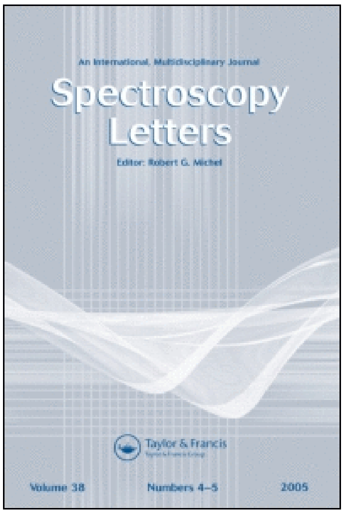

**Spectroscopy Letters**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

# Vibrational Assignment of 2-Benzoyl Pyridine and its $^{18}O$ Labelled Isomer

Ts. M. Kolev[a]; P. Bleckmann[b]
[a] Institute of Organic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria [b] Institute of Chemistry, University of Dortmund, Dortmund, FRG

**To cite this Article** Kolev, Ts. M. and Bleckmann, P.(1989) 'Vibrational Assignment of 2-Benzoyl Pyridine and its $^{18}O$ Labelled Isomer', Spectroscopy Letters, 22: 9, 1215 — 1227
**To link to this Article: DOI:** 10.1080/00387018908054018
**URL:** http://dx.doi.org/10.1080/00387018908054018

SPECTROSCOPY LETTERS, 22(9), 1215-1227 (1989)

# VIBRATIONAL ASSIGNMENT OF 2-BENZOYL PYRIDINE AND ITS $^{18}O$ LABELLED ISOMER

KEY WORDS: IR spectra; Raman spectra; isotope labelling; 2-benzoyl pyridine; 2-benzoyl pyridine-$^{18}O$; vibrational assignment

Ts.M. Kolev, and P. Bleckmann*
Institute of Organic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
*Institute of Chemistry, University of Dortmund, D-4600 Dortmund 50, F R G

## ABSTRACT

Vibrational spectra of 2-benzoyl pyridine and 2-benzoyl pyridine-$^{18}O$ have been recorded in the solid and molten state in the infrared (4000-100 cm$^{-1}$) and in the Raman (4000-50 cm$^{-1}$). Polarized Raman spectra in the molten state have also been measured. The assignment of the vibrational bands is performed using the group vibrational concept, isotopic shifts and polarization features of the normal modes.

## INTRODUCTION

Infrared and Raman spectra of 2-benzoyl pyridine have been studied by Seth-Paul et all Ref.1. Although thorough infrared and Raman studies of 2-benzoyl pyridine are available, discrepencies in the assignments of some normal modes still remain.

2-Benzoyl pyridine (BP) has found an important application as a complexation agent for the spectrophotometric determination of a great variety of metals as seen from the growing number of papers devoted to this compound and its derivatives[2-8]. Dipole moments, Kerr constants and conformations in solutions of BP have been determinated and calculated[9-12]. The assignment of the spectra takes into account the respective activity of all bands whose IR and Raman bands are associated with $C_s$ symmetry of the studied molecules. It is possible to distinguish the vibrations which belong to phenyl and pyridyl part of molecule.

The present article gives experimental data for the IR and Raman spectra of BP and its $^{18}O$ isotopically substituted isomer as well as for polarization raman spectra of molten BP.

## EXPERIMENTAL

2-Benzoyl pyridine, reagent grade (EGA Chemie), was purified by distillation under vacuum, b.p. 134-136°C 0,2 Torr, and multifold recrystallization from hexane. The preparation of BP-$^{18}O$ was carried out according to Roberts and Urey[13]. IR spectra of all the ketones were recorded in KBr and polyethylene pellets on a Brucker-113 v FTIR spectrometer in the 4000-100 $cm^{-1}$ region.

Raman spectra, 4000-50 $cm^{-1}$, were registered using a 60 mW exitation with the 514,5 nm line of an $Ar^+$ laser on a Coderg triple monochromator spectrometer. Depolarization was determined in the molten state. The isotopic content, determined by mass spectrometry, was 70,4 atomic % $^{18}O$.

## RESULTS AND DISCUSSION

The observed bands and their assignment are given in Table 1. The nomenclature of Kohlrausch and Pongratz[14], further developed by Datin and Lebas[15], La Lau and Snyder[16] and also in Ref. 17 is used here for description of the vibrational modes of monosubstituted benzene and pyridine rings.

