**Physical-Chemistry Seminar**

## Sunday 4/August/2024 Time:12:30PM

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Interaction of water on diamond(001) by density functional theory

Master seminar

Online Seminar https://technion.zoom.us/my/dgklab

**Interaction of water on diamond(001) by density functional theory**

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Abstract

The interaction between water and diamond surfaces holds significant importance1-3 in the fields of tribology, electrochemistry, and materials science. For example, the sign of electron affinity of hydrogenated diamond surfaces were found to be altered by the surface dipole arising from the adsorption of water.4 There has been numerous studies on this topic from the perspectives of both experiment5 and theory6.

In early work7, Hoffman and co-workers used X-ray photoelectron spectroscopy and high resolution electron energy loss spectroscopy to study the adsorption of water on bare diamond surfaces at room temperature. It was found that dissociative adsorption (chemisorption) occurred readily, forming hydroxyl (OH) and hydrogen (H) atoms on the surface. Upon annealing to 300, dissociative adsorption (chemisorption) occurred on the bare diamond surface. Recently, the dissociative adsorption of water on diamond surfaces were studied by the Righi group8, using density functional theory (DFT). By considering a single water molecule on the perfect diamond(001), the adsorption is found to proceed via a precursor-mediated pathway; that is, water first physisorbs as an almost intact molecule (heat of adsorption: 0.22 eV), from which dissociation thereafter occurs at a barrier of 0.38 eV. Consequently, there is a competition between desorption and dissociation, amongst which the latter is *not* favored. The seemingly discrepancy between experiment and theory calls for further investigation into the system of water on diamond.

Here, I present DFT work on the interaction of water on diamond(001) surfaces that goes beyond the scope of the work by the Righi group. In my work, the diamond(001) surface deviates from the perfect scenario, by considering pre-adsorbed species (e.g., hydroxyl and/or hydrogen) and surface dimer vacancy defects. Our findings are presented as below.

1. *Migration of hydroxyl on C(001) catalyzed by water.* We find that surface hydroxyl on C(001) is capable of interacting with water via hydrogen-bonding, forming a complex, OH(surf)…H2O(ad), that 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 C(001) in the absence of water; the barriers vary from 1.92 eV along [10] to 2.24 eV along [110].
2. *Effect of surface fragments (OH + H) on the adsorption and dissociation of water on C(001).* It has now been well established that water dissociates on C(001), leading to the formation of fragments of hydroxyl and hydrogen on the surface. Here, we study how these surface fragment affects the adsorption and dissociation of another incoming water molecule. We find that the dynamics again follows the precursor-mediated pathway, in which water is firstly molecularly adsorbed and thereafter dissociates to form surface hydroxyl and hydrogen atoms. Modification of energetics is evident in the heats of molecular adsorption of 0.36-0.52 eV, and dissociation barrier of 0.37-0.75 eV.
3. *Effect of pre-adsorbed hydrogen on the adsorption and dissociation of water on C(001).* Surface hydrogens are unavoidable on diamond synthesized by chemical vapor deposition. At the surface site of pre-adsorbed hydrogen on C(001), our simulations show that water dissociation follows a precursor-mediated pathway, where water is initially adsorbed in molecular form and then dissociates to form surface hydroxyl and hydrogen atoms. This process involves modifications in energetics, with molecular adsorption energies of 0.31 eV and a dissociation barrier of 0.52 eV.
4. *Effect of surface dimer vacancy on the adsorption and dissociation of water on C(001).* Dimer vacancies are the most common defects on C(001). Here, we study how surface dimer vacancy affects the adsorption and dissociation of water molecule. The dissociation of water on the surface also follows the precursor-mediated pathway, beginning with molecular adsorption and leading to the formation of surface hydroxyl and hydrogen atoms. The energetics are characterized by molecular adsorption energies of 0.22 eV and a dissociation barrier of 0.92 eV.

Reference

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