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# Electronic spectra and photophysics of the two stable conformers of anthracene dimer: evaluation of an ab initio structure prediction

Carlos Gonzalez<sup>a</sup>, Edward C. Lim<sup>b,\*</sup>

<sup>a</sup> Physical and Chemical Properties Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

<sup>b</sup> Department of Chemistry, The University of Akron, Akron, OH 44325-3601, USA

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## Abstract

It is shown that the spectral features and excited-state dynamics of the two Van der Waals dimers of anthracene, generated by supersonic free expansion, can be accounted for if the dimers have the crossed ( $D_{2d}$ ) and the parallel-displaced ( $C_{2h}$ ) structures predicted by an ab initio calculation with MP2 correlation. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

As the species formed due to intermolecular interactions, the geometrical structures of aromatic dimers generated by free jet expansion provide important information concerning the nature of the forces between aromatic molecules and understanding of the dimers' other properties. The simplest aromatic dimer is the Van der Waals (VdW) dimer of benzene, and much has been written about its geometrical structures [1]. However, despite the large body of work, the experiment and computation are inconsistent with each other in regard to the number of low-energy conformers in benzene. Thus, whereas the high-level

ab initio calculations predict a parallel-displacement ( $C_{2h}$ ) and a T-shaped ( $C_{2v}$ ) dimers of very similar energies, only one dimer conformer, attributed to the T-shaped geometry, has been unambiguously detected in the microwave and optical spectra of benzene [1]. Recently, we have made ab initio study of the conformational geometries of the VdW dimers of naphthalene and anthracene [2], and the VdW trimer of naphthalene [3]. For the naphthalene trimer, both the MP2/6-31G//MP2/6-31G<sup>2</sup> and MP2/6-31 + G//MP2/6-31G<sup>2</sup> yielded the minimum energy cyclic ( $C_{3h}$ ) geometry that is essentially identical to the experimental geometry [4]. For the dimers of naphthalene and anthracene, the same calculations

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\* Corresponding author. Fax: +1-330-972-6407; e-mail: elim@uakron.edu

<sup>1</sup> Holder of the Goodyear Chair in Chemistry at The University of Akron.

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<sup>2</sup> Energy calculation performed using MP2 theory and the 6-31G (or 6-31 + G) basis set on a structure previously optimized with MP2 theory and the 6-31G basis set.

yield two lowest energy conformers of very similar energies: crossed ( $D_{2d}$ ) and parallel-displaced ( $C_{2h}$ ). Other dimer conformers, including T-shaped dimers, are substantially less stable than the two lowest energy structures. Consistent with the number of the low energy conformers predicted by the *ab initio* computations, the laser-induced fluorescence (LIF) excitation and resonant two-photoionization (R2PI) spectra of jet-cooled anthracene exhibit two dimer features [5,6]. One is broad and structureless, whereas the second at lower energy is relatively sharp and structured.

Although the structural identities of the two dimer absorptions in anthracene cannot be ascertained without rotationally resolved spectra, some reasonable conjectures concerning the merit of the *ab initio* structure prediction can be made on the basis of the qualitative analyses of the electronic absorption spectra and photophysics of the two dimer conformers. We show here that the computed *ab initio* dimer structures are consistent with the observed electronic spectra as well as the excimer fluorescence arising from excitation of the two dimer absorption systems. The analyses also suggest a plausible reason for the observation of a single dimer absorption in naphthalene. In what follows, we describe the experimental spectra (absorption and emission), the computed *ab initio* dimer structures, consideration of exciton splitting for the two dimer conformers, semiempirical dimer potentials, and present the analyses leading to the structural assignments of the two dimer absorption bands in anthracene.

## 2. Results and discussion

### 2.1. Absorption and emission spectra

Fig. 1 presents the  $S_1 \leftarrow S_0$  LIF excitation spectra of anthracene dimers, first reported by Chakraborty and Lim [5]. One of the spectra is broad and structureless, whereas the other at lower energy is relatively sharp and structured. These spectral features have been assigned to two conformational isomers. Photoexcitation of the two VdW dimers leads to rapid formation of excimers [5]. Subsequent work based on hole-burning spectroscopy and mass-resolved R2PI spectroscopy by Matsuoka et al. [6]

