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COMMENTS

Comment on “Theoretical Investigation of Perylene Dimers and Excimers and Their Signatures in X-Ray Diffraction”

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Recently, Velardez et al.[1] reported TD-DFT calculations on a perylene pair in the gas phase as well as in a crystal environment in connection with a determination of the change in the X-ray diffraction pattern upon optical excitation. The calculations yielded transitions in excellent accordance with experimental results. However, we present here evidence that the spectroscopic analysis should be reconsidered. The necessity of a reanalysis is a consequence of the qualitatively incorrect ordering of some of the excited states in the context of excimer formation when using TD-DFT and the standard B3LYP functional.[2] The conclusions in ref 1 regarding the change in X-ray scattering intensity upon excimer formation are, essentially, unchanged when a more suitable functional is employed.

A perylene dimer with D_{2h} symmetry is formed by superposing one molecule on top of another with a displacement along the z-axis perpendicular to the molecular planes.[3] We have elaborated on the work of ref 1 by calculating the six lowest excited states of the dimer system at the TD-DFT B3LYP/6-31G* level of theory as a function of interplanar distance along the z-axis from $z = 2.8$ to 10.0 Å. The structure of the perylene molecule used in composing the dimer was optimized at the B3LYP/6-311++G** level of theory. All calculations were performed in Gaussian 03.[4]

By analogy with ref 1, we identify the lowest and second lowest pair of excited states as being the charge resonance (CR), $M^-M^+ \leftrightarrow M^+M^-$, and exciton resonance (ER), $M^*M \leftrightarrow MM^*$, states, respectively, Figure 1. This identification is substantiated by the fact that these pairs belong to the same irreducible representations. The CR states should converge to the energy of $M^+ + M^-$ or, equivalently, the difference ΔE of the ionization potential (IP) and electron affinity (EA) of perylene. It is found experimentally[5] that $\Delta E = 7.0 - 1.1$ eV $= 5.9$ eV, while at the UB3LYP/6-31G* level of theory,[6] $E(M^+ + M^-) = 6.0$ eV. The CR states, due to the constrained symmetry of the system, are symmetry-adapted, linear combinations of CT states and should thus show a $1/r_{12}$ ($\sim 1/z$) dependence in the asymptotic limit. Crude fitting of the CR states to a model $-\alpha/z + \beta$ for $z \geq 7.00$ Å yields the asymptotic limit $\beta = 3$ eV; thus, the energy of the CR states is grossly underestimated. The CR problem[7] is related to the well-known CT problem in TD-DFT[8] and has only very recently been discussed in the context of excimer formation.[2]

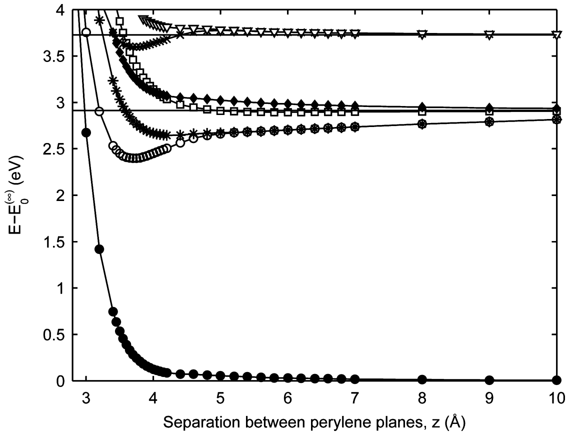

Figure 1. Energy of the perylene pair in the D_{2h} configuration as a function of interplanar distance. The energy of the ground state ^1A_g (●) and that of each of the six lowest singlet excited states $^1B_{3g}$ (○), $^1B_{2u}$ (*), 2 $^1B_{2u}$ (□), 2 $^1B_{3g}$ (♦), ^1A_u (×), and $^1B_{1g}$ (∇) is calculated at the TD-DFT B3LYP/6-31G* level of theory. The energies are given relative to the ground-state energy of the dimer at infinite separation, $E_0^{(\infty)}$. The energies of the first and second singlet excited state of the perylene molecule (at the same level of theory) are indicated by horizontal lines.