The conjugation of the carbonyl group with phenyl and pyridyl rings should favour a planar conformation. The steric repultion, however, between the nearest hydrogen atom and the free electron pair of the N atom do not cooperate to attain coplanarity, thus twisting both phenyl and pyridyl rings by 40° [12]. The molecule of 2-benzoyl pyridine has a $C_s$ molecular symmetry. A corollary of this is the simultaneous IR and Raman activity of all 63 normal vibrations. Among the 63 vibrations 51 are associated with vibrational motions of the pyridyl and phenyl rings. Exept for the carbonyl stretching vibrations the remaining 11 bands are atributed to the intragroup motions.

The new spectral information contained in Table 1 concerns the IR and Raman spectra for BP-$^{18}$O. All bands of BP and BP-$^{18}$O coincide in frequency within 1-2 cm$^{-1}$ exept for three bands reffered to the carbonyl group. The $^{18}$O isotopic substitution has a prominent effect only on the characteristic carbonyl frequencies. The $\nu_{C=O}$ stretching band of BP appears at 1670 cm$^{-1}$ (IR) the $\nu_{C=^{18}O}$ is observed at 1642 cm$^{-1}$ (Fig.1). The isotopic shift $\Delta\nu_{C=O}$ of 28 cm$^{-1}$ is equal to that of benzophenone-$^{18}$O[18] but less of di-2-pyridyl ketone-$^{18}$O[21]. The in-plane deformation vibration (Fig.2) were found at 576 cm$^{-1}$ (IR), 579 cm$^{-1}$ (Raman) for BP and at 567 cm$^{-1}$ (IR), 569 cm$^{-1}$ (Raman) for BP-$^{18}$O. A

Table 1. Vibrational assignment of 2-benzoyl pyridine and 2-benzoyl pyridine-$^{18}O$ in the solid state

| $\nu_i$ ($cm^{-1}$) | IR | | Raman | | Assignment | |
|---|---|---|---|---|---|---|
| | BP | BP-$^{18}O$ | BP | BP-$^{18}O$ | | |
| 1 | 3101 | 3102 | 3102 | 3102 | 20a | (Ph)* |
| 2 | 3101 | 3101 | | | 20a | (Py)** |
| 3 | 3083 | 3082 | 3088 | 3088 | 20b | (Ph) |
| 4 | | | 3067 | 3068 | 20b | (Py) |
| 5 | 3057 | 3056 | 3060 | 3060 | 2 | (Py) |
| 6 | 3057 | 3056 | 3060 | 3060 | 2 | (Ph) |
| 7 | 3060 | 3060 | 3060 | 3060 | 7a | (Py) |
| 8 | 3027 | 3027 | 3028 | 3027 | 7a | (Ph) |
| 9 | 2988 | 2989 | 3005 | 3005 | 13 | (Ph) |
| 10 | 1668 | | 1664 | | $\nu$(C=O) | |
| | | 1640 | | 1638 | | |
| 11 | 1594 | 1594 | 1595 | 1594 | 8a | (Ph) |
| 12 | 1585 | 1585 | 1584 | 1585 | 8a | (Py) |
| 13 | 1578 | 1577 | 1575 | 1575 | 8b | (Ph) |
| 14 | 1567 | 1567 | 1566 | 1565 | 8b | (Py) |
| 15 | 1490 | 1490 | 1596 | 1595 | 19a | (Ph) |
| 16 | 1465 | 1465 | 1467 | 1467 | 19a | (Py) |
| 17 | 1448 | 1448 | 1443 | 1443 | 19b | (Ph) |
| 18 | 1435 | 1434 | 1436 | 1436 | 19b | (Py) |
| 19 | 1322 | 1323 | 1326 | 1326 | 14 | (Ph) |
| 20 | 1316 | 1316 | 1312 | 1312 | 14 | (Py) |
| 21 | 1301 | 1302 | 1303 | 1302 | 3 | (Ph) |
| 22 | 1284 | 1284 | 1281 | 1281 | $e_2$ | |
| 23 | 1241 | 1241 | 1248 | 1248 | 3 | (Py) |
| 24 | 1180 | 1181 | 1181 | 1181 | $e_1$ | |

