

# Theoretical Investigations on Absorption and Fluorescence of Perylene and its Tetracarboxylic Derivatives

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**Summary.** Theoretical molecular geometries of the perylene derivatives 3,4,9,10-perylene tetracarboxylic dianhydride (*PTCDA*), 3,4,9,10-perylene tetracarboxylic diimide (*PTCDI*), *N,N'*-dimethyl 3,4,9,10-perylene tetracarboxylic diimide (*MePTCDI*), and 3,4,9,10-perylene tetracarboxylic disulfide (*PTCDS*) are presented for the electronic states  $S_0$  and  $S_1$ . On this basis, the electronic absorption properties can be interpreted and compared with experimental data. The vibronic structure of  $S_0 \rightarrow S_1$  absorption and  $S_1 \rightarrow S_0$  fluorescence has been reproduced. The analysis of the active vibrational modes shows a corresponding behaviour of derivatives and perylene.

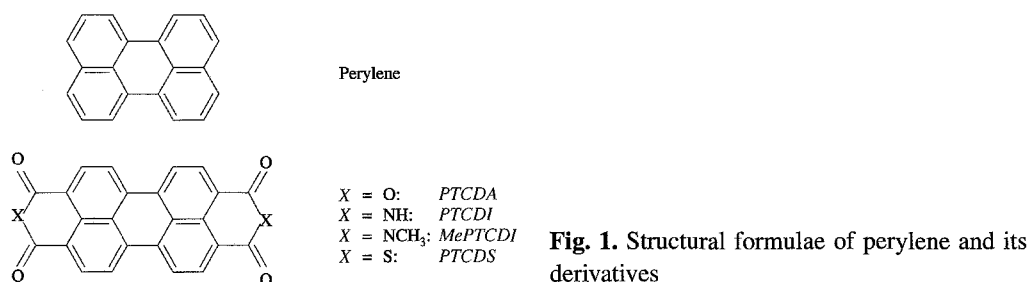
**Keywords.** Absorption/fluorescence properties; Molecular structure; Perylene tetracarboxylic derivatives; Vibronic structure.

## Theoretische Untersuchungen der Absorption und Fluoreszenz von Perylen und seinen Tetracarbonsäure-Derivaten

**Zusammenfassung.** Theoretische Molekülgeometrien der Perylen-Derivate 3,4,9,10-Perylentetracarbonsäuredianhydrid (*PTCDA*), 3,4,9,10-Perylentetracarbonsäurediimid (*PTCDI*), *N,N'*-Dimethyl-3,4,9,10-Perylentetracarbonsäurediimid (*MePTCDI*) und 3,4,9,10-Perylentetracarbonsäuredisulfid (*PTCDS*) für die elektronischen Zustände  $S_0$  und  $S_1$  werden vorgestellt. Auf dieser Grundlage können die elektronischen Absorptionseigenschaften interpretiert und mit experimentellen Daten verglichen werden. Die vibronische Struktur der  $S_0 \rightarrow S_1$ -Absorption und der  $S_1 \rightarrow S_0$ -Fluoreszenz konnte reproduziert werden. Die Analyse der aktiven Schwingungsmoden zeigen ein gegenüber Perylen vergleichbares Verhalten der Derivate.

## Introduction

The investigation of the perylene derivatives 3,4,9,10-perylene tetracarboxylic dianhydride (*PTCDA*), 3,4,9,10-perylene tetracarboxylic diimide (*PTCDI*), and *N,N'*-dimethyl 3,4,9,10-perylene tetracarboxylic diimide (*MePTCDI*) (Fig. 1) is of currently increasing interest due to their huge variety of possible future electronic and photonic applications (*e.g.* diodes [1], waveguides [2], quantum well structures [3]). Structural investigations like STM [4, 5], LEED, XPS [6] and RHEED [7] have shown that they are promising candidates for well ordered growth of thin



**Fig. 1.** Structural formulae of perylene and its derivatives

films on various substrates. However, there is little knowledge about the basic optical properties of these compounds. Though molecular structure and Raman and IR spectra are comparable, the absorption spectra of thin films of these compounds reveal significant differences [8, 9] which can be attributed to their different crystal structures and film ordering. The contributions from different intermolecular interactions and the molecular properties have still to be discussed. The aim of the present paper is to provide a theoretical description of the molecular absorption and fluorescence spectra of the perylene derivatives and a comparative analysis of experimental results obtained in liquid solution.