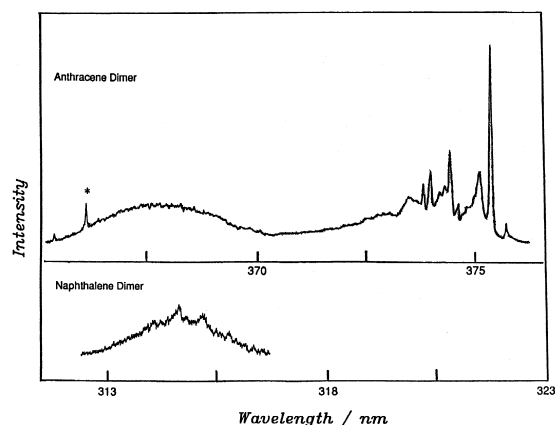


Fig. 1. The  $S_1 \leftarrow S_0$  fluorescence excitation spectra of anthracene dimer (upper trace) and naphthalene dimer (lower trace) in their origin band regions, measured by monitoring the excimer fluorescence at wavelengths longer than 500 nm (upper trace) and longer than 400 nm (lower trace). The anthracene band marked by an asterisk is a hot band of the monomer [5].

confirmed the assignment. Matsuoka et al. also showed that the excimer fluorescence from the two dimers is significantly different in lifetime. Thus, while the excitation of the dimer with broad feature results in the excimer fluorescence which has a long lifetime (300 ns), excitation of the sharp feature at lower energy leads to the excimer fluorescence with short lifetime ( $15 \pm 5$  ns). Moreover, the excimer fluorescence from the broad absorption system is red shifted with respect to that from the sharp system [6].

Unlike anthracene, only one dimer feature is clearly evident in the LIF excitation and R2PI spectra of jet-cooled naphthalene [7,8] (Fig. 1). Photoexcitation of the broad dimer feature leads to rapid formation of excimer [8].

### 2.2. *Ab initio* structures: crossed ( $D_{2d}$ ) and parallel-displaced ( $C_{2h}$ ) dimers

Since the details of the computational work will be presented elsewhere [2], only a short summary of the methodology and essential results will be given here. Briefly, molecular dynamics (MD) trajectories were computed with the molecular dynamics (MM3) force field [9] using the molecular dynamics/mechanics program TINKER [10]. These geometries were further optimized with the MM3 force field by the

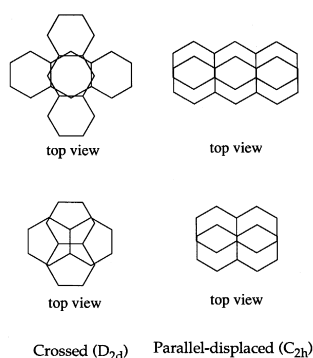


Fig. 2. The top views of the optimized MP2/6-31G dimer structures for naphthalene and anthracene.

Quasi-Newton optimizer contained in the TINKER suite of programs. The optimized geometries of the lowest-energy minima located using the MM3 force field were then used as the initial guess for additional MD simulation until no further minimum was located. The final optimized geometries found by this procedure were then used as initial guess for full geometry optimization at the MP2/6-31G level of theory [11]. All ab initio calculations were carried out with the Gaussian 94 suite of programs [12]<sup>3</sup> on a Cray-T94 at the Ohio Supercomputer Center.

Fig. 2 and Table 1 give the two stable dimer conformers of very similar energies obtained by MP2/6-31G//MP2/6-31G and MP2/6-31 + G//MP2/6-31G calculations [2]. One dimer has a crossed  $D_{2d}$  structure and the other has a parallel-displaced  $C_{2h}$  structure in both naphthalene and anthracene. The parallel-displaced (PD) dimer of naphthalene has a horizontal displacement of 1.5 Å along the short axes of the monomers, and the vertical separation of 3.5 Å. The corresponding horizontal and vertical separation in the parallel-displaced dimer of anthracene are 1.1 Å and 3.6 Å, respectively. The shorter horizontal displacement of the anthracene dimer relative to that of the naphthalene dimer is

Table 1

Optimized MP2/6-31G geometries of naphthalene and anthracene dimers<sup>a</sup>

Dimer <sup>b</sup>	Symmetry	VD <sup>c</sup> (Å)	HD <sup>d</sup> (Å)
C-naphthalene	$D_{2d}$	3.6	
PD-naphthalene	$C_{2h}$	3.5	1.5
C-anthracene	$D_{2d}$	3.3	
PD-anthracene	$C_{2h}$	3.6	1.1

<sup>a</sup>From Ref. [2].

