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The Vibrational Spectra of 9-Fluorenone and Some of Its Isotopic Isomers

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THE VIBRATIONAL SPECTRA OF 9-FLUORENONE AND SOME OF
ITS ISOTOPIC ISOMERS

KEY WORDS: IR spectra; Raman spectra; isotope labelling; 9-Fluorenone; 9-Fluorenone- ^{18}O ; 9-Fluorenone- d_8 ; vibrational assignment; differential infrared linear dichroic spectra in nematic solutions.

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ABSTRACT

Vibrational spectra of 9-Fluorenone, 9-Fluorenone- ^{18}O and 9-Fluorenone- d_8 have been recorded in the solid state and solutions in the infrared and ($4000\text{--}100\text{ cm}^{-1}$) and in the Raman ($4000\text{--}50\text{ cm}^{-1}$). Differential infrared linear dichroic spectra 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 9-fluorenone as a single crystal have been studied by Zwarich et al [1].

Although thorough infrared and Raman studies of 9-fluorenone and some related compounds are available, discrepancies in the assignments of the normal modes still remain especially in the in and out-of-plane deformation vibration. In this connection the synthesis and complete vibrational assignment of 9-fluorenone- ^{18}O and 9-fluorenone- d_8 have been undertaken. The crystallographic determination of the structure of 9-fluorenone was made by Luss and Smith [2]. The crystals belong to the orthorhombic system with the space group Pcab (D_{2h}^{15}). The sixteen molecules are packed, two per asymmetric unit, in a unit cell having dimensions $a=16.068$, $b=18.650$ and $c=12.550$ Å. The molecules in the asymmetric unit are almost parallel; the angle between the planes of the two different molecules is 5.9° [2]. The individual rings of each molecule are bent about 1° with respect to the overall molecular plane so that the covering molecular symmetry remains essentially C_{2v} . The molecule of 9-fluorenone has 60 normal vibrations distributed in $\Gamma=21\text{A}_1+9\text{A}_2+10\text{B}_1+20\text{B}_2$. All bands are Raman and IR active except for the A_2 symmetry class forbidden in the IR.

The present article contains experimental data for the IR and Raman spectra of 9-fluorenone (FL) 9-fluorenone- ^{18}O (FL- ^{18}O) and 9-fluorenone- d_8 (FL- d_8) as well as differential infrared linear dichroic spectra (DIRLD) of FL and FL- d_8 .

EXPERIMENTAL

All ketones were obtained and purified by multifold recrystallization from hexane and isooctane followed by sublimation in vacuo. Reagent grade FL- d_0 (Fluka AG) was also purified by the same double sublimation and recrystallization. The preparation of FL- ^{18}O was

carried out according to Halman and Pinchas [3]. FL-d₈ was obtained from deuterated fluorene by oxidation with Na₂Cr₂O₇. Infrared spectra of all ketones were recorded in CsI and polyethylene pellets with a Bruker IFS-113 v FTIR spectrometer in the 4000–100 cm⁻¹.

Differential infrared linear dichroic (DIRLD) spectra of the studied compounds were taken with a Bruker IFS-113 v FTIR spectrometer in the 4000–400 cm⁻¹ region applying the method described in Ref. 4.

Raman spectra, 4000–50 cm⁻¹, were registered using a 60 mW excitation with the 514,5 nm line of an Ar⁺ laser on a Coderg triple monochromator spectrometer. The deuterium and ¹⁸O content in FL-d₈ and FL-¹⁸O was determined by mass spectrometry.

RESULTS AND DISCUSSION

The observed bands and their assignment are given in Table 1. The nomenclature cited in Ref. 5 is used here for the description of the vibrational modes of o-disubstituted benzene rings simultaneously with the assignment of Zvarich [1].

Table 1.

