

## The role of hydrogen bonding in water-metal interactions

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### I. SUPPLEMENTARY INFORMATION: ELECTROSTATIC INTERACTION BETWEEN A WATER MOLECULE AND AN IDEAL METAL SURFACE

In this section we study the role of electrostatic interaction between a single water molecule and an ideal metal surface. Our aim is to understand how the water molecule orients itself under the constraint of electrostatic interaction energy due to an infinite metal surface<sup>1</sup>. We calculate the electrostatic interaction energy of the water molecule on top of an infinite metal surface. We employ method of images of point charges<sup>2</sup> to calculate the electrostatic interaction energy as a function of different orientations of the molecule. For a set of three charges we use a round up number, based on the water molecule Mulliken atomic charges obtained with siesta (O=-1C,H=0.5C,H=0.5C). We define the initial position of the molecule to lie in Y-Z plane with Hydrogen atoms facing up away from the image plane. We define  $\theta = 0$  for the initial position see Fig. I, this would be the so called vertical configuration in the main article.  $\theta = \pi/2$  is the horizontal position of the water molecule parallel to the metal surface (called flat in the main manuscript). We rotate the water molecule about the Y-axis fixed at the center of charge of the water molecule. The center of charge coordinate  $X_{CC}$  is defined as  $\vec{X}_{CC} = \sum q_i \vec{x}_{q_i} / \sum q_i$ . The center of charge corresponds to the center of the point dipole obtained from any given charge distribution. This can be easily realized by the action of a rotation matrix about Y-axis followed by translation along Z-axis. We fix the center of charge to be at height  $z$  above the metal surface.

$$\begin{pmatrix} x_o \\ y_o \\ z_o \end{pmatrix} = \begin{pmatrix} -\frac{r}{2} \cos \frac{\alpha}{2} \sin \theta \\ 0 \\ z - \frac{r}{2} \cos \frac{\alpha}{2} \cos \theta \end{pmatrix} \quad (1)$$

We can similarly obtain the most general coordinates of the hydrogen atoms

$$\begin{pmatrix} x_{h1} \\ y_{h1} \\ z_{h1} \end{pmatrix} = \begin{pmatrix} \frac{r}{2} \cos \frac{\alpha}{2} \sin \theta \\ r \sin \frac{\alpha}{2} \\ z + \frac{r}{2} \cos \frac{\alpha}{2} \cos \theta \end{pmatrix} \quad (2)$$

$$\begin{pmatrix} x_{h2} \\ y_{h2} \\ z_{h2} \end{pmatrix} = \begin{pmatrix} \frac{r}{2} \cos \frac{\alpha}{2} \sin \theta \\ -r \sin \frac{\alpha}{2} \\ z + \frac{r}{2} \cos \frac{\alpha}{2} \cos \theta \end{pmatrix} \quad (3)$$

The coordinates of the image of charges can be easily obtained by the reflection of  $z$  coordinate through the x-y plane.

$$(x_{i_o}, y_{i_o}, z_{i_o}) = \left(-\frac{r}{2} \cos \frac{\alpha}{2} \sin \theta, 0, -z + \frac{r}{2} \cos \frac{\alpha}{2} \cos \theta\right)$$

$$(x_{i_{h1}}, y_{i_{h1}}, z_{i_{h1}}) = \left(\frac{r}{2} \cos \frac{\alpha}{2} \sin \theta, r \sin \frac{\alpha}{2}, -z - \frac{r}{2} \cos \frac{\alpha}{2} \cos \theta\right)$$

$$(x_{i_{h2}}, y_{i_{h2}}, z_{i_{h2}}) = \left(\frac{r}{2} \cos \frac{\alpha}{2} \sin \theta, -r \sin \frac{\alpha}{2}, -z - \frac{r}{2} \cos \frac{\alpha}{2} \cos \theta\right)$$

In the coordinates described in Fig. I  $\alpha$  is the angle between the two arms of the water molecule and is a known constant ( $\alpha = 105^\circ$ ).  $\theta$  is the angle made by the plane containing the water molecule with the vertical. "z" is the distance between the metal surface and the center of charge of the water molecule. X-Y plane is the reflecting metal surface about which we perform method of images.

