ARTICLES

Anomalous Fluorescence of Terrylene in Neon Matrix

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Received: August 24, 2000

Fluorescence and fluorescence excitation spectra of terrylene deposited in Ne and Ar matrixes at 7 K have been studied. The (0,0) fluorescence band of terrylene in Ne matrixes is shifted by 330 cm^{-1} to low energy with respect to the (0,0) fluorescence excitation band observed at 18990 cm^{-1}. Furthermore, the vibronic structures of both spectra are different. In contrary to this observation, the fluorescence and fluorescence excitation spectra of terrylene in Ar matrixes have a common origin at 18312 cm^{-1} and demonstrate mirror symmetry. Semiempirical AM1 calculations combined with the analysis of the vibronic structure of the spectra suggest that terrylene molecules in the excited S$_1$ state are subject to relaxation. This relaxation is possible in soft Ne but it is frozen in rigid Ar matrix.

I. Introduction

Since 1992,[1] terrylene has probably been the most extensively studied molecule in the field of low-temperature single molecule spectroscopy (SMS). This molecule is characterized by all the required properties for this kind of spectroscopy.[2] It is photochemically stable, possesses the strong $S_0 \rightarrow S_1$ absorption, and its fluorescence quantum yield is close to unity (with no observable transition to triplet state). Terrylene has already been studied as a dopant in many organic hosts, such as polymers (polyethylene, polyvinylbutyral, etc.), Shpol'skii matrixes (hexadecane, dodecane, octane), as well as in single crystals (*p*-terphenyl).

Recently, we extended single molecule studies into a new environment, that of low-temperature noble gas matrixes.[3] In a preliminary step leading to these studies, we have undertaken spectroscopic investigations of bulk terrylene deposited in Ar and Ne matrixes. To our surprise we found that fluorescence and fluorescence excitation spectra of terrylene in Ne matrixes show anomalous behavior. The (0,0) origin bands of fluorescence and fluorescence excitation bands do not coincide, and these spectra lack mirror symmetry. To our best knowledge, it is the first such observation for terrylene. In this contribution we present the results of experimental studies and suggest a possible explanation based on semiempirical AM1 calculations.

II. Experimental Section

Terrylene was obtained from the PAH Research Institute in Germany. A small oven containing terrylene was placed inside a liquid helium cryostat in front of a sapphire window cooled to 7 K. Terrylene molecules were evaporated into vacuum at temperatures between 180 and 220 °C where they mixed with a delicate stream of noble gas before being deposited on a cold, sapphire window.

The excitation light source was a Lambda Physik FL 1001 dye laser pumped by an LPX 100 excimer laser. The lasing dye was Coumarin 307 (tuning range: 480−550 nm). Fluorescence photons were detected with the aid of a Jarrel-Ash monochromator, an EMI 9659 photomultiplier, a Stanford Research SR250 boxcar averager, and a Light Scan PC card equipped with a voltage-to-frequency converter.

Theoretical calculations were carried out by using the semiempirical AM1 method.[4]

III. Results and Discussion

Fluorescence and fluorescence excitation spectra of terrylene in Ar and Ne matrixes deposited and measured at 7 K are shown in Figure 1. The spectra of terrylene in Ar have approximate mirror symmetry with respect to the common (0,0) origin at about 18312 cm^{-1}. The rather broad bands observed (full width at half-maximum of about 150 cm^{-1}) have contributions from several matrix sites (such observation is typical for a sample which has not been annealed).[5] The vibronic structure of the fluorescence excitation spectrum of terrylene in Ne matrix resembles that observed in Ar but with the (0,0) origin shifted to higher energy (main site at 18990 cm^{-1}), due to lower polarizability of neon. However, the fluorescence spectrum shows several essential anomalies. Its (0,0) band has a maximum at 18660 cm^{-1}, which means that it is shifted by 330 cm^{-1} to lower energy as compared with the fluorescence excitation. Furthermore, the vibronic structures of both spectra are significantly different. We should note that the fluorescence spectrum of terrylene in neon matrix does not depend on the wavelength of excitation as well as the fluorescence excitation spectrum does not depend on the wavelength of observation.

