Spectroscopic Characteristics of Pentacene In Shpol'skii Matrixes

M. Banasiewicz, I. Deperasińska, and B. Kozankiewicz*

Institute of Physics, Al. Lotników 32/46, PL 02-668 Warsaw, Poland

Received: June 28, 2002; In Final Form: October 15, 2002

Absorption, fluorescence, and fluorescence excitation spectra of pentacene were measured in *n*-heptane, *n*-nonane, *n*-decane, *n*-dodecane, *n*-tetradecane, and *n*-hexadecane at temperature 5 K. We found that the band shift in different matrixes is well described by the intermolecular dispersive interactions with the Onsager cavity radius 5.5 ± 0.8 Å. Analysis of the fluorescence vibronic structure indicated contribution of 12 totally symmetric vibrations in the frequency range below 2000 cm^{-1}. The ab initio calculations with 6-31G(d) basis set and semiempirical AM1 calculations were carried out to explain the structure of the spectra.

I. Introduction

Pentacene (Pc) molecules occupying the O_1 (and O_2) sites in *p*-terphenyl crystal were the first and the most frequently studied systems in the exciting field of single molecule spectroscopy at pumped helium temperatures.[1,2] The intersystem crossing (ISC) yield of the $S_1 \rightarrow T_1$ relaxation of Pc is very sensitive to the matrix and site,[3−5] and for a long time it was difficult to find a matrix (other than *p*-terphenyl and naphthalene[6] crystals) where this yield is sufficiently low to allow detection of single Pc molecules. Two years ago, Durand et al.[7] succeeded to monitor single Pc molecules in *n*-tetradecane (C_{14}) and in *n*-hexadecane (C_{16}) and failed in some other Shpol'skii matrixes. Our subsequent studies of these systems[8,9] showed that the ISC yield is as low as 1.3% ± 0.4% for Pc in C_{14},[7] increases to 10% ± 8% for Pc in C_{16},[9] and is still higher in other Shpol'skii matrixes,[9] in good agreement with the experiment.[7]

In the present report, we present detailed spectroscopic studies of bulk Pc samples, which were done parallel to the kinetic investigations. We studied absorption, fluorescence, and fluorescence excitation spectra of Pc in *n*-heptane (C_7), *n*-nonane (C_9), *n*-decane (C_{10}), *n*-dodecane (C_{12}), C_{14}, and C_{16} at 5 K. The spectra were analyzed with the aid of ab initio calculations[10] with 6-31G(d) basis set and semiempirical AM1[11a,b] calculations. The goal was to get information about the surrounding of Pc molecules in Shpol'skii matrixes.

II. Experimental Section

Spectroscopic studies were performed with saturated solutions of Pc (Aldrich) in *n*-alkanes (from Aldrich or Merck). Liquid samples were bubbled with argon to remove oxygen and quickly frozen by inserting into liquid nitrogen before being transferred to a liquid helium optical cryostat. In the case of absorption study, liquid samples were also gently heated to increase Pc solubility. The fluorescence spectra of Pc samples, one that was kept at room temperature only and another that was preheated, had exactly the same shape. Thus, we did not consider the possibility that heating led to Pc aggregates.

Single beam absorption spectra were measured with the aid of a homemade cuvette in which two quartz windows were separated by a 1.5 mm Teflon ring. The light of a tungsten lamp, which was transmitted through the sample solid solution, was analyzed with a McPherson 207 monochromator and detected with an EMI9659 photomultiplier operating in the photon-counting mode.

Fluorescence and fluorescence excitation spectra were measured with the photon-sampling technique. The excitation source was a Lambda Physik FL1001 dye laser pumped by an LPX100 excimer laser. Fluorescence was analyzed with a McPherson 207 monochromator and detected with an EMI9659 photomultiplier (prepared for pulse operation) and a Stanford Research SR250 boxcar averager.

Theoretical calculations were curried out by using the ab initio[10] and the semiempirical AM1 method.[11a,b]

III. Results and Discussion

Absorption. The spectrum of the light beam emitted from a tungsten lamp, which went through the solid sample solution of Pc in a C_{14} matrix, is presented in Figure 1A. This spectrum had some contribution of Pc fluorescence, indicated by the presence of the fluorescence vibronic component at 16 825 cm^{-1}. Thus, to obtain the absorption spectrum, presented in Figure 1C, we had to remove the fluorescence contribution. Successive steps of this procedure are presented in Figure 1.

Using the above procedure, we measured absorption spectra of Pc in C_{10}, C_{12}, C_{14}, and C_{16} at 5 K, see Figure 2. The characteristic features of these spectra are the domination of the (0,0) line and the shift of this line to lower energies with increasing length of the *n*-alkane chain.

