

**Atodiresei *et al.* Reply:** In a recent Letter [1] we presented a detailed theoretical investigation on how far, for aromatic molecules adsorbed on the Cu(110) surface, the strength of the van der Waals (vdW) interaction correlates with the electronic structure if such molecules are adsorbed in a *flat* geometry on the surface.

In the Comment [2], Ji *et al.* claim that (i) the flat adsorption geometry used by us for a single pyridine ( $C_5H_5N$ ) molecule adsorbed on the Cu(110) surface is not the ground-state configuration, (ii) for the pyrazine ( $C_4H_4N_2$ ) molecule on Cu(110) a flat adsorption geometry was found by neglecting the nonlocal vdW correlations [3], which has a lower energy than the configuration considered in our study [1], in which the semiempirical van der Waals interaction [4] was employed and (iii) the authors identified a different ground-state adsorption geometry for the chemisorbed benzene on the Cu(110) surface. In the following we will give convincing arguments that these remarks are misleading and do not address the central points of our Letter [1].

As regarding the issue (i), the ground state of a single pyridine molecule adsorbed on the Cu(110) as well as on the Ag(110) surface was analyzed in detail by us in Ref. [5] (not cited in the Comment of Ji *et al.* [2]). In that study we clearly demonstrated that the pyridine molecule adopts a perpendicular adsorption geometry in the ground state in full agreement with the experimental data. In particular, for this perpendicular configuration Ji *et al.* report an adsorption energy and Cu–N bond length that are similar to those already presented in Ref. [5]. Thus, in this respect there is no disagreement between the authors of the Comment and us, but they misleadingly suggest that we are not aware of a perpendicular geometry as the ground state of the pyridine adsorbed on the Cu(110) surface.

Now we turn to (ii): In Ref. [5] we also showed that in the case of a flat adsorption configuration, depending on the specific initial position of the molecule on the surface, after relaxing the geometry *without* the semiempirical vdW corrections, the pyridine molecule either remains parallel to the substrate under consideration, i.e., it remains in a metastable state, or it becomes perpendicularly adsorbed on it in a ground-state geometry [see Fig. 4 in Ref. [5]]. Since an initially flat adsorption configuration of pyridine on Cu(110) can end up in a perpendicular one after a slight rotation of the molecule, a detailed analysis of how the strength of the vdW interaction correlates with the electronic structure of aromatic molecules (i.e., with respect to the nature of the highest occupied and the lowest unoccupied molecular orbitals) is highly desirable. To investigate the role of the van der Waals interaction for such molecules and since the flat adsorption geometry used for the pyridine-Cu(110) system in Refs. [1,5] is not the ground state one, a meaningful comparison between pyridine and pyrazine requires a similar adsorption configuration.

First we note that the structure presented in their Comment and attributed as our configuration is different

from the one presented in our Letter [1] (see Fig. 3). In our Letter the adsorption configuration of pyrazine shows that the N atoms are in a mirror symmetric position between Cu atoms of the surface, while theirs is significantly rotated. Because of their setup used in this Comment, Ji *et al.* fail to reproduce a configuration which they attributed as being ours.

But most importantly, the geometry proposed by Ji *et al.* is also a metastable one and *not* the ground state as they claim in their Comment. Using the same computational setup as in our Letter, our calculations show that in the ground state the pyrazine molecule chemisorbes perpendicular on the Cu(110) surface yielding an adsorption energy of 0.75 eV just like we demonstrated for the pyridine molecule in Ref. [5]. Our results are fully consistent with the experimental results reported for the pyrazine adsorption on the same substrate [6]. Thus, the issue (ii) mentioned by Ji *et al.* is not at all relevant for our analysis reported in the Letter [1] and is the subject of their own comment mentioned at the point (i).

A final note (iii) concerns the claim of the authors that in Ref. [7] they found for the benzene molecule ( $C_6H_6$ ) a different ground-state adsorption geometry than that used in our Letter. However, in Ref. [8] using a computational setup carefully checked, we show that the long-bridge adsorption geometry used also in our Letter is the ground state one in agreement with a previous experimental [9] as well as theoretical [10] work (also not cited by Ji *et al.*).

To conclude, we were and are fully aware of the fact that aromatic molecules like pyridine and pyrazine adsorbed in a flat geometry on the metal surface as discussed in our Letter [1] are not necessarily in the ground-state configuration and showed that in this case the van der Waals interaction plays a crucial role. Therefore, as discussed in depth in this Reply, the issues raised by Ji *et al.* are not to the point of our Letter and mislead the scientific community.

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