

Absorption and Fluorescence Spectra of some 1,3,4-Oxadiazole Derivatives in n-Paraffins at 77 K*

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The quasilinear absorption and fluorescence spectra of 2-(1-naphthyl)-5-phenyl 1,3,4 oxadiazole, 2-(2-naphthyl)-5-phenyl 1,3,4 oxadiazole, 2-(1-naphthyl)-5-(4-biphenyl)-1,3,4 oxadiazole and 2-(2-naphthyl)-5-(4-biphenyl)-1,3,4 oxadiazole have been studied in n-hexane, decane and nonane at 77 K. An analysis of the vibrational structure in the first electronic excited singlet state (S_1) and in the ground state (S_0) is given. Internal oscillations in the investigated molecules found from the quasilinear spectra are in agreement with those found in the infrared spectra.

Quasilinear absorption and luminescence spectra of simple aromatic and N-heterocyclic compounds in n-paraffins [1] and in similar solvents [2, 3], and of more complicated compounds such as oxazole and oxadiazole derivatives [4–6] have been published. The present work analyses the quasilinear vibrational structure in the ground and the first electronic excited singlet states of the following 1,3,4-oxadiazole derivatives (supplied by Nuclear Enterprises, scintillation grade):

2-(1-naphthyl)-5-phenyl 1,3,4 oxadiazole (α -NPD),
2-(2-naphthyl)-5-phenyl 1,3,4 oxadiazole (β -NPD),
2-(1-naphthyl)-5-(4-biphenyl)-1,3,4 oxadiazole (α -NBD),
2-(2-naphthyl)-5-(4-biphenyl)-1,3,4 oxadiazole (β -NBD).

Spectroscopic-grade n-hexane, decane and nonane were used as solvents. The apparatus used was similar to the one described in Ref. [7]. The absorption measurements were performed with a xenon lamp XHP 450. The fluorescence was excited with the 337.1 nm line of an N_2 -nitrogen laser. The infrared spectra were measured with a Perkin-Elmer spectrophotometer.

Tables 1 and 4 show the results and a full vibrational analysis of these quasilinear spectra. Lines

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with a half width $>10\text{ cm}^{-1}$ we call bands. The best spectra were observed in n-hexane. The quasilinear spectra of α -NPD in n-hexane and decane have a singlet structure. The absorption and fluorescence spectra of α -NPD begin with the lines 28735 cm^{-1} and 28538 cm^{-1} , respectively, which corresponds to the pure electron ($0-0'$) transition. It can be seen that the so-called mirror symmetry of absorption and fluorescence bands is not exactly fulfilled. From Table 1 it follows that only the wave-numbers 488 cm^{-1} and 1277 cm^{-1} in the absorption spectrum are approximately the same as in the

Table 5. Internal ground frequencies in molecules of α -NPD and β -NPD and some published assignments.

From kwasi- linear spectra $\tilde{\nu}[\text{cm}^{-1}]$	From infrared spectra $\tilde{\nu}[\text{cm}^{-1}]$	Interpretation	Comparison with literature $\tilde{\nu}[\text{cm}^{-1}]$
80		Lattice vibrations (n-hexane)	72 [8]
161 190 215 217 250 337 360 366 472 488		Planar deformation vibrations of aryl groups (phenyl, naphthyl) in regard to the central group (oxadiazole)	170–270 [9]
519 570 572		Planar deformation vibrations of naphthyl in regard to the oxa- diazole ring	517 [10]
874 875	875	Planar deformation vibrations of naphthyl group	
921 997 1020 1023 1061	919 990 1020	Vibrations of phenyl ring	
1372 1380 1390	1074	Vibrations of naphthyl ring	1380 [4]
1442 1436	1455	Vibrations of oxa- diazole ring	
1531 1548 1584	1536 1557 1585	Skeleton vibrations of oxadiazole ring	1510– 1570 [4]
1603– 1607	1616	Vibrations of naphthyl ring	1625 [10]



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Table 1. α -NPD at 77 K.

