Highly Resolved Vibronic Spectra of Dioxido-p-terphenyl and Trioxido-p-quaterphenyl in n-Hexane at 77 K*

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Highly resolved vibronic absorption and fluorescence spectra of dioxido-p-terphenyl and the fluorescence spectrum of trioxido-p-quaterphenyl in n-hexane at 77 K were obtained. The analysis of the vibrational structure in the excited singlet S_1 and in the ground S_0 state gives fundamental frequencies in the ground state in good agreement with those from infrared (IR) and Raman spectra.

1. Introduction

According to the results so far published on the Shpolskii spectra, vibronic spectra of oxido-p-biphenyl belong to the highest resolved ones [1–4]. Oxido-substituted p-oligophenylenes are very interesting from the point of view of their application in scintillation techniques [5–7]. A blocking of the movement of the benzene rings in p-oligophenylenes using oxygen as bridging element leads to the coplanarity of all rings [7]. Also in this case, similarly as with oxido-p-diphenylene, a highly resolved structure of the vibronic spectra should be expected.

In the present paper, quasilinear absorption and fluorescence, infrared and Raman spectra were investigated for dioxido-p-terphenyl and trioxido-p-quaterphenyl.

2. Experimental

Dioxido-p-terphenyl and trioxido-p-quaterphenyl were synthesized by Wirth et al. [7]. n-Hexane, spectrograde, from Loba-Vien was dried and its transmittance tested in the uv and visible regions. The quasilinear spectra were measured with an equipment described in [8] at 77 K by means of a PGS-2 grating spectrograph with a 1302 groove/mm grating and a reciprocal linear dispersion of 3.63 Å/mm. A 450 W Xenon lamp in combination with a SPM-2 C. Zeiss Jena monochromator has given a continuous, monochromatic excitation.

Infrared spectra of the substances, compressed into tablets of KBr, were measured by means of a Beckman Acculab 6 spectrophotometer, and the Raman spectra of the powder compounds by a VARIAN model Cary 82 Raman laser spectrophotometer for $\lambda = 5145$ Å.

3. Results and Discussion

a) *Dioxido-p-terphenyl*

In the fluorescence spectrum of dioxido-p-terphenyl in n-hexane 89 lines were observed in the region of 29935 – 25657 cm^{-1}, which can be coordinated to 17 fundamental vibrations. All frequencies active in the fluorescence spectrum accord well with those obtained by the authors from measurements of the IR and Raman vibration spectra and are given in Table 1.

Table 1. Comparison of the fundamental frequencies (in cm^{-1}) of dioxido-p-terphenyl in S_0 and S_1 states[a].

Fluorescence (in S_0)	Infrared	Raman	Absorption (in S_1)
210 (m)		215 (mw)	185 (vs)
318 (vs)		322 (w)	312 (s)
535 (s)	545 (m)	538 (mw)	518 (vs)
620 (s)	618 (m)	625 (w)	599 (s)
			648 (vs)
695 (s)	690 (ms)	695 (w)	670 (m)
758 (vs)		759 (s)	
855 (m)	860 (w)	858 (vs)	828 (m)
930 (ms)	932 (ms)		948 (vs)
1008 (m)	1008 (m)	1012 (ms)	976 (s)
			1043 (s)
1100 (m)	1104 (ms)	1102 (mw)	1073 (m)
1147 (w)	1145 (vs)	1145 (mw)	
1210 (s)	1126 (s)	1218 (mw)	1190 (m)
1308 (vs)	1295 (w)	1308 (s)	1327 (m)
1345 (m)	1340 (w)	1349 (s)	1355 (ms)
1475 (m)	1473 (vs)	1476 (m)	1459 (mw)
1600 (s)	1595 (mw)	1597 (m)	1598 (m)
1645 (vs)		1638 (vs)	1623 (m)

[a] vs — very strong, s — strong, ms — middle strong, m — middle, mw — middle weak, w — weak, vw — very weak.

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The vibronic spectra exhibit triplet structure according to Shpolskii. Three components of the 0–0 transition in the fluorescence spectrum, i.e., 29395, 29373 and 29345 cm^{-1}, agree with those of the 0–0 transition (purely electronic) in the absorption spectrum. A nonresonant line of 29436 cm^{-1} occurs in the absorption spectrum in the vicinity of the 0–0 transition, which is interpreted as the coupling between the strongest electronic transition and local lattice vibrations. The distances of the 0–0 resonance components are small (22 and 28 cm^{-1}).

The absorption spectrum of dioxido-p-terphenyl (60 lines in the region of 29344—31777 cm^{-1}) was also interpreted in terms of 17 fundamental vibrations. The vibration frequencies in the excited state are in general lower than those in the ground state. Two frequencies 648 (very weak) and 1043 cm^{-1} (weak) occur in the S_1 state which cannot be attributed to any vibrations in the S_0 state. In view of their strong intensity they cannot be coordinated to combinative vibrations. Moreover, two fundamental frequencies in the emission spectrum, 758 (very weak) and 1147 cm^{-1} (weak) without counterparts in the absorption deviate from the rule of the reflection symmetry of absorption and fluorescence.

b) Trioxido-p-quaterphenyl

The bad solubility of this compound in n-hexane enabled the investigation only of the fluorescence spectrum. In the fluorescence spectrum of trioxido-p-quaterphenyl (55 lines in the region of 27967 — 24616 cm^{-1}) 13 fundamental vibrations have been identified which are in good agreement with the values obtained from the IR and Raman spectra (cf. Table 2). Probably not all vibronic transitions were recorded on the plate. The low concentration of the solutions and the unequal population of the four emission centres (quartet spectrum according to Shpolskii) enabled the detection only of the strongest transitions in the molecule, despite long exposure times (several hours).

Table 2. Comparison of the fundamental frequencies (in cm^{-1}) of trioxido-p-quaterphenyl in S_0 state[a].

Fluorescence	Infrared	Raman
322 (m)	inactive in Raman spectrum;	
385 (w)	IR from 400 cm^{-1}	
503 (w)	510 (w)	
560 (s)	565 (mw)	
640 (mw)	642 (m)	
749 (s)	748 (vs)	749 (m)
890 (mw)	890 (w)	
933 (w)	932 (ms)	
1080 (m)	1080 (mw)	1082 (mw)
1218 (m)	1218 (m)	1220 (vw)
1308 (s)	1315 (w)	1312 (ms)
1373 (w)	1385 (m)	
1635 (vs)		1640 (vs)

[a] See Table 1.

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