Electronic supplementary information for "Possible Formation of Metastable PAH Dimers upon Pickup by Helium Droplets"

F. Calvo,[*,†] E. Yurtsever,[‡] and Ö. Birer[‡]

Univ. Grenoble Alpes, LIPHY, F-38000 Grenoble, France and CNRS, LIPHY, F-38000 Grenoble, France, and Koç University, Chemistry Department, Rumeli Feneri Yolu, Sariyer 34450, Istanbul, Turkey

E-mail: florent.calvo@ujf-grenoble.fr

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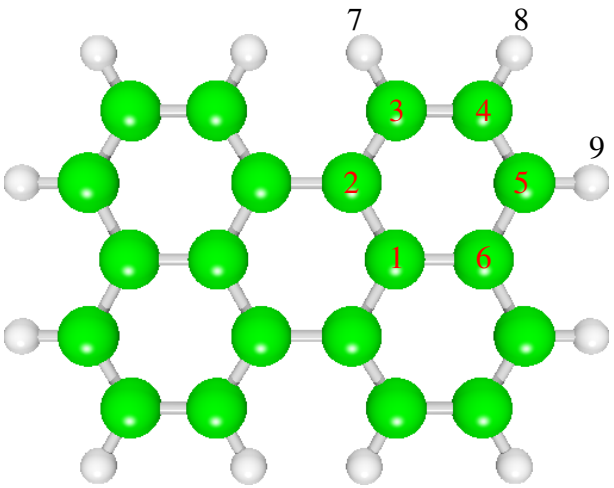
[*]To whom correspondence should be addressed
[†]Univ. Grenoble Alpes, LIPHY, F-38000 Grenoble, France and CNRS, LIPHY, F-38000 Grenoble, France
[‡]Koç University, Chemistry Department, Rumeli Feneri Yolu, Sariyer 34450, Istanbul, Turkey

1 Equilibrium geometry and charges carried by the perylene monomer



1:+0.134
2:−0.029
3:+0.160
4:−0.107
5:−0.275
6:+0.203
7:+0.129
8:+0.122
9:+0.152

The Cartesian coordinates (in Å) are given below, with the partial charges (in units of e) as the last column.

C	1.459171	0.000000	0.000000	0.134035
C	0.747434	1.269824	0.000000	−0.029359
C	−0.747427	1.269824	0.000000	−0.029359
C	−1.459164	0.000000	0.000000	0.134035
C	−0.747427	−1.269824	0.000000	−0.029359
C	0.747434	−1.269824	0.000000	−0.029359
C	2.920515	0.000000	0.000000	0.203222
C	1.485025	2.461310	0.000000	0.160389
C	−1.485018	2.461310	0.000000	0.160389
C	−2.920508	0.000000	0.000000	0.203222
C	−1.485018	−2.461310	0.000000	0.160389
C	1.485025	−2.461310	0.000000	0.160389
C	3.601259	1.268593	0.000000	−0.275454
C	2.899401	2.454943	0.000000	−0.107083
C	−2.899394	2.454943	0.000000	−0.107083
C	−3.601252	1.268593	0.000000	−0.275454
C	−3.601252	−1.268593	0.000000	−0.275454
C	−2.899394	−2.454943	0.000000	−0.107083
C	2.899401	−2.454943	0.000000	−0.107083
C	3.601259	−1.268593	0.000000	−0.275454
H	4.699673	1.272032	0.000000	0.151861
H	3.436018	3.415020	0.000000	0.122273
H	−3.436011	3.415020	0.000000	0.122273
H	−4.699665	1.272032	0.000000	0.151861
H	−4.699665	−1.272032	0.000000	0.151861
H	−3.436011	−3.415020	0.000000	0.122273
H	3.436018	−3.415020	0.000000	0.122273
H	4.699673	−1.272032	0.000000	0.151861
H	0.955352	3.423785	0.000000	0.128674
H	−0.955345	3.423785	0.000000	0.128674
H	−0.955345	−3.423785	0.000000	0.128674
H	0.955352	−3.423785	0.000000	0.128674

2 Dynamics of T-shape conformers in vacuum

Ring-polymer MD simulations were carried out for the bare perylene dimer initially in perfect T-shape conformation ($\theta_z = 90°$). For both intermolecular LJ models, 100 independent trajectories were performed and propagated for 25 ps each. The following figure shows the time variations of the angle θ_z averaged over the 100 trajectories, compared to the same quantity obtained in presence of helium, averaged over 10 trajectories (four of which are shown in the main document):