Table 1 (continued)

| $\nu_i$ | IR | | Raman | | Assignment |
|---|---|---|---|---|---|
| (cm$^{-1}$) | BP | BP-$^{18}$O | BP | BP-$^{18}$O | |
| 25 | 1167 | 1167 | 1168 | 1167 | 9a (Ph) |
| 26 | 1158 | 1157 | 1158 | 1160 | 15 (Ph) |
| 27 | 1152 | 1152 | 1150 | 1151 | 9a (Py) |
| 28 | 1094 | 1094 | 1100 | 1100 | 18a (Ph) |
| 29 | 1075 | 1075 | 1094 | 1094 | 18a (Py) |
| 30 | 1048 | 1047 | 1051 | 1051 | 18b (Py) |
| 31 | 1026 | 1025 | 1030 | 1029 | 18b (Ph) |
| 32 | 1000 | 1000 | 1005 | 1006 | 1(Ph-breath |
| 33 | 993 | 993 | 1000 | 1000 | 1(Py-breath |
| 34 | | | 980 | 980 | 5 (Ph) |
| 35 | 978 | 978 | 980 | 980 | 17a (Py) |
| 36 | 962 | 962 | 956 | 956 | 17a (Ph) |
| 37 | 942 | 942 | | | 5 (Py) |
| 38 | 942 | 942 | 940 | 940 | 17b (Ph) |
| 39 | 926 | 925 | 925 | 925 | $d_2$ (Ph) |
| 40 | 896 | 896 | 901 | 901 | $d_2$ (Py) |
| 41 | 853 | 853 | 860 | 859 | 10a (Ph) |
| 42 | 818 | 818 | 824 | 824 | 10a (Py) |
| 43 | 777 | 777 | 778 | 778 | 11 (Ph) |
| 44 | 749 | 748 | 754 | 754 | $d_1$ (Py) |
| 45 | 730 | 730 | 734 | 734 | $d_1$ (Ph) |
| 46 | 703 | 703 | | | 4 (Ph) |
| 47 | 688 | 688 | 689 | 689 | 4 (Py) |
| 48 | 668 | 668 | 651 | 651 | 6a (Ph) |
| 49 | 648 | 648 | 650 | 650 | 6a (Py) |
| 50 | 617 | 617 | 619 | 618 | 6b (Ph) |
| 51 | 576 | | 579 | | $\delta$(C=O) |
| | | 567 | | 569 | |
| 52 | 454 | 454 | | | 16a (Ph) |
| 53 | 445 | 445 | 440 | 440 | 16a (Py) |

(continued)

Table 1 (continued)

| $\nu_i$ ($cm^{-1}$) | IR | | Raman | | Assignment |
|---|---|---|---|---|---|
| | BP | BP-$^{18}$O | BP | BP-$^{18}$O | |
| 54 | 429 | 429 | 416 | 416 | 16b (Ph) |
| 55 | 401 | 401 | 404 | 404 | 16b (Py) |
| 56 | 355 | 346 | | | $\delta$(C=O) |
| 57 | 289 | 290 | 290 | 290 | $\delta(C_{Py}$-CO-$C_{Ph})$ |
| 58 | 228 | 227 | 234 | 233 | $\delta^{asym}$(Ph-plane... Py-plane) |
| 59 | 214 | 214 | 215 | 215 | $\delta^{sym}$(Ph-plane.... Py-plane) |
| 60 | 154 | 153 | 155 | 155 | $\gamma^{asym}$(Ph-plane.... Py-plane) |
| 61 | 129 | 129 | 121 | 121 | $\gamma^{sym}$(Ph-plane.... Py-plane) |
| 62 | 104 | 104 | 108 | 108 | $C_{Al}{}^{\#}$ -- $C_{Py}$ torsion |
| 63 | | | 92 | 92 | $C_{Al}{}^{\#}$ – $C_{Ph}$ torsion |

(Ph)* - phenyl part

(Py)** - pyridyl part

$C_{Al}{}^{\#}$ - alkyl C-atom

comparison of the spectra of BP and BP-$^{18}$O shows that $^{18}$O labelling results in a 10 cm$^{-1}$ of $\delta_{C=O}$. In this way we have assigned unambiguously the band at 576 cm$^{-1}$ in the IR spectrum of BP to $\delta_{C=O}$. The out-of-plane deformation vibration $\gamma_{C=O}$ appears at 355 cm$^{-1}$ (IR) for BP

