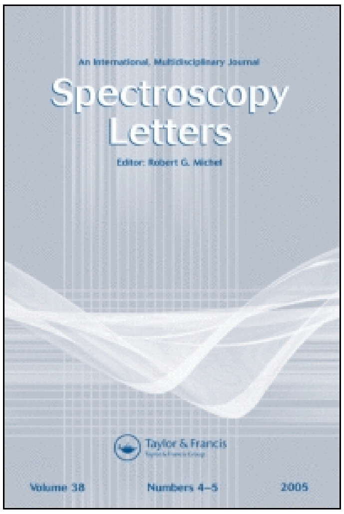

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Vibrational Spectra of 4-Benzoylpiridine and the ^{18}O Substituted Derivative

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VIBRATIONAL SPECTRA OF 4-BENZOYLPIRIDINE AND THE ^{18}O SUBSTITUTED DERIVATIVE

KEY WORDS: IR spectra; Raman spectra; isotope labelling; 4-benzoylpiridine; 4-benzoylpiridine-^{18}O; vibrational assignment

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ABSTRACT

Infrared and Raman spectra of 4-benzoylpiridine (4BP) and its ^{18}O substituted derivative have been recorded in the solid and in the molten state. Polarized Raman spectra in the molten state have also been measured. The assignment of the vibrational bands is performed on the basis of isotopic shifts, group vibrational concept and polarization features of the normal modes. The previous assignment of the in- and out-of-plane deformations of the carbonyl group and the fundamentals below 700 cm^{-1} are questioned and corrected.

INTRODUCTION

The present paper was carried out as a part of systematic study of the vibrational spectra of some compounds having structures analogous to the twisted diphenyl methanone (benzophenone). Our previously published studies were on the vibrational spectra of di-2-pyridyl ketone and 2-benzoylpiridine [1-2].

A fairly complete assignment of 4-benzoylpiridine was made by Seth-Paul et al.[3]. These authors have performed the assignment on the basis of precisely measured IR and Raman frequencies. Nevertheless, some discrepences in the attributions still remain. The molecular symmetry of 4-BP is C_s [3].

4-Benzoylpiridine has found some applications as a complexation agent although not so important as 2-benzoylpiridine and di-2-pyridyl ketone[4-6]. Dipole moments, Kerr constants and conformations in solutions of 4-BP have been determined and calculated[7-10].

The subject of this article is the vibrational assignment of the fundamentals of 4-BP-^{18}O carried out on the basis of isotopic shifts, vibrational group concept and polarization features of the normal modes.

EXPERIMENTAL

4-Benzoylpyridine, puriss.(EGA Chemie), was purified by multifold recrystallization from heptane-m.p. 74-75°C. The 4-BP-^{18}O was prepared according to Roberts and Urey from $H_2{}^{18}O$ and 4-BP under action of NaOH in methanol[11]. IR spectra of the ketones were recorded in KBr and polyethylene pellets on Brucker-113 v FTIR spectrometer in the 4000-100 cm^{-1} region. The reported wavenumbers in Table 1. are believed to be accurate to within ∓ 1 cm^{-1}.

Raman spectra were registrated using a 60 mW exitation with the 514,5 nm line of an Ar^+ laser on a Coderg triple monochromator spectrometer; frequency reproducibility within ∓1 cm^{-1}. The spectra, 4000-50 cm^{-1} of solid ketones were obtained from crystal powders contained in sealed capillary tubes. Depolarization ratios were determined in the molten state.

The isotopic content, determined by mass spectrometry, was 71,8 atomic % ^{18}O.

RESULTS AND DISCUSSION

An IR spectrum of solid 4-BP-^{18}O 1700-600 cm^{-1} is shown in Fig.1. The same spectrum between 600 and 100 cm^{-1} is shown in Fig.2. The Raman spectrum of 4-BP in solid state is presented in Fig.3 while Figs.4 and 5 represent the Raman spectra in the molten state, with parallel and perpendicular exitation respectively.

The wavenumbers (cm^{-1}) of the observed bands assigned to fundamentals in the infrared and Raman spectra of 4-BP and 4-BP-^{18}O are listed in Table 1.