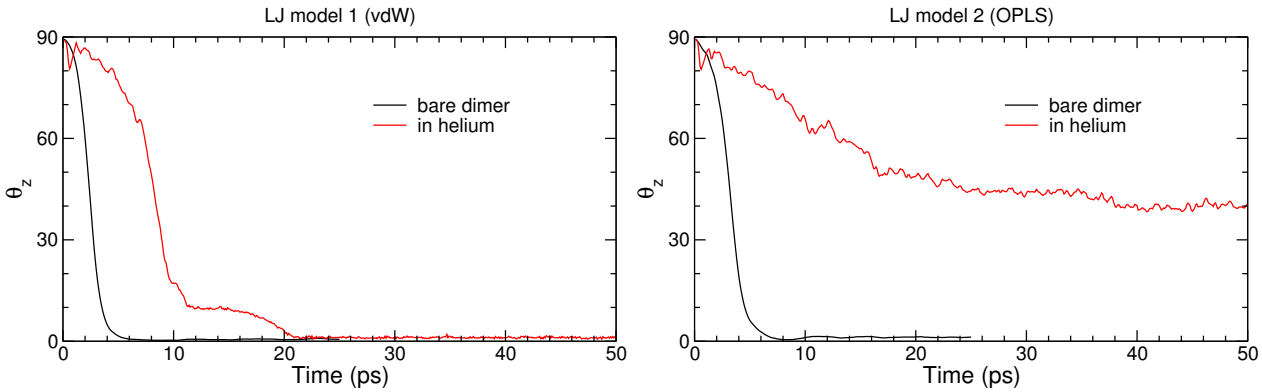


Figure 1: Average angle θ_z between the normal vectors of the perylene molecules, the dimer being initially placed in T-shaped conformations. For each intermolecular LJ model (left panel: vdW model; right panel: OPLS model), the results obtained for 100 trajectories on the isolated dimer are compared with 10 trajectories for the dimer in helium environment.

In vacuum, the bare dimer quickly rearranges into the stacked form over 4–5 ps in average, whereas the presence of helium leads to about twice this value for the vdW intermolecular model, and in excess of 100 ps for the OPLS model.

3 Stacked conformers initially separated by one monolayer

We show in the figure below the results of four RPMD trajectories performed with each intramolecular LJ potential, for conformers initially separated by one monolayer and distant by more than 6 Å. For each model, the set of four trajectories contains the specific trajectory analysed in Fig. 6 of the main article.

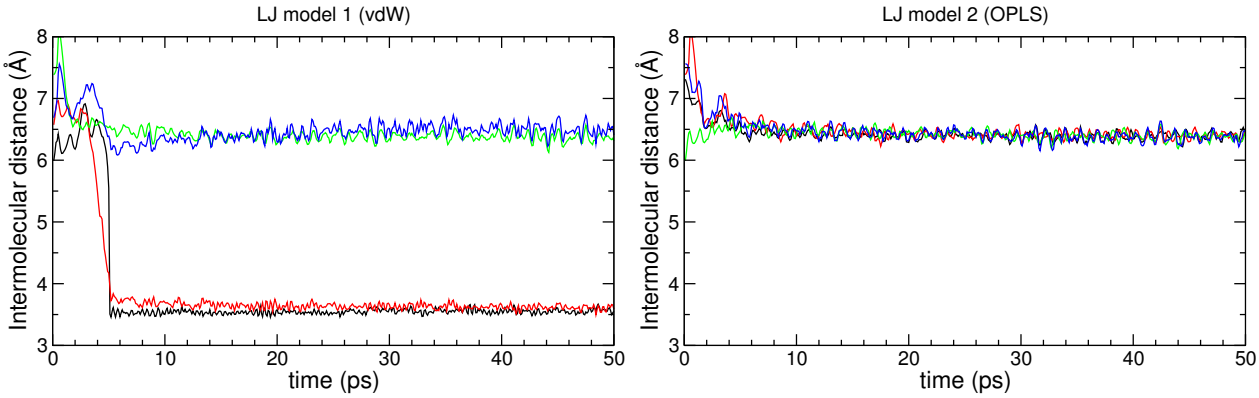


Figure 2: Distance between the centers of mass of the perylene molecules initially separated by more than 6 Å, surrounded by 500 He atoms and as obtained for four independent RPMD trajectories for the two intermolecular LJ models.

4 Full Ref. 39

(39) Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, M. J.; Klene, M.; Knox, J. E.; 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.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.