Inclusion of so-called exact exchange in the exchange-correlation functional is of immense importance in the calculation of CT and, thus, CR states.[8] Therefore, we have redone the calculation with the functional BH&HLYP, which incorporates 50% exact exchange.

The CR states are observed, Figure 2, to be moved above the lowest pair of ER states. A bound state, an excimer, is formed in the lowest ER state at $z = 3.60$ Å. The excimer is bound by $D_e = 0.42$ eV, in excellent agreement with the value of 0.44 eV obtained from solution experiments.[9] Fitting the CR states for $z \geq 7.00$ Å yields the asymptotic limit $\beta = 5$ eV, while $E(M^+ + M^-) = 6.1$ eV at the UBH&HLYP/6-31G* level of theory. Thus, the energy of the CR states is still underestimated, but the ER states represent now correctly the lowest excited states. The vertical transition energy ΔE_v from the first excited state to the ground state at $z = 3.60$ Å, that is, the excimer emission, is 2.50 eV (496 nm), Table 1 (cf. Table 1 in ref 1). At the TD-DFT BH&HLYP/6-311++G** level of theory, this value is reduced to 2.33 eV, in better agreement with experimental results, $\Delta E_v = 1.94$ and 2.145 eV.[10] In accordance with simple molecular exciton theory,[11] the strongest transition is to the second excited state at $\Delta E_v = 3.30$ eV (375 nm) with an oscillator strength of $f = 0.45$. Transition to the lowest CR state has $f = 0.24$, probably due to intensity borrowing from the bright ER state.

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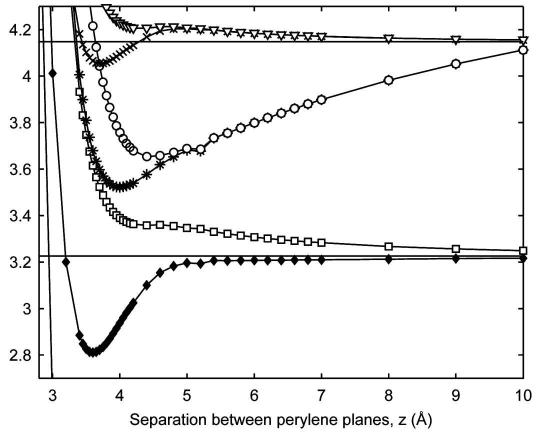

Figure 2. Energy of the perylene pair in the D_{2h} configuration as a function of interplanar distance. The energy of each of the six lowest singlet excited states $^1B_{3g}$ (♦), $^1B_{2u}$ (□), 2 $^1B_{2u}$ (*), 2 $^1B_{3g}$ (○), ^1A_u (×), and $^1B_{1g}$ (∇) is calculated at the TD-DFT BH&HLYP/6-31G* level of theory. Otherwise, this is the same as Figure 1.

TABLE 1: Type of State (ER or CR), Irreducible Representation (Γ) of the D_{2h} Point Group to Which the State Belongs, Transition Wavelength *λ*, Vertical Transition Energy ΔE_v, and Oscillator Strength *f* for the Perylene Dimer at $z = 3.60$ Å Calculated at the TD-DFT BH&HLYP/6-31G* Level of Theory[a]

type	Γ	*λ* (nm)	ΔE_v (eV)	*f*
ER	B_{3g}	496 (533)	2.50 (2.33)	0.00 (0.00)
ER	B_{2u}	375 (396)	3.30 (3.13)	0.45 (0.47)
CR	B_{2u}	368 (381)	3.37 (3.25)	0.24 (0.16)
ER	A_u	330 (353)	3.75 (3.51)	0.00 (0.00)
CR	B_{3g}	318 (326)	3.90 (3.80)	0.00 (0.00)
ER	B_{1g} (A_u)	303 (320)	4.10 (3.88)	0.00 (0.00)

[a] Values calculated at the TD-DFT BH&HLYP/6-311++G** level of theory are given in parentheses.