Vibrational assignment of fluorenone-d₀, ¹⁸O and d₈

ν_i (cm ⁻¹)	Fl-d ₀		Fl- ¹⁸ O		Fl-d ₈		Assignment
	IR	Ra	IR	Ra	IR	Ra	
1	3088	3093	3088	3092	2289	2292	a ₁
2	3080	3082	3088	3088	2281	2280	b ₂

(continued)

Table 1 Continued

3	3069	3067	3069	3067	2279	2280	a_1	20b
4	3049	3049	3049	3049	2275	2274	b_2	
5	3049	3049	3049	3049	2274	2274	a_1	2
6	3029	3025	3025	3025	2270	-	b_2	
7	3018	-	3018	-	2266	2266	a_1	7a
8	3018	-	3018	-	2266	2266	b_2	
9	1719	1715	1681	1680	1711	1708	a_1	$\nu_{C=O}$
10	1613	1613	1613	1613	1587	1583	b_2	8a
11	1598	1602	1599	1602	1572	1576	a_1	
12	1594	-	1594	-	1546	-	b_2	8b
13	1594	-	1594	-	1546	1546		
14	1481	1481	1481	1481	1386	1384	*	19a
15	1476	1470	1476	1470	1378	1376	a_1	
16	1450	1452	1450	1452	1338	-	a_1	19b
17	1444	1444	1444	1444	1330	1330	b_2	
18	1342	1341	1342	1341	1301	-	b_2	14
19	1322	1322	1322	1322	1296	1295	a_1	
20	1371	1371	1371	1372	1038	1036	a_1	3
21	1368	1367	1367	1367	-	-		
22	1297	1292	1298	1292	-	-	b_2	e_2
23	1212	1212	1212	1212	-	1200	a_1	
24	1194	1198	1194	1198	873	872	a_1	9a
25	1186	1180	1186	1180	764	765	b_2	
26	1158	1159	1158	1159	746	763	a_1	9b
27	1148	1150	1148	1150	739	736		
28	1148	1150	1148	1150	1090	1090	a_1	e_1

29	1098	1100	1097	1100	830	-	b ₂	18a
30	1084	-	1084	-	800	-		
31	1011	1016	1011	1016	939	940	a ₁	1
32	1002	-	1002	-	939		b ₂	
33	978	-	978	-	800	800		17a
34	960	-	960	-	773	-	*	
35	954	-	954	-	764	-	*	17b
36	952	950	952	950	-	-	*	
37	917	919	918	919	903	902	b ₂	d ₂
38	890	-	890	-	-	-	*	
39	880	-	880	-	696	686		15
40	814	815	814	815	786	-	*	
41	786	785	786	785	594	594	b ₁	10a
42	773	773	773	773	582	-	a ₁	
43	744	740	744	740	-		*	11
44	736	-	736	-	569	570	*	
45	724sh	724	724sh	724	696	-	a ₁	d ₁
46	-	700	-	700	520	519	a ₁	4
47	669	-	669	-	627	625	*	
48	650	650	650	650	-	-	a ₁	6a
49	617	618	617	618	ovl.	-	*	
50	411	411	411	411	407	405	*	6b
51	555	555	545	545	ovl.	555	b ₁	δ(C=O)
52	442	444	442	443	418	416	b ₁	16a
53	422	422	422	422	412	405	*	
54	407	-	407	-	376	-	a ₁	

(continued)

Table 1 Continued

55	400	—	399	—	368	—	*	16b
56	285	285	276	276	—	—		$\gamma(\text{C}=\text{O})$
57	285	285	285	285	283	281		$\delta(\text{C}-\text{CO}-\text{C})$
58	207	208	207	208	203	—		$\delta(\text{Ph.pl.Ph})$
59	175	165	175	165	—	170		$\gamma(\text{Ph.pl.Ph})$
60	120	129	120	129	—	120		$\gamma(\text{Ph.pl.Ph})$

Tentative assignments are marked with an asterisk.