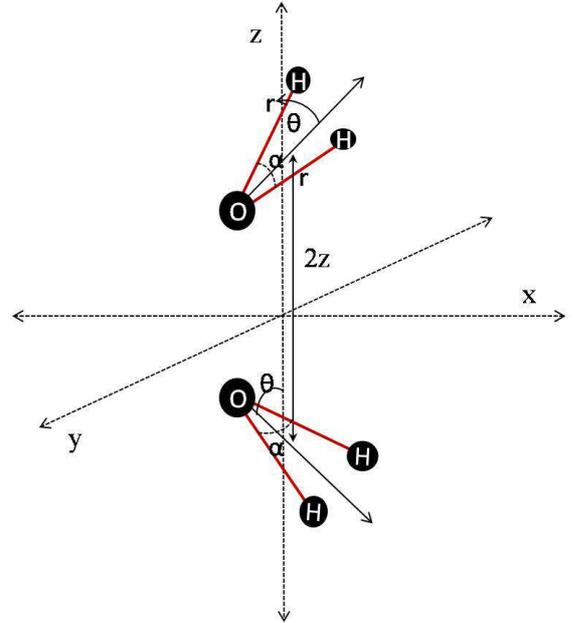


FIG. 1. Schematics showing water molecule and its image where rotation of the molecule is described about center of charge. The molecule is rotated about Y-axis fixed across its center of charge.  $\theta$  is the angle of rotation as a function of which we calculate the total electrostatic energy of the system.

The total electrostatic energy of the system (metal + monomer) can be written as

$$U_{electrostatic} = U_{rr} + U_{ir} \quad (4)$$

where  $U_{rr}$  is the interaction energy of the real charges and  $U_{ir}$  is the interaction energy of the real and image charges.

$$U_{rr} = \frac{1}{4\pi\epsilon_0} \sum_{i=1}^3 \sum_{j \neq i=1}^3 \frac{q_i q_j}{\sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}}$$

$$U_{ir}(\theta) = \frac{1}{4\pi\epsilon_0} \sum_{i=1}^3 \sum_{j=1}^3 \frac{q_i q_j^{image}}{\sqrt{(x_i - x_{i_j})^2 + (y_i - y_{i_j})^2 + (z_i - z_{i_j})^2}}$$

$U_{rr}$  is the electrostatic self energy of the molecule and is independent of the orientation of the molecule so the equilibrium configuration only depends on the interaction of the water molecule with its image. To obtain the most favorable configuration of the water molecule due to electrostatic interactions we minimize  $U_{ir}(\theta)$  with respect to the orientation angle  $\theta$ . We plot the electrostatic potential energy landscape of  $U_{ir}(\theta)$  for four distances  $z$  from the metal surface as a function of  $\theta$ .

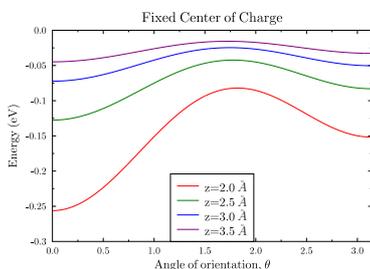


FIG. 2.  $U_{ir}(\theta)$  vs  $\theta$  for four distances from the metal surface. For all the distances we see that the vertical configurations are more stable than the parallel configuration.

On the basis of total electrostatic interaction energy landscape for the water molecule as a function of orientation angle  $\theta$  we make the following observations.

