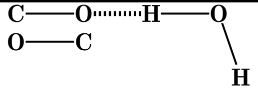
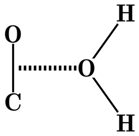
Supporting Information for: Thermal Effects on Electronic Properties of CO/Pt(111) in Water[†]

Sai Duan,[a,b] **Xin Xu,**[c] **Yi Luo,***[a,d] **Kersti Hermansson**[a] **and Zhong-Qun Tian**[b]

1 Optimized structures of water/CO complex

Table S1 Optimized r_{min} of the water/CO complex with different configurations at HF/6-31G* (HF), three-site model (TSM, TIP3P for water) force field, and current force field (SPC for water and Amber99 for CO), respectively. In each configuration, r_{min} represents the distance between the carbon, oxygen, or midbond of CO and the leftmost atom of the water molecule (shown as a dashed bond). The results at the HF and TSM levels are extracted from Ref. 1.

Configuration	HF[a]	TSM[a]	Current
	2.41	2.05	2.38
	2.56	2.15	2.59
	3.29	3.35	3.50

[a] Extracted from Ref. 1.

The optimized structural parameters of water/CO complex at different theoretical levels are listed in Table S1. Here we compared the optimized r_{min}, i.e. the distance between the carbon, oxygen, or midbond of CO and the leftmost atom of the water molecule (shown as a dashed bond in Table S1), at our current used force filed level (SPC for water and Amber99 for CO) with that at *ab initio* (HF, HF/6-31G*) and the widely used three-site model (TSM, TIP3P for water) levels.[1] Although the current level gives a slightly larger r_{min} for the center configuration (see the third row in Table S1), the results of end-on configurations at the current level are almost equivalent of that at the *ab initio* level (see the first and second rows in Table S1). One should notice that the oxygen end-on configuration (the first row in Table S1) plays an important role in the molecular dynamic simulations in the text. Therefore, we can conclude that the current force field can take the interaction between adsorbed CO molecules and solvent water molecules into account reliably for the present simulations.

References

1 J. E. Straub and M. Karplus, *Chem. Phys.*, 1991, **158**, 221–248.

2 Calculated WFs (in eV) of pure Pt(111) surfaces under different CO coverages in vacuum at the DFT level.

θ	0	4	20	52	80	100
WFs	5.85	5.87	5.80	5.73	5.70	5.70