On the Absorption Spectrum of Isoquinoline and 3-Methylisoquinoline in Tetrahydrofuran and n-Paraffin

A. Kawski, I. Gryczyński, and Z. Kojro

Luminescence Research Group, Institute of Physics, University of Gdańsk, Gdańsk, Poland

I. Janič

Department of Physics, University, Novi Sad, Yugoslavia

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The quasilinear absorption spectra of isoquinoline and 3-methylisoquinoline have been studied in tetrahydrofuran and n-paraffin solvents at 77 °K. An analysis of the vibrational structure in the first electronic excited singlet state (S_1) is given. Different multiplicities of the absorption spectra have been studied and explained.

1. Introduction

The electronic absorption and luminescence spectra of many aromatic and N-heterocyclic compounds in well chosen crystalline n-paraffin solvents consist of a series of very narrow bands, called quasilines. This is the Shpolskii effect (see ref. for a review [1]). Recently [2], quasilinear luminescence spectra have been found for some compounds in tetrahydrofuran (THF) too.

Reprint requests to Prof. Dr. A. Kawski, Luminescence Research Group, Institute of Physics, University of Gdańsk, *Gdańsk/Polen*.

Table 1. Absorption spectrum of isoquinoline at 77 °K.

No	Intensity	Wavelength (Å)	Wavenumber (cm^{-1})	Multiplet $\Delta\tilde{\nu}$	$\Delta\tilde{\nu}$	Mean value $\Delta\tilde{\nu}$	Possible assignment	Accurateness of the analysis
			in n-pentane (doublet structure)					
1	m	3184.1	31406	35			0 — 0′	
2	m	3180.5	31441				0_1 — 0_1′	
3	w	3137.5	31872	40	466	469	0 — 466	
4	w	3133.6	31912		471		0_1 — 471	
5	w	3112.5	32128	42	722	726	0 — 722	
6	w	3108.5	32170		729		0_1 — 729	
7	vw	3085.8	32406	43	1000	1004	0 — 1000	
8	vw	3081.7	32449		1008		0_1 — 1008	
9	m	3049.6	32791	41	1385	1388	0 — 1385	
10	n	3045.8	32832		1391		0_1 — 1391	
			in THF (triplet structure)					
1	s	3183.7	31410	41			0 — 0′	
2	m	3179.5	31451	60			0_1 — 0_1′	
3	vw	3173.4	31511				0_2 — 0_2′	
4	vw	3155.6	31689		279	279	0 — 279	
5	vw	3136.9	31878		468	468	0 — 468	
6	mw	3111.9	32134	37	724	722	0 — 724	
7	w	3108.3	32171		720		0 — 720	
8	vw	3088.7	32376		966	966	0 — 966	
9	w	3085.0	32414		1004	1004	0 — 1004 $\approx$ 279+724	+1
10	w	3050.7	32779		1369	1369	0 — 1369	
11	w	3048.5	32803		1393	1393	0 — 1393	
12	vw	3042.6	32866		1456	1456	0 — 1456 $\approx 2\times$724	+8
13	ww	3017.6	33138		1728	1728	0 — 1728 = 279+2×724	+1
14	vvw	2985.8	33491		2081	2081	0 — 2081 = 724+1369	−12

Table 2. Absorption spectrum of 3-methylisoquinoline at 77 °K.

No	Intensity	Wavelength (Å)	Wavenumber (cm^{-1})	Multiplet $\Delta\tilde{\nu}$	$\Delta\tilde{\nu}$	Mean value $\Delta\tilde{\nu}$	Possible assignment	Accurateness of the analysis
			in n-hexane (quintet structure)					
1	vw	3265.6	30622				$0 - 0'$	
2	S	3255.2	30720	39			$0_1 - 0_1'$	
3	w	3251	30759	31			$0_2 - 0_2'$	
4	vw	3247.8	30790	39			$0_3 - 0_3'$	
5	vw	3243.6	30829				$0_4 - 0_4'$	
6	w	3214.3	31110		390		$0_1 - 390$	
7	m	3204.3	31208	40	488		$0_1 - 488$	
8	vw	3200.2	31248	68	489	488	$0_2 - 489$	
9	vw	3193.2	31316		487		$0_4 - 487$	
10	w	3179.8	31448		728	728	$0_1 - 728$	
11	w	3176.2	31484		764	764	$0_1 - 764$	
12	w	3154.1	31704		984	984	$0_1 - 984 = 2\times488$	+8
13	vw	3131	31938		1218	1218	$0_1 - 1218 = 488+728$	+2
14	vw	3129.5	31954		1234	1234	$0_1 - 1234$	
15	vw	3122.5	32026		1306	1306	$0_1 - 1306$	
16	vw	3120.4	32047		1327	1327	$0_1 - 1327$	
17	w	3112.5	32128		1408	1408	$0_1 - 1408$	
18	vw	3108	32173		1453	1453	$0_1 - 1452 = 2\times728$	−3
19	vw	3106	32196		1476	1476	$0_1 - 1476 = 3\times488$	+12
			in THF (triplet structure)					
1	S	3268.2	30598	55			$0 - 0'$	
2	mw	3262.3	30653	44			$0_1 - 0_1'$	
3	w	3257.6	30697				$0_2 - 0_2'$	
4	w	3227.0	30988	61	390	393	$0 - 390$	
5	vw	3220.7	31049		396		$0_1 - 396$	
6	m	3216.7	31088	56	490		$0 - 490$	
7	vw	3210.9	31144	46	491	491	$0_1 - 491$	
8	vw	3206.1	31190		493		$0_2 - 493$	
9	w	3192.1	31327		729	729	$0 - 729$	
10	vw	3166.7	31578		980	980	$0 - 980 = 2\times490$	0
11	vw	3142.8	31819		1221	1221	$0 - 1221 = 490+729$	+2
12	vw	3132.5	31923		1325	1325	$0 - 1325$	
13	vw	3124.7	32003		1405	1405	$0 - 1405$	
14	vw	3118.9	32062		1464	1464	$0 - 1464 = 2\times729$	+6
							$= 3\times490$	−6

