

Molecular versus excitonic transitions in PTCDA dimers and oligomers studied by helium nanodroplet isolation spectroscopy

M. Wewer and F. Stienkemeier*

Fakultät für Physik, Universität Bielefeld, D-33615 Bielefeld, Germany

(Received 26 December 2002; published 6 March 2003)

Laser-induced fluorescence of 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) oligomers embedded in helium nanodroplets has been studied in the spectral region where the strongest absorptions of PTCDA crystals and single PTCDA molecules dissolved in organic solvents have been observed before. The cold helium droplet environment allows a separation of excitonic and molecular excitations. We find narrow ($<1\text{ cm}^{-1}$) as well as broad ($\approx 500\text{ cm}^{-1}$) absorptions which can be attributed to electronic molecular transitions of the PTCDA dimer and, respectively, to excitonic transitions of sandwichlike PTCDA oligomers. The maximum of the excitonic absorption lies at $22\,190\text{ cm}^{-1}$, slightly shifting to lower energies upon addition of more PTCDA molecules. The results are discussed in comparison with existing theories of exciton states in thin organic films or crystals.

DOI: 10.1103/PhysRevB.67.125201

PACS number(s): 36.40.-c, 36.20.Kd, 71.35.Cc

There is a considerable current interest in the understanding of charge carrier injection and exciton generation in thin films of large polyaromatic molecular systems. This interest is based on the importance of these phenomena in a wide range of electronic and optoelectronic applications.¹ Among the different molecules 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) has recently been the subject of numerous studies in several laboratories because of its favorable semiconductor properties. The growth of highly ordered crystalline films on different substrates has been demonstrated.^{2,3} Measurements of photon absorption,⁴ electroabsorption,⁵ photoluminescence,⁶ photoconduction,⁷ high resolution electron energy loss, x-ray induced photoelectron, low-energy electron diffraction, Fourier transform infrared,⁸ and Raman spectroscopy⁹ as well as theoretical studies^{10–15} have been performed to understand the fundamental excitonic properties of these films. Soos *et al.* have suggested the lowest excited state observed at 2.23 eV in the crystal may be a one-dimensional charge transfer (CT) exciton.¹⁵ A subsequent theory by Hennessy *et al.* proposes the exciton-phonon-CT dimer model, which includes the mixture of monomerlike Frenkel excitons and neighboring CT excitons.¹⁴ This model is supported by a successful fit of the experimental absorption spectrum of PTCDA stacks. Recent papers by Mazur *et al.*¹³ give the absolute values of the lowest lying CT states by using Fourier transform and self-consistent polarization field (SCPF) methods. The calculations suggested that all CT states are in the same energy range between 2.5 – 3.05 eV. The measured absorption spectra of PTCDA films show a resolved maximum at 2.23 eV, interpreted as an excitonic transition. At higher energies the spectra are dominated by a broad structureless absorption. Better resolved studies are required to test these existing theories in order to shed more light on the conduction properties of organic semiconducting films.

Here we apply helium nanodroplet isolation (HENDI) spectroscopy^{16,17} to form oligomers of PTCDA molecules in a liquid helium environment at temperatures below 1 K. The experimental setup has been reported in detail elsewhere.¹⁸ In short, helium droplets (He_N , $N \approx 5000$) are produced in a

supersonic expansion of He gas at a stagnation pressure of 60 bar through a cold nozzle of $10\ \mu\text{m}$ diameter kept at 17 K. PTCDA molecules are picked-up further downstream in a heated cell at a partial pressure of around 10^{-4} mbar. Selection of different cell temperatures enables us to vary the number of picked-up molecules. At relatively low cell temperatures each droplet only contains one single molecule. Increasing the cell temperature, oligomers of PTCDA molecules can be aggregated inside the droplet after consecutive pick-up of two or more molecules. The superfluid environment cools the embedded species down to 380 mK,¹⁹ hence simplifying spectra in a way that only vibrational ground states are expected to be populated. Moreover, the weakly interacting environment has been proved to introduce only little shifts and broadenings. To excite the molecules we have used a ring dye laser providing 60–150 mW of power at the position of the molecular beam with an effective bandwidth of 0.05 cm^{-1} .