Fluorescence. The fluorescence spectra of Pc in the studied matrixes are presented in Figure 3. The characteristic features of these spectra, like in the case of absorption, are the much higher intensity of the (0,0) line as compared to the vibronic components and its shift to lower energies with increasing length of the *n*-alkane chain. The maxima of fluorescence (0,0) lines are shifted to lower energies by less than 10 cm^{-1} with respect to the maximum of corresponding absorption lines. This observation may indicate a small reorganization of the cavity containing the Pc molecule during the lifetime of the excited S_1 state.[12]

Beside the above spectra, we observed a progression of much weaker fluorescence lines from high-energy sites, which had their origin (0,0) lines at 17 384, 17 364, 17 357, 17 391, and 17 348 cm^{-1} for Pc in C_7, C_9, C_{10}, C_{12}, and C_{14} matrixes,

---

* To whom correspondence should be addressed. E-mail: kozank@ifpan.edu.pl. Fax: (+48-22) 843 09 26.

10.1021/jp021527w CCC: $25.00

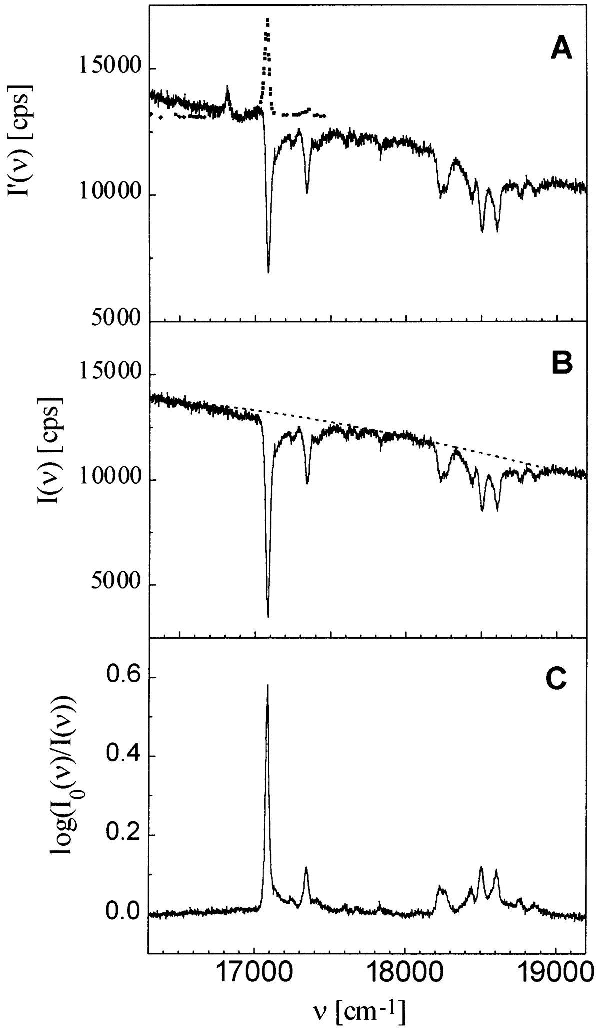


Figure 1. Experimental determination of the absorption spectrum of Pc in a C_{16} Shpol‘skii matrix: (A) single-beam spectrum of a tungsten lamp light that went through a solid sample solution of Pc in C_{16} (solid line) and the fluorescence contribution indicated by the dashed line; (B) single-beam spectrum without the fluorescence contribution ($I(\nu)$, solid line) and spectrum observed for a solid solution of C_{16} without Pc ($I_0(\nu)$, dotted line); (C) calculated absorbance ($\log(I_0(\nu)/I(\nu))$) spectrum of Pc in C_{16} matrix.