The quasilinear phosphorescence spectra of isoquinoline are analysed in the literature [3, 2]. The fluorescence of isoquinoline is quenched in some solvents by spin-orbital interaction, caused by the n-electrons [4]. Addition of a methyl group to the isoquinoline skeleton diminishes the spin-orbital interaction. For 3-methylisoquinoline both phosphorescence and fluorescence occur in hydrocarbon solvents. The best quasilinear fluorescence spectrum of 3-methylisoquinoline was obtained in n-hexane and the values of internal vibrational frequencies in the ground electronic state (S_0) were determined [3].

The present work analyses the quasilinear vibrational structure in the first absorption transition of isoquinoline and 3-methylisoquinoline in n-paraffins and in THF at 77 °K.

2. Experimental

Isoquinoline (Merck) and 3-methylisoquinoline (Koch-Light LTD.) Isoquinoline were purified by

vacuum distillation. The solvents used, n-pentane, n-hexane and n-heptane were of spectral quality. Tetrahydrofuran (THF) was purified as in the work of Kirkbright and De Lima [2]. The solutions ($5 \cdot 10^{-4} < C < 5 \cdot 10^{-3}$ mol/l) in a quartz cuvette (0.5 to 1 mm) were rapidly cooled by liquid nitrogen to 77 °K in a quartz Dewar and the quasilinear absorption spectra measured with the apparatus described elsewhere [5].

3. Results and Discussion

The analysis of the quasilinear absorption spectra of isoquinoline in n-pentane and THF are given in Tables 1 and 2. The quasilinear absorption spectrum of isoquinoline in n-pentane has a doublet structure with average intervals between the components of 40 cm^{-1}. In THF it has a triplet structure with very different intensities. The strongest line is the first one in the group $O - O'$. A much higher relativ intensity of one line in a given group allowes the observation of this line only in the remaining groups.

Table 2 represents the quasilinear absorption spectrum of 3-methylisoquinoline in n-hexane and THF. The spectrum of 3-methylisoquinoline in n-hexane consists of 13 groups of lines forming a quintet structure with the second as the strongest line. An exact determination of the sites of the remaining lines in the quintets (pose the first) was impossible because of their very weak intensity. The quasiline absorption spectrum of 3-methylisoquinoline in THF shows, similar to the case of isoquinoline, a triplet structure the strongest line of which is the first one ($O - O'$ transition).

The obtained values of the $O - O'$ ($S_0 \rightarrow S_1$) transitions of isoquinoline in n-pentane (31406 cm^{-1}) agree well with those in THF (31410 cm^{-1}). For 3-methylisoquinoline in THF we observed a small shift in the wavelength of the $O - O'$-transition compared with $O - O'$ in n-hexane. The obtained values of the basic vibrations of isoquinoline and 3-methylisoquinoline in their first electronic states are the same within the limits of experimental error for the used solvents (see Table 1 and 2). Further details are given in Table 1 and 2. The different multiplets we ascribe to different centres whose electron levels are shifted relative to one another. The intensities of the particular lines in a multiple are tightly connected with the population of different possible positions of the solute molecule in the crystalline lattice of the solvents [1]. It follows that the quasilinear spectra of molecules with a similar structure (the greatness of the molecule) should be characterized with the same multiplicities, as is the case at isoquinoline and 3-methylisoquinoline in THF.

Table 3. Comparison of the fundamental oscillations of isoquinoline and 3-methylisoquinoline.

Ground state			First excitet singlet state
	Isoquinoline		
Infrared [6]	Raman bands [6]	Phospho-rescence [3]	Absorption (the mean values from different solvents)
182	183		
278.5			279
458.6	460		468.5
		607	
741.5	747		724
970.6	959	961	966
1013.5	1014		1004
1376.8			1369
1381.6	1383	1381	1390.5
	3-methylisoquinoline		
Infrared [3]		Fluo-rescence [3]	Absorption (the mean values from different solvents)
410		410	391.5
510		510	489.5
754		792	728.5
946		940	
1040		1039	
1376		1394	1324
1425			1406.5

Table 3 gives the observed frequencies of the investigated molecules in the first excited electronic state and the corresponding vibrational frequencies in the ground electronic state found in the phosphorescence [3] and fluorescence [3] and also from the Raman [6] and infra-red [3, 6] spectra.

[1] E. V. Shpolskii and T. N. Bolotnikova, Pure and Applied Chemestry, **37**, 183 [1974].
[2] G. F. Kirkbright and C. G. De Lima, Chem. Phys. Letters **37**, 165 [1976].
[3] I. Janić and A. Kawski, Advan. Mol. Relaxation Proc. **5**, 185 [1973].
[4] V. L. Ermolayev and I. P. Kotlar, Opt. Spektrosk. **9**, 359 [1960].
[5] A. Kawski, Z. Kojro, I. Gryczyński, and P. Bałuk, Bull. Acad. Polon. Sci. Ser. Sci. Math. Astr. Phys. **35** [1977], in press.
[6] S. C. Wait, Jr., and J. C. McNerney, J. Mol. Spectrosc. **34**, 56 [1970].