In Fig. 1 the measured laser induced fluorescence (LIF) spectra of single PTCDA molecules (d) as well as PTCDA oligomers (b) attached to helium nanodroplets are compared to absorption spectra of the PTCDA molecules in DMSO (c) (Ref. 21) and spectra of a thin film of PTCDA on quartz (a).²⁰ The advantage of using the helium droplet environment is clearly visible from the striking difference in achievable spectral resolution. The spectrum in (d) reveals fully vibrationally resolved the $S_1(\tilde{\nu}') \leftarrow S_0(\tilde{\nu}''=0)$ transition of PTCDA monomers. The most intense line determines the 0–0 transition at $20\,988\text{ cm}^{-1}$.²⁷ A discussion of the spectrum in comparison with Raman spectra and theoretical calculations will be given in a forthcoming paper.²² The spectrum is shown here to demonstrate that in our experiments the monomer absorption can be clearly separated from the spectra of PTCDA complexes. In comparison, the spectrum of PTCDA in DMSO (c) has been attributed to the monomer absorption with three strong absorption bands in the visible range which belong to the lowest π - π^* transition of the extended π -electron system of the molecule. A considerable shift and broadening is induced by solvent interaction.

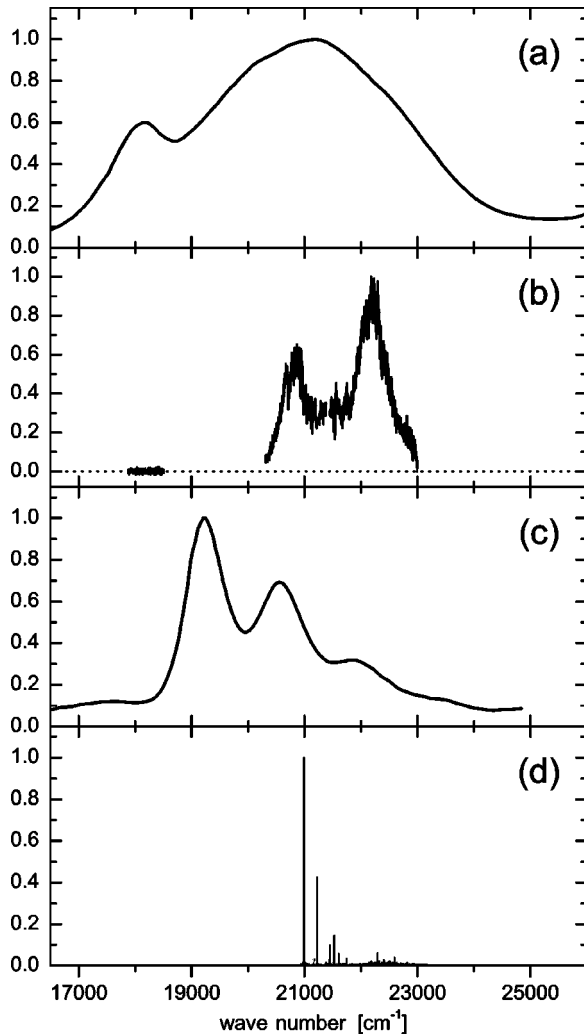


FIG. 1. Comparison between different techniques to measure the absorption of PTCDA. (a) Absorption spectrum of a 200 nm PTCDA film on a quartz substrate (Ref. 20). (b) LIF spectrum of PTCDA complexes in helium nanodroplets at a pick-up pressure of 1.8×10^{-3} mbar. (c) Monomer absorption spectrum of PTCDA in DMSO (concentration: $0.25 \mu\text{M}$) (Ref. 21). (d) LIF spectrum of single PTCDA molecules in helium nanodroplets.

At elevated pick-up pressure several more narrow lines appear in the spectral region of the strong 0-0 monomer transition (Fig. 2). From the Poissonian distributions (see Fig. 4) the lines are identified as PTCDA dimers. We ascribe these to T-shaped complexes analogous to the assignment in Ref. 25. In these studies the polycyclic aromatic hydrocarbons naphthalene and anthracene have been addressed. Sharp lines of T-shaped dimers have been found to be redshifted from the 0-0 transition of the monomer by a few hundreds of wave numbers.²⁶ We find doublet structures split by 2.2 cm^{-1} , redshifted from the monomer origin by 110 and 223 cm^{-1} , respectively. Van der Waals vibrational progressions, which could be interpreted as intermolecular vibrations of the stem to the top site of T-shaped PTCDA dimers cannot be unambiguously identified. Other intense peaks are at 44, 54, 96, and 329.5 cm^{-1} redshifted from the monomer origin. We interpret these lines as 0-0 transitions of different T-shaped