The conjugation of the carbonyl group with both phenylene groups favors a planar molecular configuration. The crystallographic data of Luss and Smith show as mentioned that the dihedral angle between the individual rings of each molecule is about 1° . The IR spectra of FL- ^{18}O are shown in the Fig. 1 and 2. The IR spectrum of FL- d_8 is presented in Fig. 3. Differential infrared dichroic (DIRLD) spectrum of FL- d_0 oriented in the nematic liquid crystal ZLI 1538 (Merck), measured by 30°C is shown in Fig. 4. The Raman spectrum of FL- ^{18}O in the $4000\text{--}50\text{ cm}^{-1}$ Raman shifts frequency region is presented in the Fig. 5 and 6.

The new spectral information contained in Table 1 concerns the IR and Raman spectra of FL- ^{18}O and FL- d_8 . Data for FL- ^{18}O were also included in Table 1 although except for three carbonyl bands they coincide with those for FL within $1\text{--}2\text{ cm}^{-1}$. The ^{18}O isotopic substitution prominently influences only the characteristic carbonyl frequencies. The $(\text{C}=\text{O})$ stretching bands appears at 1680 in the Raman and 1681 cm^{-1} in IR. The in-plane

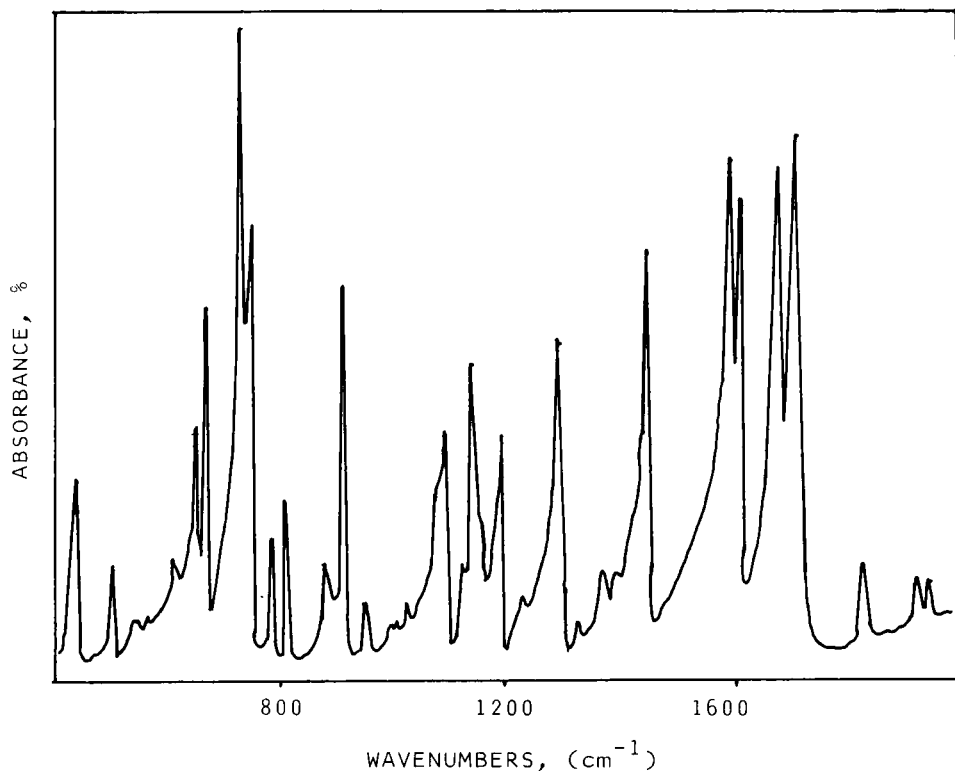


Fig.1. Infrared spectrum of fluorenone - ^{18}O in the middle-frequency region $2000\text{--}400\text{ cm}^{-1}$.

deformation vibration $\delta(\text{C}=\text{O})$ is found at 555 cm^{-1} in both IR and Raman while the out-of-plane one, $\gamma(\text{C}=\text{O})$ lies at 285 cm^{-1} .

Isotopic shifts of 10 cm^{-1} for $\delta(\text{C}=\text{O})$ and 9 cm^{-1} for $\gamma(\text{C}=\text{O})$ confirm unambiguously the band assignment.

