# 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-biphenylyl)-1,3,4 oxadiazole and 2-(2-naphthyl)-5-(4-biphenylyl)-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 ($\alpha$-NPD),
2-(2-naphthyl)-5-phenyl 1,3,4 oxadiazole ($\beta$-NPD),
2-(1-naphthyl)-5-(4-biphenylyl)-1,3,4 oxadiazole ($\alpha$-NBD),
2-(2-naphthyl)-5-(4-biphenylyl)-1,3,4 oxadiazole ($\beta$-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 with a half width $>10\,\mathrm{cm}^{-1}$ we call bands. The best spectra were observed in n-hexane. The quasilinear spectra of $\alpha$-NPD in n-hexane and decane have a singlet structure. The absorption and fluorescence spectra of $\alpha$-NPD begin with the lines 28735 $\mathrm{cm}^{-1}$ and 28538 $\mathrm{cm}^{-1}$, 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 fullfiled. From Table 1 it follows that only the wavenumbers 488 $\mathrm{cm}^{-1}$ and 1277 $\mathrm{cm}^{-1}$ in the absorption spectrum are approximately the same as in the

Table 5. Internal ground frequencies in molecules of $\alpha$-NPD and $\beta$-NPD and some published assignments.

| From kwasi-linear spectra $\tilde{\nu}$ [$\mathrm{cm}^{-1}$] | From infrared spectra $\tilde{\nu}$ [$\mathrm{cm}^{-1}$] | Interpretation | Comparison with literature $\tilde{\nu}$ [$\mathrm{cm}^{-1}$] |
|---|---|---|---|
| 80 | | Lattice vibrations (n-hexane) | 72 [8] |
| 161<br>190<br>215<br>217<br>250<br>337<br>360<br>366<br>472<br>488 | | Planar deformation vibrations of aryl groups (phenyl, naphthyl) in regard to the central group (oxadiazole) | 170–270 [9] |
| 519<br>570<br>572 | | Planar deformation vibrations of naphthyl in regard to the oxadiazole ring | 517 [10] |
| 874<br>875 | 875 | Planar deformation vibrations of naphthyl group | |
| 921<br>997<br>1020<br>1023<br>1061 | 919<br>990<br>1020<br><br>1074 | Vibrations of phenyl ring | |
| 1372<br>1380<br>1390 | | Vibrations of naphthyl ring | 1380 [4] |
| 1442<br>1436 | 1455 | Vibrations of oxadiazole ring | |
| 1531<br>1548<br>1584 | 1536<br>1557<br>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 ($cm^{-1}$) | $\Delta\tilde{\nu}$ ($cm^{-1}$) | Possible assignment | Accurateness of the analysis | Remarks |
|---|---|---|---|---|---|
| Absorption in n-hexane ($c=5\times10^{-5}$ 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 ≈ 1277+825 | +8 | band |
| 9 | 31220 | 2485 | 0−2485 ≈ 3×825 | +10 | band |
| 10 | 31546 | 2811 | 0−2811 ≈ 1531+1277 | +3 | band |
| 11 | 31807 | 3072 | 0−3072 ≈ 2×1531 | +10 | band |
| 12 | 32072 | 3337 | 0−3337 ≈ 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 ≈ 80+1313 | +8 | band |
| 13 | 26990 | 1548 | 0−1548 | | band |
| 14 | 26838 | 1700 | 0−1700 ≈ 1548+161 | −9 | band |
| 15 | 26476 | 2062 | 0−2062 ≈ 1548+519 | −5 | line on a band |
| 16 | 26096 | 2442 | 0−2442 ≈ 1548+875 | +19 | line |
| 17 | 25740 | 2798 | 0−2798 ≈ 1548+1260 | −10 | band |
| 18 | 25445 | 3093 | 0−3093 ≈ 2×1548 | −3 | band |
| 19 | 25336 | 3202 | 0−3202 ≈ 2×1548+80 | +26 | line |
| 20 | 25233 | 3315 | 0−3315 ≈ 2×1548+217 | +2 | line |
| 21 | 25088 | 3450 | 0−3450 ≈ 2×1260+921 | +9 | line |
| 22 | 24931 | 3607 | 0−3607 ≈ 2×1548+519 | −9 | line |
| 23 | 24857 | 3681 | 0−3681 ≈ 2×1401+875 | +4 | line |
| 24 | 24691 | 3847 | 0−3847 ≈ 2×1260+1313 | +14 | line |
| 25 | 24540 | 3998 | 0−3998 ≈ 2×1548+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 ≈ 1584+337 | +30 | band |
| 11 | 26336 | 2122 | 0−2122 ≈ 1584+572 | −34 | band |
| 12 | 26082 | 2376 | 0−2376 ≈ 1584+793 | −1 | line |
| 13 | 25846 | 2612 | 0−2612 ≈ 1584+1023 | +5 | band |
| 14 | 25523 | 2935 | 0−2935 ≈ 1584+1380 | −29 | band |
| 15 | 25316 | 3142 | 0−3142 ≈ 2×1584 | −26 | band |