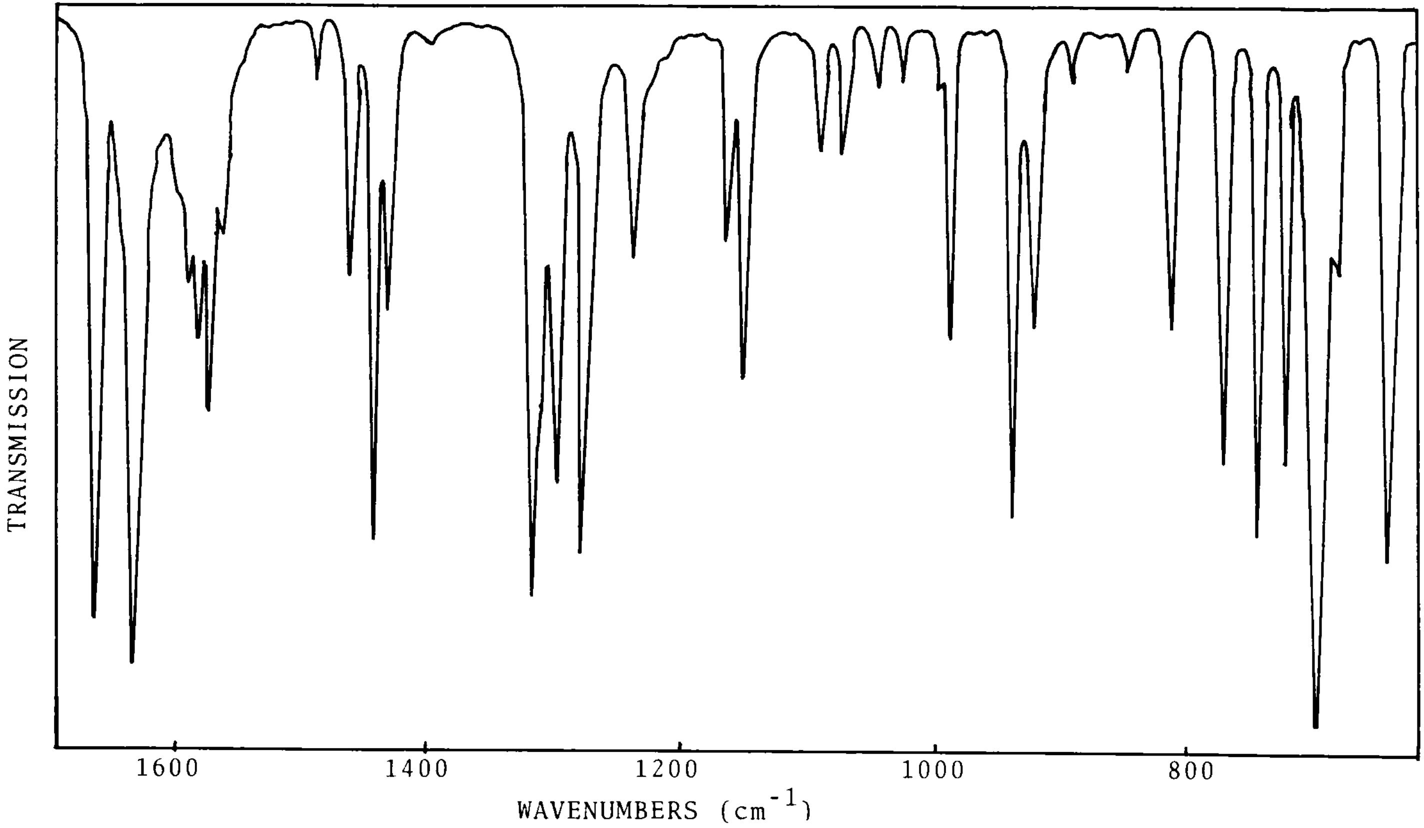

Fig. 1. Infrared spectrum of 2-pyridyl ketone-$^{18}$O (70,4 atomic %-$^{18}$O) in the solid state, KBr pellet

