

LASER RAMAN SCATTERING STUDIES OF N-(2-PYRIDYL) THIOACETAMIDE*

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The N-(2 Pyridyl) thioacetamide molecule is of considerable biological and pharmaceutical importance. Very little work has been done on the vibrational spectra of thioacetamide. In order to extend this study further, the laser Raman spectrum of thioacetamide has been recorded in the region $60\text{--}2500\text{cm}^{-1}$ on a Cary Model-82 spectrophotometer using Argon laser source with exciting radiation 5145\AA for the first time. The spectrum has been analysed assuming C_s point group symmetry and the observed fundamentals have been assigned to different normal modes of vibration. The assignment of the fundamental frequencies is made on the basis of magnitude and relative intensities of the observed bands. Some of the assignments (C—H, C=S, C=C, N—H, C=N) have been discussed.

Key Words : Laser Raman Spectroscopic Investigation—N-(2Pyridyl) Thioacetamide Molecule

INTRODUCTION

THE knowledge of the vibrational analysis of the benzene molecule is very important since it can be applied to many compounds of similar structure. Because of the simplicity and highly symmetrical nature of this molecule, it is very suitable as a model in methodological research work and structural studies. Whiffen¹ and Varsanyi² in their study of different monosubstituted benzene *viz* C_6H_5X have shown that of all thirty fundamental vibrations of the aromatic ring, twenty four frequencies do not change much when the X group is changed. The remaining six frequencies alone are sensitive to the X -group. They have also concluded that two of the frequencies occur at fairly high frequency region and the other four at lower frequency region. For simplicity and convenience, the modes of vibration of aromatic compounds are considered as separate C—H or ring C=C vibrations. However, as with any 'complex' molecule, vibrational interactions occur and these labels really indicate the predominant vibrations. An in-plane vibration mode of the aromatic ring may interact with the stretching vibration of an (aromatic carbon)— X bond. This type of stretching vibration is known as an X -sensitive mode and is dependent on the mass of the substituent X . The X -sensitive bands normally occur in the regions $1300\text{--}1050\text{cm}^{-1}$, $850\text{--}620\text{cm}^{-1}$ and $580\text{--}200\text{cm}^{-1}$. These vibrational modes are due to (a) the ring carbons 1, 3, and 5 moving radially in phase while the substituent on carbon 1 moves radially out of phase, (b) the in-

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plane bending of a quadrant of the ring in which the C—X bond length increases as the distance between the carbons 1 and 4 decrease and (c) of the distance between carbon 1 and 4 and C—X bond length both increases simultaneously. The current investigation presents the laser Raman spectrum of N-(2 pyridyl) thioacetamide.

EXPERIMENTAL

N-(2 pyridyl) thioacetamide is obtained from Fluka A G Chemische Fabrik, Schweiz. The laser Raman spectrum of this molecule has been recorded at I.I.Sc., Bangalore, using Cary Model-82 laser Raman spectrophotometer in the region 60–2500 cm^{-1} and is presented in Fig 1. The observed frequencies are listed in Table I.

RESULTS AND DISCUSSION

The molecule N-(2 pyridyl) thioacetamide would belong to the C_s point group and all the vibrations are allowed in both the Raman and infrared spectra. The totally symmetric vibrations A' should give polarised Raman lines, whereas non-totally symmetric vibrations A'' should give depolarised Raman lines.

Aromatic C—H Stretching Vibrations

These bands occur in the region 3080–3010 cm^{-1} and are of strong to medium intensity.³ A band with upto five peaks may be observed in this region. Alkene C—H stretching vibrations also cause bands in this region.