In a molecule with C_s symmetry it is possible to define only a plane symmetry. Thus studied molecule has 63 fundamentals, 30 (21a′ + 9a′′) of which belong to the phenyl and 27 (19a′ + 8a′′) to the pyridyl group. The remaining 6 fundamentals can be described as C(C=O)C vibrations. All vibrations are infrared and Raman active. Only the fundamentals in the Wilson notation[12] of the title compound are given in Table 1 while the nomenclature of Kohlrausch and Pongratz[13] for X-sensitive vibration, further developed in Refs.14 and 15, is used here for description of the vibrational modes. Since pyridyl modes resemble phenyl modes, distinction is made by means of Ph or Py depending upon whe-

Table 1. Vibrational assignment of 4-benzoylpiridine and 4-benzoylpiridine-^{18}O in the solid state

ν_i	4BP		4BP^{18}O		Assignment
(cm^{-1})	i.r.	Raman	i.r.	Raman	
1	3085	3086	3085	3085	20a (Ph)
2	3059	3075	3060	3074	20b (Py)
3	3059	3060	3060	3060	20a (Ph)
4	3059	3060	3060	3060	20b (Py)
5	3045	3036	3044	3036	2 (Ph)
6	3059	3060	3060	3060	2 (Py)
7	3022	3016	3023	3015	7a (Py)
8	3045	3036	3044	3036	7a (Ph)
9	3022	3016	3023	3015	13 (Ph)
10	1657	1662	1624	1629	$\nu_{C=O}$
11	1597	1598	1596	1598	8a (Ph)
12	1597	1596	1597	1596	8a (Py)
13	1576	1570	1577	1571	8b (Ph)
14	1549	1551	1548	1551	8b (Py)
15	1491	1490	1490	1490	19a (Ph)
16	1491	1488	1489	1487	19a (Py)
17	1446	1449	1447	1449	19b (Ph)
18	1409	1412	1409	1411	19b (Py)
19	1330	1331	1331	1332	14 (Ph)
20	1321		1321		14 (Py)
21	1309		1308		3 (Ph)
22	1285	1289	1285	1289	e_2
23		1289		1289	3 (Py)
24	1178	1180	1178	1281	9a (Ph)
25	1151	1158	1150	1159	e_1
26		1108		1109	9a (Py)
27	1075	1071	1075	1071	18a (PY)
28	1063	1071	1063	1071	18b (Ph)

Table 1. (continued)

29	1063	....	1062	....	18b	(Py)
30	1027	1030	1027	1029	18b	(PY)
31	1001	1006	1001	1005	1(breath.)	(Ph)
32	999	1000	999	1001	1(breath.)	(Py)
33	991	990	991	990	5	(Ph)
34	976		976		17a	(Py)
35	974sh.	965sh.	974sh.	965sh.	17a	(Ph)
36	946	940	946	939	5	(Py)
37	930	930	931	931	d_2	
38	930		930		10b	(Ph)
39	886	870	885	870	10a	(Py)
40	848	853	848	852	10a	(Ph)
41	848	850	847	849	11	(Ph)
42	785	786	785	786	11	(Py)
43	747	750	746	751	d_1	
44	721	725	721	725	d_1	
45	696		697		4	(Ph)
46	696		697		6a	(Ph)
47	663	666	662	666	6a	(Py)
48	640	647	639	647	6b	(Ph)
49	637		637		6a	(Py)
50	616	620	616	621	6b	(Py)
51	570	573	562	565	$\delta_{C=O}$	
52	447	455	447	455	16a	(Ph)
53	437	449	437	449	16a	(Py)
54	416	412	415	412	16b	(Ph)
55	404	405	404	404	16b	(Py)
56	379	381	370	372	$\gamma_{C=O}$	
57	288	293	288	292	$\delta(C_{Py}COC_{Ph})$	
58	238	244	238	244	$\delta^{as}(C_{Py}\cdots C\cdots C_{Ph})$	
59	222	226	222	227	$\delta^{sym}(C_{Py}\cdots C\cdots C_{Ph})$	
60	219		219		$\gamma^{as}(C_{Py}\cdots C\cdots C_{Ph})$	
61	154	156	154	156	$\gamma^{sym}(C_{Py}\cdots C\cdots C_{Ph})$	
62		105		105	torsion	
63		66		66	torsion	

ther the mode pertains to the phenyl or the pyridyl ring. The ring stretching vibrations for the phenyl and pyridyl rings (8a, 8b, 19a, 19b and 14) appeared in the region 1600-1300 cm^{-1}. The molecules of 2-benzoylpiridine and di-2-pyridyl ketone absorb in the nearly same frequency interval.