<sup>b</sup>C, crossed; PD, parallel displaced.

<sup>c</sup>Vertical displacement.

<sup>d</sup>Horizontal displacement along the short axes of the monomers.

consistent with the greater dispersion forces (favoring the face-to-face sandwich structure) expected of the larger dimer. The vertical separations of the aromatic rings in the crossed dimer are 3.6 Å for naphthalene and 3.3 Å for anthracene. The binding energies of the dimers, corrected for basis set superposition error (BSSE), are listed in Table 2.

### 2.3. Exciton splitting and energy-level diagram for the crossed and the parallel-displaced dimers

The Hamiltonian operator for the electronically excited dimer (AB) of interacting chromophores can be written as

$$\hat{H} = \hat{H}_A + \hat{H}_B + \hat{V} \quad (1)$$

where  $\hat{H}_A$  and  $\hat{H}_B$  represent the terms for the individual chromophores (A and B), and  $\hat{V}$  is the operator describing the interaction between the two chromophores. If the interchromophore distance is large compared to the size of the molecule, and if there is

Table 2

BSSE-corrected binding energies (in kJ/mol) computed at MP2/6-31 + G//MP2/6-31G level<sup>a</sup>

Dimer	$-\Delta E_{\text{elec}}$
C-naphthalene	15.75
PD-naphthalene	15.66
C-anthracene	36.42
PD-anthracene	31.83

<sup>a</sup>From Ref. [2].

<sup>3</sup> Certain commercial materials and equipment are identified in this paper in order to specify procedures completely. In no case does such identification imply recommendation or endorsement by the National Institute of Standard and Technology, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

no overlap between the chromophore orbitals, the interaction between the two chromophores in the dimer can be described by the dipole–dipole interaction [14]

$$\hat{V} = \frac{\vec{M}_A \cdot \vec{M}_B}{r^3} - \frac{3(\vec{M}_A \cdot \vec{r})(\vec{M}_B \cdot \vec{r})}{r^5} \quad (2)$$

where  $\vec{M}_A$  and  $\vec{M}_B$  are the transition dipoles,  $\vec{r}$  represents the vector from one center of mass to the other center of mass, and  $r$  is the distance between the two centers of mass. These two conditions are clearly not met for the aromatic dimers under consideration, and the interaction between the two monomers is expected to involve electron exchange [15]. Nonetheless, for the qualitative interpretation of spectral features which we seek, it is useful to consider only the electrostatic dipole–dipole interaction which splits the excited state of the dimer into two exciton components. The wave functions for the two exciton components are given by in-phase (+) and out-of-phase (−) combinations of the excited states of the two subsystems.

$$\psi_{\pm} = \frac{1}{\sqrt{2}} (\psi_A^* \psi_B \pm \psi_A \psi_B^*) \quad (3)$$

The energies of the two-exciton components can be obtained by evaluating the expectation values of the Hamiltonian in Eq. (1). The results are [16]

$$E_+ = \langle \psi_+ | \hat{H}_A + \hat{H}_B + \hat{V} | \psi_+ \rangle = E_g + E_e + \varepsilon \quad (4a)$$

and

$$E_- = \langle \psi_- | \hat{H}_A + \hat{H}_B + \hat{V} | \psi_- \rangle = E_g + E_e - \varepsilon \quad (4b)$$

where  $E_g$  and  $E_e$  represent the energy of the ground and excited states of the monomer, respectively, and  $\varepsilon$  represents the excitation resonance interaction energy

$$\varepsilon = \langle \psi_A^* \psi_B | \hat{V} | \psi_A \psi_B^* \rangle \quad (5)$$

Thus, the excited state of the dimer is split by  $2\varepsilon$  ( $= E_+ - E_-$ ).