- The absolute minimum energy configuration of the water molecule is when  $\theta = 0$  with respect to the vertical, when the molecule about the center of charge and  $\theta = \pi$  when the molecule is rotated about a fixed oxygen atom (for smaller distances).
- $\theta = 0$  or the vertical configuration with Hydrogen atoms pointing up is more favored than the  $\theta = \frac{\pi}{2}$  parallel configuration in both the cases.
- We see a clear asymmetry in the  $\theta = 0$  and the  $\theta = \pi$  configurations for distances  $z = 2 - 2.5 \text{ \AA}$  which will not be seen if an extended dipole approximation of the water molecule is used to model the system.
- With increasing distance from the metal surface the water molecule can be approximated as a point

dipole for which all the orientations will have almost same energy value.

### A. Validity of Dipole approximation.

Based on the above observations we emphasize the fact that a permanent dipole approximation does not distinguish between the cases where the hydrogen atoms point up or down. This picture yields the same energy for both the configurations due to the symmetry in dipole. On the other hand, accounting for the full charge density distribution of the water molecule clearly distinguishes between the configuration where hydrogen atoms are pointing up or pointing down. Also the permanent dipole approximation of the water molecule is only valid for the case when the water molecule is sufficiently far away from the metal surface in comparison to the O-H bond length. The distance at which the water molecules are adsorbed on the metal surface is roughly  $2.5 \text{ \AA}$ . Which is not much greater than the water molecule bond lengths (of the order of  $1 \text{ \AA}$ ). The more realistic approach is to do a full electrostatic interactions of the water molecule.

### B. Electrostatic energy for full charge density for water molecule.

Motivated by our previous calculations it will be worth calculating the metal-water molecule interaction energy using the full charge density function of water molecule. Our electronic charge distribution is obtained using the Kohn-Sham eigenstates of an isolated water molecule obtained from a previous DFT calculation using the SIESTA<sup>3</sup> code. These Kohn-Sham wave functions are linear combinations of atomic orbitals, we used a single- $\zeta$  polarized basis set. We obtain the linear combination coefficients from self-consistent DFT calculation and use them to compute the Kohn-Sham wave functions of the water molecule and with them the analytical charge density distribution function. The charge density distribution depends the orientation angle  $\theta$ . For the core and the nuclear charge we use highly localized Gaussian functions centered at the coordinate position of the atoms. These coordinates are defined in the same way as for the point charges which allow for the  $\theta$  rotation about the Y-axis. We define the charge density in the following way

$$\rho(\vec{r}, R_i(z, \theta)) = q \left| \sum_{i \in \text{atom}} \sum_{n=1}^4 C_{nlm} Y_{lm}(\widehat{\vec{r} - \vec{R}_i}) R(|\vec{r} - \vec{R}_i|) \right|^2 \quad (5)$$

$Y_{lm}$  is the spherical harmonics and  $R(|\vec{r} - \vec{R}_i|)$  is the radial function, which in our case is a set of truncated gaussian functions we fitted to match the original, confined, SIESTA radial functions. The vector  $\vec{R}_i$  gives the most general position for each atom as given in the equation 1, 2, and 3.  $q$  is the total charge in each eigenstate of the basis.  $C_{nlm}$  is the linear combination coefficients obtained from the SIESTA calculation. We can also write

the core charge distribution using a localized gaussian function

$$\rho_{core}(\vec{r}, R_i(z, \theta)) = \sum_{i \in atom} q_i |e^{-\kappa(|\vec{r} - \vec{R}_i|^2)}|^2 \quad (6)$$

where  $\kappa = \frac{1}{R_c^2}$ .  $R_c$  is the radius of the core ( $R_c = 0.61 \text{ \AA}$  for oxygen and  $R_c = 0.21 \text{ \AA}$  for hydrogen). Since we have chosen localized atomic orbitals as the basis set for the full wave function, we can rigid rotate the full charge distribution by rotating the water molecule as described for the point charge case. The atomic orbitals rotate with its atomic center. Hence we can calculate the electrostatic energy between the full charge distribution of the water molecule and the full image charge distribution as a function of orientation angle  $\theta$  and  $z$  (distance of the center of charge from the image plane). We define the full charge distribution of the water molecule and its image in the following way