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10.1021/jp003051r CCC: $20.00

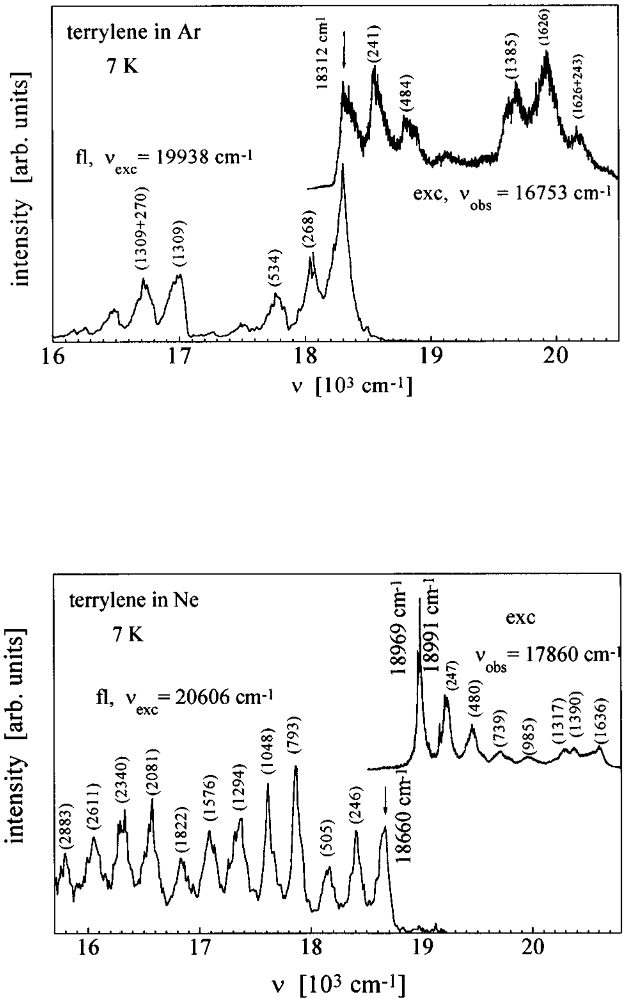


Figure 1. Fluorescence (fl) and fluorescence excitation (exc) spectra of terrylene in Ar and in Ne matrixes at 7 K. Fluorescence spectra were corrected for the spectral sensitivity of detection system, fluorescence excitation spectra were not corrected for the wavelength dependence of the intensity of the exciting laser light.

This anomalous fluorescence of terrylene in Ne matrix suggests that there is some relaxation process present in the lowest excited S_1 singlet state. To elucidate this suggestion we performed theoretical calculations of the structure of electronic states and an analysis of the vibronic structure of the spectra.

We used the semiempirical AM1 method[4] to optimize the geometry of terrylene in the ground (S_0) and the lowest excited (S_1) singlet electronic states, to calculate the S_0-S_1 transition energy corresponding to the geometrical structures of both states, and finally, to calculate the vibronic frequencies. The main results of these calculations (which do not take into account the matrix) are collected in Tables 1 and 2.

Terrylene molecules in the S_0 state (G-structure) have a planar structure of D_{2h} symmetry. After being excited to the S_1 state terrylenes can rearrange to a new structure of C_i symmetry (E-structure) with the relaxation energy of 1078 cm^{-1}. It is noted that the proposed[6,7] "helicoidal" structure of terrylene, with two terminal naphthalene planes twisted by 6° with respect to the central naphthalene ring, has been not confirmed by our calculations which neglect molecule−matrix interactions. Destabilization energy in the S_0 state, which is the difference between the ground-state energy of the E-structure and the energy of the G-structure, is 1534 cm^{-1}. Therefore, our AM1 calculations predict the possibility of a large Stokes shift, from the (0,0) transition energy of 20439 cm^{-1} in absorption to 17827 cm^{-1} in relaxed fluorescence. The calculated transition energies and oscillator strengths (collected in Table 1) are in good agreement with the experimental data (the S_0-S_1 transition energies in different media are within the range 17200−18900 cm^{-1}). The S_0-S_1 transition energy (ΔE) calculated for the G-structure (which corresponds to absorption) is polarized along the long axis of terrylene, while this transition calculated for the E-structure (appropriate for fluorescence) has a very small (1%) contribution polarized along the short axis of terrylene. Bond lengths of terrylene in the G- and E-structures are slightly different—see Table 1. The bond lengths in the G-structure obtained in this work are in good agreement with those predicted by the ab initio calculations.[8] The biggest disagreement was found for the longest *peri* bond e−h (−0.024 Å) but even in this case it is within the limit of experimental error encountered for molecules of comparable size.[8] Analysis of the bond lengths

