Electronic Supplementary Information (ESI)

Low-dimensional HfS$_2$ as SO$_2$ adsorbent and gas sensor: Effect of water and sulfur vacancies

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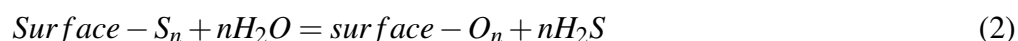
Analysis of water influence on 1T-HfS$_2$ monolayer

To simulate the effect of water, we consider that H$_2$O can depose oxygen atoms on the unsaturated hafnium atoms and modify the surface state according to the following equation[1,2]:

$$surface + nH_2O = surface - H_{2n}O_n \tag{1}$$
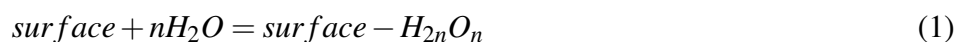
Sulfur/oxygen exchanges can take place on the stable reference surface

$$Surface - S_n + nH_2O = surface - O_n + nH_2S \tag{2}$$

Taking water as the oxygen source, successive exchanges were studied. Gibbs free energy of Reaction (1), for example, was computed according to:

$$\Delta_r G = \mu(Surface - O_n) - \mu(Surface - S_n) + n\mu(H_2S) - n\mu(H_2O) \tag{3}$$

Assuming that the difference between the chemical potential of solid phases can be approximated by the difference in their electronic energy[1,2]:.

$$\Delta_r G = \Delta_r G^0 + nRT\,ln10\,log\frac{(P(H_2S)}{P(H_2O))} \tag{4}$$

Here $\Delta_r G^0$ being equals to $\Delta E_n + \Delta\mu^0(T)$[3,4]. ($\Delta\mu^0(T)$) includes the effect of temperature by accounting for the vibrational contribution of the system in the following equation :