The molecular structure and the spectroscopic properties of perylene are well known both experimentally [10, 11] and theoretically [12]; they are used as a reference for its derivatives in this paper. The experimental comparison of perylene with its derivatives is performed on the basis of degassed dilute solutions in  $CHCl_3$ . However, due to the poor solubility of the derivatives in general, direct absorption spectra can be measured merely for MePTCDI, otherwise the relative absorption is obtained indirectly *via* fluorescence excitation. The details of absorption and fluorescence experiments have been described elsewhere [13]. Both absorption and fluorescence of the three perylene derivatives show a similar spectral shape with a vibronic progression comparable to perylene. The 0-0 energies of the  $S_0 \rightarrow S_1$  absorption vary slightly (PTCDA:  $19390\text{ cm}^{-1}$ , PTCDI:  $19240\text{ cm}^{-1}$ , MePTCDI:  $19040\text{ cm}^{-1}$ ) and are red-shifted by about  $3600\text{ cm}^{-1}$  with respect to perylene.

The paper is organized as follows: after presenting the completely optimized molecular geometries of the  $S_0$  and  $S_1$  state as a basis of the spectroscopic behaviour, the electronic transition energies and strengths will be shown. Finally, the vibronic structure of the  $S_0 \rightarrow S_1$  absorption and the  $S_1 \rightarrow S_0$  fluorescence will be characterized. The investigated compounds are PTCDA, PTCDI, MePTCDI, and the hypothetical 3,4,9,10-perylene tetracarboxylic disulfide (PTCDS, see Fig. 1).

## Methods

The modified QCFFVC method [14–17] was used to calculate the completely optimized molecular geometries dependent on all  $3N$  molecular coordinates as well as the electronic  $S_0 \rightarrow S_p$  transition energies and oscillator strengths. As compared with other known quantum chemical procedures, this method is especially favoured for the geometry optimization of excited electronic states and the determination of transition energies with reasonable accuracy for  $\pi$  conjugated organic molecules. In addition, vibrational energies, the corresponding wave functions, and vibronic coupling constants can be obtained. The latter data are necessary for the theoretical description of vibrationally

structured spectra. For the complete optimization, 64 and 120 single-excited configurations were taken into account for perylene and its derivatives, respectively. The sum  $\gamma$  of the squared first derivatives which indicates the numerical accuracy of the minimization of the energy is approximately  $10^{-23}$  for all investigated compounds in the  $S_0$  and  $S_1$  electronic states except for MePTCDI ( $\gamma \approx 10^{-16}$ ). The necessary  $S$ -potential parameters that have been generally developed for the QCFFVC method [18] are used for the calculations of the hypothetical sulfur compound PTCDS.

