Role of proton ordering in adsorption preference of water molecule on ice surface

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I. Introduction

Adsorption of polar monomers on ice surface, relevant to the physical/chemical reaction in ice clouds as well as growth of ice, remains an open issue partially due to the unusual surface characteristics with protons at the top layer of ice. Using first-principle calculations, we explore the adsorption properties of ice surface in terms of a surface proton order parameter, which characterizes the inhomogeneity of the dangling atoms on ice surface. Our findings suggest that the physical/chemical reactions as well as growth of ice may prefer to occur firstly at surfaces with larger proton order parameter [1].

II. Methods

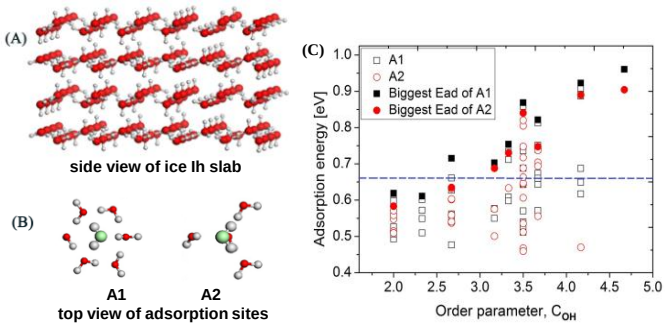
Density function theory

- VASP, CP2K/Quickstep
- PAW, PBE
- Maximally localized Wannier function centers

Molecular dynamics simulations

- LAMMPS
- TIP4P/Ice empirical potential
- NVT-ensemble

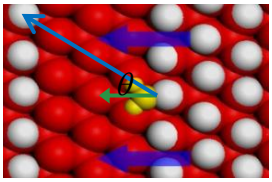
III. Adsorption energy



The larger the order parameter [2] (the more inhomogeneous the ice surface) is, the higher the adsorption energy. There exists a large variation in the adsorption energy for a fixed order parameter, among which the largest adsorption energy is lower than the bulk cohesive energy (dashed line) for C_{OH}<2.5 but higher than the bulk cohesive energy for C_{OH}>2.5 (see C).

IV. Effective electric field

Dangling atoms of ice surface acting like an electric field affects the adsorption of polar water molecule. Here we define an effective electric field to qualify the effect of dangling atoms of ice surface.



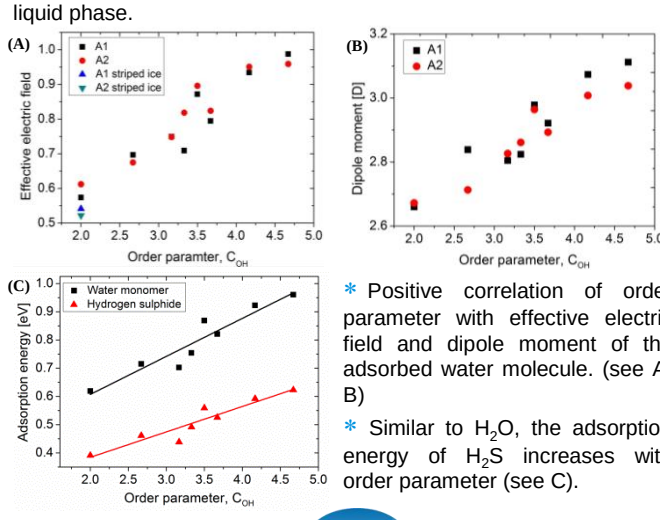
$$E_{eff} = \frac{q}{4\pi\varepsilon_0}\sum_i^{N_{OH}} \frac{-1}{r_i^2}\Theta(r_i)\cos\theta$$

$\hat{r}$ dipole electric field

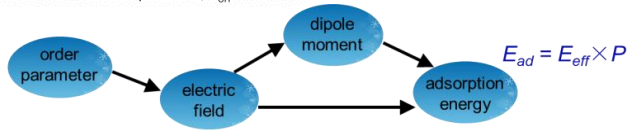
where q=0.21e is the effective charge of dangling atoms [2], r is the distance from the oxygen atom of the adsorbed water molecule to the dangling proton or oxygen atom on ice surface, θ is the angle between $\hat{r}$ and the direction of the dipole of adsorbed molecule, and d_H is the distance from oxygen atom of the adsorbed molecule, $\Theta(r_i)$=1 within d_H, while $\Theta(r_i)$=0 outside d_H.

V. Relation of order parameter and adsorption property

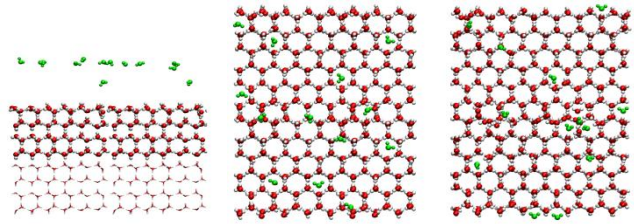
The dipole moment (P) of water molecules varies under different polarization conditions, e.g., P~1.855D in gas phase and ~3.1D in liquid phase.



* Positive correlation of order parameter with effective electric field and dipole moment of the adsorbed water molecule. (see A, B)
* Similar to H_2O, the adsorption energy of H_2S increases with order parameter (see C).



VI. Dynamics process of water molecules adsorption



(A) side view of initial state (B) top view of initial state (C) after 2ns equilibration

* Water molecules randomly distributional are dropped at a distance to ice surface of 6~9Å. After 2ns (2×10^6 timestep) equilibration under 50K, water molecules are trapped to sites with large local electric field on ice surface.

VII. Conclusions

* Larger order parameter leads to larger adsorption energy.
* Order parameter affects on adsorption energy through effective electric field and dipole.
* Results of H_2S and MD simulation shows that the physical/chemical reactions and the initial growth of ice prefer to occur on the ice surface with higher inhomogeneity (larger order parameter).

[1] Zhaoru Sun, Ding Pan, Limei Xu, Enge Wang, Proc. Nat. Acad. Sci. (online).
[2] Ding Pan, Li-Min Liu, Gareth A. Tribello, Ben Slater, Angelos Michaelides, Enge Wang, Phys. Rev. Lett. 101, 155703 (2008).

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