TABLE 1: Results of AM1 Calculations. G and E Denote Geometric Structures of Terrylene Which Have Been Optimized in the Ground and First Excited Electronic State, Respectively

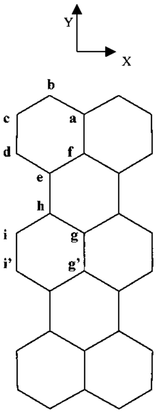
Energetic (energy and oscillator strength for S_0/S_1 transition) and structural data (bond lengths) for G and E structure of terrylene				
		AM1		*ab initio*[8]
		G -structure	E-structure	G -structure
 Y X a b c d e f h i i' g g'	excitation energy ΔE =	20439 cm^{-1}	17827 cm^{-1}	
	oscillator strength f =	1.078	1.175	
	bond lengths [all in Å]	r_G	r_E	r_G
	b - c	1.372	1.382	1.355
	d - e	1.386	1.405	1.370
	i - h	1.384	1.414	1.367
	c - d	1.411	1.397	1.405
	i - i'	1.403	1.378	1.393
	a - f	1.419	1.426	1.413
	g - g'	1.423	1.437	1.422
	e - f	1.431	1.423	1.426
	g - h	1.430	1.427	1.426
	a - b	1.420	1.415	1.414
	e - h	1.458	1.439	1.482

TABLE 2: AM1 Calculation Results for Vibration Frequencies

frequencies ($h\nu$) and reduced displacements (Δ)
for 19 totally symmetric vibronic modes of terrylene
[Δ_Y is reduced displacement for the hypothetical case where
terrylene bonds can change along the long molecular axis only]

AM1 − this work			Ohno[12]		ab initio[8]
$h\nu$ [cm^{-1}]	Δ	Δ_Y	$h\nu$ [cm^{-1}]	Δ	$h\nu$ [cm^{-1}]
278	0.40	0.40	248	0.53	263
491	0.05	0.01	484	0.10	490
597	0.06	0.05	554	0.23	587
684	0.23	0.10	606	0.15	645
856	0.10	0.04	834	0.05	883
1029	0.06	0.05	880	0.01	897
1177	0.07	0.04	1089	0.05	1117
1218	0.04	0.04	1110	0.04	1201
1231	0.05	0.04	1165	0.01	1289
1352	0.06	0.05	1213	0.12	1344
1407	0.09	0.06	1313	0.74	1387
1476	0.33	0.30	1333	0.25	1435
1532	0.06	0.01	1365	0.12	1440
1588	0.20	0.06	1385	0.04	1489
1599	0.18	0.08	1451	0.02	1564
1624	0.20	0.16	1499	0.03	1615
1751	0.30	0.26	1593	0.09	1737
1777	0.08	0.07	1622	0.33	1758
1790	0.07	0.07	1630	0.27	1781

presented in Table 1 shows that the main changes in the geometry on relaxation of terrylene in the excited S_1 state are the shortening of the i−i′ (by −0.025 Å) and e−h (by −0.019 Å) bond lengths and parallel increase of the d−e (by 0.019 Å) and h−i (by 0.03 Å) bond lengths. It is interesting to notice that our results predict similar overall changes in the molecular geometry (and destabilization energy) upon the $S_0 \rightarrow S_1$ excitation as the ab initio calculations performed for naphthalene[9] (terrylene can be considered as a molecule composed of three naphthalene units).