Hence, the assignment of the deformation vibrations reported in ref. 1 is revised here.

Ring vibrations

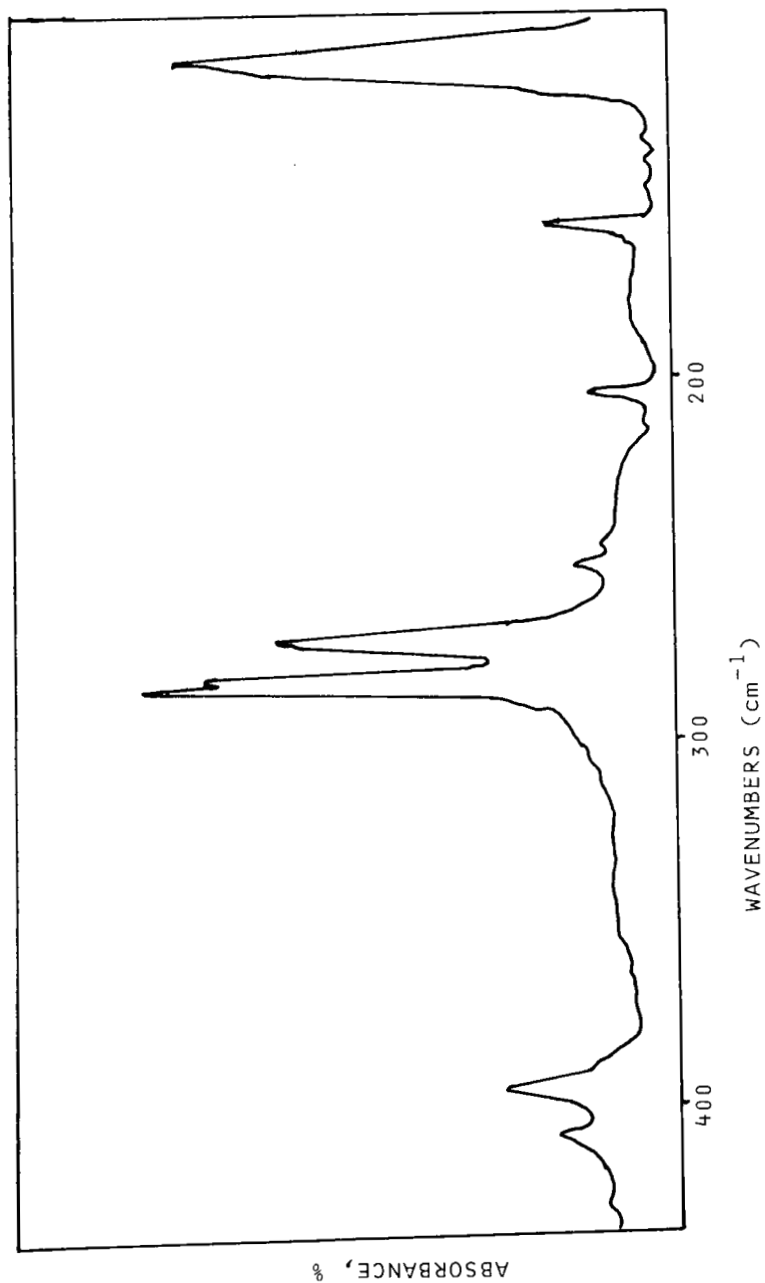


Fig. 2. Infrared spectrum of fluorenone - ^{18}O in the low frequency region 400-100 cm^{-1}