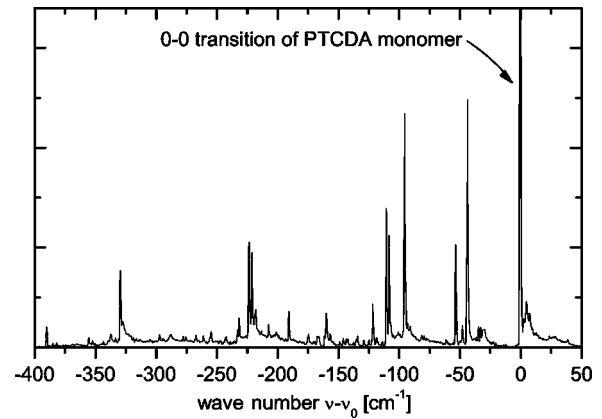


FIG. 2. LIF spectrum of T-shaped PTCDA dimers in helium nanodroplets. Frequencies are given with respect to the 0-0 transition of the PTCDA monomer at 20988 cm^{-1} .

geometries. Furthermore, since there are also redshifted satellites of monomer lines,²⁸ which are interpreted as complexes with attached localized helium atoms,^{17,22} many of the weak dimer lines may be due to complexes with helium atoms as well. A closer look at the vibrational excited lines of the LIF spectrum shows the same group of dimer lines redshifted by the same amount at each vibrational absorption. This means that the van der Waals binding of these T-shaped dimers does not perturb the intramolecular vibrations of the PTCDA subunits.

The thin film spectrum in Fig. 1(a) contains monomer excited states as well as intermolecular interactions. The peak at $\approx 18000 \text{ cm}^{-1}$, is attributed to a mixed Frenkel and CT state of the crystal.¹⁴ A separation of molecular and excitonic contributions cannot be accomplished. Again, the amount of shift and broadening induced by the interaction with the substrate is not obvious.

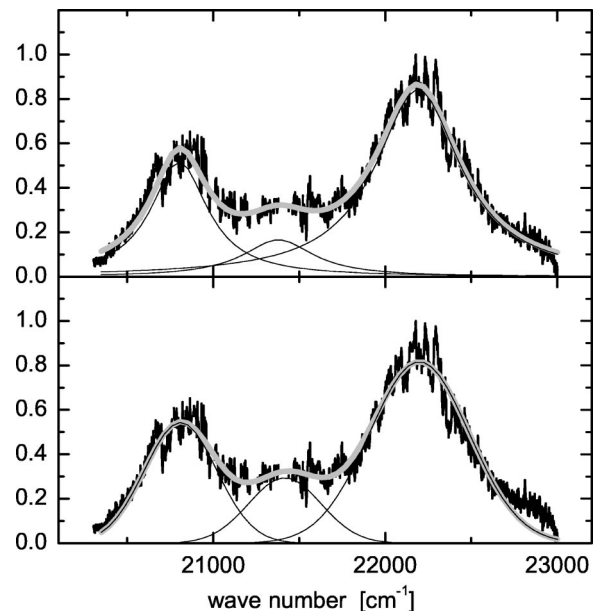


FIG. 3. Fit using Lorentzian (upper panel) and Gaussian (lower panel) functions to the LIF spectrum in Fig. 1(b).

TABLE I. Parameters of the fits in Fig. 3. Given are the position of the maximum, the width and the relative amplitudes.

	Position [cm^{-1}]	FWHM [cm^{-1}]	Amplitude
Lorentz	20 800	400	0.61
	21 380	500	0.2
	22 190	600	1
Gauss	20 810	420	0.67
	21 416	420	0.36
	22 198	580	1

Panel (b) in Fig. 1 gives the LIF spectrum of PTCDA oligomers in helium nanodroplets. Fits to the spectrum comparing Lorentzian and Gaussian functions are shown in Fig. 3. Corresponding fit parameters are given in Table I. The Gauss fit does not reproduce the slim upper part of the maxima as good as the Lorentz function; furthermore, the large deviations in the blue tail of the most pronounced maximum favor the Lorentz fit as the correct functional form. The Lorentzian character of the line shapes coupled with the narrowness of the monomer lines indicates a fast decay mechanism generating homogenous broadening. A dephasing time on the order of 10 fs follows from the observed linewidth. This time does not correspond to the radiative lifetime which has been measured to be in the 10 ns range.⁶ One should note that quenching and subsequent substantial reduction in radiative lifetimes of electronic transitions in similar molecules embedded in helium droplets has not been observed so far.¹⁷ The preferred geometry for an