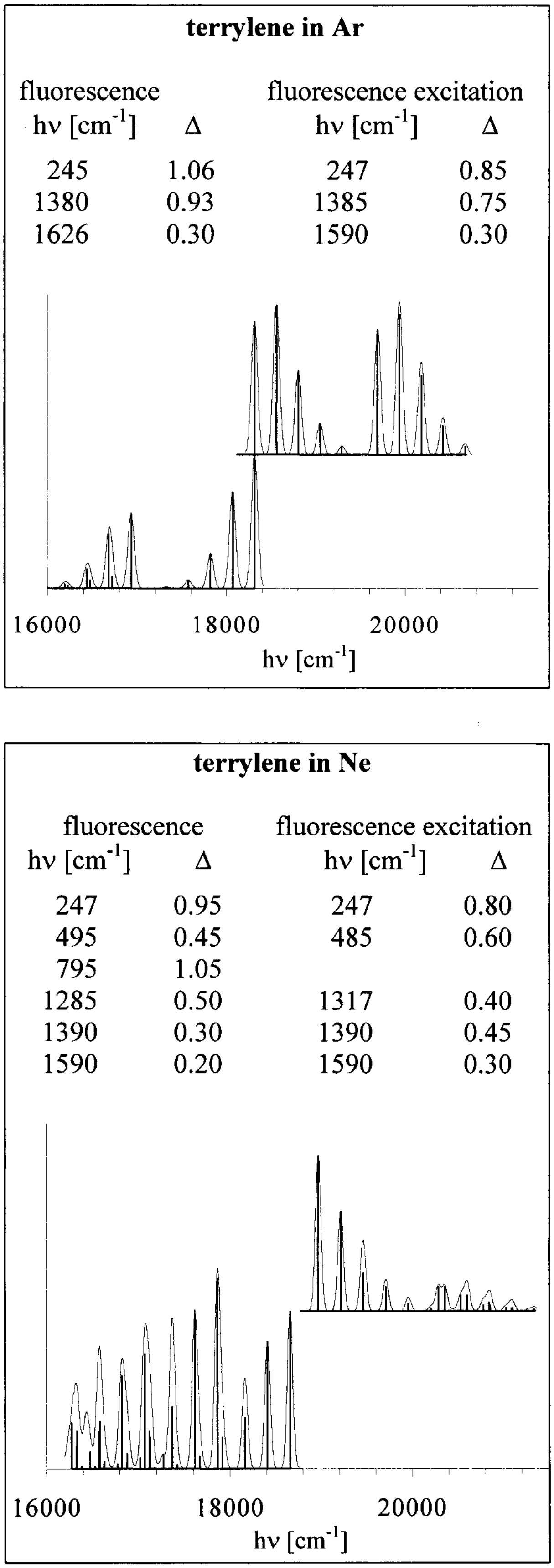
Vibrational frequencies, calculated in this work by the AM1 method, are in good agreement with previous calculations, which used the AM1,[6,7] ab initio,[8] and Ohno[11,12] methods. Table 2 contains 19 frequencies of the normal vibrational modes of the non CH-stretching a_{1g} vibrations and their displacement parameters Δ (which are the absolute magnitude of the difference between the equilibrium geometry of the S_0 and S_1 state for each considered vibration, given in dimensionless normal coordinates of the S_0 state).[10,11] The totally symmetric modes are expected to be strongly active in the S_0−S_1 transition.[10,11] The intensity distribution over the vibronic structure of electronic spectra is described by the Franck−Condon factors, which are dependent on the displacement parameters Δ. The reduced displacements Δ_Y, given in Table 2, correspond to the hypothetical case, where terrylene bonds can change only along the long molecular axis.

In a next step, we made the analysis of the vibronic structure of experimental fluorescence and fluorescence excitation bands. We simulated the experimental spectra by using expressions for the multi-vibrational Franck−Condon factors for harmonic and displaced oscillators given in ref 10. Best fit procedure provided frequencies and reduced displacements of the active modes. Simulated spectra are shown in Figure 2.

This analysis revels, that the [240], [1385], and [1620] frequencies are common in the spectra of terrylene in Ar and Ne matrixes, whereas the [485], [795], and [1300] frequencies are necessary to reproduce the spectra of terrylene in Ne. We should point out at this point, that in order to reproduce the intensities of the vibronic bands the frequency [485] has to be considered, despite contribution at the same spectral position from the harmonic of the [240]. To understand the structure of the spectra, we attributed the most probable vibrational modes (obtained by the AM1 calculations) for each experimentally determined frequency (found by the spectral simulation procedure). The criteria for the selection of the vibration mode were close frequency and high reduced displacement of the vibration. The results of our assignment are presented in Table 3.

