4252 *J. Phys. Chem. A* **2007,** *111,* 4252−4258

Fluorescence Studies of Terrylene in a Supersonic Jet: Indication of A Dark Electronic State Below the Allowed Transition

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Received: January 15, 2007; In Final Form: March 7, 2007

Jet-cooled terrylene has been studied in helium buffer gas using a pulsed nozzle by means of laser-induced fluorescence. Fluorescence excitation and two-color depletion experiments (resulting in hole burning spectra) are presented. Analysis of the spectra leads to the conclusion that another excited electronic state is present in the vicinity of the allowed $^1B_{1u}$ state. Assuming (according to previous literature suggestions Karabunarliev, S.; Baumgarten, M.; Müllen, K. *J. Phys. Chem. A* **1998**, *102*, 7029) that this dark state is the 2^1A_g state, we discuss the vibrational structure of the fluorescence excitation spectrum in terms of two manifolds of vibronic states belonging to $S_d(2^1A_g)$ and $S_1(^1B_{1u})$ states. The anomalous shift between excitation and dispersed fluorescence spectra observed earlier for terrylene in a neon matrix is discussed as a consequence of terrylene electronic relaxation to the low-energy dark state.

1. Introduction

Terrylene, a molecule representative for oligorylenes, presents the properties required for single molecule spectroscopy (large oscillator strength and quantum yield). As a polycyclic aromatic molecule, this molecule is also a possible carrier of diffuse interstellar bands. For these reasons, it has been investigated carefully in the past few years.[1−9] The structure of this molecule, together with the coordinate system used in this work (Mulliken convention[10]), is shown in Figure 1.

The $S_0(1^1A_g) \rightarrow S_1(1^1B_{1u})$ transition in terrylene is allowed by symmetry and polarized along the long molecular axis.[1,4,5,8] The energy of this transition depends on the interactions of terrylene with the environment[2,4−7,9] and is estimated to be located between 19 181 cm^{-1} and 19 203 cm^{-1} for the free terrylene molecule.[7,9] High-resolution measurements[11] recently performed by Hoheisel and Hese placed the 0−0 transition at 19 237.8 cm^{-1}.

It is known that the allowed $S_0(1^1A_g) \rightarrow S_1(1^1B_{1u})$ transition involves progressions of several totally symmetric vibrations a_g, such as the long axis stretch at a frequency[1−8] of ∼240 cm^{-1}. The fluorescence $S_1(1^1B_{1u}) \rightarrow S_0(1^1A_g)$ of terrylene taking place from a state well separated from the other excited electronic states has a large fluorescence quantum yield ∼0.74.[1,2] However, it has been noted that absorption and emission of terrylene in low-temperature matrixes does not always display mirror image symmetry.[5] Namely, whereas fluorescence and excitation spectra of terrylene in an argon matrix display approximate mirror symmetry, anomalous fluorescence of terrylene was observed in a neon matrix, with an unexpected energy gap relative to excitation. The origin band of the dispersed fluorescence was shifted down in energy by 330 cm^{-1} with respect to the (0−0) excitation band. Simultaneously mirror symmetry between the two spectra was lost. The lowering of the symmetry of terrylene upon electronic excitation in the “soft” neon matrix was considered as a possible explanation of this observation.[5] The problem of the lowering of symmetry of terrylene in the excited-state has been suggested in some other works.[9] More generally, it can be considered in context of the “rigidity” of large polycyclic aromatic hydrocarbons.[12]

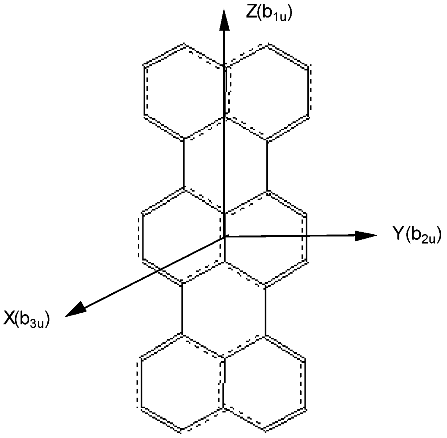

Figure 1. Terrylene molecule and coordinate system used in this work.

Very recently, Hoheisel and Hese[11] have reported high resolution fluorescence excitation spectra of terrylene expanded in a continuous supersonic jet with argon as a buffer gas. They concentrated on a very narrow spectral range performing analysis of rotational contours of three bands separated by 14 cm^{-1} and located around 19 200 cm^{-1}. The central band at 19 237.8 cm^{-1} was assigned to the allowed $S_0(1^1A_g) \rightarrow S_1(1^1B_{1u})$ vibrationless (0,0) transition. The weaker band located at 14 cm^{-1} further to the blue has been assigned to the $v = 2 \leftarrow v = 0$ transition involving a 7 cm^{-1} accordion mode in the S_1 state. Surprisingly, the band located at −14 cm^{-1} from the origin band could not be fitted with the same set of molecular

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10.1021/jp070337o CCC: $37.00