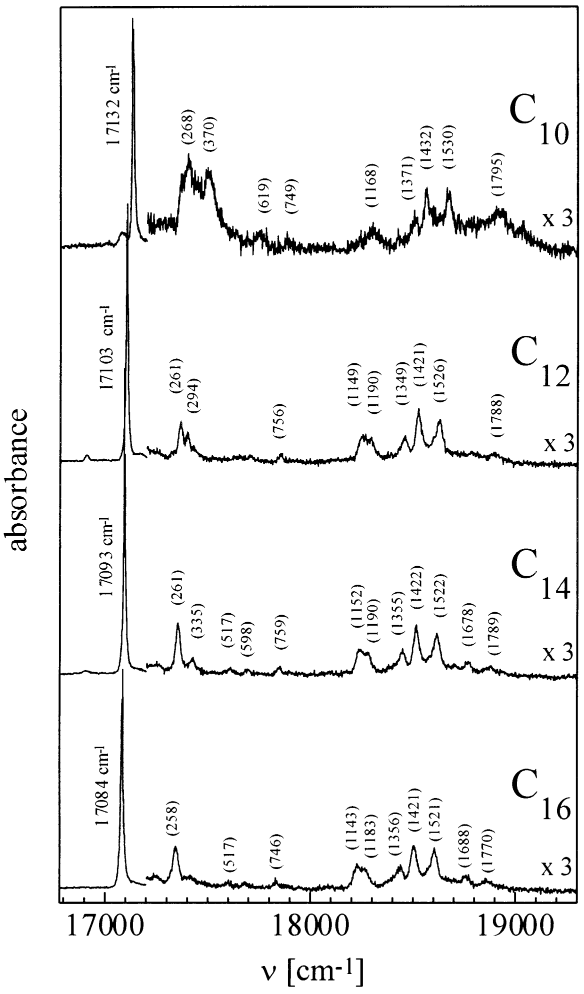


Figure 2. Absorption spectrum of Pc in different Shpol'skii matrixes at 5 K. The numbers in parentheses indicate the vibrational frequencies (given in cm^{-1}) obtained with respect to the (0,0) origin line.

respectively. The fluorescence intensity from the high-energy site, with respect to the fluorescence intensity from the main Pc site, increases with decreasing length of the *n*-alkane chain. Thus, taking into account that a good match of the long axis Pc structure and the zigzag structure of *n*-alkane can be expected only for C_{12}, C_{14}, and C_{16}, we may conclude that Pc molecules in the main site are tightly surrounded by *n*-alkane chains whereas in the high-energy sites there is some empty space around Pc. In the remaining part of this report, we limit our study to the main sites of Pc.

Fluorescence Excitation. Fluorescence excitation spectra of Pc in the studied Shpol'skii matrixes are shown in Figure 4. They have similar structure and spectral position to the absorption spectra presented in Figure 2.

Spectral Shift of the (0,0) Origin Line of Pc in Shpol'skii Matrixes. The solvent shift of nonpolar (or weakly polar) molecules can be described by the simple expression, proposed by Bakshiev et al.,[13]

$$\nu = \nu_0 - [(n^2 - 1)/(n^2 + 2)]3II'(\alpha_e - \alpha_g)/[2(I + I')a^3] \quad (1)$$

where ν and ν_0 are the maxima of the (0,0) lines of the studied molecule in the solvent and in a vacuum, n is the refractive index of the solvent, I and I' are the ionization energies of the studied guest and solvent molecules, $\Delta\alpha = (\alpha_e - \alpha_g)$ is the average static polarizability difference between the excited (e) and the ground (g) state, and a is the Onsager cavity radius of the molecule. Except the Onsager cavity radius, all other values in eq 1 can be determined experimentally for Pc in the Shpol'skii matrixes.

The $\nu_0 = 18\,649\ cm^{-1}$ is known from Pc studies in expanding supersonic beam.[14] The maxima of the (0,0) lines, ν, for Pc in Shpol'skii matrixes were determined in the present work, see Figures 2−4. The refractive indexes of *n*-alkanes are given in the literature for their liquid solutions at 20 °C.[15] To estimate the refractive index in frozen *n*-alkanes, we used the Lorentz−Lorentz relation,[16] which shows that the function $\Phi(n^2) = (n^2 - 1)/(n^2 + 2)$ is proportional to the matrix density. Density of liquid C_7 is 0.683 76 g/cm^3,[15] whereas it increases to 0.890 g/cm^3 for solid C_7 at 100 K.[17] Thus, $\Phi(n^2)$ is 1.30 times bigger for solid than for liquid C_7. Calculated in this way, the n value should be considered as some kind of averaged refractive index of a Shpol'skii matrix (which in reality is anisotropic). Neglecting compression of the solid between 100 and 5 K and assuming the same factor (1.30) for other Shpol'skii solvents, we calculated that the average refractive indexes for solid C_7, C_9, C_{10}, C_{12}, C_{14}, and C_{16} at 5 K are 1.525, 1.550, 1.558, 1.574, 1.585, and 1.593, respectively. Let us mention that a similar approach was already used for the frozen solutions of C_7 and