The carbonyl group of 4-benzoylpyridine is conjugated with the phenyl and pyridyl rings but the molecule is not planar. The steric repultion between the ortho hydrogen atoms do not cooperate to attain coplanarity and thus twisting both pyridyl and phenyl nuclei by 38° [7-10]. The new spectral information presented in Table 1 concerns the IR and Raman spectra for BP-^{18}O. All bands of 4-benzoylpyridine (4-BP) and 4-benzoylpyridine-^{18}O (4-BP-^{18}O) coincide within 1-2 cm^{-1} exept for three bands reffered to the carbonyl group. The ^{18}O isotopic substitution affects only the characteristic carbonyl frequencies. The carbonyl stretching band of 4-BP appears at 1657 cm^{-1} (IR) and 1662 cm^{-1} (Raman). The corresponding bands for 4-BP-^{18}O are observed at 1624 cm^{-1} and 1629 cm^{-1} respectively. (Fig.1). The isotopic shift $\nu_{C=O}$ of 33 cm^{-1} is equal to that of di-2-pyridyl ketone-^{18}O[1]. The in-plane deformation vibration (Fig.2) were found at 570 cm^{-1} (IR), 573 cm^{-1} (Raman) (Fig.3) for 4-BP and at 562 cm^{-1} (IR), 565 cm^{-1} (Raman) for 4-BP-^{18}O. A comparison of the spectra of both isotopic isomers shows that ^{18}O labelling results in a 8 cm^{-1} shift of $\delta_{C=O}$. In this way the band at 570 cm^{-1} in the IR spectrum of 4-BP is unambiguously assigned to $\delta_{C=O}$. The out-of-plane deformation vibration $\gamma_{C=O}$ appears at 379 cm^{-1} (IR) and 381 cm^{-1} (R) for 4-BP and at 370 cm^{-1} (IR), 372 cm^{-1} (R) for 4-BP-^{18}O. Hence, the