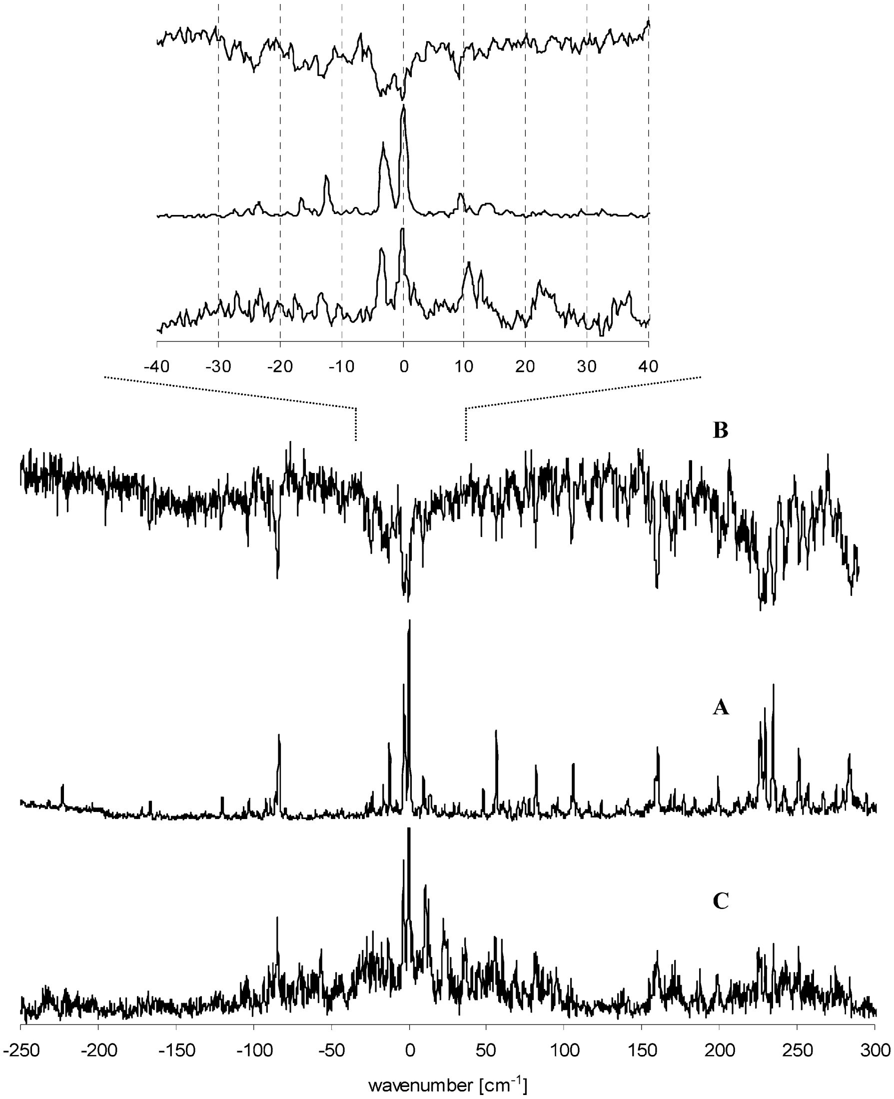

Figure 2. Fluorescence excitation and hole burning spectra of terrylene (not corrected by the laser power). (A) Fluorescence excitation spectrum in helium supersonic jet ($h\nu_{00} = 19\,226.5$ cm^{-1}), (B) hole burning spectrum corresponding to spectrum A (probe laser set at 19 226.5 cm^{-1}), and (C) fluorescence excitation spectrum in argon supersonic jet.

constants as the two others. One of the possibilities was to assign this band to a hot band, but the authors have not ruled out the possible influence of a close-lying dark state.

In this work, we present a spectroscopic study of jet-cooled terrylene using a pulsed nozzle and helium as the buffer gas and we investigate a much broader spectral region than that reported in reference 11. To clarify the origin of many bands observed in the fluorescence excitation spectrum, two-color depletion studies (resulting in hole burning spectra) have also been performed. Moreover, several single vibronic level (SVL) emission spectra resulting from the excitation of selectively chosen vibronic levels were measured, for a better understanding of the excitation spectrum. Calculations of vibrational frequencies were also done to assist in the analysis of the spectra.

2. Experimental Section

Terrylene used in our work was received from Dr. Werner Schmidt (Institut fuer PAH-Forschung, Germany).

Spectroscopic studies of terrylene in supersonic beams have been performed using similar set ups in Orsay[13] and in Warsaw.[14] To get sufficient fluorescence signal, the terrylene sample was heated to a temperature of about 280 °C. A pulsed nozzle was used to save the terrylene sample. A standard nozzle (General Valve Corporation) was modified by changing the standard wire in the electromagnetic coil for a temperature-resistant one, to allow the temperature to be raised from 200 °C up to around 300 °C. He at a pressure of 2−3 atm seeded with terrylene vapor was expanded through a 0.3 or 0.4 mm orifice. With Ar as a buffer gas, a stagnation pressure of 0.5 atm was used. The temperature has been varied between 260 and 280° to check that no new band due to clusters appears. For routine experiments, it has been maintained as low as possible, at the onset of a satisfying signal-to-noise ratio. Laser-induced fluorescence excitation spectra were measured by exciting the molecule in the cold region of the jet by a dye laser (Sirah) operating at 10 Hz, and used with Coumarin 307 (C 307). Fluorescence was detected by a Hamamatsu R2949 photomultiplier using a Schott CG550 cutoff filter. Selectively excited dispersed fluorescence was recorded using a 60 cm monochromator (Jobin-Yvon), with a 1200 grooves/mm grating. Two-color laser depletion spectra were measured in Warsaw with the setup already described,[14] using the tuneable 10 Hz pulses of an OPO as a pump, and the synchronized C307 dye