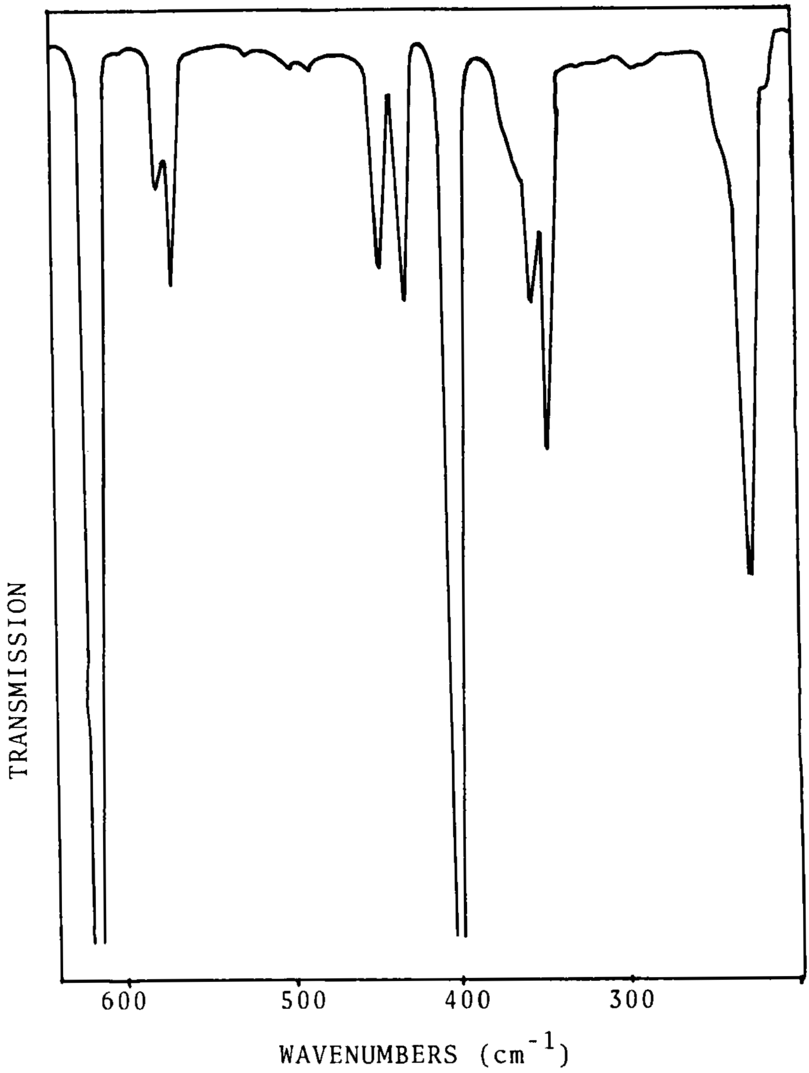

Fig.2. Infrared spectrum of 2-pyridyl ketone-$^{18}$O (70,4 atomic %-$^{18}$O) in the solid state, polyethylene pellet