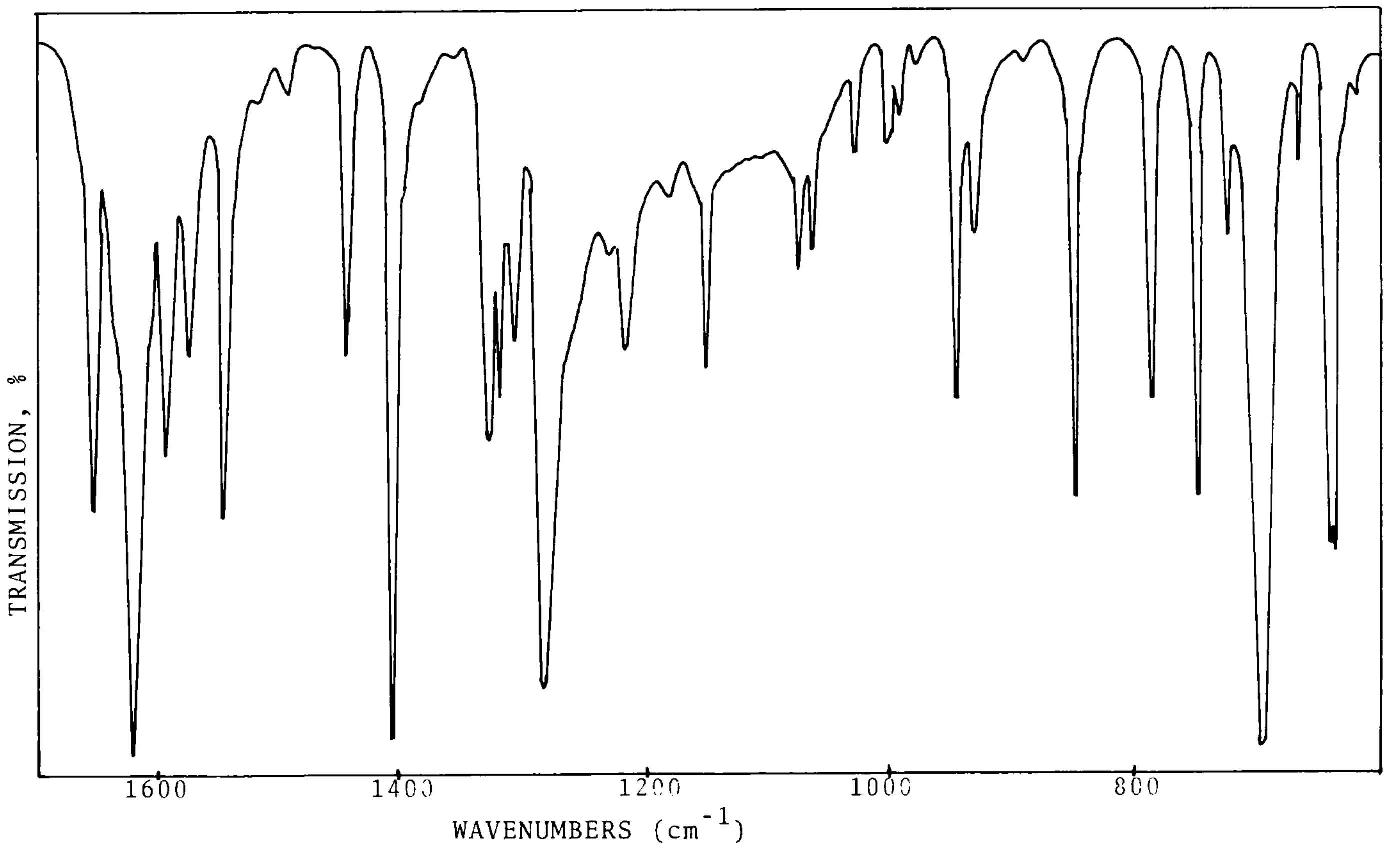

Fig.1. Infrared spectrum of 4-pyridyl ketone-^{18}O (71,8 atomic % -^{18}O) in the solid state, KBr pellet