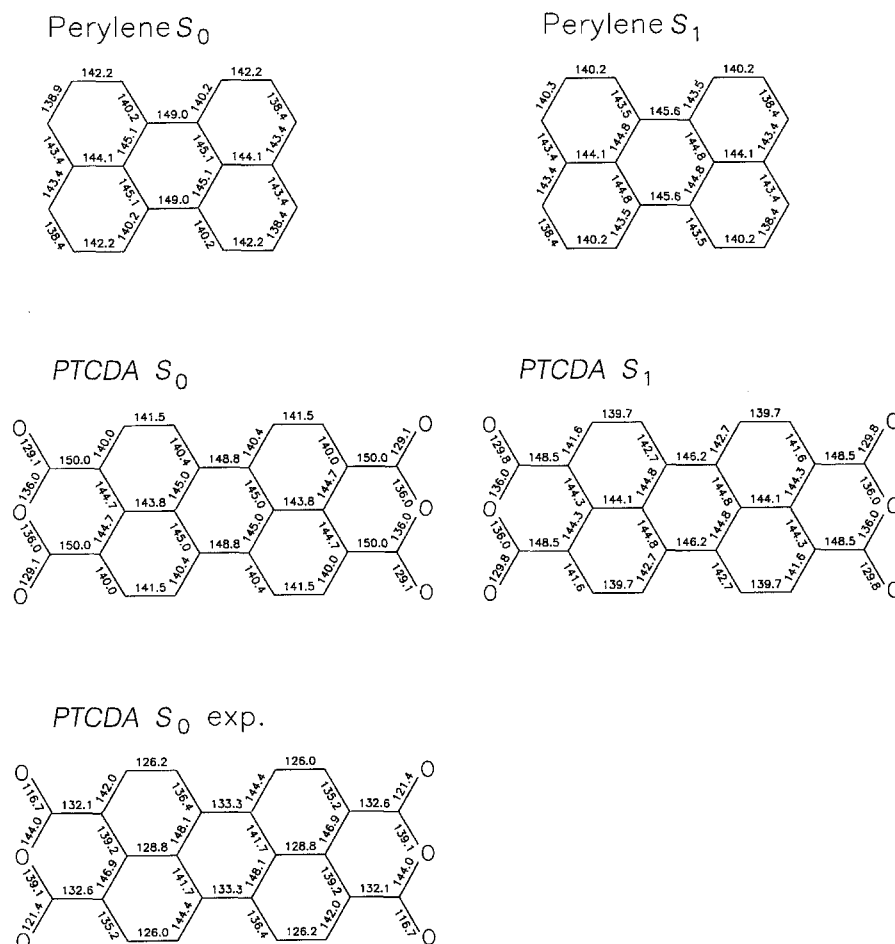
The substructure of the  $S_0 \rightarrow S_1$  absorption and  $S_1 \rightarrow S_0$  fluorescence spectra were calculated as vibronic line spectra (with a defined graining of  $\Delta = 100 \text{ cm}^{-1}$ ) by the FCHT method [16, 21] on the basis of the  $S_0$  and  $S_1$  data obtained by the QCFFVC method within the framework of the model of non-interacting oscillators (NIO approach). In detail, the FCHT method allows the determination of the (Franck-Condon and Herzberg-Teller, respectively) weighted state density functions by use of the BS (Beyer-Swinehart) algorithm [19, 20] and the characterization of the vibronic structure of the respective electronic transitions by an analysis of the vibrational modes.

## Results and Discussion

The completely optimized molecular geometries of the  $S_0$  and  $S_1$  states are presented in Fig. 2 for perylene and PTCDA. For clarity, only the C–C bond lengths are shown. The calculated bond angles which are all between  $119^\circ$  and  $122^\circ$ , and also the nearly equal C–H bond lengths ( $R_{\text{CH}} \approx 108 \text{ pm}$ ) have been omitted. The molecular structures of both molecular states are coplanar for perylene and its derivatives<sup>1</sup> except for MePTCDI (due to the  $\text{CH}_3$  groups). In all cases, the symmetry is  $D_{2h}$ . Remarkably, the two C–C-bonds between the two naphthalene moieties in the  $S_1$  state are much shorter than in  $S_0$  (3.4 pm). The differences in the other distances are less than 2 pm. In contrast to perylene, the corresponding changes in its derivatives are generally smaller. The additional carboxylic group causes that the shortening of the distance between the naphthalene moieties (2.6 pm) is less than in perylene. The shortening is equally distributed over all C–C-bonds that are parallel to the long axis of the molecule. As will be shown later this causes a major contribution of perylene stretching modes to the electronic transitions. The peripheric bonds that are diagonal with respect to the axes of the molecule are shorter in  $S_1$  whereas all other bonds, including C=O and C–O–C, remain almost unchanged. Generally speaking, the alterations of bond distances are little significant and of the order of or less than 2 pm for all derivatives. Therefore, the Stokes shift should be small, and thus the centre of gravity of both the  $S_0 \rightarrow S_1$  absorption band and the  $S_1 \rightarrow S_0$  fluorescence is close to the 0,0 transition.

