Comment on "Vibrational Recognition of Hydrogen-Bonded Water Networks on a Metal Surface"

Meng *et al.* [1] report *ab initio* total-energy and molecular-dynamics calculations for $\sqrt{3} \times \sqrt{3}R30°$ adsorption layers of H_2O/Pt(111). Their inference that "theoretical energetics and vibrational dynamics indicate the existence of a well-ordered molecular bilayer on this surface" is unpersuasive for several reasons. One is that the reported bilayer binding energy, 534 meV per H_2O excluding zero-point energy [2], is ~0.2 eV below the theoretical lattice energy of a water molecule in ice-I*h* [3]. Thus, the bilayer is thermodynamically unstable against forming a three-dimensional ice mound. Another is that both He-atom and electron diffraction have shown that the wetting layer on Pt(111) has $\sqrt{39} \times \sqrt{39}R16.1°$ periodicity with 32 water molecules per primitive surface unit cell, not $\sqrt{3} \times \sqrt{3}R30°$ periodicity with two [4,5]. The reason is that the Pt-Pt distance is too large compared to the lattice constant of ice. In the $R16.1°$ superlattice, with ~23% more water molecules per unit area than in a $\sqrt{3} \times \sqrt{3}R30°$ bilayer, this problem is solved.

Figure 1 shows a representative "H-down" [6] $\sqrt{39} \times \sqrt{39}R16.1°$ water adlayer. Note that because of the unit cell's 16.1° rotation, *few O atoms are in atop sites*. Thus, the discussion in Ref. [1] of atop-site bonding is largely beside the point [7]. More important, the adsorption energy of the optimized structure of Fig. 1 is 0.60 eV [8] (using the VASP computer code [9] as in Ref. [1]). Though still ~0.1 eV too small to explain why wetting occurs, this energy is 66 meV larger than the result of Meng *et al.*, implying that the $\sqrt{3} \times \sqrt{3}R30°$ bilayer in Ref. [1] is far from optimal, even among 2D adsorption structures.

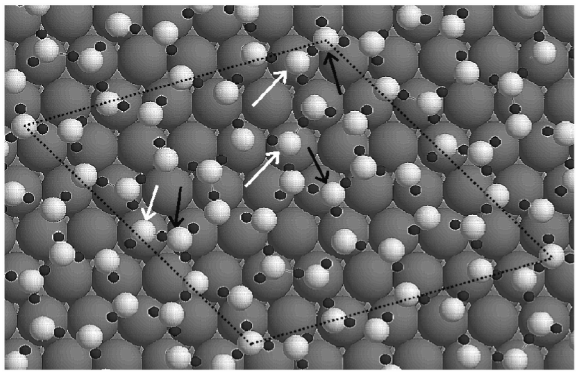

FIG. 1. An "H-down" $\sqrt{39} \times \sqrt{39}R16.1°$ water layer on Pt(111) [6]. Top view, with Pt, O, and H atoms shown as gray, white, and black spheres. Dashed line indicates the surface unit cell. Black and white arrows point to H_3O- and OH-like adspecies formed as this structure was optimized.

To understand why Pt(111) wets, analysis of the $\sqrt{39} \times \sqrt{39}R16.1°$ structure is unavoidable. Of considerable interest are the energetic significances of local proton disorder in the $R16.1°$ water adlayer [10] and of the formation of H_3O- and OH-like surface species. Both are apparent in Fig. 1.

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Peter J. Feibelman*
Sandia National Laboratories
Albuquerque, New Mexico 87185-1413, USA

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*Electronic address: pjfeibe@sandia.gov

[1] S. Meng *et al.*, Phys. Rev. Lett. **89**, 176104 (2002).
[2] Meng *et al.* do not mention zero-point energy. Without including it, I reproduce the energy they report.
[3] P. J. Feibelman, Science **295**, 99 (2002), Table I.
[4] A. Glebov *et al.*, J. Chem. Phys. **106**, 9382 (1997).
[5] S. Haq, J. Harnett, and A. Hodgson, Surf. Sci. **505**, 171 (2002).
[6] "H-down" means that H atoms not participating in H bonds have O atoms above them and Pt's below, as in Ref. [1], Fig. 1(d).
[7] A similar criticism applies to the effort of H. Ogasawara *et al.*, to deduce water-adlayer structure from x-ray spectroscopic measurements [see Phys. Rev. Lett. **89**, 276102 (2002)]. These authors appeal to yet another first-principles optimization of a $\sqrt{3} \times \sqrt{3}R30°$ water layer on Pt(111) adsorption layer data to interpret their spectra.
[8] The optimization was on a three-layer Pt(111) slab with bottom layer Pt atoms fixed at theoretical bulk Pt-Pt separations. Particulars of the calculation were as in Ref. [1], but for a larger plane wave basis cutoff, 400 eV, and a surface Brillouin zone sample consisting of $\overline{\Gamma}$ only.
[9] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993); **49**, 14 251 (1994); G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996); Phys. Rev. B **54**, 11 169 (1996).
[10] The $\sqrt{3} \times \sqrt{3}R30°$ bilayer *must* be perfectly proton ordered because there are only two water molecules in its unit cell.