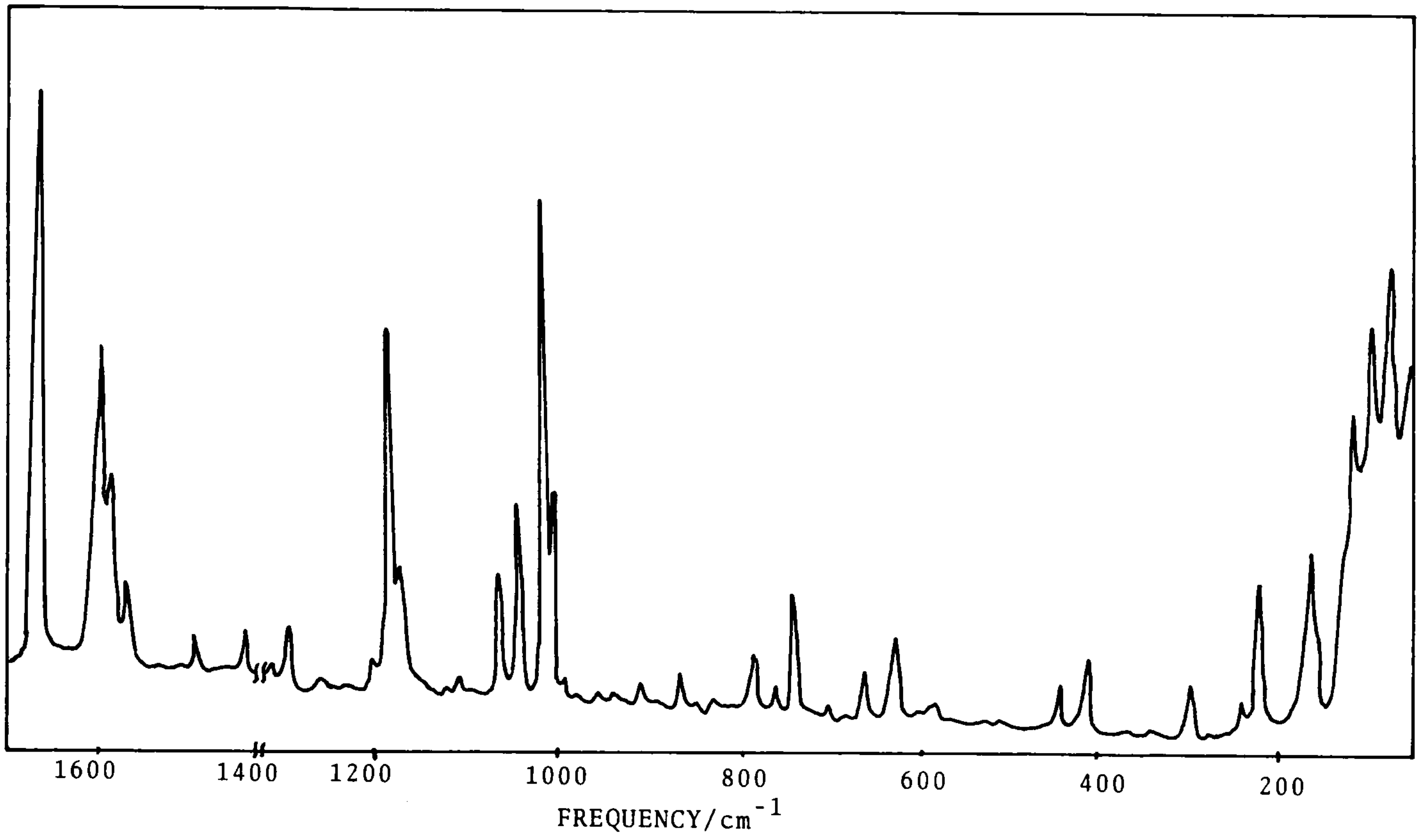

Fig.3.Raman spectrum of 2-pyridyl' ketone in the solid state

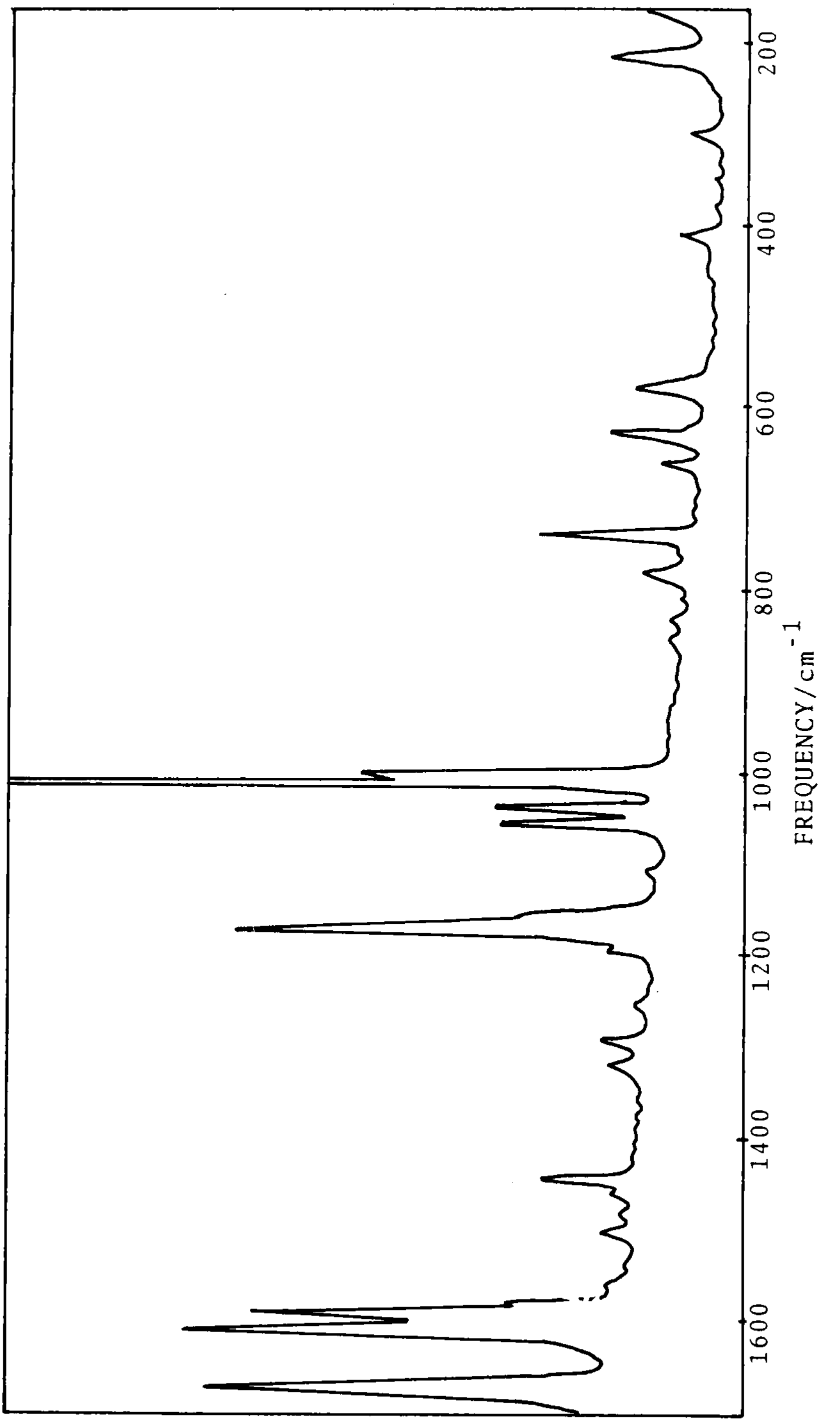

Fig.4. Raman spectrum of 2-pyridyl ketone; parallel polarization in molten state

and at 346 $cm^{-1}$ for BP-$^{18}O$.The isotopic shift is 9 $cm^{-1}$; like in the case of benzophenone[18]. Hence, the $^{18}O$ isotopic shifts 9 $cm^{-1}$ for $\gamma_{C=O}$, 10 $cm^{-1}$ for $\delta_{C=O}$ and 28 $cm^{-1}$ for $\nu_{C=O}$ confirm the band assignment.

The ring stretching vibrations (8a, 8b, 19a, 19b and 14) having predominantly C—C character appear in the region 1600-1300 $cm^{-1}$. The bands at 1594, 1578, 1490, 1448 and 1322 $cm^{-1}$ (IR) are assigned to the phenyl ring motions and the bands at 1585, 1567, 1467, 1435 and 1316 $cm^{-1}$ (IR) are connected with pyridyl ring vibrations. The ring vibration 14 analogous to "Kekule vibration" of benzene is found in a frequency interval established by Whiffen[19] and Varsanyi[20] and confirmed in many other works[1,18,21].

The very strong IR band at 1284 $cm^{-1}$ and the very weak Raman band at 1281 $cm^{-1}$ of 2-benzoyl pyridine is assigned here to the $e_2$ vibration. Hence, we confirm the assignment of Seth-Paul and coworkers[1].

The frequences of the planar C H bonds are known to cover a larger region. The vibration modes namely 3, 15, 18a, 18b and 9a for the phenyl ring and 3, 9a, 18a and 18b for the pyridyl nucleus.

Di-2-pyridyl keton displays the breathing mode at 1000 and 1014 $cm^{-1}$ Ref.21 and benzophenone at 1004 and 999 $cm^{-1}$ (IR)[18]. Therefore, the bands at 1000 $cm^{-1}$ (IR) and 1006 $cm^{-1}$ (R) and 993 $cm^{-1}$ (IR) and 996 $cm^{-1}$ (R) are due to 1 of phenyl and 1 of pyridyl part of molecule respectively.

The out-of-plane C—H bends (5a, 17a, 17b, 10a and 11) for phenyl ring are placed at 980, 956, 940, 860 and 778 $cm^{-1}$ in the Raman spectrum while these belonging to pyridyl one are placed at 980, 942, 860 and 824 $cm^{-1}$ (R).

