0.5635 |
| | $f_\theta$ | N C H | 0.2110 |
| Interaction constants stretch-stretch | $f_{dd}$ | C C C C | 0.6415 |
| | $f_{dr}$ | C C C N | 0.3921 |
| | $f_{Dd}$ | C H C C | 0.2413 |
| | $f_{rD}$ | C N C H | 0.1127 |
| | $f_{rr}$ | C N C N | 0.1015 |
| Stretch – bend | $f_{d\infty}$ | C C C C C | 0.1235 |
| | $f_{d\beta}$ | C C C N C | 0.1137 |
| | $f_{r\infty}$ | C N C C C | 0.0916 |
| | $f_{r\beta}$ | C N C N C | 0.0735 |
| | $f_{r\theta}$ | C N N C H | 0.0561 |
| | $f_{d\theta}$ | C C N C H | 0.0315 |
| Bend - Bend | $f_{\infty\infty}$ | C C C C C C | 0.0261 |
| | $f_{\infty\beta}$ | C C C C N C | 0.0175 |
| | $f_{\infty\theta}$ | C C C N C H | 0.0102 |

**Table2:** Vibrational assignment of fundamental frequencies in $(Cm^{-1})$ of Iso quinoline.

| Species | Observed frequency and Intensity | | Calculated frequency | Assignments (% P E D) |
|---|---|---|---|---|
| | FT IR | FT Raman | | |
| a′ | 3102 W | | 3090 | C – H stretching(98) |
| a′ | 3057 W | 3057 ms | 3045 | C – H Stretching(94) |
| a′ | 3005 W | | 2994 | C – H Stretching(96) |
| a′ | 2967 W | | 2956 | C –H  Stretching(96) |
| a′ | | 2931ms | 2924 | C – H Stretching(94) |
| a′ | 2927VW | 2911W | 2916 | C – H Stretching(98) |
| a′ | 2881mS | | 2870 | C – H Stretching(92) |
| a′ | 1631S | 1625W | 1625 | C – N Stretching(94) |
| a′ | 1600m | | 1594 | C – N Stretching(92) |
| a′ | 1498VW | 1484W | 1490 | C – C Stretching(98) |
| a′ | 1462W | 1462W | 1454 | C – C Stretching(97) |
| a′ | 1450W | 1434VS | 1442 | C – C Stretching(94) |
| a′ | 1384m | 1384VS | 1376 | C – C Stretching(92) |
| a′ | 1355mS | 1328W | 1348 | C – C Stretching(94) |
| a′ | 1273W | 1254W | 1266 | C – C Stretching(93) |
| a′ | 1233W | 1203W | 1226 | C – C Stretching(98) |
| a′ | 1167W | 1169W | 1161 | C – C Stretching(96) |
| a′ | 1124W | 1140W | 1118 | C – C Stretching(99) |
| a′ | 1070W | | 1066 | C – H in-plane bending(83) |
| a′ | 1066W | | 1062 | C – H in-plane bending(82) |
| a′ | 1035W | 1036S | 1031 | C – H in-plane bending(80) |
| a′ | 1013W | 1015mS | 1009 | C – H in-plane bending(81) |
| a′ | 983W | | 930 | C-C-C Torisonal bending (72) |
| a′ | 943W | | 892 | |
| a′ | 862W | | 859 | C-C-C Torisonal bending (69) |
| a′ | 850W | | 804 | |
| a′ | 826m | | 823 | C-N in-plane bending (75) |
| a′ | 799W | | 796 | C-C-C in-plane bending (73) |
| a″ | 775ms | 783m | 772 | |
| a″ | 744W | | 704 | C-N in-plane bending(71) |
| a″ | 717W | | 714 | C-H out-of-plane bending(69) |
| a″ | 637W | 638W | 633 | |
| a″ | | | | C-H out-of-plane bending(61) |
| a″ | 565W | 523S | 535 | |
| a″ | 517W | | 515 | C-C-C- out-of-plane bending(63) |
| a″ | 507W | 503S | 505 | |
| a′ | 450W | | 426 | C-H- out-of-plane bending(65) |
| a′ | 446W | | 390 | |
| a″ | 409W | 383W | 381 | C-C- out-of-plane |

| | | | | |
|---|---|---|---|---|
| a″ | 356W | 375W | 375 | bending(66) |
| a″ | 223W | | 214 | |
| a″ | 196W | | 195 | C-C-C out-of-plane |
| a′ | 178ms | | 164 | bending(59) |
| a′ | 100W | 99S | 96 | C-N out-of-plane |
| | 81W | | 84 | bending(57) |
| | 89W | | 76 | C-N out-of-plane |
| | | | | bending(58) |
| | | | | C-C-C out-of-plane |
| | | | | bending(60) |
| | | | | N-C-C in-plane |
| | | | | bending(82) |
| | | | | C-N-C out-of-plane |
| | | | | bending(64) |
| | | | | N-C-H in-plane |
| | | | | bending(81) |
| | | | | N-C-C out-of-plane |
| | | | | bending(56) |
| | | | | C-N-C out-of-plane |
| | | | | bending(62) |
| | | | | N-C-H out-of-plane |
| | | | | bending(69) |
| | | | | N-C-H out-of-plane |
| | | | | bending(67) |
| | | | | C-N-C-H torsional |
| | | | | mode(54) |
| | | | | C-C-C-H torsional |
| | | | | mode(51) |

VS- Very strong; S-Strong; M-medium; MS-Medium strong; W-Weak.


## Conclusion

The values of force constants obtained in present investigation would help to understand the physical and chemical properties of "Isoquinoline" and its derivatives. The force constants reported here reproduce the observed frequencies. The potential energy distributions obtained in the analysis provide some insight into the nature of normal modes of "Isoquinoline".

A close agreement between the observed and calculated frequencies confirms the validity of the assignment.

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