No	Wavenumber (cm^{-1})	$\Delta\bar{\nu}$ (cm^{-1})	Possible assignment	Accurateness of the analysis	Remarks
Absorption in n-hexane ($c=5 \times 10^{-5}$ M)					
1	28735		0-0'		band
2	28985	250	0-250		line
3	29223	488	0-488		band
4	29560	825	0-825		band
5	29850	1115	0-1115		line
6	30012	1277	0-1277		band
7	30266	1531	0-1531		band
8	30845	2110	0-2110 $\approx$ 1277+825	+8	band
9	31220	2485	0-2485 $\approx$ 3 $\times$ 825	+10	band
10	31546	2811	0-2811 $\approx$ 1531+1277	+3	band
11	31807	3072	0-3072 $\approx$ 2 $\times$ 1531	+10	band
12	32072	3337	0-3337 $\approx$ 3072+250	+15	band
Fluorescence in n-hexane ($c=10^{-4}$ M)					
1	28538		0-0		band
2	28458	80	0-80		band
3	28377	161	0-161		band
4	28321	217	0-217		line
5	28066	472	0-472		line
6	28019	519	0-519		line
7	27663	875	0-875		band
8	27617	921	0-921		line
9	27518	1020	0-1020		band
10	27278	1260	0-1260		band
11	27225	1313	0-1313		band
12	27137	1401	0-1401 $\approx$ 80+1313	+8	band
13	26990	1548	0-1548		band
14	26838	1700	0-1700 $\approx$ 1548+161	-9	band
15	26476	2062	0-2062 $\approx$ 1548+519	-5	line on a band
16	26096	2442	0-2442 $\approx$ 1548+875	+19	line
17	25740	2798	0-2798 $\approx$ 1548+1260	-10	band
18	25445	3093	0-3093 $\approx$ 2 $\times$ 1548	-3	band
19	25336	3202	0-3202 $\approx$ 2 $\times$ 1548+80	+26	line
20	25233	3315	0-3315 $\approx$ 2 $\times$ 1548+217	+2	line
21	25088	3450	0-3450 $\approx$ 2 $\times$ 1260+921	+9	line
22	24931	3607	0-3607 $\approx$ 2 $\times$ 1548+519	-9	line
23	24857	3681	0-3681 $\approx$ 2 $\times$ 1401+875	+4	line
24	24691	3847	0-3847 $\approx$ 2 $\times$ 1260+1313	+14	line
25	24540	3998	0-3998 $\approx$ 2 $\times$ 1548+921	-19	line
Fluorescence in decane ($c=10^{-4}$ M)					
1	28458		0-0		band
2	28377	81	0-81		band
3	28121	337	0-337		line
4	27886	572	0-572		line
5	27665	793	0-793		line
6	27435	1023	0-1023		band
7	27181	1277	0-1277		band
8	27078	1380	0-1380		band
9	26874	1584	0-1584		band
10	26567	1891	0-1891 $\approx$ 1584+337	+30	band
11	26336	2122	0-2122 $\approx$ 1584+572	-34	band
12	26082	2376	0-2376 $\approx$ 1584+793	-1	line
13	25846	2612	0-2612 $\approx$ 1584+1023	+5	band
14	25523	2935	0-2935 $\approx$ 1584+1380	-29	band
15	25316	3142	0-3142 $\approx$ 2 $\times$ 1584	-26	band

Table 2. β -NPD at 77 K.

No	Wavenumber (cm^{-1})	Multiplet $\Delta\tilde{\nu}$	$\Delta\tilde{\nu}$ (cm^{-1})	Possible assignment	Accurateness of the analysis	Remarks
Absorption in n-hexane ($c=10^{-5}$ M)						
1	30030			0 - 0'		line
2	30084	54		0 ₁ -0 ₁ '		line
3	30111	27		0 ₂ -0 ₂ '		line
4	30220		190	0 - 190		line
5	30276	56	192	0 ₁ -192		line
6	30312	36	201	0 ₂ -201		line
7	30395		365	0 - 365		line
8	30450	55	366	0 ₁ -366		line
9	30902		872	0 - 872		line
10	30960	58	876	0 ₁ -876		line
11	31027		997	0 - 997		line
12	31201		1171	0 - 1171		line
13	31259	58	1175	0 ₁ -1175		line
14	31299	40	1188	0 ₂ -1188 $\approx$ 997+190	+1	line
15	31466		1436	0 - 1436		band
16	31726		1696	0 - 1696		band
17	32165		2135	0 - 2135		band
18	32584		2554	0 - 2554 $\approx$ 2 $\times$ 1175+190	+14	band
19	32841		2811	0 - 2811		band
20	32949		2919	0 - 2919 = 2 $\times$ 872+1175	0	band
21	33289		3259	0 - 3259 $\approx$ 2 $\times$ 1436+366	+21	band
Fluorescence in n-hexane ($c=10^{-4}$ M)						
1	29438			0 - 0'		line
2	29223		215	0 - 215		line
3	29120		318	0 - 318		line
4	29078	42	360	0 - 360		line
5	28868		570	0 - 570		band
6	28703		735	0 - 735		line
7	28377		1061	0 - 1061		band
8	28066		1372	0 - 1372		line
9	28019	47	1419	0 - 1419		line
10	27996		1442	0 - 1442		line
11	27832		1606	0 - 1606		line
12	27670		1768	0 - 1768 $\approx$ 1442+318	+8	band
13	27225		2213	0 - 2213 $\approx$ 1061+2 $\times$ 570	+12	band
14	26441		2997	0 - 2997 $\approx$ 1606+1372	+19	line
15	26295		3143	0 - 3143 $\approx$ 1768+1372	+3	line
Fluorescence in decane ($c=10^{-4}$ M)						
1	29053			0 - 0		line
2	29019	34		0 ₁ -0 ₁ '		line
3	28969		84	0 - 84		line
4	28425		628	0 - 628		line
5	27988		1065	0 - 1065		line
6	27624		1429	0 - 1429		line
7	27586	38	1433	0 ₁ -1433		line
8	27450		1603	0 - 1603 $\approx$ 1429+2 $\times$ 84	+6	line
9	27412	38	1607	0 ₁ -1607		line
10	26406		2647	0 - 2647 $\approx$ 1065+1603	-21	band
11	25887		3166	0 - 3166		band
Fluorescence in nonane ($c=10^{-4}$ M)						
1	29163			0 - 0'		line
2	29120	43		0 ₁ -0 ₁ '		line
3	27770		1393	0 - 1393		line
4	27732	38	1388	0 ₁ -1388		line
5	27601		1562	0 - 1562		line
6	27563	38	1557	0 ₁ -1557		line

