Comment on "Chemical versus van der Waals Interaction: The Role of the Heteroatom in the Flat Absorption of Aromatic Molecules C_6H_6, C_5NH_5, and $C_4N_2H_4$ on the Cu(110) Surface"

In a recent Letter [1], Atodiresei *et al.* found that standard density function theory (DFT) suggests chemisorption of benzene (Bz), but physisorption of Pyridine (Py) and Pyrazine (Pz) on Cu(110). However, the inclusion of non-self-consistent van der Waals (vdW) corrections to standard DFT could change the suggested physisorption of Py on Cu(110) to chemisorption, while that of Pz remains physisorbed also with vdW corrections. Based on this change and some supplementary analysis, the authors concluded that vdW corrections are crucial for a reliable study of π-conjugated heterocycle molecules adsorbed on Cu(110). But as a more thorough analysis, presented here, reveals, the structures adopted in the Letter are not in fact the most stable configurations. A different, and more stable adsorption configuration leads to a much shorter molecule-substrate distance (MSD) even within *standard DFT* methods, strongly indicating the chemisorbed nature of Pz adsorbed on Cu(110), and contradicting the primary conclusion in the Letter [1].

Concerning Bz adsorbed on Cu(110), although the structure adopted by the authors [1] is neither the experimentally observed one [2], nor the ground state we found [3], we concur with the authors that it is chemisorbed [1,3]. In terms of Py adsorbed on Cu(110), the "flat adsorption" configuration investigated by the authors has not been reported experimentally [4], where two configurations were found, namely, a perpendicular and a tilted configuration. In both configurations the contact of the molecule and surface is through Cu-N bonds, while in the Letter the semiempirical vdW corrections give rise to the formation of a few Cu-C bonds, which conflicts with the experimental result. We also carried out a calculation with the same method as the authors, i.e., a standard DFT method (VASP) using Perdew-Burke-Ernzerhof exchange-correlation functional, and, based on our experience [5–7], an energy cutoff of 400 eV and a convergence criterion of 0.02 eV/Å for the forces on ions. It shows that the Cu-N bond length is 2.05 Å (0.86 Å shorter than that in the Letter) in a perpendicular configuration which is 0.64 eV more stable than the authors' configuration. The authors' conclusion concerning Py/Cu(110), according to which vdW interactions are essential for the change of physisorption to chemisorption, is thus misleading.

In addition, their assertion that the molecule-substrate interaction weakens as one replaces Bz by Py or Pz [1] seems unfounded, given our previous results on similar molecules [5–7], where we established that interactions are accompanied by a charge transfer from substrate to molecule. The molecule-substrate interaction depends on the energy value of the lowest unoccupied molecular orbital, increasing as the eigenvalue is shifted to a lower level.
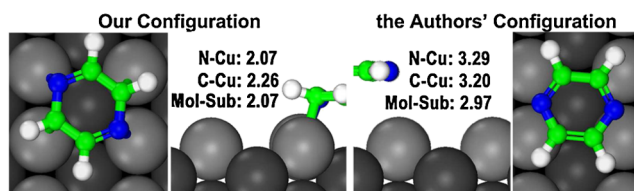

FIG. 1 (color online). Top and half-side views of our (left) and the authors' (right) configurations, together with relaxed N-Cu and C-Cu bond lengths and molecule-substrate distances.

This argument is confirmed by our calculation which show that Pz bonds to Cu(110) much more strongly than Bz. We shall now focus on the adsorption mechanism of Pz on Cu(110), which reveals the largest discrepancy between our results and the results published in this Letter.

Our previous results on similar molecules [3,5–7] suggest, for Pz adsorbed on Cu(110), a more stable flat structure (Fig. 1 left) than the one adopted in the Letter (Fig. 1 right). Reproducing the calculation by the authors we find that the averaged MSD is 2.97 Å, consistent with the authors' value of 2.99 Å. However, in the improved configuration the total energy is 0.34 eV *more stable* than for the authors' configuration, and the MSD is 0.90 Å *shorter*. The N-Cu bond length in this case is 2.07 Å, or 0.19 Å shorter than the adjacent C-Cu bond length. Such a short MSD (bond length) accompanied by a larger adsorption energy suggests that Pz is chemically adsorbed on Cu(110) in its ground state and most likely flat configuration. The authors of the Letter even failed to reach this conclusion after the adsorption energy has been corrected by nonlocal correlation effects or vdW interactions.

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