The bands at 926 $cm^{-1}$ and 896 $cm^{-1}$ (IR) 925, 901 $cm^{-1}$ (R) refer to the X-sensitive vibration $d_2$. In case of benzophenone[18] it is shown that the deuteration does not practically affect the band positions. The high IR intensities of this bands also confirm the assignment. The strong Raman band at 731 $cm^{-1}$ and the weak one at 754 $cm^{-1}$ are assigned to the X-sensitive phenyl and pyridyl ring vibration respectively.

The bands at 650 $cm^{-1}$ (IR, R) previuosly assigned as $\delta_{C=O}$ in Ref.1 is most probably the 6a vibration - in-plane radial ring C—C deformation. Normal coordinate analysis predicts a frequency range 650-690 $cm^{-1}$ for the 6a vibration and 620-650 $cm^{-1}$ for the 6b vibration[20]. We reassign the band at 576 $cm^{-1}$ to $\delta_{C=O}$, which is refered to 6a mode in Ref.1. The medium IR band is atributed to 16a vibration. The previous assignment of this band to band to $\delta_{C=O}$ is wrong, because that band is completely unsensitive to $^{18}O$ isotopic substitution. The assignment of the band at 355 $cm^{-1}$ (IR) to 18b mode[1] is revised here. The unambiguously assignment is $\gamma_{C=O}$. The bands between 300-100 $cm^{-1}$ are characteristic for the motion of both phenyl and pyridyl planes with respect to the directions of their neighbouring (Ph-C-Py) bonds. These fundamentals are found in the expected frequency range[15,18,20,21] although some differences from previous assignments occur, especially for the band at 286 $cm^{-1}$ considered as arising from the 9b X-sensitive vibration[1].

## ACKNOWLEDGEMENT

One of us (Ts.K.) thanks to Alexander von Humboldt Stiftung for a research fellowship. This study was also supported by the Institute of Chemistry, University of Dortmund.

## REFERENCES

1. W.A.Seth-Paul, B.Van Der Veken and M.Herman, Spectros.Int.J.,1,120(1982).
2. R.Dutta and Kuntala De,Indian J.Chem.,27A,133(1988).
3. E.Anders,H.Boldt,T.Clark,R.Fuchs and T.Gaßner,Chem. Ber.,119,279(1986).
4. R.Dutta and M.Hossain, Indian J.Chem.,23A,30(1988).
5. I.Ahuja,R.Singh and R.Spiramulu,Spectrochim.Acta, 36A,383(1980).
6. M.Mohan and B.Paramhans,Croat.Chem.Acta,54,173(1981).
7. R.Dutta and A.Sarkar,J.Inorg.Nucl.Chem.,43,57(1981).
8. I.Ahuja and R.Singh,Inorg.Nucl.Chem.Lett.,9,289(1973).
9. S.Trovato,F.Zuccarello and A.Millefiori,J.Mol.Struct., 28,216(1975).
10. S.Trovato,F.Zuccarello,A.Favini and A.Millefiori, Spectrochim.Acta,32A,351(1976).
11. Ch.Lai Cheng and G.L.D.Ritchie,J.Chem.Soc.Perkin II, 1973,1461.
12. J.Barassin,G.Queguiner and H.Limbroso,Bull.Soc.Chim. France,1967,4707.
13. I.Roberts and H.Urey,J.Am.Chem.Soc.,60,880(1938).
14. K.W.F.Kohlrausch and A.Pongratz,Monatsh.Chem.,64, 374(1934).
15. A.Perrier-Datin and J.M.Lebas,Spectrochim.Acta, Part A,25,169(1969).
16. C.La Lau and R.W.Snyder,Spectrochim.Acta,Part A,27, 2073(1971).
17. E.B.Wilson,Phys.Rev.,45,706(1934).
18. Ts.Kolev,B.Nikolova,B.Jordanov and I.Juchnovski, J.Mol.Struct.,129,1(1985).
19. D.H.Whiffen,J.Chem.Soc.,1350(1956).
20. G.Varsanyi,Vibrational Spectra of Benzene Derivatives,Academic Press,New York,1969.
21. Ts.Kolev and P.Bleckmann,Spectrosc.Lett.,22,No6, (1989), in press.

Date Received: 06/22/89
Date Accepted: 07/27/89