The vibration [240] (245 and 247 cm^{-1} in Ar and 247 cm^{-1} in Ne) is the main vibration contributing to the spectra of terrylene. It corresponds to the 243 cm^{-1} vibration of terrylene in polyethylene,[11,12] 241−243 and 249 cm^{-1} in *n*-hexadecane[7,13] and 245−248 cm^{-1} in crystalline *p*-terphenyl.[6] We identify it as the 277 cm^{-1} long axis stretch of terrylene obtained by the AM1 (it is easily seen in Table 2 that $\Delta = \Delta_Y$ for this mode). Our assignment agrees with those proposed by other authors.[6,8,11]

The vibration [1385], contributing to the spectra of terrylene in both studied matrixes (1380 and 1385 cm^{-1} in Ar and 1390 cm^{-1} in Ne) can be identified with the 1272 and 1283 cm^{-1} vibrations observed in polyethylene,[11,12] 1269 and 1279 cm^{-1} in *n*-hexadecane,[7] and 1285−1291 and 1293−1298 cm^{-1} in crystalline *p*-terphenyl.[6] We attribute it to the calculated frequency 1476 cm^{-1}. Our calculated vibration 1476 cm^{-1} is of the same type as the vibration 1333 cm^{-1}, considered in ref 10. Also for this vibration $\Delta \approx \Delta_Y$ (see Table 2).



terrylene in Ar

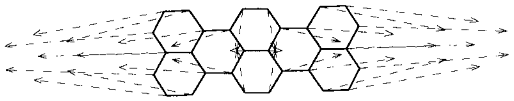
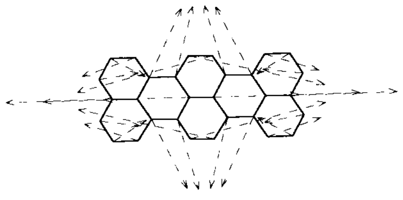
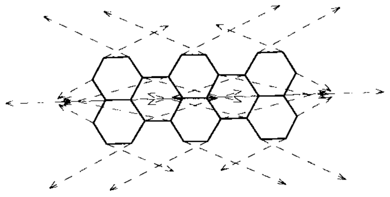
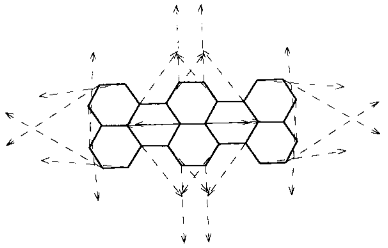
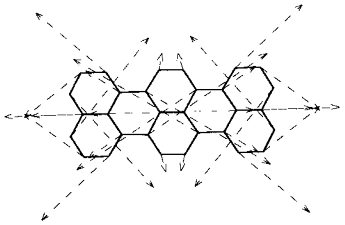
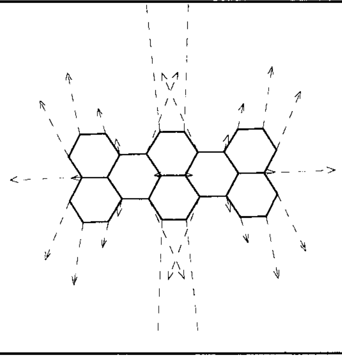
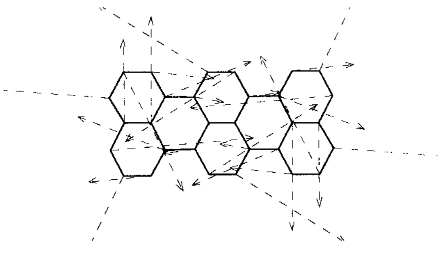
fluorescence hν [cm^{-1}]	Δ	fluorescence excitation hν [cm^{-1}]	Δ
245	1.06	247	0.85
1380	0.93	1385	0.75
1626	0.30	1590	0.30

terrylene in Ne

fluorescence hν [cm^{-1}]	Δ	fluorescence excitation hν [cm^{-1}]	Δ
247	0.95	247	0.80
495	0.45	485	0.60
795	1.05		
1285	0.50	1317	0.40
1390	0.30	1390	0.45
1590	0.20	1590	0.30

Figure 2. Simulated fluorescence (fl) and fluorescence excitation (exc) spectra of terrylene in Ar and in Ne matrixes. Bands were drawn as Gaussian curves with full width at half-maximum of 15 cm^{-1}. Frequencies and displacement parameters of vibrations that were used to simulate the spectra are given above the spectra.