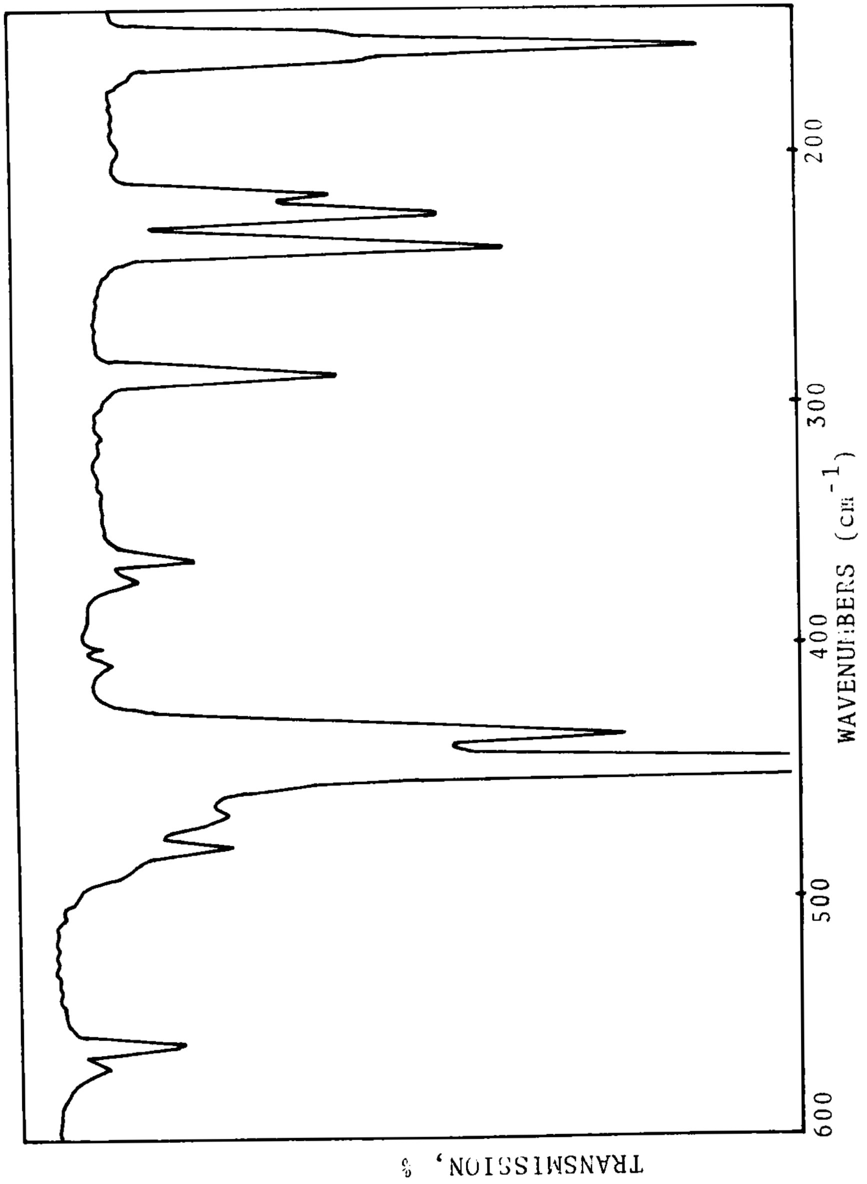

Fig.2. Infrared spectrum of 4-pyridyl ketone-^{18}O (71,8 atomic % -^{18}O) in the solid state, polyethylene pellet