$$\Delta\mu^0(T) = \Delta ZPE + \Delta H_{vib} + \Delta H_{rot} + \Delta H_{tr} - T(\Delta S_{vib} + \Delta S_{rot} + \Delta S_{tr})$$
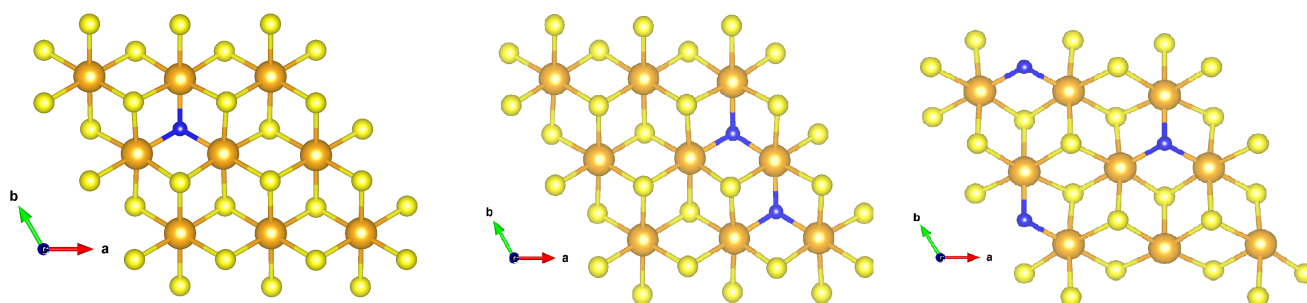
and ΔE_n being the electronic energy contribution to the S/O exchange reaction defined as $\Delta E_n = E(Surface - O_n) - E(Surface - S_n) + nE(H_2O) + nH_2S$