TABLE 3: Assignment of Vibronic Frequencies Given by the AM1 Method (see Table 2) to Those Obtained from Experiment (see Figures 1 and 2)

hν [cm^{-1}]		Graphical presentation of vibrations
experiment	AM1 calulations	
[240]	277	
[1385]	1476	
[1620]	1751	
[485]	491	
[1300]	1407	
[795]	*on the left:* 684 in D_{2h} 681 in C_i *on the right*: 787 in C_i (see text for details)	 

The vibration [1620] (1626 and 1590 cm^{-1} in Ar, 1590 cm^{-1} in Ne) can be identified with the vibration 1562 and 1580 cm^{-1} observed in polyethylene,[11,12] with 1553 cm^{-1} in *n*-hexadecane[7] and 1574−1582 cm^{-1} in *p*-terphenyl.[9] We can attribute this vibration to the calculated frequencies 1751 and/or 1624 cm^{-1}, both have close frequency and sufficiently high parameter Δ.

All of the above vibrations are related to the stretch of the terrylene molecule along its long axis. These vibrations alone lead to a sufficiently good description of the spectra of terrylene in Ar matrixes.

However, to simulate the spectra of terrylene in Ne matrix we have to consider three more vibrations, the [485], [795], and [1300]. Possible relatives of these vibrations observed in other media (in polyethylene, *n*-hexadecane, and *p*-terphenyl) have slightly different frequencies and, as a rule, a weak intensity. We attribute the vibration [485] to the AM1 frequency 491 cm^{-1}, and the vibration [1300] to the calculated 1407 cm^{-1}. The most important vibration [795], which is responsible for the lack of mirror symmetry of fluorescence and fluorescence excitation spectra, can be attributed to the calculated frequency 684 cm^{-1}, obtained for the D_{2h} symmetry or to the 787 cm^{-1}, appearing in only the C_i symmetry for molecule geometry of the excited state. A common property of the [485], [795], and [1300] vibrations is the nonnegligible stretch of terrylene along the short molecular axis (in this case $\Delta > \Delta_Y$).

In conclusion, vibrations characterized by a large amplitude along the short terrylene axis (these vibrations concern mainly terrylene carbon atoms h and i) contribute selectively to the spectra observed in Ne matrixes. Contribution of these vibrations to the spectra in Ar matrix (as well as in other media) can be neglected. Relaxation of the S_1 state, observed in Ne but absent in Ar, is also dependent on the possibility of terrylene to be deformed along the short axis. Both these facts suggest that the anomalous fluorescence of terrylene in Ne matrix (which seems to be soft at 7 K) is related to deformation along the short molecular axis, with the carbon atoms h and i (and their symmetric partners) at the central naphthyl unit involved the most. A rigid structure of Ar matrix (as well as that of other previously mentioned media) protects terrylene molecules against the short axis deformation.

The anomalous fluorescence of terrylene has been observed for the first time and in Ne matrix only. Our effort to observe Stokes shifted fluorescence of terrylene in Ar matrix at elevated temperatures was unsuccessful, although the sample was heated to evaporation of the matrix. Increased mobility of the matrix does not seem to be sufficient and does not lead to anomalous fluorescence of terrylene. Possibly, the quantum mechanical effects[14,15] operating in the Ne matrix should be included to explain our observation. We are however not ready to discuss this point at the present state of our knowledge.

It should also be mentioned, that a close relative of terrylene, di-*tert*-butyl-terrylene demonstrates normal fluorescence behavior in low-temperature Ne matrix. We observed that fluorescence and fluorescence excitation spectra of this compound had a common (0,0) origin and showed mirror symmetry of their vibronic structure. Di-*tert*-butyl-terrylene is, however, of C_2 symmetry and does not have the analogue of the 787 cm^{-1} vibration (which contributes to the anomalous fluorescence of terrylene in Ne matrix).

Normal fluorescence behavior was recently observed for perylene in Ne matrix.[5] Perylene molecules are, however, lacking the central naphthyl unit of terrylene and a possibility of deformation of this structural unit seems to be the most important candidate for explaining the anomalous fluorescence of terrylene.

Anomalous fluorescence of terrylene in Ne matrix has been puzzling and highly unexpected. Its better understanding needs still more elaborate studies. We are currently considering extending the study to terrylene in Ne matrix at pumped helium temperatures, combined with hole burning.

Acknowledgment. This work was partly supported by the State Committee for Scientific Research of the Republic of Poland, Project: 2P03B 046 12.

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