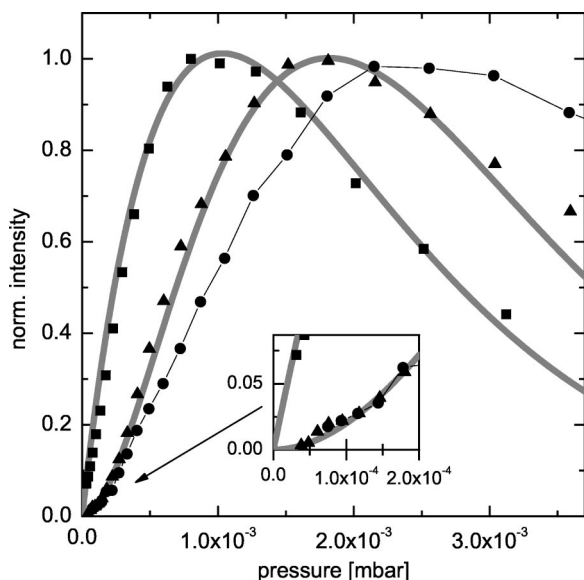


FIG. 4. Normalized LIF signals of $(\text{PTCDA})_n$ complexes in helium nanodroplets are plotted vs pick-up cell partial pressure. The symbols represent measured data (squares: monomer line, $21\,217.5\text{ cm}^{-1}$; triangles: narrow dimer line, $21\,173.5\text{ cm}^{-1}$; circles: exciton signal, $21\,148\text{ cm}^{-1}$). The thick solid lines give the Poissonian functions of order 1 and 2. The inset shows the low pressure region (exciton signal multiplied by 1.2)

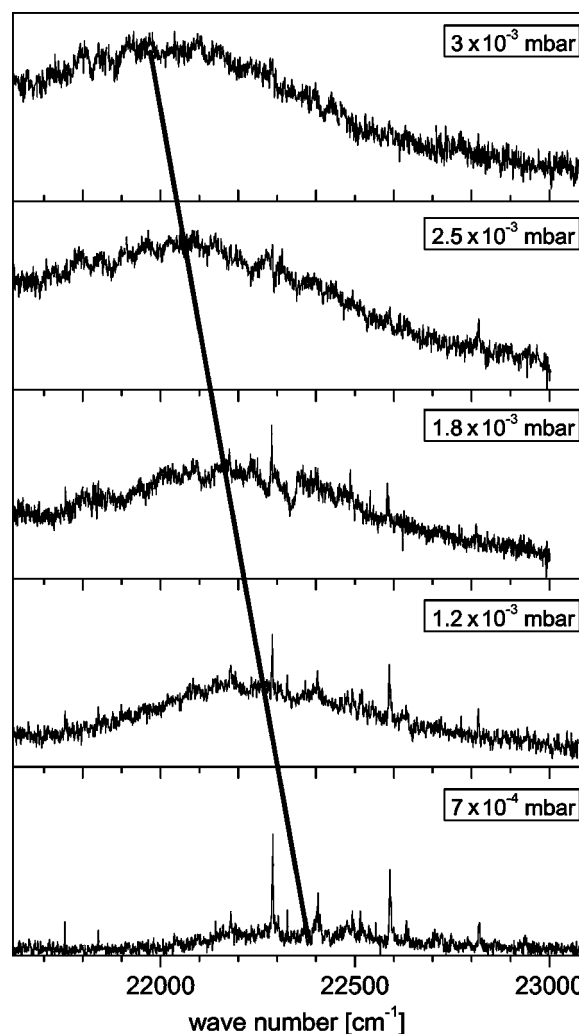


FIG. 5. LIF spectra of the most intense exciton state at different pick-up cell pressures.

exciton state is the sandwich geometry, where both molecules have the closest approach of 3.37 \AA (Ref. 23) and the overlapping aromatic π orbitals are responsible for the charge exchange. The first remarkable result from our measurement is the absence of the lowest energy absorption, found at $\approx 18\,000\text{ cm}^{-1}$ (2.23 eV) in the spectrum of the PTCDA film. However, since 3000 cm^{-1} is a reasonable matrix-induced shift, the higher absorption energies found in the helium environment are to be expected, because in helium shifts of only $\leq 100\text{ cm}^{-1}$ are induced.¹⁷ On the other hand, shifting the spectrum does not resemble pronounced energies found in the film absorption.