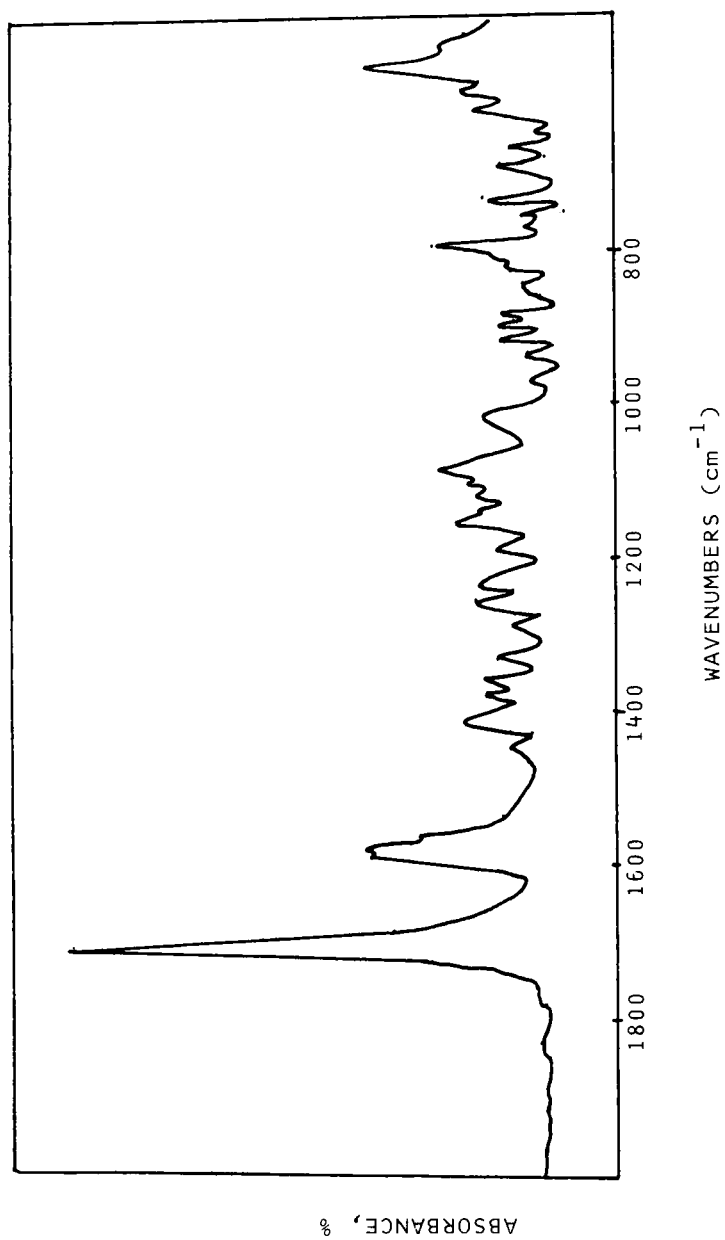


Fig.3. Infrared spectrum of fluorenone - d_8 in the middle-frequency region 2000-400 cm^{-1}