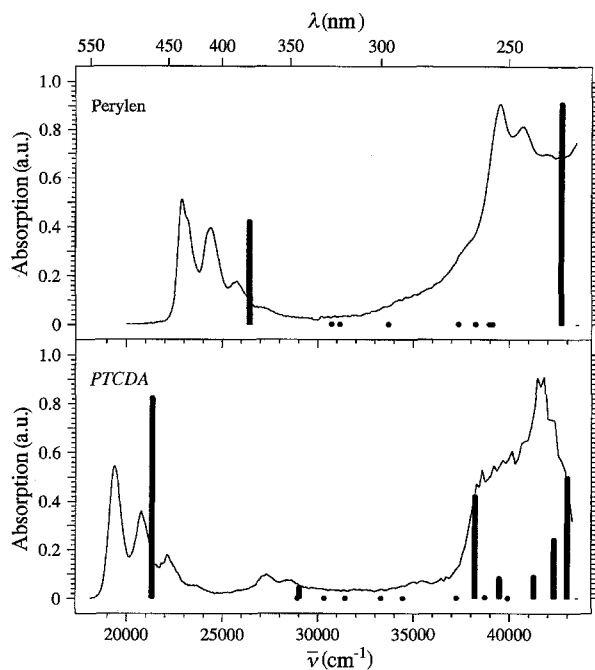
Figure 3 shows the energies of the electronic transitions calculated by the QCFFVC method for perylene and PTCDA compared with the experimental absorption spectra of these compounds in solution. The lengths of the bars indicate the oscillator strength and the black dots the energy of the forbidden electronic transitions (electronic oscillator strength = 0). The calculations reveal that the  $S_0 \rightarrow S_1$  transition is electronically allowed, has a large oscillator strength ( $\approx 1.5$ ), and is characterized by the HOMO-LUMO configuration for perylene as well as for its derivatives. The calculated transition moment is parallel to the long axis of the

<sup>1</sup> Theoretical and experimental X-ray results ([22]; see also Fig. 2) can not be compared directly, because the molecular symmetry is disturbed by intermolecular interactions.



**Fig. 2.** Completely optimized geometries of the  $S_0$  and  $S_1$  states of perylene and PTCDA determined theoretically (bond distances in pm); the experimentally obtained data of the ground state of PTCDA are shown for comparison

molecule for all investigated compounds. As shown in Fig. 3, the calculated energies of the allowed transitions are comparable with the energies of the measured absorption bands. The structural similarities of the four derivatives cause that the calculated transitions of PTCDI, MePTCDI, and PTCDS show electronic structures comparable to those of PTCDA; they are only slightly shifted in energy (calculated  $S_0 \rightarrow S_1$ : PTCDA: 21348  $\text{cm}^{-1}$ , PTCDI: 21385  $\text{cm}^{-1}$ , MePTCDI: 21330  $\text{cm}^{-1}$ , PTCDS: 21142  $\text{cm}^{-1}$ ). The analysis of the transition overlap densities (not shown) confirms the correspondences. There is no transition overlap density at the respective substituents O, N, and S for the  $S_0 \rightarrow S_1$  transition. Therefore, the energy of this transition is basically independent of the hetero atoms and similar for all derivatives. However, the hetero atoms are involved in some of the transitions at energies higher than 37000  $\text{cm}^{-1}$ , and therefore variations between the experimentally observed broad bands at these energies occur. This broad absorption consists of several electronic transitions (e.g. calculated transition energies for PTCDA:  $S_0 \rightarrow S_9$ : 38232  $\text{cm}^{-1}$ ,  $S_0 \rightarrow S_{11}$ : 39506  $\text{cm}^{-1}$ ,  $S_0 \rightarrow S_{13}$ : 41286  $\text{cm}^{-1}$ ,