Table 2. $\beta$-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 | 54 | | $0 - 0'$ | | line |
| 2 | 30084 | 27 | | $0_1 - 0_1'$ | | line |
| 3 | 30111 | | | $0_2 - 0_2'$ | | line |
| 4 | 30220 | 56 | 190 | $0 - 190$ | | line |
| 5 | 30276 | 36 | 192 | $0_1 - 192$ | | line |
| 6 | 30312 | | 201 | $0_2 - 201$ | | line |
| 7 | 30395 | 55 | 365 | $0 - 365$ | | line |
| 8 | 30450 | | 366 | $0_1 - 366$ | | line |
| 9 | 30902 | 58 | 872 | $0 - 872$ | | line |
| 10 | 30960 | | 876 | $0_1 - 876$ | | line |
| 11 | 31027 | | 997 | $0 - 997$ | | line |
| 12 | 31201 | 58 | 1171 | $0 - 1171$ | | line |
| 13 | 31259 | 40 | 1175 | $0_1 - 1175$ | | line |
| 14 | 31299 | | 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 | $0 - 2554 \approx 2\times1175 + 190$ | +14 | band |
| 19 | 32841 | | 2811 | $0 - 2811$ | | band |
| 20 | 32949 | | 2919 | $0 - 2919 = 2\times872 + 1175$ | 0 | band |
| 21 | 33289 | | 3259 | $0 - 3259 \approx 2\times1436 + 366$ | +21 | band |
| Fluorescence in n-hexane ($c=10^{-4}$ M) | | | | | | |
| 1 | 29438 | | | $0 - 0'$ | | line |
| 2 | 29223 | | 215 | $0 - 215$ | | line |
| 3 | 29120 | 42 | 318 | $0 - 318$ | | line |
| 4 | 29078 | | 360 | $0 - 360$ | | line |
| 5 | 28868 | | 570 | $0 - 570$ | | band |
| 6 | 28703 | | 735 | $0 - 735$ | | line |
| 7 | 28377 | | 1061 | $0 - 1061$ | | band |
| 8 | 28066 | 47 | 1372 | $0 - 1372$ | | line |
| 9 | 28019 | | 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 | $0 - 2213 \approx 1061 + 2\times570$ | +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 | 34 | | $0 - 0$ | | line |
| 2 | 29019 | | | $0_1 - 0_1'$ | | line |
| 3 | 28969 | | 84 | $0 - 84$ | | line |
| 4 | 28425 | | 628 | $0 - 628$ | | line |
| 5 | 27988 | | 1065 | $0 - 1065$ | | line |
| 6 | 27624 | 38 | 1429 | $0 - 1429$ | | line |
| 7 | 27586 | | 1433 | $0_1 - 1433$ | | line |
| 8 | 27450 | 38 | 1603 | $0 - 1603 \approx 1429 + 2\times84$ | +6 | line |
| 9 | 27412 | | 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 | 43 | | $0 - 0'$ | | line |
| 2 | 29120 | | | $0_1 - 0_1'$ | | line |
| 3 | 27770 | 38 | 1393 | $0 - 1393$ | | line |
| 4 | 27732 | | 1388 | $0_1 - 1388$ | | line |
| 5 | 27601 | 38 | 1562 | $0 - 1562$ | | line |
| 6 | 27563 | | 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 ≈ 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 ≈ 2090+470 | −26 | band |
| 10 | 31506 | 2770 | 0−2770 ≈ 2534+241 | −5 | band |
| 11 | 31786 | 3050 | 0−3050 ≈ 1258+1789 | +3 | band |
| 12 | 32062 | 3326 | 0−3326 ≈ 2534+780 | +12 | band |
| 13 | 32852 | 4116 | 0−4116 ≈ 3326+780 | +10 | band |
| 14 | 33102 | 4366 | 0−4366 ≈ 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 ≈ 2×489 | +29 | band |
| 5 | 27270 | 1285 | 0−1285 | | band |
| 6 | 27064 | 1491 | 0−1491 ≈ 1285+226 | −20 | band |
| 7 | 26518 | 2037 | 0−2037 ≈ 2×1007 | +23 | band |
| 8 | 26035 | 2520 | 0−2520 ≈ 1491+1007 | +22 | band |
| 9 | 25714 | 2841 | 0−2841 | | band |
| 10 | 25510 | 3045 | 0−3045 ≈ 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 ≈ 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 ≈ 212+1619 | −14 | band |
| 8 | 25208 | 3078 | 0−3078 ≈ 1244+1817 | +17 | band |
| 9 | 24691 | 3595 | 0−3595 ≈ 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 $\beta$-NPD in n-hexane, decane and nonane has a doublet structure with average intervals between the components ob about 40 $cm^{-1}$. However, for $\beta$-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 $\alpha$-NPD and $\beta$-NPD from the infrared and quasilinear electronic spectra, and also their interpretation.


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