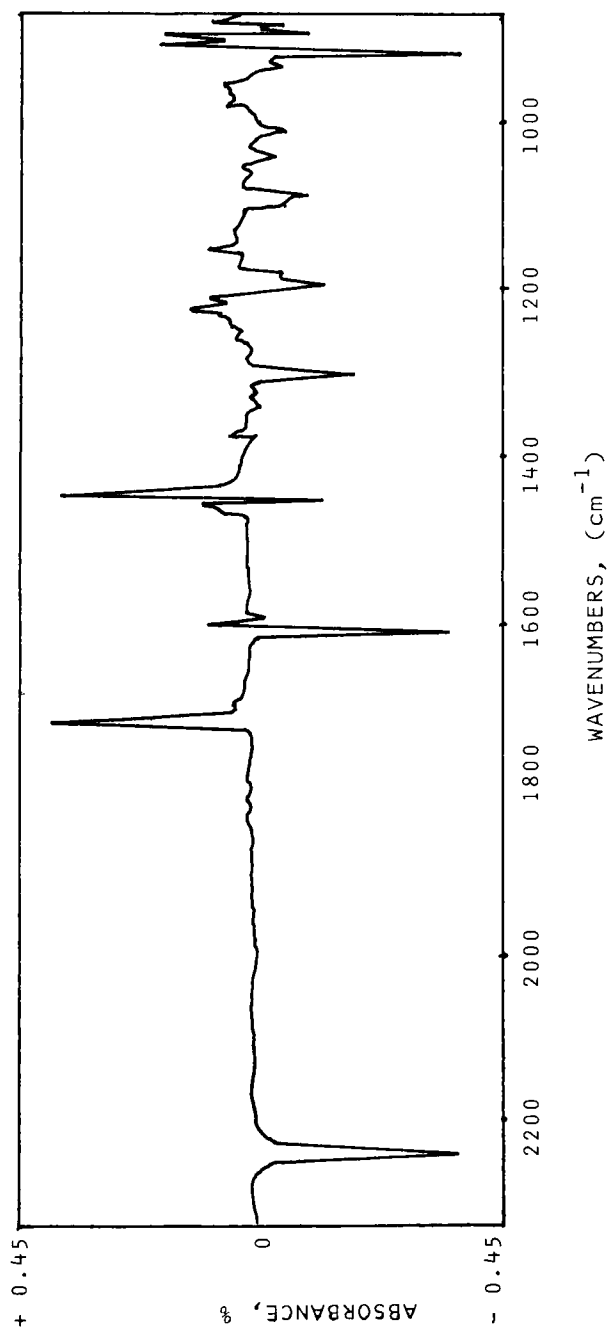


Fig. 4. Differential infrared linear dichroic (DIRLD) spectrum of fluorenone-d₈ oriented in the nematic liquid crystal ZLI 1538.
The spectrum is measured at 30 °C.