In contrast to the assignment of the low energy maximum in the film spectrum by Hennessy *et al.*,¹⁴ Scholz and co-workers¹⁰ present a microscopic model in the framework of Frenkel excitons coupled with intramolecular vibrations, neglecting any charge transfer contributions. They model the rather complex vibrational structure of PTCDA by a single effective internal mode with an energy of 0.17 eV . In this regard it is noticeable that this energy of 0.17 eV coincides with the spacing of the two main maxima in our spectrum. From our results one cannot directly approve or disapprove

the various interpretations of the lowest absorption mentioned above because theoretical models are adopted to specific conditions and, e.g., the influence of an extended crystal structure is partially incorporated within the theory. However, the absorption of the isolated complexes presented here, should be very well suited to be compared with refined models and test the proposed mechanisms.

A closer look at the spectrum (Figs. 3, 5) reveals an overlying substructure containing maxima characterized by a typical width on the order of 50 cm^{-1} . This substructure resembles additional absorptions of different isomers which are probably mixed sandwich and T geometries. An apparent coincidence of these relatively broad maxima with narrow molecular lines of T-shaped dimers gives evidence that these are relics of vibrational structures.

During their flight through the scattering cell the helium droplets capture statistically a certain number of molecules, corresponding to the density in the cell which is determined by the vapor pressure of dopants. Varying the density, the measured intensities follow Poissonian distributions

$$P(\eta) = \frac{(\eta\sigma L)^n}{n!} \exp(-\eta\sigma L)$$

(η = density, σ = pick-up cross section, L = length of scattering region).²⁴ The order n determines the number of picked-up molecules. Figure 4 shows such Poissonian distributions for a monomer line ($\nu = 21\,217.5 \text{ cm}^{-1}$) and the narrow dimer absorption shifted by -44 cm^{-1} (see Fig. 2). Both features are well reproduced by a Poissonian fit of the order 1 and 2, respectively, thus confirming the correct assignments. Figure 4 also includes the signal dependence of the broad excitonic absorption. When compared to the dimer, the maximum of the distribution is shifted towards higher dopant density. This indicates that also larger oligomers absorb at that wavelength. To study further the evolution of the excitonic excitation towards larger complexes we recorded spectra adding more molecules by increasing the cell temperature. In this manner stacks of PTCDA molecules are formed. Figure 5 shows the most intense peak with increasing dopant partial pressure in the pick-up cell. Starting at a pressure of 7×10^{-4} mbar the LIF-spectrum contains the

sharp transitions of PTCDA monomer modes, but already exhibits the broad absorption of PTCDA dimers. At 3×10^{-3} mbar, up to PTCDA hexamers are expected to be present in the droplets. The maximum of the absorption is shifted continuously to lower energies with increasing number of PTCDA molecules. Obviously, excitonic transitions occur already in PTCDA dimers. This is supported by the Poissonian distributions: At very low pick-up pressures the slope of the exciton signal matches the dimer signal (inset in Fig. 4). The deposition of further subunits only shifts the excitation energy. The other absorption maxima show the same behavior. Since at higher cell temperatures the droplet beam is already depleted by scattering, the oscillator strength of the exciton transition has to increase substantially for larger complexes.

In conclusion, our measurements show high resolution excitation spectra of PTCDA oligomers embedded in superfluid helium nanodroplets. We find narrow dimer excitation lines redshifted of the monomer origin, interpreted as excitations of different dimer structures in T-shaped geometries. Vibrational resolution provides information about the structure and binding of such complexes in geometries that only represent local minima with respect to their binding energy. On the other hand, broad absorptions of PTCDA complexes are observed that represent the transition into excitonic states of sandwichlike structures. Transitions of such type appear to be already present in PTCDA dimers. Forming larger PTCDA complexes in the droplets shifts the exciton states towards lower energies. The results presented here demonstrate that the application of HENDI to PTCDA complexes offer the possibility to probe and distinguish molecular and excitonic excitations. In this way, the energetic structure of excitonic transitions as well as decay times from line broadening provides fundamental insight into the semiconducting properties of organic materials.