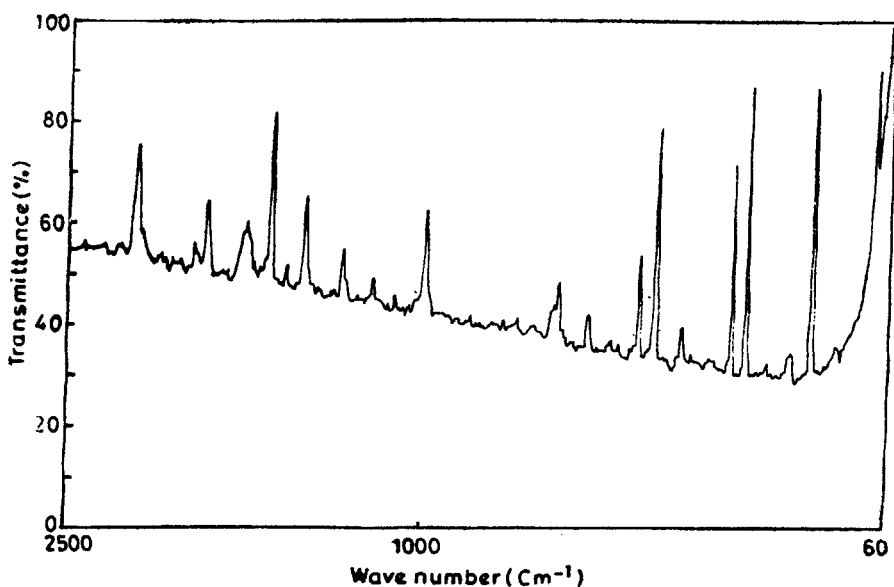


FIG 1 Laser Raman spectrum of N(2-pyridyl) thioacetamide

TABLE I

Vibrational frequencies of Laser Raman Spectrum of N(2 Pyridyl) Thioacetamide

Frequency (cm ⁻¹)	Intensity*	Assignment
95	VS	815-734
176	VW	997-815
229	VS	1020-784
274	W	1020-741
320	VW	1064-734
358	VS	1106-741
338	S	1106-734
434	VW	1165-734
464	W	1240-784
479	M	1279-784
532	VS	1275-734
568	M	1440-862
601	VW	1467-862
617	VW	1440-815
666	W	1440-784
722	VW	1581-862
734	M	aromatic C-H out of plane deformation
741	M	aromatic C-H out of plane deformation
784	VW	ring out of plane bending
815	VW	ring out of plane bending
862	VW	ring out of plane bending
908	VW	2 × 1275-2 × 815
997	M	aromatic in plane C-H deformation
1020	VW	aromatic inplane C-H deformation
1064	W	aromatic inplane C-H deformation
1106	M	aromatic in plane C-H deformation
1135	VM	aromatic inplane C-H deformation
1165	M	aromatic inplane C-H deformation
1240	M	C=S stretching vibration
1278	W	C=S stretching vibration
1313	S	2 × 1064-815
1328	VW	2 × 1167-997
1337	VW	2 × 1167-997
1362	M	2 × 1240-1106
1400	VW	2 × 1440-2 × 734
1440	M	aromatic C = N ring stretching
1467	W	aliphatic C-H deformation
1491	VW	734 + 741
1511	VW	784 + 741
1540	VW	815 + 734
1570	W	815 + 741
1581	S	aromatic C = C stretching vibration
1625	VW	2 × 815
1949	VW	1135 + 815

*VS : Very strong; S : Strong; M : Medium; W : Weak; VW : Very Weak

Aromatic In-Plane C—H Deformation Vibrations

The number of C—H inplane deformation bands occur in the region 1290–1000 cm^{-1} , the bands being sharp but of weak to medium intensity. These bands are not normally of importance for interpretation purposes although they can be used. In fact, a number of interactions are possible, thus necessitating great care in interpretation of bands in this region. Further the band appears at 1467 cm^{-1} may be due to the aliphatic C—H deformation.

Aromatic Out-of-Plane Deformations and Ring Out-of-Plane Vibrations

The frequencies of the C—H out of plane deformation vibrations are mainly determined by the number of adjacent hydrogen atoms on the ring and not very much affected by the nature of substituents^{4,5} although strongly electron attracting substituent groups. These bands give an important means for determining the type of aromatic substitution. The C—H out of plane deformation bands in the present study occur at 734 cm^{-1} and 741 cm^{-1} . The rings out of plane bending vibrations are found at 784, 815 and 862 cm^{-1} .

Aromatic C=C Stretching Vibrations

The ring carbon—carbon stretching vibrations occur in the region 1625–1430 cm^{-1} .^{6–10} In general *ortho*, disubstituted benzenes have strong bands at 1625–1590 cm^{-1} . The strongest band appeared at 1581 cm^{-1} refers the C=C stretching vibrations for the compound under investigation. Further the band at 1440 cm^{-1} may be due to the Aromatic C=N ring stretching vibration and the medium intensity band appears at 1240 cm^{-1} is due to C=S stretching vibrations.

CONCLUSION

The vibrational frequencies identified in the analysis of laser Raman spectrum of N(2 pyridyl) thioacetamide have been assigned to specific modes of vibration.

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