TABLE 1: Highest Intensity Lines Observed in the Fluorescence Excitation Spectrum of Terrylene in Helium Supersonic Jet and their Tentative Assignment

experimental data		tentative assignment - the numbering and the frequencies of particular vibrations for both 1^1B_{1u} and 2^1A_g states are done in Table 4 - in parenthesis the difference between experimental and attributed position of lines: $\delta = \mid h\upsilon_i^{cal} - h\upsilon_i \mid$				
wavenumbers [cm^{-1}]			vibrational states of dark 2^1A_g state for 4 modes (C_i) of b_{1u} symmetry coupling 2^1A_g and 1^1B_{1u} excited states			
$h\nu_i$	$h\upsilon_i - h\upsilon_0^0$	vibrational states of bright 1^1B_{1u} state	C1	C2	C3	C4
19 000.5	−226.0		$0_0^0 + h\upsilon_{C1}$			
19 055.2	−171.3		1_0^2 (8.3)			
19 060.6	−165.9			$0_0^0 + h\upsilon_{C2}$		
19106.9	−119.6		2_0^2 (0.4)			
19123.7	−102.8		1_0^4 (2.8)	1_0^2 (0.1)		
19143.2	−83.3				$0_0^0 + h\upsilon_{C3}$	
19167.5	−59.0		$1_0^2 2_0^2$ (2.0)	2_0^2 (0.9)		
19 203.5	−23.0				1_0^2 (2.7)	
19 210.5	−16.0		2_0^4 (2.0)			
19 214.2	−12.3		3_0^2 (0.3)			
19 223.4	−3.1					$0_0^0 + h\upsilon_{C4}$
19 226.5	0.0	0_0^0 (0.0)				
19 236.0	9.5	1_1^1 (2.8)	$1_0^4 2_0^2$ (3.5)			
19 241.2	14.7		4_0^1 (0.7)			
19 250.1	23.6				2_0^2 (0.9)	
19 274.6	48.1		$1_0^2 3_0^2$ (2.9)	3_0^2 (0.0)	1_0^4 (5.4)	
19 283.1	56.6	1_0^2 (0.0)				1_0^2 (3.3)
19 308.8	82.3				$1_0^2 2_0^2$ (3.4)	
19 332.7	106.2	2_0^2 (0.0)				2_0^2 (3.3)
19 387.1	160.6	$1_0^2 2_0^2$ (2.2)		$2_0^2 3_0^2$ (6.4)	4_0^1 (3.9)	$1_0^2 2_0^2$ (5.3)
19 425.9	199.4	3_0^2 (0.0)				
19 453.2	226.7		$3_0^2 4_0^1$ (1.3)		$1_0^2 4_0^1$ (6.9)	
19 456.2	229.7				$2_0^2 3_0^2$ (7.0)	
19 461.1	234.6	4_0^1 (0.0)				
19 469.0	242.5					4_0^1 (5.6)
19 477.8	251.3	$1_0^2 3_0^2$ (4.7)				
19 483.9	257.4		4_0^2 (3.4)			
19 493.8	267.3			3_0^4 (5.2)	$2_0^2 4_0^1$ (4.6)	

laser pulses delayed by 200 ns as a probe. We estimate the error of calibration of lasers as ±2 cm^{-1}.

Ground-state optimization of the terrylene geometry and calculations of the harmonic vibrational frequencies were performed at the DFT B3LYP/6-31G* level employing the Gaussian 98 program package.[15] Vertical excited states were calculated by the TD DFT B3LYP/6-31G* method.

3. Results and Discussion

Figure 2 displays the fluorescence excitation spectrum of terrylene expanded in helium (middle trace). The main band at 19 226.5 cm^{-1} has been assigned to the origin of the $S_1 \leftarrow S_0$ transition. Figure 2 also shows the hole-burning spectrum obtained with the probe set on the main band at 19 226.5 cm^{-1} (upper trace). It is seen that most of the details of the excitation spectrum are present in the hole-burning spectrum proving that most of the excitation spectrum originates from a single species.

Despite its signal-to-noise ratio being not as good as with He, the fluorescence excitation spectrum recorded with Ar as a carrier gas displays at first sight the same features. However, a closer look at the origin region shows that instead of the +9.5 cm^{-1} band, a new stronger one at +11 cm^{-1} appears. This latter band is part of a four-member progression or sequence built on a ~11 cm^{-1} frequency mode.