For a dimer with the arbitrary orientation of the transition moments ( $\vec{M}_A$  and  $\vec{M}_B$ ) where  $\theta$  denotes the angle the transition moment makes with the line

joining the two centers of mass, and  $\phi$  represents rotation of the transition dipoles about the line joining them, i.e.,  $\phi = \phi_B - \phi_A$ , the dipole–dipole interaction energy  $\varepsilon$  is given by [14]

$$\varepsilon(r, \theta_A, \theta_B, \phi) = \frac{M_A M_B}{r^3} (2 \cos \theta_A \cos \theta_B - \sin \theta_A \sin \theta_B \cos \phi) \quad (6)$$

The exciton splitting is therefore large if the transition moment is large and if the two chromophores are separated by a short distance. The splitting also depends strongly on the orientation of the two monomer transition moments, and hence on the conformation of the dimer. For the crossed dimers of naphthalene and anthracene, for which  $\theta = 90^\circ$  and  $\phi = 90^\circ$ , the excitation resonance interaction vanishes. Conversely, the interaction is finite for the parallel-displaced dimer with  $\phi = 0^\circ$ . The intensities of the electronic absorption to the two-exciton components can be deduced by considering the electrostatic interaction between the transition moments. The transition to lower-energy exciton component ( $\psi_-$ ) of the parallel-displaced dimer is forbidden, whereas the transition to the higher-energy exciton component ( $\psi_+$ ) is allowed [16].

The  $S_1 \leftarrow S_0$  absorption system of anthracene is due to the allowed  ${}^1B_{2u} \leftarrow {}^1A_g$  transition, which is polarized along the short axis of the molecule. For the crossed dimer of anthracene, with the two chromophores arranged perpendicular to each other (Fig. 2), the angle  $\phi$  between the two transition moments is  $90^\circ$ , and the excitation resonance interaction vanishes ( $\cos 90^\circ = 0$  and  $\theta = 90^\circ$ , Eq. (6)). Thus, the interaction energy, and hence the exciton splitting, is zero. The energy of the  $S_1$  state of the crossed dimer relative to the monomer state is given by

$$E = E_m + E_{vdw} \quad (7)$$

where  $E_{vdw}$  is the Van der Waals energy (composed mostly of attractive electrostatic and dispersion contributions) that stabilizes the dimer relative to the monomer.

For the parallel-displaced dimer of anthracene, with  $\phi = 0^\circ$  and  $\theta \neq 90^\circ$ , the excitation resonance

interaction is finite, so that the energy of the  $S_1$  state of the dimer is given by

$$E = E_m + E_{\text{vdW}} \pm \varepsilon \quad (8)$$

where  $\varepsilon$  is the interaction energy. Since the attractive interaction between the opposing transition dipoles is expected to stabilize  $S_1$ ,  $\psi_-$  will be the lower-energy exciton component of the dimer. The electronic transition from the ground state to the lower-energy, exciton component ( $\psi_-$ ) in  $S_1$  is forbidden, whereas that of the higher-energy component ( $\psi_+$ ) is allowed. If the VdW energy is similar for both the crossed and the parallel-displaced dimers, the higher-energy exciton component of the parallel-displaced dimer is expected to lie above the  $S_1$  states of the crossed dimer. A schematic diagram comparing the energy levels of the  $S_0$  and  $S_1$  states of the two dimer conformers is given in Fig. 3.

#### 2.4. Structural assignments of the two dimer absorption bands and excited-state dynamics

Based on the supposition that the higher-energy exciton component of the  $S_1$  parallel-displaced dimer should lie above the  $S_1$  state of the crossed dimer (Fig. 3), it is reasonable to assign the structureless absorption band at higher energy to the parallel-displaced dimer, and the structured absorption at lower energy to the crossed dimer. If we assume for sim-

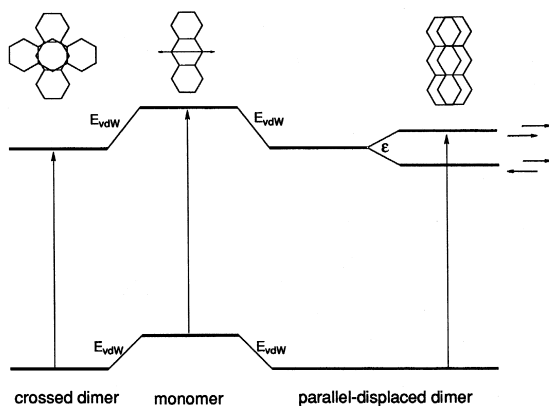


Fig. 3. The schematic energy level diagram for the crossed dimer (left) and the parallel-displaced dimer (right) of anthracene, relative to the monomer, showing the Van der Waals stabilization ( $E_{\text{vdW}}$ ) and exciton splitting ( $2\varepsilon$ ). The horizontal arrows for the excited state of the parallel-displaced dimer represent the monomer transition moments in the dimer.

plicity that VdW energy is the same for both dimers, exciton splitting of  $1000 \text{ cm}^{-1}$  or greater can be estimated for the parallel-displaced dimer, based on the energy difference of  $\sim 500 \text{ cm}^{-1}$  between the structured and the structureless absorption bands. Considering the allowed character of the  $S_1 \leftarrow S_0$  transition in anthracene ( $f \approx 0.1$ ), the exciton splitting of this magnitude is quite reasonable.