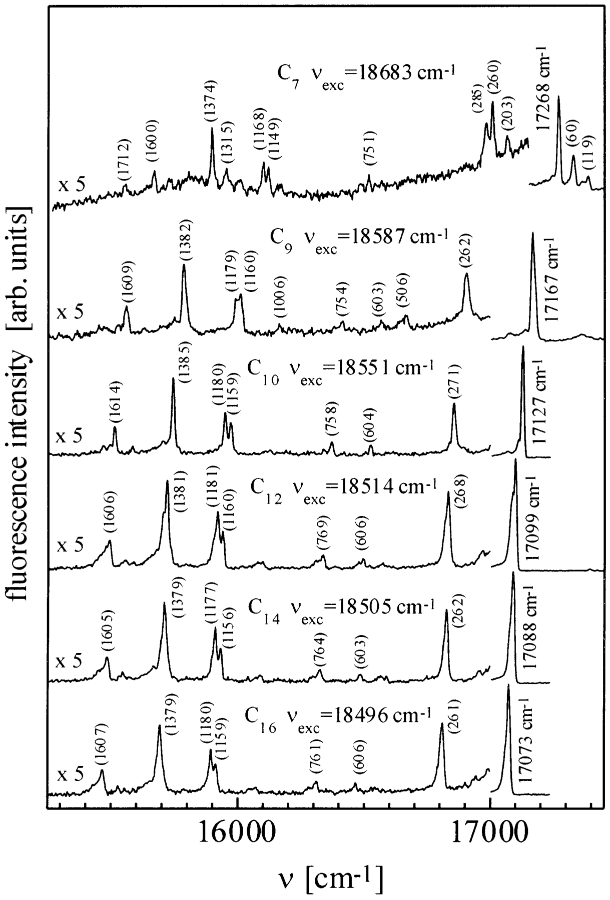


Figure 3. Fluorescence spectra of Pc in different Shpol'skii matrixes at 5 K. The numbers in parentheses indicate the vibrational frequencies (given in cm^{-1}) obtained with respect to the origin (0,0) line.

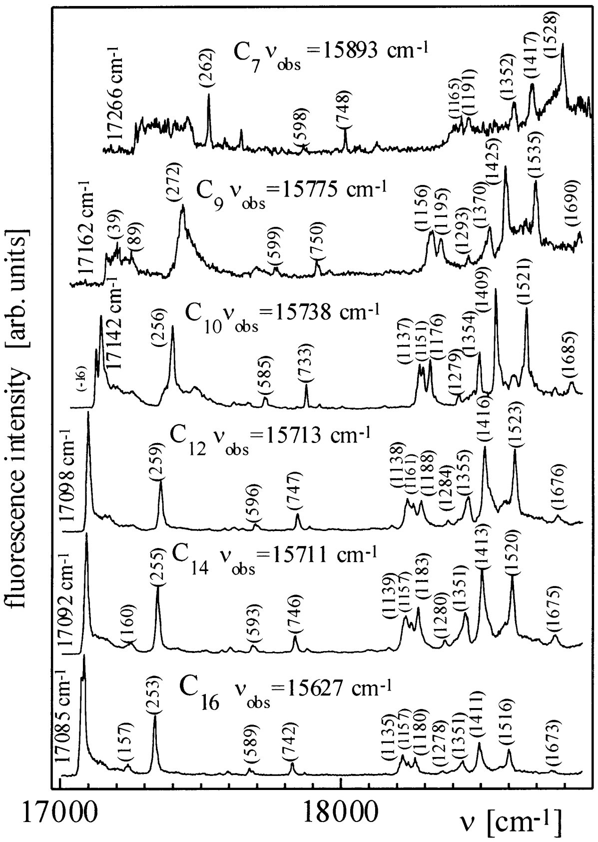


Figure 4. Fluorescence excitation spectra of Pc in different Shpol'skii matrixes at 5 K. The numbers in parentheses indicate the vibrational frequencies (given in cm^{-1}) obtained with respect to the origin (0,0) line.

C_8.[18] Ionization energy of Pc is 6.68 ± 0.10 eV.[19] Ionization energies of *n*-alkanes are 9.93 ± 0.10, 9.71 ± 0.10, and 9.65 eV for C_7, C_9, and C_{10}, respectively.[15] Thus, for all studied Shpol'skii matrixes, we used the common value of 9.75 ± 0.25 eV. Polarizability difference for Pc, $\Delta\alpha = (18 \pm 7) \times 10^{-40}$ F m^2, is known from the Stark effect observed for single Pc molecules in a *p*-terphenyl crystal.[20]

Substituting the above values into eq 1, we find the Onsager cavity radius of 5.5 ± 0.8 Å. On the other hand, the Onsager cavity radius calculated theoretically for the molecular structure of Pc optimized in the 6-31 G(d) basis set [10] is 5.05 Å. Thus, taking into account the experimental error, both values of the Onsager cavity radius, obtained from the experimental data and calculated, are equal. This is a rather unexpected result because the Bakhshiev formula was derived with several simplifying assumptions and was applied in principle to isotropic, liquid solvents. Our work shows that this approach can be successfully used to describe the (0,0) line shift in anisotropic Shpol'skii matrixes as well.