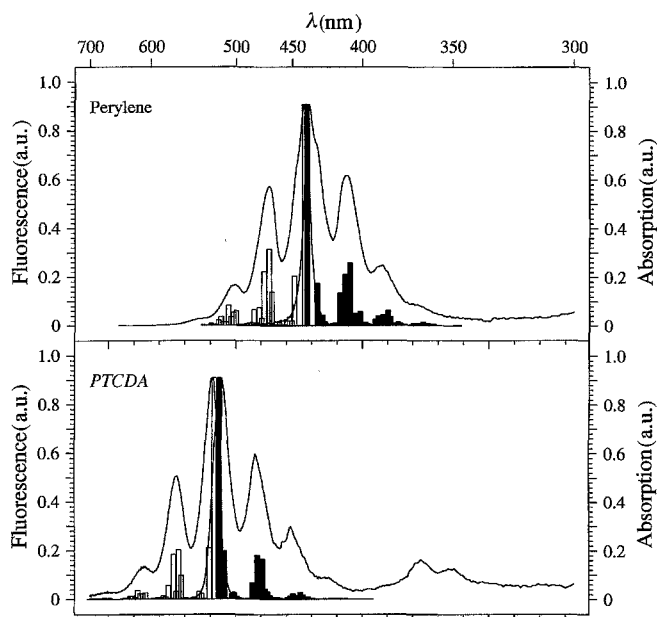
**Fig. 3.** Experimental optical absorption of perylene (top) and *PTCDA* (bottom) in  $\text{CHCl}_3$  compared with the calculated electronic transitions shown as bars; the lengths of the bars indicate the oscillator strength, the black dots stand for electronically forbidden transitions

$S_0 \rightarrow S_{14}$ :  $42331 \text{ cm}^{-1}$ ,  $S_0 \rightarrow S_{15}$ :  $43019 \text{ cm}^{-1}$ ). An additional weak but pronounced absorption band between  $27000 \text{ cm}^{-1}$  and  $30000 \text{ cm}^{-1}$  occurs in the measured absorption spectra of *PTCDA*, *PTCDI*, and *MePTCDI* that does not exist in the perylene spectrum. This absorption is attributed to the weak  $S_0 \rightarrow S_3$  transition found in the theoretical calculations for the four derivatives.

In this context it should be mentioned that the hypothetical mixed perylene derivatives *PTCMAI*, *PTCDMAS*, and *PTCMIS*, where different anhydride substituents are introduced on each side of the molecule (combinations of the above mentioned derivatives), show an analogous electronic spectroscopic behaviour as regards the energies of  $S_0 \rightarrow S_1$  and the other  $S_0 \rightarrow S_p$  transitions, the oscillator strengths, and the location of the transition moments. Thus, the modifications remain meaningless for the molecular spectroscopic behaviour.

In order to identify the vibronic structure of the  $S_0 \rightarrow S_1$  absorption and the  $S_1 \rightarrow S_0$  fluorescence band of perylene and its derivatives, the above calculations were combined with the FCHT method. As mentioned above the measured vibronic structure of both the  $S_0 \rightarrow S_1$  absorption and the  $S_1 \rightarrow S_0$  fluorescence is comparable in all cases to that observed for perylene (Fig. 4 shows a comparison of *PTCDA* and perylene; the calculated vibronic structure is presented by histograms). The calculated vibronic line spectra show the same vibrational progression as the measured spectra both in  $S_0 \rightarrow S_1$  absorption and in  $S_1 \rightarrow S_0$  fluorescence.

Table 1 compares the vibrational modes that contribute to the  $S_0 \rightarrow S_1$  absorption for perylene and its derivatives. It turns out that only seven (*PTCDA*, *PTCDI*, and *MePTCDI*) and nine (*PTCDS*) out of  $3N - 6$  vibrational modes have a significant intensity for all derivatives. The energies and characteristics of the modes are similar for all four compounds. The stretchings  $\nu_{\text{CC}}$  and also the bendings  $\delta_{\text{CCX}}$ ,  $\delta_{\text{CX}}(\text{X: O, N, S})$ , and  $\delta_{\text{CCH}}$  occur typically. Instead, pronounced



**Fig. 4.** Vibronic structure of  $S_0 \rightarrow S_1$  absorption and  $S_1 \rightarrow S_0$  fluorescence spectra measured in  $\text{CHCl}_3$  and the calculated vibronic line spectra