The assignment of the two dimer absorption bands in anthracene to the crossed and the parallel-displaced dimers is in accord with the semiempirical  $S_1$  and  $S_0$  intermolecular potentials of Sadygov and Lim [17], who incorporated the intermolecular distance dependence of  $\pi$ - $\sigma$  interaction into the INDO 1/S for the calculation. In this work, the INDO 1/S SCF-CI energy of the excited state (or the ground state) was first computed as a function of the angle of rotation about the  $C_2$  axis, and the displacement along the in-plane short axes of the monomers, to determine how the energy varies as the sandwich dimer of  $D_{2h}$  symmetry is distorted to produce the crossed and the parallel-displaced dimers. This  $S_1$  (or  $S_0$ ) intermolecular potential was then combined with the INDO 1/S SCF-CI  $S_1$ - $S_0$  transition energy to generate the  $S_0$  (or  $S_1$ ) potential. Although INDO 1/S is certainly not the best choice for the study of  $S_0$  potential (PM3 for example would be better), this approach avoids the uncertainty associated with the use of the two different computational methods for the ground and the excited states. Fig. 4 illustrates the intermolecular potentials so obtained for naphthalene dimer. The results are remarkable in several respects. First, whereas the horizontal displacement as well as the rotation lead to destabilization of the electronically excited dimer, they lead to stabilization of the ground-state dimer. The minimum-energy ground-state structure has rotation angle ( $\phi$ ) of  $90^\circ$  for the crossed dimer and horizontal displacement (D) of about  $1.3 \text{ \AA}$  for the parallel-displaced dimer, in essential agreement with the results of the ab initio calculations. The binding energies of the crossed and the parallel-displaced dimers, relative to the sandwich dimer, are also similar to those from the ab initio computation. Second, the  $S_1 \leftarrow S_0$  transition energy is slightly smaller for the crossed dimer than for the parallel-displaced dimer, consistent with the assignment of the higher-energy absorption band of anthracene to the parallel-displaced dimer and the

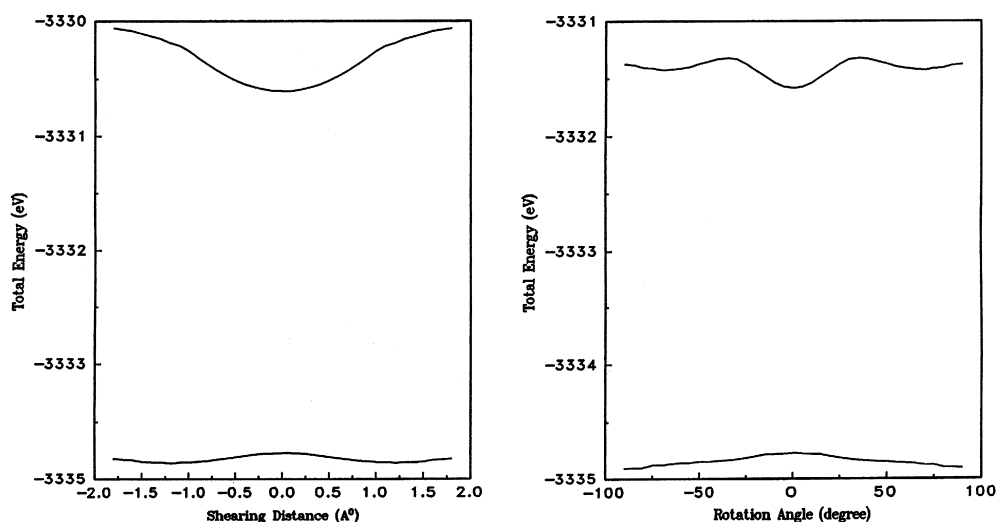


Fig. 4. The INDO1/S energies for the ground and the first excited states of naphthalene dimer (with an interplanar separation of 3.3 Å) as a function of the displacement along the short molecular-axis (left) and rotation about the  $C_2$  axis (right) [17]. The angle of  $0^\circ$  or the displacement of 0 Å corresponds to the parallel sandwich-pair ( $D_{2h}$ ) configuration of the dimer, which is the most stable conformation of the excimer. The results for the anthracene dimers are also very similar, except for the smaller electronic gap between the excited and ground states.