Vibronic Structure Analysis of Fluorescence and Absorption Spectra of Pentacene. Absorption and fluorescence spectra of Pc in Shpol'skii matrixes (Figures 2 and 3) are composed of vibronic bands with widths of 15−20 cm^{-1}. Vibrational frequencies (except probably the lowest frequency vibration, 262 cm^{-1}) and their relative intensities within the error limit are not dependent on the matrix. The absorption−fluorescence mirror symmetry is observed in the frequency region up to 1300 cm^{-1} from the (0,0) origin line. Above this frequency, the mirror symmetry breaks. Intensities of vibronic bands in the absorption spectrum of Pc are higher in comparison to the intensity of vibronic bands in the fluorescence spectrum. This effect can be explained by the Herzberg−Teller coupling with higher-lying electronic state with strongly allowed electronic transition, the feature observed already for several other polycyclic hydrocarbons.[12,21,22]

The Franck−Condon (FC) analysis[23,24] of the electronic spectra provides information about the frequencies (ν) of the vibrational modes and their displacement parameters (Δ), which describe geometric changes when the molecule is transferred from its electronic ground (S_0) to the lowest excited (S_1) state.

Results of the FC analysis of the fluorescence spectrum of Pc in the C_{14} matrix are collected in Table 1 (experiment) and visualized in Figure 5. It appears that 12 vibronic modes with relatively small displacement parameters (in other words with short progression in the spectrum) can perfectly describe the fluorescence spectrum of Pc.

Generally, small values of the displacement parameters (as well as small Stokes shift between the position of (0,0) lines in absorption, Figure 2, and fluorescence, Figure 3, denote that the geometric structures of Pc in the S_0 and S_1 states are similar. The relatively biggest Δ values were found for the 262, 1179, and 1379 cm^{-1} modes.

To understand the structure of the spectra, we should compare the experimental results with the results of theoretical calculations. Normal-mode calculations for Pc were already done by Ohno.[25] Recently, the semiempirical CNDOM calculations of the electronic spectra[26] and ab initio calculations of the geometry and rotational constants were reported.[14] In this work, we carried out both ab initio calculations with 6-31G(d) basis set[10] and semiempirical AM1[11] calculations.

TABLE 1: Experimental (Figure 5) and Calculated Properties of the Vibrational Modes of Pc[a]

experiment		calculation		
ν (cm^{-1})	Δ	ν (cm^{-1})	Δ	Δ_L/Δ_S[b]
262	0.52	257	0.78	39.0
603	0.18	601	0.61	2.5
		636	0.31	1.6
764	0.23	753	0.17	0.7
790	0.17	778	0.36	1.6
1000	0.18	981	0.18	0.6
1155	0.36	1180	0.08	1.6
1179	0.45	1197	0.30	6.0
1300	0.14	1305	0.42	2.6
1379	0.54	1396	0.50	6.3
1421	0.21	1463	0.25	2.5
		1488	0.24	1.2
1542	0.20	1594	0.44	1.1
1605	0.31	1605	0.37	0.6

[a] Calculated frequencies of the totally symmetric vibrations of Pc were obtained with the aid of ab initio 6-31G(d) method, while the displacement parameters were obtained for the geometry of the ground and excited singlet states of Pc calculated with the AM1 method. [b] The ratio Δ_L/Δ_S, where Δ_L and Δ_S are displacements along the long and short molecular axes, respectively, informs about the preferred direction of the molecular vibration.

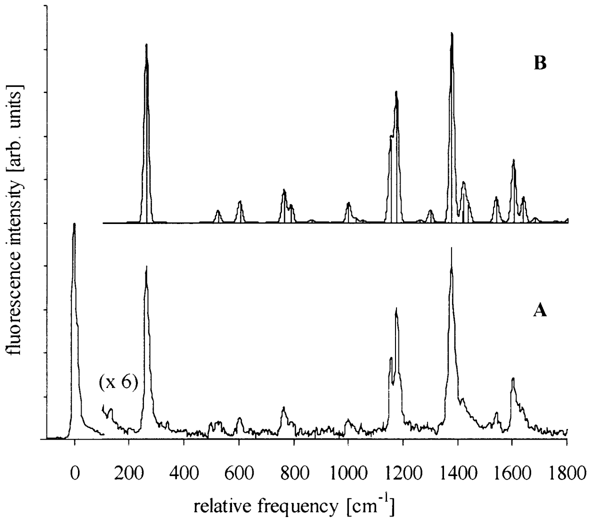


Figure 5. Fluorescence spectrum of Pc in C_{14} matrix (A) and the simulated spectrum (B), which took into account 12 vibronic modes. The vibronic frequencies and their reduced displacement parameters are given in Table 1. All lines in the simulated spectrum were drawn as Gaussian curves with the fwhm of 16 cm^{-1}.