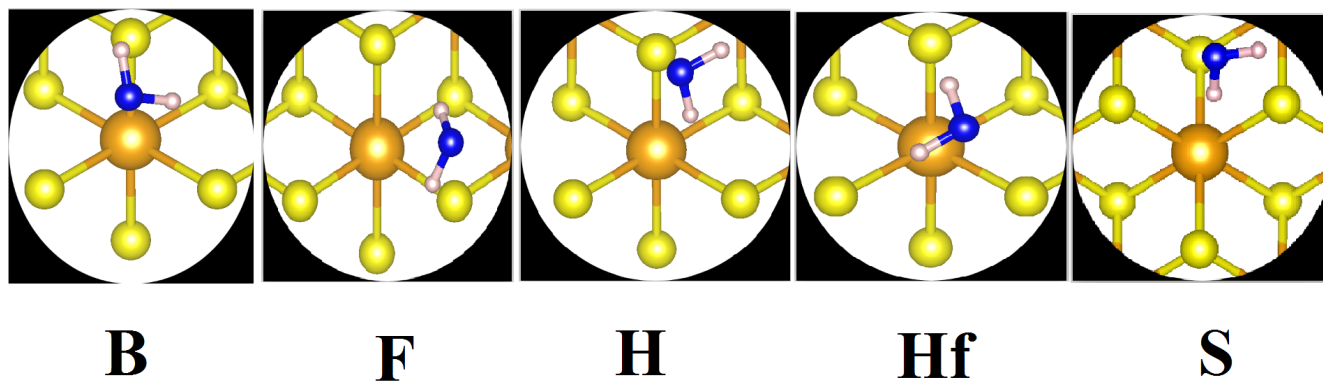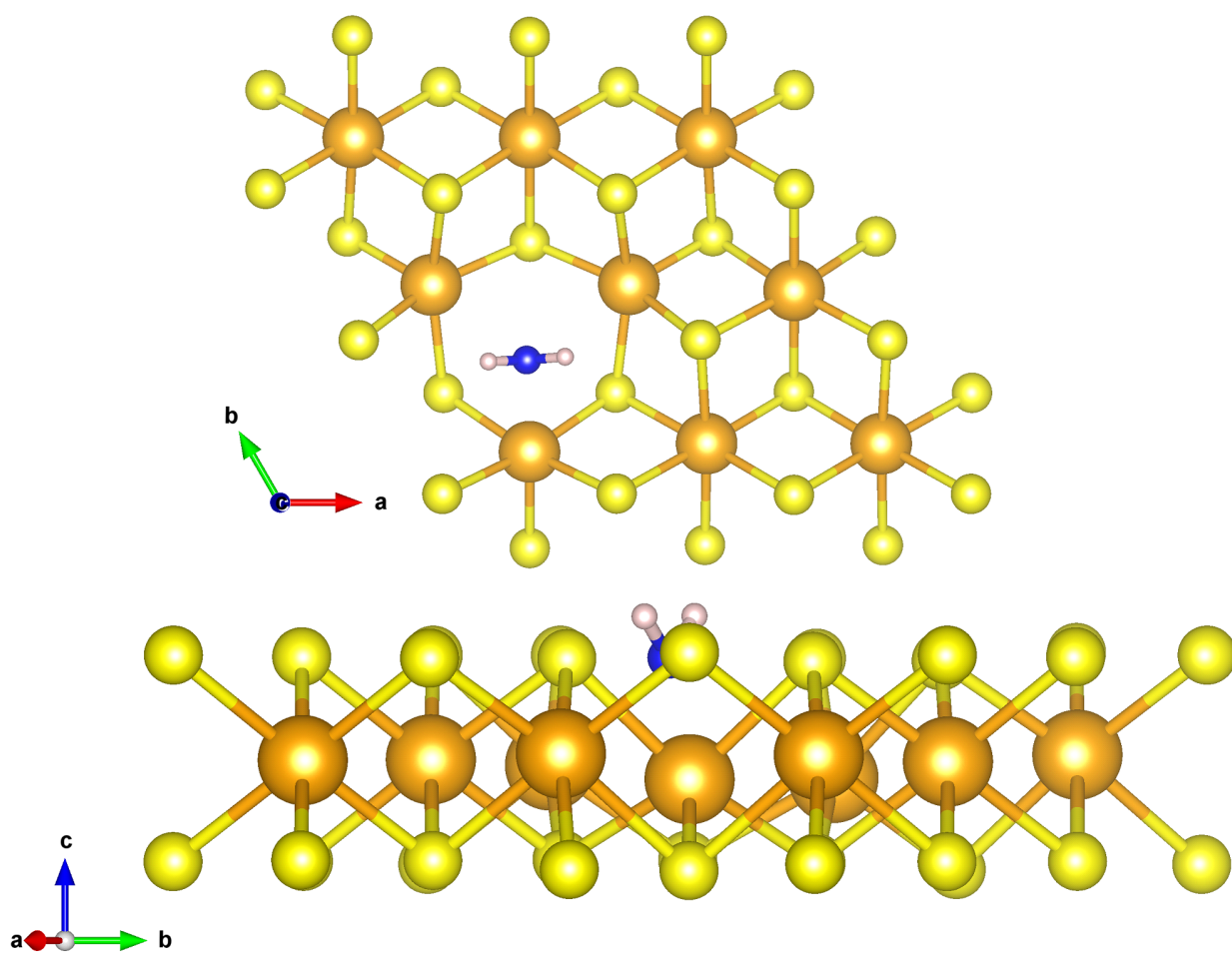
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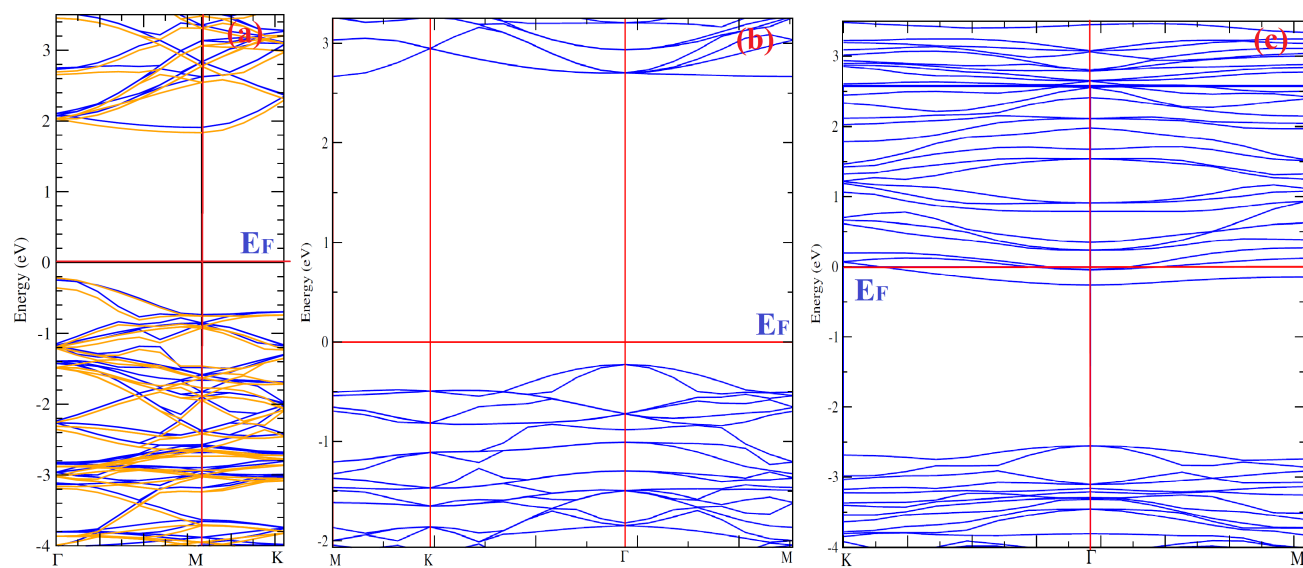
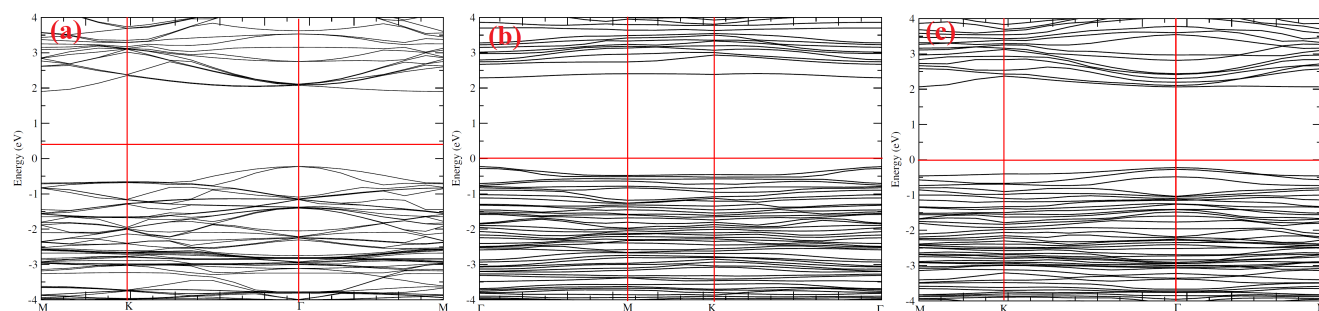| S site	H site	B site	Hf site	F site
-12.6	-16.4	-17.4	-20.3	-16.4