There is also some correspondence between our observations and the data reported in reference 11 for terrylene in an argon continuous jet. The three transitions A (19 223.5 cm^{-1}), B (19 237.8 cm^{-1}), and C (19 251.2 cm^{-1}) observed in ref 11 are within contours of respective bands observed by us for terrylene in argon (compare Figure 2).

Detailed inspection of Figure 2 indicates that the excitation spectrum of terrylene exhibits very intriguing features showing a very complicated and irregular structure. As already mentioned, the main band at 19 226.5 cm^{-1} (tentatively assigned as the 0−0 transition) is accompanied by a less intense one shifted to the red by c.a. 3 cm^{-1}. The two components of the doublet appear with comparable intensity ratio in the excitation spectra recorded in He or in Ar, as well as in the hole-burning spectrum. This shows unambiguously that they arise from the same ground-state level.

Moreover, the excitation spectrum extends down to ~230 cm^{-1} below the energy of the 0−0 transition. We can essentially expect in this region the presence of hot bands involving vibrational modes for which the frequency in the ground state (S_0) is larger than the frequency in the excited state (S_1). However, such an interpretation seems to be unlikely because of the excellent correspondence between fluorescence excitation and hole burning spectra (see Figure 2A and B).

The first two columns of Table 1 report the frequencies of the highest intensity bands observed in the fluorescence excitation spectrum of terrylene. The most prominent feature among the lines composing the vibrational structure above the (0−0) energy is a strong band at 234.6 cm^{-1}. This band corresponds to the vibronic transition (S_0 $\upsilon'' = 0$) → (S_1 $\upsilon' = 1$) for the well-known and previously assigned[1−8] totally symmetric long

TABLE 2: Low-Frequency Vibrations of Terrylene in the Ground Electronic State (S_0) Calculated at the B3LYP/6-31G* Level (Frequencies Given without Scaling Factor) and Vibrations of b_{1u} Symmetry with Lowest Frequencies

	symmetry	frequency [cm^{-1}]
	(A)	
1	a_u	20.8
2	b_{1g}	28.5
3	b_{3u}	37.0
4	b_{2g}	111.7
5	b_{3u}	112.9
6	b_{2u}	151.1
7	b_{2g}	168.8
8	b_{3u}	181.4
9	a_u	214.4
10	b_{1g}	221.4
11	a_g	246.7
	(B)	
18	b_{1u}	435.9
23	b_{1u}	478.8
26	b_{1u}	528.4
39	b_{1u}	684.3
47	b_{1u}	801.9

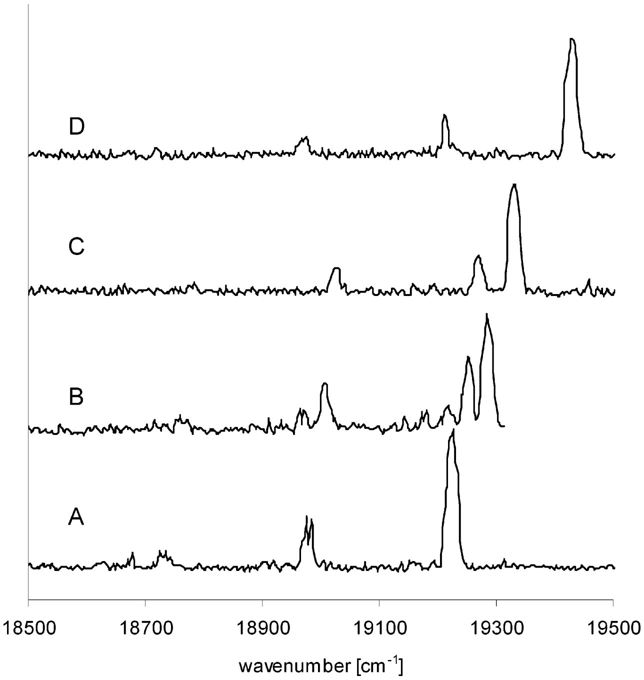

Figure 3. Selected single vibronic level dispersed fluorescence spectra of terrylene in helium supersonic jet. (A) (0,0) Excitation at 19 226.5 cm^{-1}, (B) excitation at (0,0) + 56.6 cm^{-1}, (C) excitation at (0,0) + 106.2 cm^{-1}, and (D) excitation at (0,0) + 199.4 cm^{-1} (see Table 2).

axis stretch (a_g) vibrational mode calculated here for the S_0 state at 246.7 cm^{-1} (see Table 2).

Below 234.6 cm^{-1}, we observe a few lines at 56.6, 106.2, and 199.4 cm^{-1}, which probably correspond to different low-energy modes. Only one band at 160.6 cm^{-1} can be assigned to a combination band involving the two different modes observed at 56.6 and 106.2 cm^{-1}. We shall now refer to the results of the calculations of the terrylene vibrational frequencies for the S_0 state by the B3LYP/6-31G* method shown in Table 2 to assign the low-frequency vibrations observed. It is seen that all of the 10 vibrational modes lower in frequency than the first a_g vibration (see Table 2) are nontotally symmetric. Moreover, they are all, with one exception (of b_{2u} vibration 151 cm^{-1}), out-of-plane vibrations. In the Franck−Condon treatment of the vibronic spectra of the $S_0 \leftrightarrow S_1$ transition in planar polycyclic aromatic hydrocarbons (for example, perylene[12]), the activity of out-of-plane vibrations is well described by the selection rule $\Delta\upsilon = 0, 2, 4...$, obtained within the frame of the distorted oscillator[16] approximation. This means that the frequencies of the observed lines should correspond to twice the fundamental frequencies of a given mode.