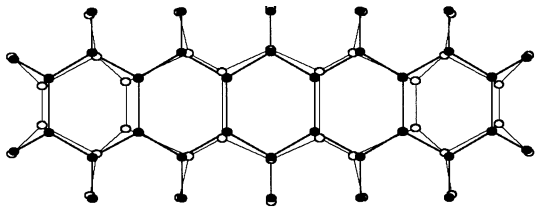


Figure 6. Geometric structure of Pc in the electronic ground S_0 state (full circles) and in the lowest excited singlet state S_1 (open circles) calculated with the AM1 method.

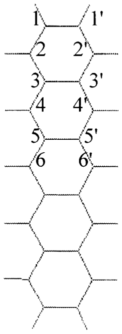
First, we optimized the geometric structure of Pc in the electronic ground state (S_0) and in the lowest excited singlet (S_1) state. The results of geometry optimization within the framework of different calculation methods are collected in Table 2, together with the existing experimental data of the bond lengths[27] and rotational constants.[14] It is seen that the geometry of Pc in the S_0 state optimized by the ab initio and AM1 methods are both similar and in very good agreement with the experimental data.[27] The similar geometry was also optimized recently with the B3LYP/cc-pVDZ basis set.[28] The geometry of Pc in the S_1 state was investigated in this work by the AM1 method only. The corresponding bonds lengths are given in the last column of Table 2, section A, and the predicted geometry change upon the $S_0 \rightarrow S_1$ excitation is visualized in Figure 6. It is seen that the Pc molecule in the relaxed S_1 state becomes stretched along its long axis, which is intuitively expected as a result of loosened binding upon an electronic excitation. The total geometry change is, however, small. To test whether the geometry change predicted by the AM1 method is correct, we calculated the rotational constants of Pc in the S_0 and S_1 states and compared them with the experimental data.[14] The result is shown in Table 2, section B. The rotational constants obtained by the AM1 method are in quantitative agreement with the experimentally determined ones. Furthermore, calculated and measured constants change the same way when Pc is excited from the S_0 to the S_1 state.

Frequencies of the totally symmetric vibrations of Pc in the harmonic approximation were obtained in this work by ab initio calculations with the 6-31G(d) basis set and using scaling factor 0.92. The displacement parameters were estimated with the aid of the AM1 method. The calculated frequencies quite well reproduce the experimental spectrum, see frequencies collected in Table 1. However, in the fluorescence spectrum of Pc in the frequency range below 2000 cm^{-1}, we observed 12 modes instead of 14 totally symmetric modes, which were theoretically predicted. Therefore, we propose that in reality the displacement parameters of the two lacking modes, calculated at 636 cm^{-1} and probably at 1488 cm^{-1}, are very small. The calculated displacement parameters are generally larger in comparison to the experimentally determined ones, and this effect can be explained by the fact that a frozen Shpol'skii matrix hinders the geometry changes during the S_1 state relaxation process. The largest experimentally determined displacement parameters, and thus the highest intensity of vibronic bands, correspond to the 262, 1179, and 1379 cm^{-1} vibrations. All of these vibrations (see Table 1) are characterized by very large Δ_L/Δ_S ratio. The most interesting is the vibration 262 cm^{-1}, which is nearly a pure long-axis vibration. A close inspection of the frequency of this vibration in the absorption, fluorescence, and fluorescence excitation spectra (Figures 2−4) seems to show that this frequency is smaller the longer the *n*-alkane chain is (in series C_{10}, C_{12}, C_{14}, and C_{16}). In other words, Pc is more tightly packed in *n*-alkanes with a longer chain.

Calculation of the Transition Energies. Energies of electronic states of Pc were calculated within the AM1 method. It is important to mention that energies of these states, and even the order of states, were strongly dependent on the number of considered excited electronic configurations. The result of AM1 calculation with as much as 250 electronic configurations, when the states order and their energies seemed to be finally established, is presented in Table 3 for both geometries of Pc, corresponding to that in the S_0 and in the S_1 states.

