

Meng *et al.* Reply: Feibelman [1] argued that the $\sqrt{39} \times \sqrt{39} R16.1^\circ$ (RT39) bilayer of water on Pt(111) [2,3] is energetically more favored than the $\sqrt{3} \times \sqrt{3} R30^\circ$ (RT3) bilayer [4], which was studied in our recent Letter [5]. Indeed, both structures have been observed experimentally. As a matter of fact, another phase, $\sqrt{37} \times \sqrt{37} R25.3^\circ$ (RT37), has also been found [2] before a complete bilayer is formed. The appearance of a different water phase depends on the temperature, pressure, and growth kinetics involved in a given experiment. The RT3 phase has, however, been observed on many metal surfaces [6] including Pt(111). Figure 1 plots the adsorption energies, obtained from our calculations, which show that the RT39 phase, with adsorption energy of 615 meV, is energetically more favorable (by ca. 70 meV) than the RT3 phase, 534 meV, at one-bilayer coverage. The adsorption energy for the RT37 phase, 597 meV, lies in between. As the coverage increases, the RT3 phase becomes more stable. At three bilayers, it is more stable than the RT39 phase. Experimentally, the RT39 structure is also found to transform into RT3 by a structural reorientation [3] at higher coverages.

The RT39 (and RT37) phase was, however, not of our concern in our previous Letter. Instead, the central issue of our work was, as indicated by the title, to study the possibility of *vibrational recognition of the hydrogen-bonded water networks at a surface* by *ab initio* molecular dynamics simulation. We started specifically from the RT3 structure, calculated the vibrational spectra of the RT3 structure, and compared with the electron energy loss spectroscopy and helium atom scattering experiments for the RT3 structure.

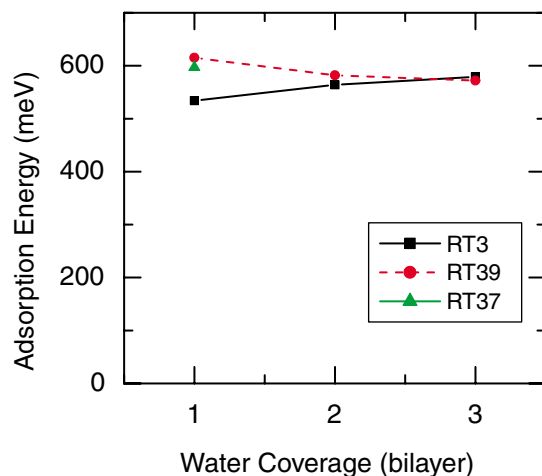


FIG. 1 (color online). The adsorption energy of various bilayer structure on Pt(111) as a function of coverage in bilayers. The square, circle, and triangle correspond to the $\sqrt{3} \times \sqrt{3} R30^\circ$ (RT3), $\sqrt{39} \times \sqrt{39} R16.1^\circ$ (RT39), and $\sqrt{37} \times \sqrt{37} R25.3^\circ$ (RT37) structures, respectively.

Although the RT39 and RT37 structures show slightly larger adsorption energy at one bilayer, it was (and still is) our belief that these two structures bear qualitatively the same physics as the simple RT3 phase. This view is based on the following obvious observations and extensive calculations for all three structures: (i) Water in both RT37 and RT39 bilayers forms the same type of hexagonal hydrogen-bonded 2D lattice, as the RT3 does, although the lattice constant differs slightly in the three cases [the lattice constants (percentage of expansion/compression) are RT3, 4.81 Å (7.2%); RT37, 4.68 Å (4.4%); and RT39, 4.33 Å (-3.3%)]. (ii) As a result, the energy difference between the three phases is small, up to 20–70 meV, and is a small fraction (ca. 10%) of the physical quantities, such as hydrogen bond energy and water adsorption energy, that are of physical interest. (iii) The RT39 phase occurs only under certain conditions, i.e., only in the perfectly ordered 2D bilayer at 130–140 K. In finite domain and islands, the RT3 structure is usually observed. (iv) It is unclear whether the appearance of different adstructures is determined by the small energy difference obtained from zero-temperature density functional calculations, or by other factors involved in the growth kinetics and dynamics at finite temperature and pressure. This question is particularly relevant because the three phases were observed under different experimental conditions. (v) For these reasons, we can hardly agree that the 10% energy difference between RT3 and RT39 at one-bilayer coverage is essential to the understanding of wetting, although this was once again not the subject of our previous Letter.

Sheng Meng,^{1,2} L. F. Xu,¹ E. G. Wang,¹ and Shiwu Gao²

¹Institute of Physics
Chinese Academy of Sciences
P.O. Box 603, Beijing, 100080, China

²Department of Applied Physics
Chalmers University of Technology
and Göteborg University
SE-412 96 Göteborg, Sweden

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