However, the assignment of the observed modes to the calculated vibrations is still difficult. The frequencies observed in the Single Vibronic Level dispersed fluorescence spectra, showed in Figure 3, provide us part of the information needed for the interpretation of these lines. These frequencies are listed in Table 3, together with the corresponding calculated values.

Inspection of these data indicates that the 244 cm^{-1} frequency appears very often in the fluorescence spectra obtained for different excitations. This frequency corresponds to the S_0 totally symmetric long axis stretch vibrations (a_g) already observed in the excitation spectrum, and reported in the literature as ranging from 241 to 249 cm^{-1}. This vibration is calculated here at 246.7 cm^{-1} and found experimentally at 244 and 234.6 cm^{-1} in the ground and excited electronic states, respectively (Table 4). It was established that this vibration is well approximated by a displaced harmonic oscillator[16] with a large change in the equilibrium geometry in S_1 relative to S_0, which results in a large value of the "reduced displacement parameter" Δ.[1,4,5] Surprisingly, the 244 cm^{-1} line is missing in the dispersed fluorescence spectrum resulting from the excitation at 234.6 cm^{-1}. In other words, the (S_1 $\upsilon' = 1$) → (S_0 $\upsilon'' = 1$) transition is not observed after (S_0 $\upsilon'' = 0$) → (S_1 $\upsilon' = 1$) excitation of this a_g vibration. This seemingly surprising fact can be explained by the value of the "reduced displacement parameter" (Δ), estimated to be near 1.[1,4,5] At such a value of Δ, the corresponding Franck−Condon (FC) factor is near zero for the (S_1 $\upsilon' = 1$) → (S_0 $\upsilon'' = 1$) transitions, in accordance to the relation for displaced oscillator:[16]

$$\mathrm{FC}(S_1\ \upsilon' = 1 \rightarrow S_0\ \upsilon'' = 1) = \mathrm{FC}(S_1\ \upsilon' = 0 \rightarrow S_0\ \upsilon'' = 0) * (1 - \Delta)^2$$

Therefore, the lack of (S_1 $\upsilon' = 1$) → (S_0 $\upsilon'' = 1$) transition for the symmetric long axis stretch vibrations a_g does not result from coincidental selection rules but is connected to the value of Δ.

The hypothesis of a distorted oscillator with a large value of Δ can also explain the spectral activity of the long axis stretch vibration a_g observed as a (S_1 $\upsilon' = 0$) → (S_0 $\upsilon'' = 1$) transition in different SVL emission spectra.

The assignment of other vibrations contributing to the $S_0 \leftrightarrow S_1$ transition can be made with the aid of the data reported in Table 2. The fluorescence spectra obtained after excitation of terrylene levels at +56.6, +106, and +199 cm^{-1} above the origin show bands at frequencies of 32, 61, and 215 cm^{-1}, respectively, together with their combinations with the 244 cm^{-1} frequency. Within the frame of the distorted oscillator model, the frequencies observed at 32, 61, and 215 cm^{-1} could be considered as twice the fundamental of out-of plane modes of 16, 30.5, and 107.5 cm^{-1} frequencies. Similarly, the bands observed in the excitation spectra at 56.6, 106.2, and 199.4 cm^{-1} could correspond to twice the fundamental at 28.3, 53.1, and 99.7 cm^{-1}, respectively. On the basis of our calculations and with the hypothesis that these modes are active by $\Delta\upsilon = 2$ transitions, we can assume that the 28.3, 53.1, and 99.7 cm^{-1} S_1 values are the counterpart of the S_0 16, 30.5, and 107.5 cm^{-1}

TABLE 3: Experimental Vibrational Frequencies Deduced from the SVL Fluorescence Spectra of Terrylene

position of the excitation		
wavenumbers [cm^{-1}]	relative position in the excitation spectrum	transitions observed in the corresponding fluorescence spectrum (shift from the excitation line)
19 143.2	−83.3	0 244
19 223.4	−3.1	0 244
19 226.5	0	0 244 488 (2*244)
19 236.0	9.5	0 244
19 283.1	56.6	0 32 65 276 (32 + 244)
19 332.7	106.2	0 61 305 (61 + 244)
19 425.9	199.4	0 215 459 (215 + 244)
19 461.1	234.6	0 488 (2*244)

frequencies. These values are collected in Table 4 together with their possible assignments (unfortunately still not unequivocal).