It is well-known that theoretical calculations are usually not very precise in determining energies of the excited electronic states of large molecules, such as pentacene. The calculated energy difference between the S_0 and S_1 states of 20 655 cm^{-1} is not far from the experimentally determined value of 18 649 cm^{-1}.[14] Let us mention that according to our AM1 calculations it is the T_4 triplet state that is close to the lowest excited singlet state S_1 and the ordering of both states is different in the S_0 state geometry (where T_4 is below S_1) than in the S_1 state geometry (where T_4 is above S_1). The relative ordering of the

TABLE 2: Experimentally Determined and Calculated Geometric Structure of Pc in the Electronic Ground (S_0) and in the Lowest Excited Singlet (S_1) States[a]

{A}		$r_{ab}(S_0)$				$r_{ab}(S_1)$
	bond length	experiment [from ref. (27)]	6-31G(d) [this work]	AM1 [this work]	B3LYP /cc-pVDZ [from ref. (28)]	AM1 [this work]
	$r_{11'}$	1.43	1.447	1.433	1.435	1.414
	r_{12}	1.35	1.339	1.359	1.368	1.376
	r_{23}	1.42	1.449	1.441	1.438	1.420
	$r_{33'}$	1.44	1.448	1.442	1.457	1.432
	r_{34}	1.38	1.364	1.381	1.391	1.407
	r_{45}	1.40	1.420	1.421	1.417	1.402
	$r_{55'}$	1.45	1.435	1.434	1.458	1.451
	r_{56}	1.39	1.391	1.401	1.405	1.405
{B}	**Rotational constant**	experiment [from ref. (14)]	6-31G(d) [this work]	AM1 [this work]		AM1 [this work]
S_0 state	A”	44.050	44.458	44.205		
	B”	3.935	3.959	3.933		
	C”	3.612	3.636	3.612		
S_1 state	A’	44.490				44.332
	B’	3.909				3.922
	C’	3.594				3.603

[a] In part A, the bond lengths are given in Å units; in part B, the rotational constants are given in 10^{-3} cm^{-1} units.

TABLE 3: Energies of Some Lowest-Energy Excited Electronic States of Pc Calculated with 250 Singly Excited Electronic Configurations for the Geometry of Pc Optimized in the S_0 and S_1 States

Pc optimized in the S_0 state		Pc optimized in the S_1 state	
state	E (cm^{-1})	state	E (cm^{-1})
T_1 (B_{1u})	7 327	T_1 (B_{1u})	4 467
T_2 (B_{3g})	12 309	T_2 (B_{3g})	10 945
T_3 (B_{1u})	17 354	T_3 (B_{1u})	16 443
T_4 (B_{2u})	19 895	S_1 (B_{2u})	18 681
S_1 (B_{1u})	20 655	T_4 (B_{1u})	18 853
T_5 (B_{2u})	21 570	S_2 (B_{2u})	20 361
S_2 (B_{2u})	21 885	T_5 (B_{2u})	20 741

S_1 and T_4 states cannot be verified experimentally. However, observation of the small Stokes shift between the absorption and fluorescence spectra may indicate some reorganization of the Pc geometry in the S_1 state. This reorganization may result in modification of the corresponding wave functions and the ISC transition probabilities of Pc (for the analysis of ISC pathways in Pc see refs 5 and 26) and may result in high sensitivity of the S_1 state relaxation to the environment.

IV. Conclusions

Absorption, fluorescence, and fluorescence excitation spectra of Pc in *n*-heptane, *n*-nonane, *n*-decane, *n*-dodecane, *n*-tetradecane, and *n*-hexadecane at temperature 5 K are composed of narrow quasi-lines. The solvent shift of the (0,0) line of Pc spectra in different matrixes was described by the Bakshiev model, which takes into account the intermolecular dispersive interactions. This approach yielded the Onsager cavity radius of Pc, 5.5 ± 0.8 Å, in good agreement with the theoretically calculated value.

The structure of the electronic spectra of Pc was investigated in terms of the Franck−Condon analysis. On the other hand, the ground and excited states of Pc were studied by quantum chemistry methods, and the Franck−Condon parameters were evaluated for the totally symmetric modes. The comparison of the Franck−Condon parameters derived from the experiment and from the calculations shows that the most prominent components of Pc spectra in Shpol'skii matrixes correspond to the modes that operate practically along the long axis of Pc. Other vibrations, those with high contribution along the short axis of Pc, are less active or absent in the spectra.

This observation indicates that the Shpol'skii matrix hinders the geometry changes occurring during the S_1 state relaxation, especially in the direction of the short axis of Pc. Unfortunately, the differences between the spectra in the investigated matrixes are too small to go deeply into the analysis.