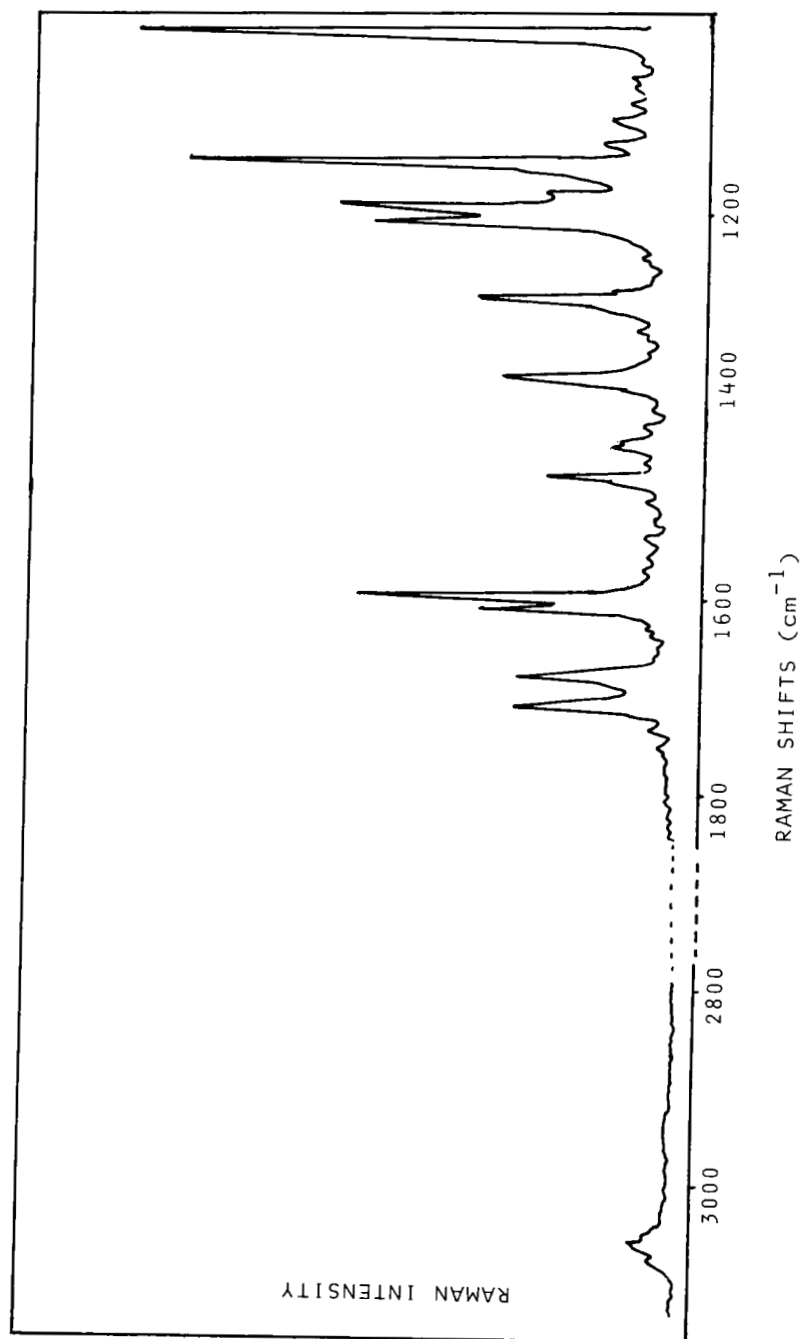


Fig. 5. Raman spectrum of fluorenone-¹⁸O in the 3200-1000 cm⁻¹ Raman shifts frequency region.

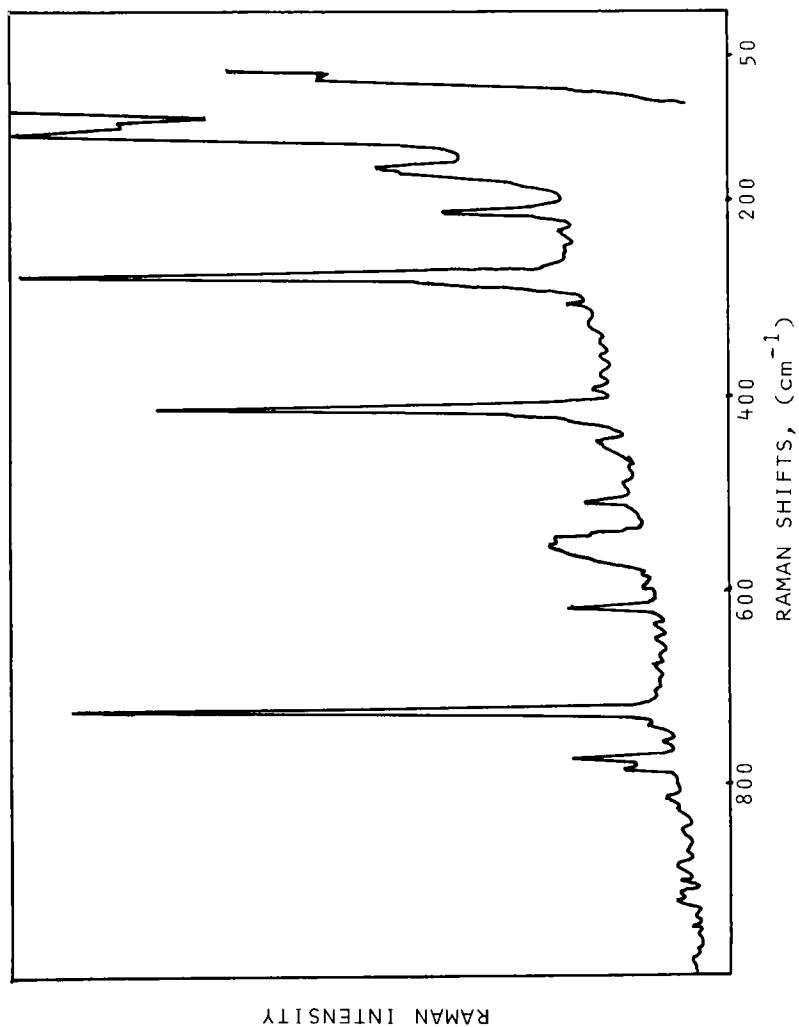


Fig.6. Raman spectrum of fluorenone-¹⁸O in the 1000-50 cm⁻¹ Raman shifts frequency region.