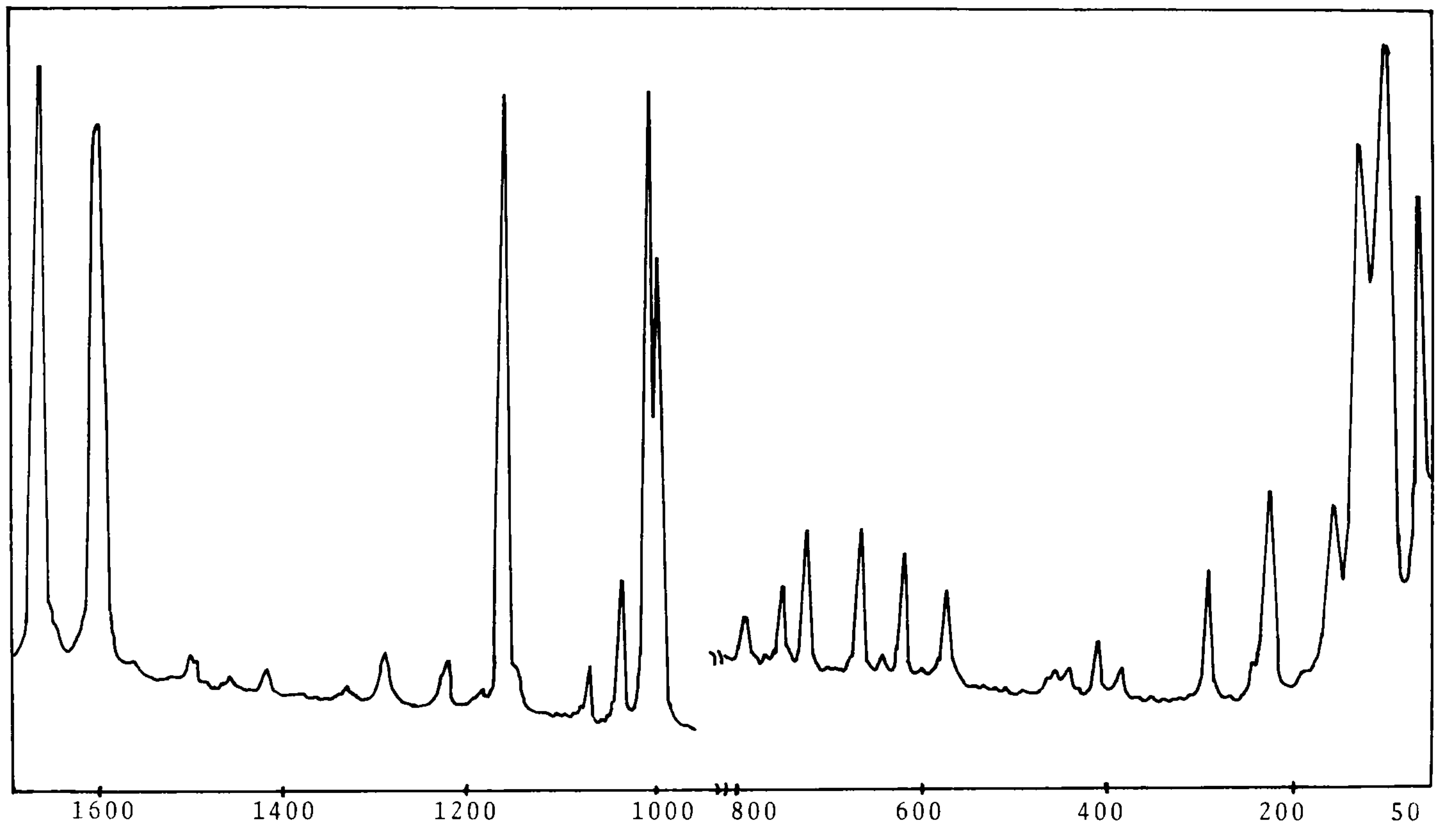

Fig.3. Raman spectrum of 4-pyridyl ketone in the solid state

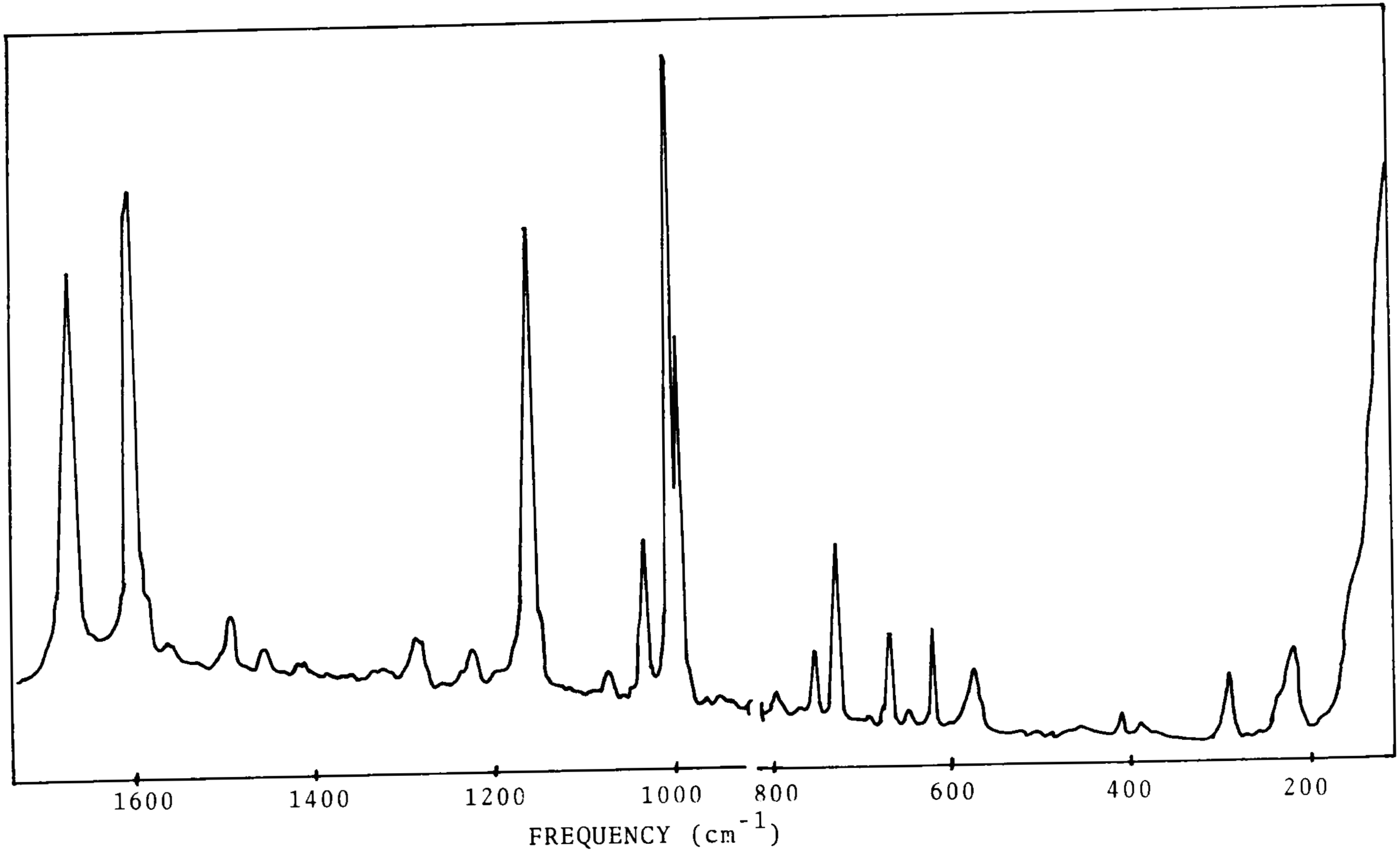

Fig.4. Raman spectrum of 4-pyridyl ketone; parallel polarization in molten state

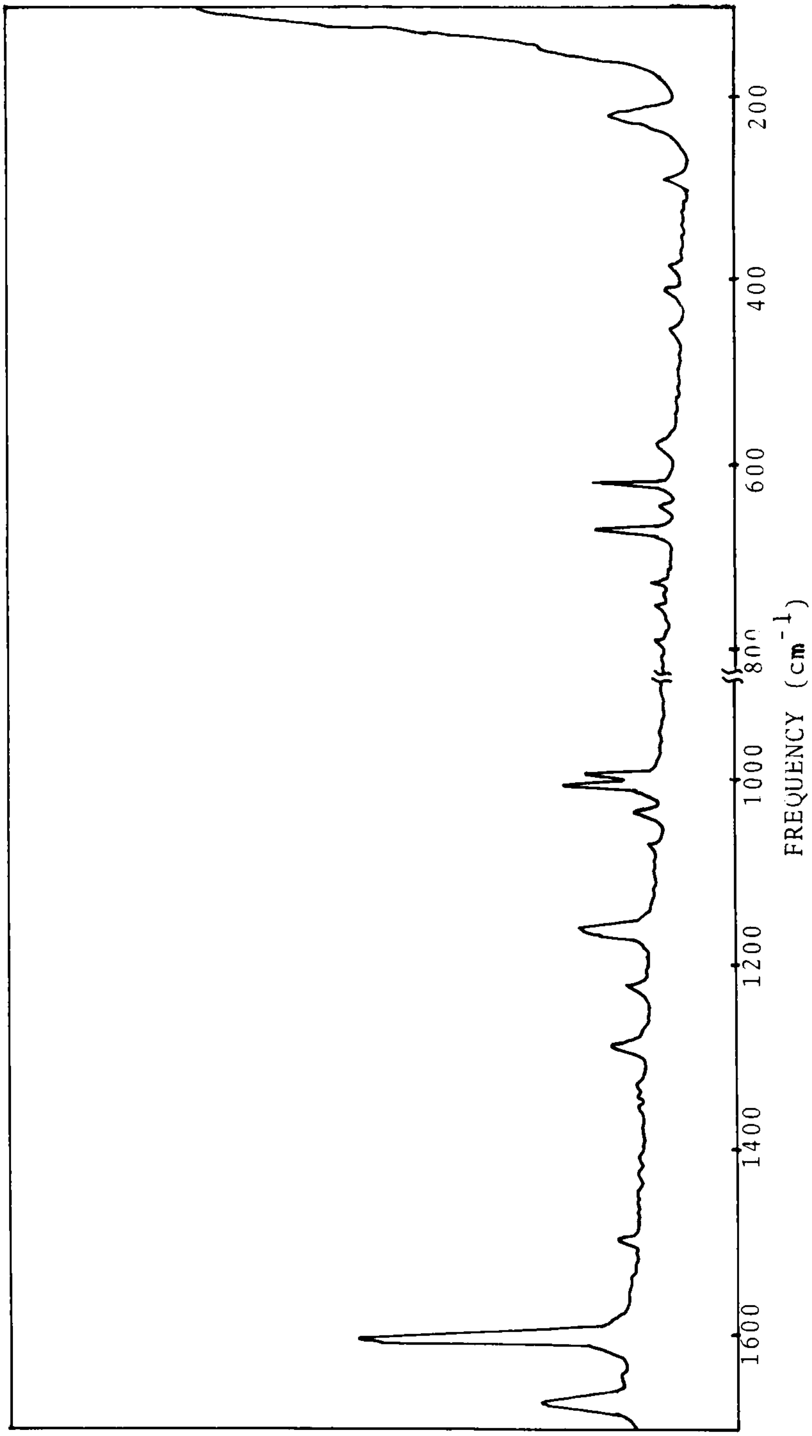

Fig.5. Raman spectrum of 4-pyridyl ketone, perpendicular polarization in molten state

^{18}O isotopic shifts 8 cm^{-1} for $\delta_{C=O}$, 9 cm^{-1} for $\gamma_{C=O}$ and 33 cm^{-1} for $\nu_{C=O}$ confirm the band assignment.

Di-2-pyridyl ketone and 2-benzoylpyridine display the breathing modes (1) in the frequency range 1000 - 1015 cm^{-1} while in the spectra of the benzophenone the same vibration appears at 999 cm^{-1}. Therefore, the bands at 1001, 999 cm^{-1} (IR) and 1006, 1000 cm^{-1} (R) are due to pyridyl and phenyl parts respectively.

The X-sensitive vibrations e_2 and e_1 are associated with stretching motions of the carbonyl carbon atom against the phenyl and pyridyl rings respectively. The strong IR band at 1285 cm^{-1} and very weak Raman band at 1289 cm^{-1} are