We thank G. Scoles for stimulating this work and his continuing support. Helpful discussions with Professor Umbach and his group are gratefully acknowledged. This work has been supported by the Deutsche Forschungsgemeinschaft.

*Electronic address: franks@physik.uni-bielefeld.de; URL: <http://www.physik.uni-bielefeld.de/cluster>

¹S. Forrest, *Chem. Rev.* **97**, 1793 (1997).

²S. Forrest, P. Burrows, E. Haskal, and F. So, *Phys. Rev. B* **49**, 11 309 (1994).

³E. Haskal, F. F. So, P. Burrows, and S. Forrest, *Appl. Phys. Lett.* **60**, 3223 (1992).

⁴U. Gómez, M. Leonhardt, H. Port, and H. Wolf, *Chem. Phys. Lett.* **268**, 1 (1997).

⁵E. Haskal, Z. Shen, P. Burrows, and S. Forrest, *Phys. Rev. B* **51**, 4449 (1995).

⁶A. Y. Kobitski, G. Salvan, H. Wagner, and D. Zahn, *Astron. Astrophys., Suppl. Ser.* **179**, 209 (2001).

⁷V. Bulovic and S. Forrest, *Chem. Phys. Lett.* **238**, 88 (1995).

⁸F. Tautz, S. Sloboshanin, J. Schaefer, R. Scholz, V. Shklover, M. Sokolowski, and E. Umbach, *Phys. Rev. B* **61**, 16 933 (2000).

⁹R. Scholz, A. Y. Kobitski, T. Kampen, M. Schreiber, D. Zahn, and J. Jungnickel, M. Elstner, M. Sternberg, and T. Fraunhein, *Phys. Rev. B* **61**, 13 659 (2000).

¹⁰I. Vragovic, R. Scholz, and M. Schreiber, *Europhys. Lett.* **57**, 288 (2002).

¹¹E. Tsiper and Z. Soos, *Phys. Rev. B* **64**, 195124 (2001).

¹²M. Hoffmann, K. Schmidt, T. Fritz, T. Hasche, V. Agranovich, and K. Leo, *Chem. Phys.* **258**, 73 (2000).

¹³G. Mazur and P. Petelenz, *Chem. Phys. Lett.* **324**, 161 (2000).

¹⁴M. Hennessy, Z. Soos, R. A. Pascal Jr., and A. Girlando, *Chem. Phys.* **245**, 199 (1999).

¹⁵Z. Soos, M. Hennessy, and G. Wen, *Chem. Phys.* **227**, 19 (1998).

¹⁶J. P. Toennies and A. F. Vilesov, *Annu. Rev. Phys. Chem.* **49**, 1 (1998).

¹⁷F. Stienkemeier and A. F. Vilesov, *J. Chem. Phys.* **115**, 10119 (2001).

- ¹⁸F. Stienkemeier, F. Meier, and H. O. Lutz, *Eur. Phys. J. D* **9**, 313 (1999).
- ¹⁹M. Hartmann, N. Pörtner, B. Sartakov, and J. P. Toennies, *J. Chem. Phys.* **110**, 5109 (1999).
- ²⁰K. Akers, R. Aroca, A. Hor, and R. Loutfy, *J. Phys. Chem.* **91**, 2954 (1987).
- ²¹V. Bulovic, P. Burrows, S. Forrest, J. Cronin, and M. Thompson, *Chem. Phys.* **210**, 1 (1996).
- ²²M. Wewer and F. Stienkemeier (unpublished).
- ²³A. Lovinger, S. Forrest, M. Kaplan, P. Schmidt, and T. Venkatesan, *J. Appl. Phys.* **55**, 476 (1984).
- ²⁴M. Lewerenz, B. Schilling, and J. P. Toennies, *J. Chem. Phys.* **102**, 8191 (1995).
- ²⁵C. Gonzales and E. C. Lim, *Chem. Phys. Lett.* **322**, 382 (2000).
- ²⁶A. Das, K. Mahato, and T. Chakraborty, *J. Chem. Phys.* **114**, 8310 (2001).
- ²⁷In the PTCDA monomer spectrum in Ref. 17 the vibrationally excited mode at $21\,217\text{ cm}^{-1}$ was mistakenly assigned to the 0-0 line.
- ²⁸A group of four lines is present at each vibrational monomer line, redshifted 20 to 45 cm^{-1} .