$$\rho_{total}(\vec{r}, R_i(z, \theta)) = \rho_{core}(\vec{r}, R_i(z, \theta)) + \rho(\vec{r}, R_i(z, \theta)) \quad (7)$$

$$\rho_{image}(\vec{r}, R_i(z, \theta)) = \rho_{total}(\vec{r}, R_i(-z, \pi - \theta)) \quad (8)$$

Once we establish a charge distribution as a function of atomic positions we can easily rotate the water molecule about the Y-axis fixed at the center of charge and calculate the electrostatic interaction energy<sup>2</sup> with the image charge distribution as a function of orientation angle  $\theta$ .

$$U_{ir}(z, \theta) = \frac{-1}{8\pi\epsilon_0} \iint \frac{\rho_{total}(\vec{r}, R_i(z, \theta))\rho_{image}(\vec{r}', R_i(z, \theta))}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' \quad (9)$$

We plot the electrostatic energy for full charge distribution and its image as a function of  $\theta$  (see Fig. 1B) for  $z = 3.12 \text{ \AA}$ . We compare it to the plot for the three point charge model. According to the plot we observe that  $\theta = 0$  (vertical) is the most stable configuration. We also observe that electrostatic energy for the full charge distribution increases compared to three point charge model. It is very interesting to notice how the energy dependence of the full charge distribution is much more complex than the simple dipole or 3 point charges model. In particular, we can see that there is an inflection point at  $\theta = \frac{\pi}{4}$ , which coincides with the angular direction of the O lone pairs.

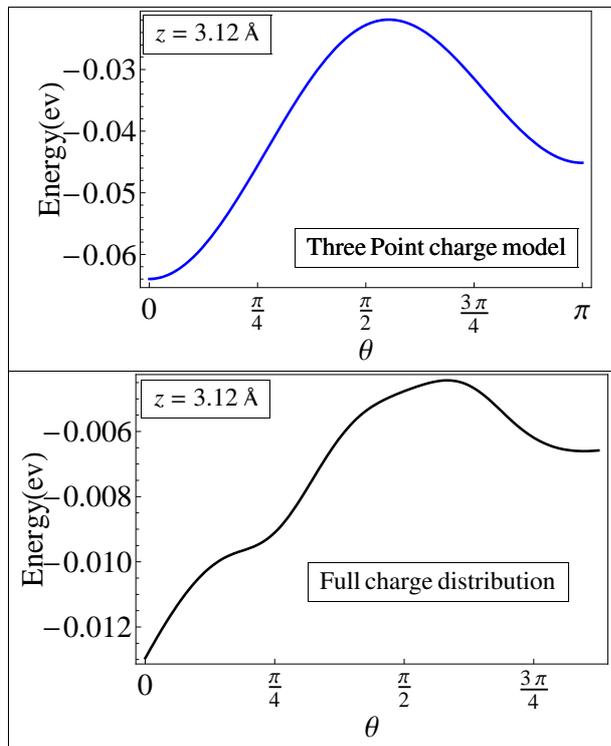


FIG. 3.  $U_{ir}(\theta)$  vs  $\theta$  for  $3.12 \text{ \AA}$  from the metal surface 1) For three point charge model. 2) For full charge distribution of water molecule.

In conclusion, we were able to calculate the electrostatic energy between the water molecule with metal for three point charge model, and full charge distribution calculated from SIESTA. We were able to identify vertical alignment (with hydrogen atoms facing up) as the most stable configuration of the water molecule under the constraint of electrostatic interactions with the metal surface. We also have shown that the full charge distribution provides a much more complex interaction energy landscape, where the lone pairs of the oxygen contribute to minimize the interaction energy for an intermediate alignment.

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