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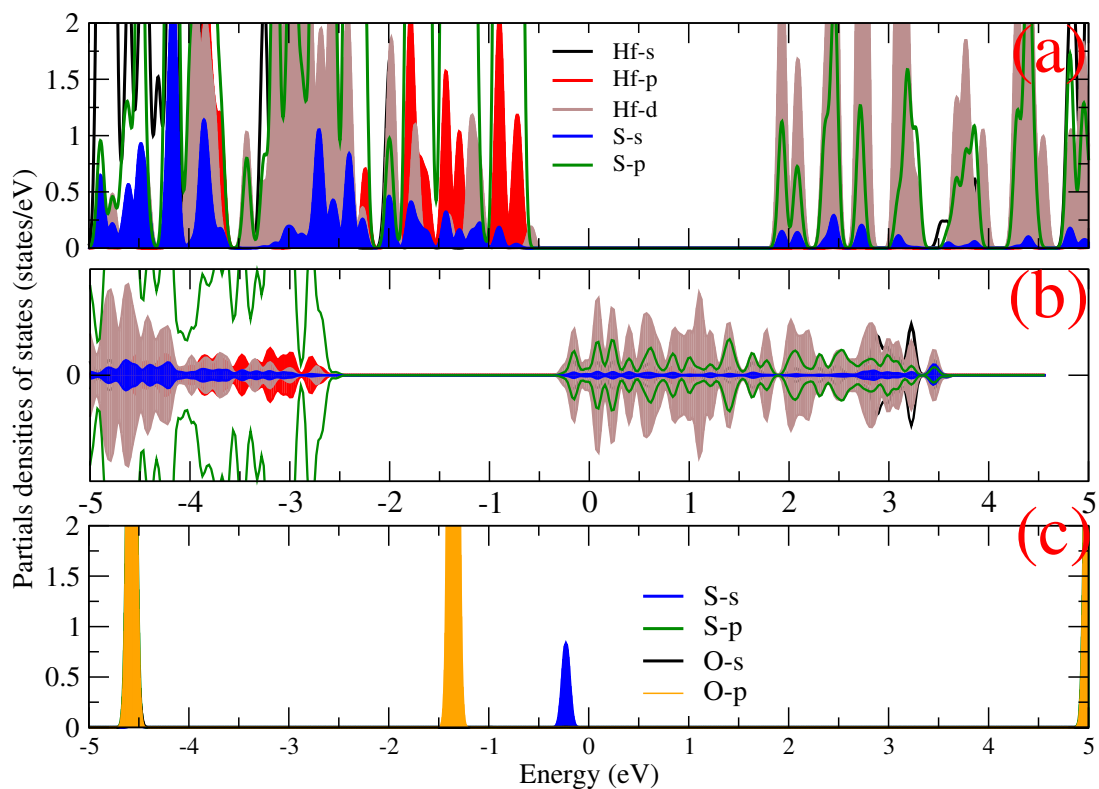
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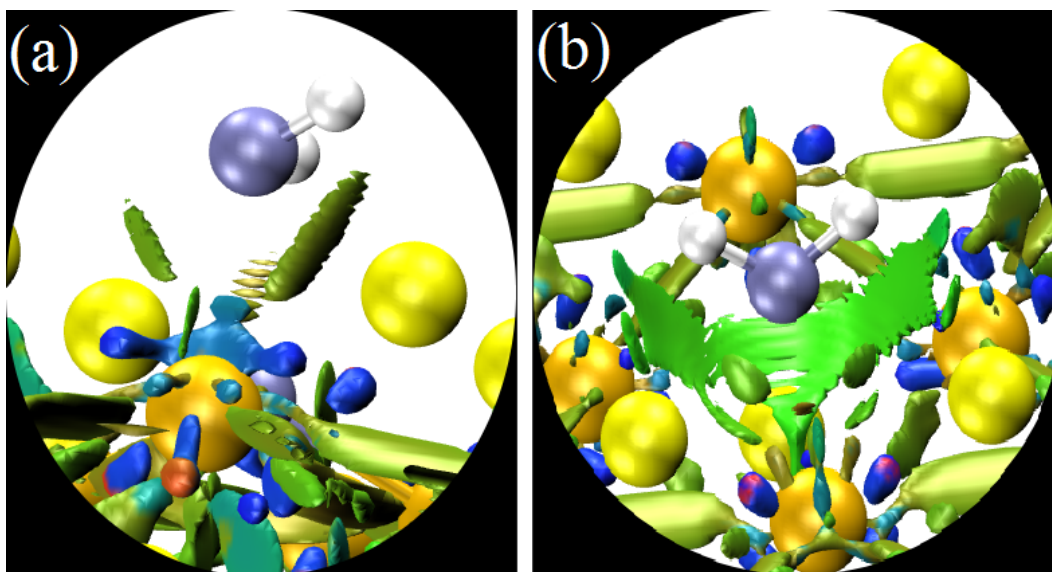
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