The calculated relative ordering of the lowest excited singlet state S_1 and the ladder of triplet states (it concerns in particular to the S_1 and T_4 states) is different for the two geometrical structures of Pc, optimized in the ground S_0 and in the excited S_1 state. Although the relative ordering of states, which can alter during relaxation of the excited S_1 state of Pc in a matrix, is difficult to verify experimentally, we propose that this process can be responsible for observed variation of the probability of intersystem crossing.

References and Notes

(1) Basché, T.; Moerner, W. E.; Orrit, M.; Wild, U. P. *Single-Molecule Optical Detection, Imaging and Spectroscopy*; VCH: Weinheim, Germany, 1997.

(2) Tamarat, Ph.; Maali, A.; Lounis, B.; Orrit, M. *J. Phys. Chem. A* **2000**, *104*, 1.

(3) de Vries, H.; Wiersma, D. A. *J. Chem. Phys*. **1979**, *70*, 5807.

(4) Williams, J. O.; Jones, A. C.; Davies, M. J. *J. Chem. Soc., Faraday Trans. 2* **1983**, *79*, 263.

(5) Corval, A.; Kryschi, C.; Astilean, S.; Trommsdorff, H. P. *J. Phys. Chem.* **1994**, *98*, 7376.

(6) Kummer, S.; Bräuchle, C.; Basché, T. *Mol. Cryst. Liq. Cryst.* **1996**, *283*, 255.

(7) Durand, Y.; Bloess, A.; van Oijen, A. M.; Kohler, J.; Groenen, E. J. J.; Schmidt, J. *Chem. Phys. Lett.* **2000**, *317*, 232.

(8) Kozankiewicz, B.; Banasiewicz, M.; Dresner, J.; Orrit, M. *Chem. Phys. Lett.* **2001**, *343*, 71.

(9) Banasiewicz, M.; Deperasińska, I.; Fabjanowicz, D.; Kozankiewicz, B. *Chem. Phys. Lett.* **2002**, *356*, 541.

(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

(11) (a) Dewar, M. J. S.; Zoebsh, E. W.; Haels, E. E.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. (b) *HyperChem for Windows*, release 5.1; HyperChem Computation Chemistry Publication HC50-00-03-00; Hypercube Inc.: Gainesville, FL, 1996.

(12) Crepin, C.; Tramer, A. *Chem. Phys.* **2001**, *272*, 227.

(13) Bakshiev, N. G.; Girin, O. P.; Piterskaya, I. V. *Opt. Spectrosc.* **1968**, *24*, 313.

(14) Heinecke, E.; Hartmann, D.; Muller, R.; Hese, A. *J. Chem. Phys.* **1998**, *109*, 906.

(15) *CRC Handbook of Chemistry and Physics*, 60th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1980.

(16) Jackson, J. D. *Classical Electrodynamics*; Wiley: New York, 1975.

(17) Merle, A. M.; Lamotte, M.; Risenberg, S.; Hauw, C.; Gaultier, J.; Grivet, J. Ph. *Chem. Phys.* **1977**, *22*, 207.

(18) Renge, I. *J. Phys. Chem.* **1995**, *99*, 15955.

(19) (a) Boschi, R.; Clar, E.; Schmidt, W. *J. Chem. Phys.* **1974**, *60*, 4406. (b) Schmidt, W. *J. Chem. Phys.* **1977**, *66*, 828.

(20) Wild, U. P.; Guttler, F.; Pirotta, M.; Renn, A. *Chem. Phys. Lett.* **1992**, *193*, 451.

(21) Zilberg, S.; Samuni, U.; Fraenkel, R.; Haas, Y. *Chem. Phys*. **1994**, *186*, 303.

(22) Ohno, K. *Chem. Phys. Lett.* **1977**, *53*, 571.

(23) Henry, B.; Siebrand, W. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: London, 1973; Vol. 1, pp 196−210.

(24) Deperasińska, I.; Kozankiewicz, B.; Biktchantaev, I.; Sepioł, J. *J. Phys. Chem. A* **2001**, *105*, 810.

(25) Ohno, K. *J. Mol. Spectrosc*. **1979**, *77*, 329.

(26) Kryschi, C.; Fleischhauer, H.-C.; Wagner, B. *Chem. Phys*. **1992**, *161*, 485.

(27) Campbell, R. B.; Robertson, J. M. *Acta Crystallogr*. **1962**, *15*, 289.

(28) Deleuze, M. S.; Trofimov, A. B.; Cederbaum, L. S. *J. Chem. Phys.* **2001**, *115*, 5859.