Knowing these frequencies in both S_0 and S_1 electronic states makes it possible to investigate the question of the presence of hot bands. The two lowest frequency vibrations show an increase of their frequencies in S_1 relative to the S_0 state. This means that hot bands involving these vibrations are expected higher in energy than the (0,0) transition. In particular, for the lowest-energy experimentally observed vibration, whose frequency is supposed to be 16 and 28.3 cm^{-1} in the S_0 and S_1 states, respectively, we expect the presence of hot bands equally spaced by 12.3 cm^{-1}. Indeed we do observe bands in the excitation spectrum recorded in helium, at 9.5 and 14.7 cm^{-1} from the origin, which do not appear clearly in the hole-burning spectrum. One of these bands could be a candidate for a hot band. An additional argument is given by the fact that these bands are more prominent in the excitation spectrum recorded in Argon, for which the low backing pressure does not ensure good cooling conditions. Moreover, they are followed by bands at 22 and 33 cm^{-1}, which could be the members of a sequence, built on an 11 cm^{-1} frequency difference.

Although these hypotheses allow us to interpret the position of several lines observed in the excitation spectrum, with the aid of the data given in Table 4, several questions remain open as to the assignment of several other bands. The following remarks should be made:

(a) The data of Table 4 do not make it possible to interpret the part of the excitation spectrum lying below the (0,0) transition, as hole-burning spectra definitely ruled out the possibility of them being hot bands.

(b) The Franck−Condon factors[16,17] calculated by means of the data given in Table 4 do not reproduce the intensities of the observed bands in a satisfying manner. Such an effect is expected in the case of strong vibronic interactions between the considered electronic state and some other states of the molecule (for example, this is the case of the excitation spectra of benzo[ghi]perylene, reported recently[18]).

TABLE 4: Experimental Frequencies of the Vibrations Observed in the S_0 (A_g) ↔ S_1 (B_{1u}) Transitions of Terrylene (from Tables 1 and 3), Corresponding Calculated Values (from Table 2), and Frequencies of Vibrations in S_d ($2A_g$) State Derived on the Analysis of Experimental Data

	$S_d = 2A_g$	$S_1 = 1B_{1u}$	$S_0 = 1A_g$	assignment (B3LYP/6-31G* calculations for S_0)	
1[a]	31.5	28.3	16	20.8	a_u
2[a]	53	53.1	30.5	28.5 37.0	b_{1g} b_{3u}
3[a]	107	99.7	107.5	111.7 112.9	b_{2g} b_{3u}
4	240	234.5	244.1	246.7	a_g

[a] These vibrations are observed only by $\Delta v = 2$ transitions.

In our opinion, these features suggest the existence of another excited electronic state in the vicinity of the $^1B_{1u}$ state. Searching for such an excited-state interacting with the S_1 state, we looked at previous works on the spectroscopy of terrylene.

According to the absorption spectrum of terrylene measured in a neon matrix,[8] the transition energy to the next allowed electronic state is 30 694 cm^{-1} in comparison to the 18 993 cm^{-1} value observed for the transition to the S_1 state. Therefore, it is located 11 900 cm^{-1} higher in energy than the S_1 state. Clearly, this state is by far too high in energy to be involved in the spectra reported here.

On the other hand, the calculations done in the present work (TDDFT B3LYP/6-31G*//B3LYP/6-31G*) evidence eight dark excited singlet states located between the two lowest bright states mentioned above. The lowest one is still 8270 cm^{-1} higher in energy than the S_1 state. However, the TDDFT method might overestimate the energy gap between the S_1 and S_d states. Indeed, the calculated energy seems to be very sensitive to the basis set. The corresponding theoretical calculations by means of TD DFT B3LYP/6-31G //B3LYP 6-31G* method place[8] the $S_1 \leftarrow S_0$ transition at 16 326 cm^{-1} and at 17 081 cm^{-1} in our TD DFT B3LYP/6-31G*//B3LYP 6-31G* calculations which is much lower than the observed value of 19 226.5 cm^{-1}.

Therefore, it seems that the explanation can be found in the results of semiempirical calculations obtained by Karabunarliev et al.[2] On the basis of PM3 calculations with expanded configuration interactions Karabunarliev et al. have predicted the existence of a relatively low-lying dark state $2A_g$ of terrylene, which involves single and double excitations. It was suggested by Karabunarliev et al. that the decrease in fluorescence quantum yield from perylene to quaterylene is due to the increasing role played by the forbidden $2A_g$ state in the relaxation processes. If this is the case, the problem of the terrylene molecule becomes formally similar to the wide class of molecules whose photophysical behavior is dependent on the couplings between three states:[19−25] $S_0(1^1A_g)$, $S_d(2^1A_g)$, and $S_1(^1B_{1u})$ where the 2^1A_g state is sometimes called “phantom” state.[22]

We assume that the dark state $S_d(2^1A_g)$ lies just below the bright state $S_1(^1B_{1u})$ in the Franck−Condon region of the $S_0(1^1A_g) - S_1(^1B_{1u})$ transition of terrylene, and that these states are vibronically coupled (what should be realized by b_{1u} vibrations). The vibronic levels of the dark S_d state and the bright state S_1 are mixed and borrowing and redistribution of intensity become possible. The detailed investigation of the coupling scheme at play in molecules of the size of terrylene is a difficult task and beyond the scope of this paper. At the present stage of our knowledge of molecules with similar $S_0(1^1A_g)$, $S_d(2^1A_g)$, and $S_1(^1B_{1u})$ states,[19−25] we do not intend to calculate the vibronic coupling at play in this system. Instead, we propose the following qualitative model to reconstruct the ladder of

