

The interplay between gaseous water and surface hydroxyl on diamond(001) via hydrogen bonding

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Hydrogen bonding plays a pivotal role in water sciences, governing dynamics such as proton transfer,¹⁻³ phase transition,⁴ solvation,⁵ and dissociation.⁶ For example, Kumagai et al.¹ have demonstrated a relay reaction of proton-transfer of a chain of H₂O(OH)_n (n ≤ 4) on Cu(110) via hydrogen bonding by inelastic electrons. For thermal reaction, Huang et al.⁶ reported on the enhanced dissociation of (H₂O)₂ on Si(001) by intermolecular hydrogen bonding; the dissociation barrier of (H₂O)₂ was computed as 73-87 meV as against that of a single H₂O of 273-307 meV. Here, we describe the interplay between a surface hydroxyl on diamond(001) and a gaseous water via hydrogen bonding, as revealed by density functional theory simulations given in parts.

1. Migration of hydroxyl on C(001) catalyzed by water. It is found that surface hydroxyl on diamond(001) is capable of interacting with a gaseous water via hydrogen-bonding, forming a complex, OH(surf)...H₂O(ad), which exhibits enhanced adsorption energies of 0.47 eV. By a series of cooperative motions of this complex and the underlying substrate atoms, the adsorbed water molecule is dissociated; the resulting fragment of hydrogen recombines with the prior OH(surf) to form water, whereas the other fragment of hydroxyl is deposited to the adjacent carbon-dimer site. Effectively, this process represents the water-catalyzed migration of surface hydroxyl on C(001), exhibiting an isotropic barrier of 0.33 eV. These findings are in contrast to anisotropic migration of hydroxyl on diamond(001) in the absence of water; the barriers vary from 1.96 eV along [1 $\bar{1}$ 0] to 2.24 eV along [110].

2. Self-catalyzed dissociation of water on C(001). It has been established that the water physisorbs on C(001), from which there is a competition that strongly favors desorption (adsorption energy computed as 0.24 eV) over dissociation (barrier computed as 0.39 eV). The dissociation products are fragments of hydrogen (H) and hydroxyl (OH) at a surface dimer of C(001), at which the dynamics of a new incoming water molecule is altered. We find that this new incoming water is molecularly adsorbed over the surface hydroxyl via hydrogen bonding, leading to an enhanced adsorption energy of 0.52 eV. Subsequent dissociation proceeds in two steps, in which the adsorbed water first overcomes a barrier of 0.25 eV to a metastable state, and thereafter dissociates to form surface hydroxyl and hydrogen atoms at the neighboring dimer site (dissociation barrier computed as 0.39 eV). It follows that the dissociation of water proceeds in a self-catalyzed fashion, in which one product fragment (surface hydroxyl) enhances the dissociation significantly.

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- (1) Kumagai, T.; Shiotari, A.; Okuyama, H.; Hatta, S.; Aruga, T.; Hamada, I.; Frederiksen, T.; Ueba, H. *Nat Mater* **2011**, *11* (2), 167-172.
- (2) Lu, D.; Voth, G. A. *Journal of the American Chemical Society* **1998**, *120* (16), 4006-4014.
- (3) Marx, D.; Tuckerman, M. E.; Hutter, J.; Parrinello, M. *Nature* **1999**, *397* (6720), 601-604.
- (4) Ma, R.; Cao, D.; Zhu, C.; Tian, Y.; Peng, J.; Guo, J.; Chen, J.; Li, X.-Z.; Francisco, J. S.; Zeng, X. C.; et al. *Nature* **2020**, *577* (7788), 60-63.
- (5) Decornez, H.; Drukker, K.; Hammes-Schiffer, S. *The Journal of Physical Chemistry A* **1999**, *103* (15), 2891-2898.
- (6) Huang, X.; Tian, R.-Y.; Yang, X.-B.; Zhao, Y.-J. *The Journal of Physical Chemistry C* **2014**, *118* (42), 24603-24610.