**Table 1.** Vibrational wave numbers ( $\text{cm}^{-1}$ ) contributing theoretically to the  $S_0 \rightarrow S_1$  absorption of perylene and its derivatives; numbers in brackets indicate the denumeration of the mode and the vibrational quantum numbers  $\nu_i$

Perylene	<i>PTCDA</i>	<i>PTCDI</i>	<i>MePTCDI</i>	<i>PTCDS</i>	Characteristics
365.8( $9_0^{1,2}$ )	236.6( $10_0^{1,2}$ )	238.4( $11_0^{1,2}$ )	225.4( $14_0^{1,2}$ )	221.4( $12_0^{1,2}$ )	$\nu_{\text{CC}}, \delta_{\text{CCC}}$
484.4( $15_0^1$ )					
571.3 ( $19_0^1$ )				543.7( $34_0^1$ )	
	557.4( $31_0^1$ )	555.3( $34_0^1$ )		618.9( $40_0^1$ )	$\delta_{\text{CX}}$
			589.0( $41_0^1$ )		$\tau_{\text{CNCC}}$
1338.2( $59_0^{1,2}$ )	1342.2( $76_0^1$ )	1344.1( $78_0^1$ )	1347.2( $88_0^1$ )	1350.8( $74_0^1$ )	$\delta_{\text{CCH}}$
1405.8( $62_0^1$ )	1401.3( $79_0^1$ )	1406.5( $81_0^1$ )	1413.7( $91_0^1$ )	1445.6( $80_0^{1,2}$ )	
1454.0( $65_0^{1,2}$ )	1460.3( $83_0^{1,2}$ )	1459.0( $87_0^{1,2}$ )	1463.3( $99_0^{1,2}$ )		$\nu_{\text{CC}}, \delta_{\text{CCH}}$
1492.5( $68_0^1$ )				1614.8( $92_0^1$ )	
1665.4( $78_0^{1,2}$ )	1673.5( $96_0^{1,2}$ )	1670.6( $100_0^{1,2}$ )	1673.9( $114_0^{1,2}$ )	1686.9 ( $96_0^{1,2}$ )	
	1779.2( $100_0^1$ )	1787.5( $104_0^1$ )	1786.5( $118_0^1$ )	1865.9( $100_0^1$ )	$\nu_{\text{C=O}}$

differences become apparent in comparison with perylene: due to the additional carboxylic group, a new high energy mode appears at approximately  $1780 \text{ cm}^{-1}$  ( $\tilde{\nu}_{100}$  for *PTCDA*) which is responsible for the  $\nu_{\text{C=O}}$  stretching, whereas the lowest vibrational mode (long axis stretching of the perylene moiety,  $\tilde{\nu}_{10}$  for *PTCDA*) is shifted by approximately  $130 \text{ cm}^{-1}$  to lower energies. Torsions occur only due to the methyl group of *MePTCDI*. However, most of the vibrational states are only

**Table 2.** Vibrational wave numbers ( $\text{cm}^{-1}$ ) contributing theoretically to the  $S_1 \rightarrow S_0$  fluorescence of perylene and its derivatives; numbers in brackets indicate the denumeration of the mode and the vibrational quantum numbers  $\nu_i$ 

