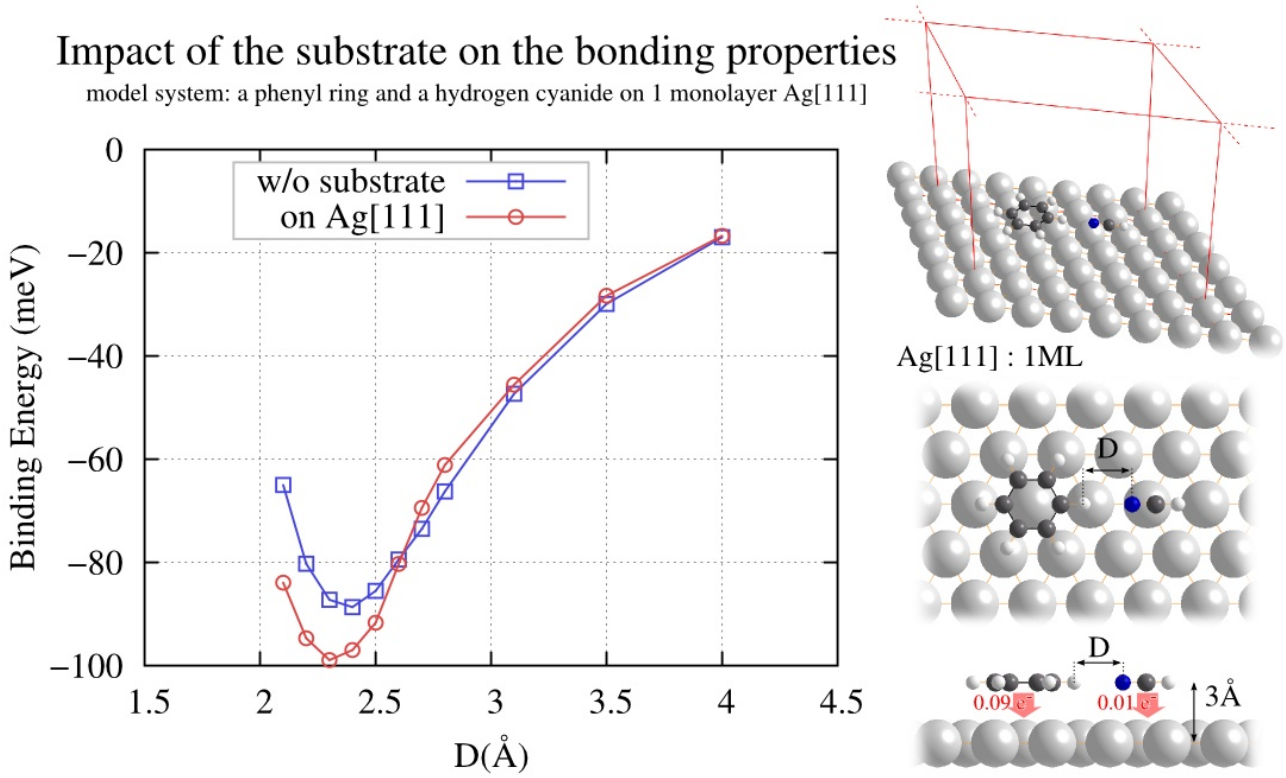
Supporting Informations



In the theoretical part of the article, we have not taken into account explicitly the presence of a substrate when investigating the different bonding motifs between molecules, because of the obvious computational cost of such simulations. It is a question however to which effect the substrate might have an effect on the molecular bonding, beyond the simple sticking and corrugation due to Van der Waals interactions.

In order to evaluate this effect, we have used a model system of our bonding motifs with reduced lateral extension, therefore economizing the computational effort. We studied the lateral interaction between a hydrogen cyanide and a phenyl ring, placed over a monolayer of silver atoms arranged as in a 111 plane (as shown on the right part of the figure). We calculate the interaction energy versus the distance D from a H atom of the phenyl ring to the N atom of the hydrogen cyanide. Results are plotted on the left part of the figure, in the free standing case (blue), and in the presence of the Ag substrate (red).

We can draw 4 conclusions from this results, regarding the effect of the substrate:

1. The intermolecular **bonding energy is increasing by 10 meV**, and reached 99 meV.
2. The **bonding length is shortened by 0.1 Å**, down to 2.3Å (-4%) .
3. There is an overall **charge transfer of 0.1 electron** (e^-) from the molecules to the substrate (on a total of 36 "valence" electrons, *i.e.*, without 1s electrons of C and N).
4. The **dipole moment of the hydrogen cyanide decreases by less than 0.01 e^-·Å**, to 0.62 e^-·Å (-1.3%).

From these results, we conclude that the effect of the substrate on the molecular bonding properties is minimal, and can be left aside in the study, provided of course that the simple sticking and corrugation effect due to Van der Waals interactions is taken into account, for example by restricting the molecules in-plane.

Computational details:

- All points are single point calculations : no geometric relaxation
- The distance between the molecules and the Ag[111] substrate is fixed to 3Å
- The size of the unit cell is : 16.9 x 11.3 x sin(60°) x 16 Å^3 , and comprises 24 Ag atoms.
- The k-point mesh is 2x3x1, without shift