Table 3. α -NBD in n-hexane ($c=10^{-5}$ M) at 77 K.

No	Wavenumber (cm^{-1})	$\Delta\tilde{\nu}$ (cm^{-1})	Possible assignment	Accurateness of the analysis	Remarks
Absorption					
1	28736				band
2	28977	241	0-241		band
3	29206	470	0-470		
4	29516	780	0-780		band
5	29994	1258	0-1258 $\approx$ 470+780	+8	band
6	30211	1475	0-1475		band
7	30525	1789	0-1789		band
8	30826	2090	0-2090		band
9	31270	2534	0-2534 $\approx$ 2090+470	-26	band
10	31506	2770	0-2770 $\approx$ 2534+241	-5	band
11	31786	3050	0-3050 $\approx$ 1258+1789	+3	band
12	32062	3326	0-3326 $\approx$ 2534+780	+12	band
13	32852	4116	0-4116 $\approx$ 3326+780	+10	band
14	33102	4366	0-4366 $\approx$ 4116+241	+9	band
Fluorescence					
1	28555		0-0		band
2	28329	226	0-226		band
3	28066	489	0-489		band
4	27548	1007	0-1007 $\approx$ 2 $\times$ 489	+29	band
5	27270	1285	0-1285		band
6	27064	1491	0-1491 $\approx$ 1285+226	-20	band
7	26518	2037	0-2037 $\approx$ 2 $\times$ 1007	+23	band
8	26035	2520	0-2520 $\approx$ 1491+1007	+22	band
9	25714	2841	0-2841		band
10	25510	3045	0-3045 $\approx$ 2037+1007	+1	band

Table 4. β -NBD in n-hexane ($c=10^{-5}$ M) at 77 K.

No	Wavenumber (cm^{-1})	$\Delta\tilde{\nu}$ (cm^{-1})	Possible assignment	Accurateness of the analysis	Remarks
Absorption					
1	28736				band
2	29240	496	0-496		band
3	29568	832	0-832		band
4	29762	1026	0-1026		band
5	29985	1249	0-1249		band
6	30211	1475	0-1475		band
7	31153	2417	0-2417		band
8	31516	2780	0-2780		band
9	31666	2930	0-2930 $\approx$ 496+2417	+17	band
Fluorescence					
1	28286				band
2	28074	212	0-212		band
3	27778	508	0-508		band
4	27285	1001	0-1001		band
5	27042	1244	0-1244		band
6	26667	1619	0-1619		band
7	26469	1817	0-1817 $\approx$ 212+1619	-14	band
8	25208	3078	0-3078 $\approx$ 1244+1817	+17	band
9	24691	3595	0-3595 $\approx$ 508+3078	+9	band

fluorescence spectrum (472 cm^{-1} and 1260 cm^{-1}). The progression frequency 1531 cm^{-1} (1548 cm^{-1}) combines with the remaining frequencies. The fluorescence spectrum of β -NPD in n-hexane, decane and nonane has a doublet structure with average intervals between the components of about 40 cm^{-1} . However, for β -NPD in n-hexane in the absorption spectrum the lines form a triplet structure, the average intervals between the components of the

triplet being 40 cm^{-1} and 56 cm^{-1} (Table 2). An exact determination of the sites of the remaining lines in the triplets was impossible because of their weakness. This can be the cause for different multiplicities observed in absorption and fluorescence from the same compound in the same solvent. Table 5 contains the fundamental frequencies of α -NPD and β -NPD from the infrared and quasilinear electronic spectra, and also their interpretation.

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