lower-energy absorption to the crossed dimer. Third, while the transformation of the locally excited (LE) state of the parallel-displaced dimer to the sandwich-pair structure of the singlet excimer is a barrierless process, the transformation of the LE state of the crossed dimer to the sandwich structure has an activation energy barrier. Thus, electronic excitation of the crossed dimer would lead to an excimer of non-zero rotation angle (i.e.,  $\phi \neq 0$ ). The vastly different spectral shapes of the two dimer absorption bands can therefore be rationalized based on the simple one-dimensional potential energy diagrams and Franck–Condon principle. The absorption band of the parallel-displaced dimer would be broad and structureless, since the excitation takes the ground-state dimer to an excited state of very different equilibrium geometry (i.e., sandwich). Conversely, the absorption band of the crossed dimer would be sharp since the equilibrium geometry of the local minimum in the excited state (reached by the vertical transition) is not very different from the global minimum of the ground state. Finally, the structural assignments of the absorption bands provide a rationale for the observation of Matsuoka et al. [6] pertaining to the excimer fluorescence. They have shown

that the excimer fluorescence from the excitation of the broad absorption feature is long-lived (300 ns), whereas that generated by excitation of the sharp feature is short-lived (15 ns). Since the excitation of the parallel-displaced dimer leads to barrierless formation of the sandwich excimer of  $D_{2h}$  symmetry, as suggested in Fig. 4, the excimer fluorescence represents the dipole-forbidden  ${}^1B_{3g} \rightarrow {}^1A_g$  radiative transition, and hence would be long lived. On the other hand, excitation of the crossed dimer would trap the dimer in a local minimum with  $\phi \neq 0$ , from which the radiative transition to the ground state becomes allowed due to the reduced symmetry ( $D_{2d}$ ). The results in Fig. 4 further predict that the emission maximum of the ‘excimer fluorescence’ from the crossed dimer should be at higher energy relative to the excimer fluorescence from the parallel-displaced dimer, in agreement with the experiment.

The electronic absorption spectra and excimer fluorescence of the anthracene dimers are therefore consistent with the conclusion that the two dimer features observed in the optical spectra of anthracene belong to the crossed ( $D_{2d}$ ) dimer and the parallel-displaced ( $C_{2h}$ ) dimer, predicted by the ab initio calculations.

### 3. Conclusion

We have shown here that the spectral features and excited-state dynamics of the two Van der Waals dimers of anthracene, generated by supersonic free expansion, can be accounted for on the basis of semiempirical intermolecular potential, exciton splitting, and the Franck–Condon principle, if it is assumed that the dimers have the crossed ( $D_{2h}$ ) and the parallel-displaced ( $C_{2h}$ ) structures predicted by an ab initio calculation with MP2 correlation. The conformer with the structureless absorption band is assigned to the parallel-displaced dimer, whereas the conformer with the structured absorption at lower energy is assigned to the crossed dimer. As for the naphthalene dimer, the similarity of its absorption spectrum to the broad absorption band of the anthracene dimer (Fig. 1) suggests that the dimer conformer responsible for the broad absorption feature is also a parallel-displaced dimer. Because the exciton splitting is expected to be rather small in the parallel-displaced dimer of naphthalene due to the very small  $S_1 \leftarrow S_0$  oscillator strength ( $f < 0.001$ ), it is plausible that the  $S_1 \leftarrow S_0$  electronic absorptions of the crossed and the parallel-displaced dimers occur in the similar spectral region for naphthalene (Fig. 2). Consistent with such a conjecture, the broad absorption band of naphthalene appears to contain some sharp features (Fig. 1), which are not apparent in the corresponding spectrum of the anthracene dimer. Clearly, a careful search for the possible second dimer conformer of naphthalene, as well as rigorous geometry characterization based on rotationally resolved spectra, are essential for a definitive test of the ab initio structure prediction. Unfortunately, the measurement of the rotational constants by high resolution spectroscopy (in frequency or time domain [4]) is very difficult due to the size of

the species and the loss of excited-state coherence by rapid excimer formation [5,6,8].

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