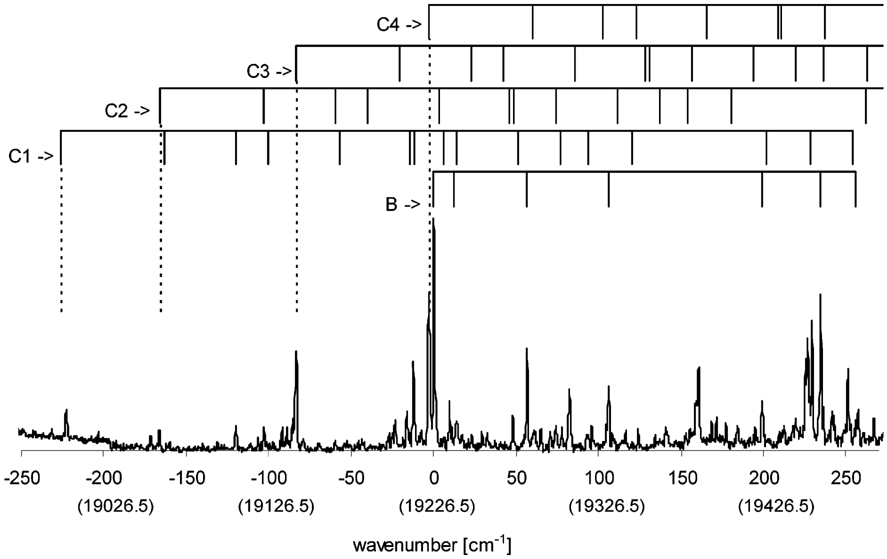

Figure 4. Interpretation of the lines observed in excitation spectrum of terrylene as connected to the transitions: $S_0(1^1A_g) \rightarrow S_1(1^1B_{1u})$ (B) and $S_0(1^1A_g) \rightarrow S_1(2^1A_g)$ for 4 coupling modes (C1−C4).

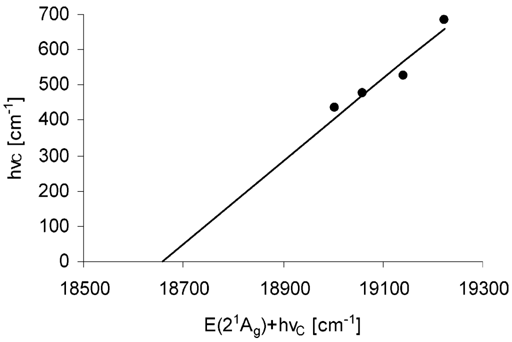

Figure 5. Linear regresion between frequencies of b_{1u} modes calculated by B3LYP/6-31G* method (compare part B of Table 2) and frequencies corresponding to the 4 false origins in the excitation spectrum of terrylene (compare Figure 2 and Table 1). The energy of dark state $E(2^1A_g)$ determined on the base of this correlation is 18657.6 cm^{-1}.

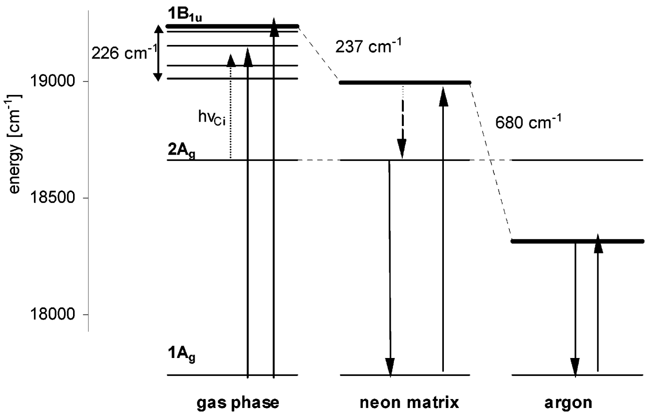

Figure 6. Schematic description of the energy levels involved in the S_1 and S_d states.

vibronic states for two manifolds: $S_d(2^1A_g)$ and $S_1(^1B_{1u})$. This model rests on the experimental spectroscopic data obtained in the present work.

We have to keep in mind that the origin band of the transition to the dark state cannot be seen as the $2^1A_g \leftarrow 1^1A_g$ transition is forbidden. Therefore, we have followed the procedure described hereafter to estimate the position of the origin band.

The lowest allowed transition in the $2^1A_g \leftarrow 1^1A_g$ excitation spectrum is located above the (0,0) transition by $h\nu_c$, where $h\nu_c$ is the frequency of the coupling mode. This lowest allowed transition is the false origin. The bands observed above the false origin are built on vibrations of terrylene in the $2A_g$ state.