As a means of investigating the crystal excimer, by analogy with ref 1, we have performed ONIOM[12] calculations at the BH&HLYP/6-31G*:BH&HLYP/3-21G* level of theory for the ground state and BH&HLYP TD/6-31G*:BH&HLYP/3-21G* for the excited states. We use the α-perylene crystal structure,[13] incorporating all nearest-neighbor pairs around the central pair for a total cluster size of nine pairs. The energy minimum in the ground state is at displacements from the eclipsed structure in the *x*- and *y*-directions[3] of 1.25 and 1.19 Å, respectively, and $z = 3.62$ Å, the experimental value being 3.45 Å. The strongest transition ($f = 0.60$) is again to the second excited state at 3.25 eV (381 nm) (3.10 eV (400 nm) using the 6-311++G** basis set), in excellent agreement with the center of the absorption band at 3.10 eV (400 nm) observed in α-perylene at room temperature.[10] The minimum on the first excited-state surface is at displacements in the *x*- and *y*-directions of 0.95 and 0.79 Å, respectively, and at $z = 3.54$ Å. This corresponds to a relative displacement of $\Delta x = -0.30$, $\Delta y = -0.40$, and $\Delta z = -0.08$ Å upon excitation from the ground-state minimum. The transition energy from the first excited state to the ground state at the excited state minimum, that is, excimer fluorescence from α-perylene, is found to be 2.89 eV (429 nm) (2.71 eV (458 nm) using the 6-311++G** basis set).

Concerning the possibility of observing excimer formation via time-resolved X-ray diffraction, the 110, 004, and 005 reflections are still predicted to be the most sensitive reflections. However, the sensitivity of the fairly intense 110 reflection to excimer formation is now about 25% smaller, whereas the weak 004 and very weak 005 reflections are about 2.5 and 3 times more sensitive, respectively, than those reported in ref 1 upon displacement of the experimental ground-state structure by the calculated Δ values. These changes are in perfect agreement with the sensitivity analysis in ref 1.

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References and Notes

(1) Velardez, G. F.; Lemke, H. T.; Breiby, D. W.; Nielsen, M. M.; Møller, K. B.; Henriksen, N. E. *J. Phys. Chem. A* **2008**, *112*, 8179–8187.

(2) Fink, R. F.; Pfister, J.; Zhao, H. M.; Engels, B. *Chem. Phys.* **2008**, *346*, 275–285.

(3) The *x*- and *y*-axes are parallel to the short and long molecular axes, respectively.

(4) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision E.02; Gaussian, Inc.: Wallingford, CT, 2004.

(5) Pope, M.; Swenberg, C. E. *Electronic Processes in Organic Crystals and Polymers*, 2nd ed.; Oxford Science Publications: New York, 1999.

(6) All energies are relative to $E_0^{(\infty)}$.

(7) Hieringer, W.; Gorling, A. *Chem. Phys. Lett.* **2006**, *419*, 557–562.

(8) Dreuw, A.; Weisman, J. L.; Head-Gordon, M. *J. Chem. Phys.* **2003**, *119*, 2943–2946.

(9) Katoh, R.; Sinha, S.; Murata, S.; Tachiya, M. *J. Photochem. Photobiol., A* **2001**, *145*, 23–34.

(10) (a) Ferguson, J. *J. Chem. Phys.* **1966**, *44*, 2677–2683. (b) Tanaka, J. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 1237–1249.

(11) Kasha, M.; Rawls, H. R.; El-Bayoumi, M. A. *Pure Appl. Chem.* **1965**, *11*, 371–392.

(12) Svensson, M.; Humbel, S.; Froese, R. D. J.; Matsubara, T.; Sieber, S.; Morokuma, K. *J. Phys. Chem.* **1996**, *100*, 19357–19363.

(13) Camerman, A.; Trotter, J. *Proc. R. Soc.* **1964**, *279*, 129–146.

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