attributed to e_2 vibration. In this way we confirm the assignment of Seth-Paul and coworkers[3]. The strong Raman band at 1158 cm^{-1} and the midle IR one at 1151 cm^{-1} can be assigned to e_1 mode. Hence, we correct the assignment in Ref.3 for this X-sensitive. The X-sensitive vibration d_2 is found at 930 cm^{-1} in both IR and Raman spectra of 4-benzoylpyridine. The vibrational mode d_1 appears at 721 cm^{-1} (IR) and 725 cm^{-1} (Raman). In the case of benzophenone[16] it was shown that this band is practically insensitive to deuteration.Its high IR intensity also supports the assignment.

The band at 640 cm^{-1} (IR) and 647 cm^{-1} (Raman) previously assigned as $\delta_{C=O}$ in Ref.3 is most probably the 6a vibration - in-plane radial ring C—C deformation. Normal coordinate analysis predicts a frequency range 640-670 cm^{-1} for the 6a vibration and 620-650 cm^{-1} for the 6b vibration. The assignment given in Table 1 for these modes is in a good agreement with the theory. We reassign the band at 570 cm^{-1} (IR) and 573 cm^{-1} (Raman) to $\delta_{C=O}$, which is refered to 6a mode in Ref.3.

The very weak Raman band at 458 cm^{-1} is attributed to 16a vibration. The previous assignment of this band to $\gamma_{C=O}$ is incorrect, since it is completely insensitive to ^{18}O isotopic substitution. The assignment of the band at 379 cm^{-1} (IR) to 6a mode[3] is revised here. The unambiguous assignment is $\gamma_{C=O}$. As it is shown in earlious papers[1,2] the bands between 300 and 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.

The results of the present study can be summerized as follows. All fundamental vibrations of 4-BP are situated in, or close to, the frequency ranges of the respective ones of benzophenone, 2-benzoylpyridine and di-2-pyridyl ketone. The carbonyl stretching band shows the ^{18}O shift equal to that of di-2-pyridyl ketone. By means of ^{18}O isotopic substitution in- and out-of-plane vibration of the carbonyl group were reliably assigned and some literature assignments were corrected.

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