Our first hypothesis was that the observed spectrum is built on a single false origin, i.e., that only one vibration is active as a coupling mode. This assumption resulted from the expected very low-energy gap between bright and dark states. Analysis carried within the framework of this hypothesis led to the conclusion that the mode of c.a. 82.3 cm^{-1} is involved in a very long progression extending over the whole excitation spectrum. In practice this means that such a mode should behave not only like a distorted but also displaced oscillator with a very large (in our estimations ≈ 2) displacement parameter. We assumed that a b_{2u} planar vibration, with a frequency of 151.1 cm^{-1} in the S_0 state, can play such a role. However, such a large value of the displacement parameter involves large and specific changes of the terrylene geometry in the $2A_g$ state in comparison with its ground $1A_g$ state. This is not confirmed in a sufficient manner by the results of the semiempirical calculations of Karabunarliev et al.[2]

The second hypothesis is that the observed excitation spectrum $2^1A_g \leftarrow 1^1A_g$ is built with the participation of more than one coupling mode. In such a case, we have several false origins and for each of them we should find progressions containing the frequencies of vibrations in the 2^1A_g state. The corresponding analysis of distances between the lines in the excitation spectrum led to the conclusion that the observed spectrum can be interpreted in terms of overlapping lines of $S_0(1^1A_g) \rightarrow S_1(1^1B_{1u})$ transition and $S_0(1^1A_g) \rightarrow S_d(2^1A_g)$ transitions for 4 coupling modes. This is shown in Figure 4. The deduced values of the vibration frequencies for the $S_d(2^1A_g)$ state are collected in Table 4 whereas the details of the assignment of particular lines are given in Table 1. It is seen (compare data of Table 4) that the deduced values of the vibration frequencies for $S_d(2^1A_g)$ are not very different from that of the bright $S_1(1^1B_{1u})$. The results of the assignment of the lines observed in the excitation spectrum (see Table 1 and Figure 3) are quite acceptable. In several cases, the differences between experimental and attributed position of spectral lines seem to be large, but it is necessary to remember the tentative character of our analysis (zero-order states without interaction between them and therefore without shift of the energy levels, the omitted vibration anharmonicity).

The estimation of the position of the origin band for 2^1A_g requires the knowledge of the frequencies of the coupling modes. In part B of Table 2, we list the frequencies of the b_{1u} vibrations of terrylene with relatively low values which can be responsible for vibrational coupling between the dark 2^1A_g and the bright 1^1B_{1u} states (predicted as nearly degenerate[2]). These frequencies characterize terrylene in the ground electronic state but we assume that the differences between frequencies in S_0 and S_1 are less than 10%, similarly as in the case of perylene.[12] We have correlated the frequencies of these b_{1u} vibrations with spectral positions of four chosen by us false origins for dark state (see Table 1). The results of this correlation are shown in Figure 5. Within approximation by linear regression we have obtained estimation of energy of the dark state as $E(2^1A_g) = 18\,657.6\ \mathrm{cm}^{-1}$.

The existence of the dark state could have implications on the understanding of the anomalous red-shifted fluorescence observed for terrylene in a Ne matrix.[5] Our earlier interpretation of some conformational changes of electronically excited terrylene in this rather soft matrix should be revised. It seems plausible that the anomalous shift of 330 cm^{-1} between excitation and dispersed fluorescence spectra is a consequence of the terrylene electronic internal conversion to the dark state. The energetics are summarized in Figure 6.

According to our estimations, in jet-cooled conditions, the energy gap $E(1^1B_{1u}) - E(2^1A_g)$ is c.a. 570 cm^{-1}. It is well-known from studies performed on polyenes that energy gap between B_u and $2A_g$ states depends strongly on the solvent polarizability mainly due to the shift of B_u energy whereas energy of A_g practically does not change.[25] Asssuming the same for terrylene, the energy gap $E(1^1B_{1u}) - E(2^1A_g)$ is estimated to be c.a. 330 and -350 cm^{-1} in Ne and Ar matrices, respectively (see Figure 5). So, in Argon matrix the 1^1B_{1u} lies lower than the 2^1A_g state and terrylene emits from 1^1B_{1u} state. Indeed, it was observed that fluorescence and fluorescence excitation spectra of terrylene in Ar matrix have a common origin and demonstrate mirror symmetry.[5] However, polarizability of Ne matrix is not sufficient to make inversion between the allowed and dark states. Owing to the vibronic coupling, the 2^1A_g state can be populated from $^1B_{1u}$ state and after vibrational relaxation, emission takes place from the 2^1A_g origin. Experimentally observed fluorescence of terrylene in Ne matrix was found as anomalous,[5] because of the large Stokes shift of fluorescence and lack of the mirror symmetry between absorption and emission spectra. The lifetime measurement performed very recently[26] in Neon and Argon matrices confirms hypothesis about state inversion. The fluorescence lifetime of terrylene is much longer in a Neon matrix (27 ns) than in Argon (4 ns), which shows unambiguously that the emission observed in Ne is due to a weakly allowed transition from 2^1A_g state.

In conclusion, the study of the gas-phase spectrum of terrylene has evidenced the existence of a 2^1A_g dark state lying in the vicinity of the strongly allowed the $^1B_{2u}$ state. This state plays a role in the deactivation processes of terrylene in a low polarizability medium like the Neon matrix and these results have made it possible to explain the lack of mirror-symmetry relation between the emission and absorption spectra of terrylene embedded in a Neon matrix.

Acknowledgment. We are indebted to Dr. Schmidt, who generously provided the terrylene used in this work.

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