Perylene	<i>PTCDA</i>	<i>PTCDI</i>	<i>MePTCDI</i>	<i>PTCDS</i>	Characteristics
360.7(9 <sub>1,2</sub> <sup>0</sup> ) 486.7(14 <sub>1</sub> <sup>0</sup> ) 571.9(19 <sub>1</sub> <sup>0</sup> )	233.5(10 <sub>1,2</sub> <sup>0</sup> )	235.3(11 <sub>1,2</sub> <sup>0</sup> )	221.6(14 <sub>1,2</sub> <sup>0</sup> )	218.7(12 <sub>1,2</sub> <sup>0</sup> )	$\nu_{\text{CC}}, \delta_{\text{CCC}}$
	555.0(31 <sub>1</sub> <sup>0</sup> )	553.8(34 <sub>1</sub> <sup>0</sup> )		545.6(34 <sub>1</sub> <sup>0</sup> )	
			585.6(41 <sub>1</sub> <sup>0</sup> )		$\delta_{\text{CXC}}$
					$\tau_{\text{CNCC}}$
				1329.4(74 <sub>1</sub> <sup>0</sup> )	$\delta_{\text{CCH}}$
1347.5(60 <sub>1,2</sub> <sup>0</sup> ) 1418.5(64 <sub>1</sub> <sup>0</sup> )	1345.1(78 <sub>1</sub> <sup>0</sup> ) 1387.6(81 <sub>1,2</sub> <sup>0</sup> )	1347.4(80 <sub>1</sub> <sup>0</sup> ) 1387.6(83 <sub>1,2</sub> <sup>0</sup> )	1349.2(89 <sub>1</sub> <sup>0</sup> ) 1387.3(93 <sub>1,2</sub> <sup>0</sup> )	1356.8(75 <sub>1,2</sub> <sup>0</sup> ) 1383.4(78 <sub>1,2</sub> <sup>0</sup> )	
1629.8(77 <sub>1,2</sub> <sup>0</sup> )	1636.4(95 <sub>1,2</sub> <sup>0</sup> )	1634.3(99 <sub>1,2</sub> <sup>0</sup> )	1633.6(112 <sub>1</sub> <sup>0</sup> ) 1633.7(113 <sub>1</sub> <sup>0</sup> )	1606.3(91 <sub>1</sub> <sup>0</sup> ) 1647.0(94 <sub>1</sub> <sup>0</sup> )	$\nu_{\text{CC}}, \delta_{\text{CCH}}$
	1780.8(100 <sub>1</sub> <sup>0</sup> )	1789.4(104 <sub>1</sub> <sup>0</sup> )	1789.1(118 <sub>1</sub> <sup>0</sup> )	1862.0(100 <sub>1</sub> <sup>0</sup> )	$\nu_{\text{C=O}}$

slightly modified in energy because they are essentially characteristic vibrations of the perylene moiety of the molecules. Therefore, the vibronic shape of the spectra of the derivatives is similar to that of perylene.

The vibronic structure of the  $S_1 \rightarrow S_0$  fluorescence spectra of the four compounds show a similar behaviour Table 2. Only six vibrational modes for *PTCDA* and *PTCDI*, seven for *MePTCDI*, and eight for *PTCDS*, respectively, take part in the electronic  $S_1 \rightarrow S_0$  transition. Deviations in energy as compared with the absorption spacings can be observed at modes where  $\delta_{\text{CCH}}$  bendings are involved. With respect to the fluorescence data on perylene, comparable differences are found as in absorption.

The vibrational modes shown in the tables above contribute to the electronic transitions mainly by their *Franck–Condon* factors. The *Herzberg–Teller* factors have an insignificant influence on the spectroscopic behaviour as a consequence of the strong  $S_0 - S_1$  electronic oscillator strength for all compounds.

As mentioned in the introduction, the experimentally measured absorption and fluorescence spectra of all investigated compounds show a similar vibronic progression of approximately  $1400 \text{ cm}^{-1}$ . However, the theoretical analysis shows that the progression is not caused by a single vibrational mode with different vibrational quantum numbers, but by the sum of different modes at lower energies and the sum of the combinations of different modes at higher energies.

## Conclusion

We have shown that the completely optimized molecular geometries of the perylene derivatives *PTCDA*, *PTCDI*, *MePTCDI*, and *PTCDS* reveal smaller changes in bond distances between  $S_0$  and  $S_1$  than perylene. The energy of the calculated electronic transitions are comparable with the experimentally obtained data. The experimentally observed weak absorption band between  $27000 \text{ cm}^{-1}$  and

$30000\text{ cm}^{-1}$ , not existent in perylene, was characterized as the  $S_0 \rightarrow S_3$  transition for all derivatives. The calculated vibronic structure of  $S_0 \rightarrow S_1$  absorption and  $S_1 \rightarrow S_0$  fluorescence could verify the experimental data. The obtained vibrational modes could be characterized as basically in-plane stretchings and bendings. Generally speaking, the influence of the hetero atoms in the perylene derivatives was found to be small on all investigated properties.

### Acknowledgements

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