

## Comment on “Molecular Distortions and Chemical Bonding of a Large $\pi$ -Conjugated Molecule on a Metal Surface”

In a recent Letter, Hauschild *et al.* [1] presented density-functional theory (DFT) calculations to demonstrate the chemisorption of 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) on Ag(111). This result is in contrast with previous calculations [2] and is an artifact of the basis superposition error effect [3] caused by excessively confined basis orbitals.

The calculations discussed in Ref. [1] were done within the linear combination of atomic orbitals approximation. They use a basis set of numerical orbitals centered on the atoms (numeric atomic orbitals, or NAO's), confined inside a cutoff radius. The chemisorption results are due to excessively confined basis functions, as we show here by performing calculations with different values of the confinement radius  $r_C$  for the NAO's [4,6]. As in Ref. [1], our calculations are done using the SIESTA code [5], with the same generalized gradients approximation functional and bases sets but exploring the effect of the orbital cutoffs.

We have considered the herringbone phase of PTCDA on Ag(111) and performed a set of total energy calculations varying the distance of the PTCDA monolayer from the surface without relaxing the atomic positions. Although such calculations do not provide the optimal intramolecular structure as a function of molecule-surface separation, they quite accurately describe the interaction energy curves and the location of the minimum energy distance. Figure 1 shows the results for several values of the cutoff radius  $r_C$  of the NAO's. We find that the equilibrium distance and interaction energy depend strongly on  $r_C$  for strongly confined orbitals: For cutoff radii below 3.0 Å, the equilibrium distance is in the range of 2.5–3.0 Å (which encloses the value of 2.83 Å reported in Ref. [1]). However, for longer radii (i.e., sufficiently extended basis functions) the molecules and the surface interact very weakly: The distance is increased and the interaction energy is dramatically reduced (indeed, Picozzi *et al.* [2] find that the interaction is slightly repulsive).

An important feature of the results of Ref. [1] is that the oxygen atoms bend toward the surface [see, for instance, Fig. 3(a) in Ref. [1]]. This is once again an effect of the basis superposition error. We have placed the PTCDA monolayer at a distance of  $\sim 3.0$  Å, as in Ref. [1], but now we allow the oxygen atoms to relax. We find that the angle of the carboxyl C-O bond with the plane of the molecule decreases significantly and monotonically with the cutoff radius: We obtain 9.3°, 5.6°, and 4.6° for values of the radii of 2.58, 2.92, and 3.57 Å, respectively. For highly confined basis functions, the C-O bond bends toward the surface: The oxygen orbitals are too short to account properly for the interaction with the neighboring hydrogens, i.e., intermolecular H bond, and the interaction with the orbitals of the Ag surface attracts the oxygens

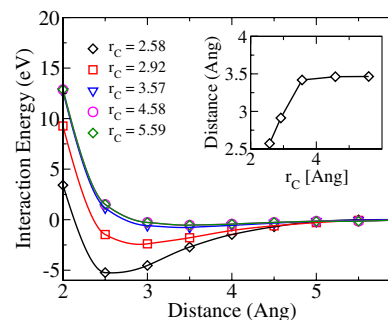


FIG. 1 (color online). Interaction energy vs distance of the PTCDA layer from the surface. The inset shows the chemisorption distance as a function of the basis cutoff radii  $r_C$  in Å.

atoms towards the surface. As the value of  $r_C$  is increased, a planar geometry is gradually recovered.

In conclusion, correctly converged calculations with present DFT functionals do not permit one to explain the experimental adsorption geometry of PTCDA on Ag(111).

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- [3] The basis set superposition error is an artificial decrease of the total energy of a system of interacting fragments, and it is caused by the use of the orbitals of a fragment to cover the deficiencies of the basis set of the other one in describing its internal energy.
- [4] The extension of the atomic orbitals used for the different chemical species involved is different, though of the same order, and has been defined via a unique parameter (see Ref. [5] and references therein). The data here are given with respect to the extension of the orbitals used for carbon.
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- [6] Note that, by virtue of the variational principle, the most accurate basis set is the one which yields the lowest total energy, which in this case corresponds to that with longer cutoff radii.