The five normal vibrations having a predominant character as (C-C)-ring stretching modes, namely 8a, 8b, 19a, 19b and 14 are situated in the $1612\text{--}1290\text{ cm}^{-1}$ frequency region and they are not greatly influenced by the conjugation with the carbonyl group in fluorenone. The frequencies of the vibrational pair 8a and 8b are at 1613 and 1601 cm^{-1} (Ra) and $1612\text{--}1599\text{ cm}^{-1}$ (IR). Deuteration causes a shift of about 26 cm^{-1} , the corresponding isotopic shift by the benzophenone is 29 cm^{-1} [6]. Our assignment is in a good agreement with the prediction of Fuson et al [5] and Varsanyi [7]. As it is known [8,9], the frequencies of the vibrational pair 8 in disubstituted benzenes are rather insensitive to the nature of the substituent whilst the deuteration influences these frequencies to a greater extent. For this reason, the isotopic shift of 26 cm^{-1} observed in FL- d_8 is in accordance with the observed shift for deuterated chlorobenzenes [5]. The assignment of vibrations 19a and 19b of FL and its isotopic species is also in a good agreement with our previous results [6] and with the results of other authors [8]. The strong IR bands at 1451 cm^{-1} in the FL spectrum splits in the DRLD spectrum into two bands of opposite polarisation at 1459 and 1453 cm^{-1} (Fig. 4), due to in-plane ring-ring interaction.

The ring vibration 14 "Kekule" is found in a frequency range established by Whiffen [9] and Varsanyi [7].

In the Fig.4 one can see that all bands belonging to the symmetry class A_1 have positive (+) signs while the bands of class B_2 are found to have negative ones. The bands of class B_1 cannot be distinguished from those of A_1 because of the averaging around the director of the nematic solvent, therefore it is difficult to determine their signs.

The very weak infrared band at 1149 cm^{-1} of FL is assigned here to the vibration $e_1(a_1\text{ band})$. The high intensity of the Raman counterpart at 1150 cm^{-1} support unambiguously this attribution.

The band at 1297 cm^{-1} and that one at 1149 cm^{-1} have opposite polarization in DIRLD spectrum that confirm the assignment to e_2 and e_1 stretching vibrations of FL.

C-H in plane vibrations

The bands at 1371, 1368, 1194, 1186, 1097, 1084, 1060 and 1034 cm^{-1} are assigned to syn- and anti-phase components of vibrations 3, 9a, 9b and 18a. The splittings between 3 and 26 cm^{-1} are close to those of benzophenone [6].

C-H out-of-plane vibrations

We started the vibrational analysis of those rather complex spectra, with the normal vibrations arising from the phenylene rings. For comparison purposes we have utilized the assignment for the normal modes of benzophenone [6] has been subject of our previous investigation. Our proposed assignment for the phenylene C-H out-of-plane bending vibration of FL and its isotopic isomers is given in Table 1 together with the observed IR and Raman spectra. As be seen the above mentioned frequencies lie very close to those of benzophenone and its isotopic derivatives [6]. A normal coordinate calculation might probably confirm the assignment proposed here.

Ring bending vibration

The strong Raman band at 1016 cm^{-1} and weak IR one at 1011 cm^{-1} are assigned to the breathing vibration of the FL. The band at 724 cm^{-1} is attributed to d_1 mode. The remaining vibrations of this group are d_2 , 4, 6a, 6b, 16a and 16b. They coincide with the corresponding

vibrations of benzophenone or lie in their vicinity. The bands above 285 cm^{-1} are assigned to the bending motion of the carbonyl group with respect to the both phenylene rings.

On the basis of measurements of the infrared and Raman spectra of FL, FL- d_8 , FL- ^{18}O in solution in the solid state and in oriented nematic solutions, we propose an assignment of the observed bands to the internal fundamental vibrations. The assignments are supported by the comparison of the present data with the corresponding vibrational analysis of benzophenone [6]. The used isotopic substitution with ^{18}O in the carbonyl group led to an unambiguous detection of the in-plane and out-of-plane carbonyl bands.

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