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Supporting Information

Understanding divergent behaviors in the photocatalytic hydrogen evolution reaction on CdS and ZnS: A DFT based study

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Table S1. Length of *M*-S bonds (*M* = Cd or Zn) closest to the adsorption site of various geometries: $L_{M\text{-S-}//}$ (in Å) within the topmost layer and $L_{M\text{-S-}\perp}$ (in Å) between the topmost layer and sublayer. For the definition of *M*-S bonds and various adsorption geometries, please refer to Figure 1. Values in parentheses are derived with the 2×2 slab.

		H*(*M*)	H*(S)	HO*(*M*)	HO*(S)	O*(*M*)	O*(S)	H*(*M*) /HO*(S)	H*(S) /HO*(*M*)
CdS	$L_{M\text{-S-}//}$	2.54 (2.55)	2.63 (2.63)	2.56 (2.57)	2.56 (2.50)	2.63 (2.61)	2.57 (2.56)	2.69 (2.85)	2.68 (2.84)
	$L_{M\text{-S-}\perp}$	2.54 (2.55)	3.73 (2.73)	2.64 (2.64)	3.06 (2.61)	2.48 (2.46)	2.61 (2.61)	2.58 (2.62) 2.59 (2.65)	2.56 (2.61) 2.57 (2.64)
ZnS	$L_{M\text{-S-}//}$	2.30 (2.32)	2.38 (2.38)	2.34 (2.38)	2.27 (2.28)	2.40 (2.40)	2.33 (2.33)	2.42 (2.58)	2.45 (2.65)
	$L_{M\text{-S-}\perp}$	2.36 (2.34)	3.24 (3.91)	2.43 (2.40)	2.38 (2.36)	2.29 (2.28)	2.37 (2.38)	2.36 (2.38) 2.38 (2.41)	2.37 (2.39) 2.37 (2.40)

Table S2. Adsorption energy (ΔE), bond length (L) and magnetic moment (μ) for adsorption geometries with H* species on pure and Pt loaded CdS and ZnS (110). For the definition of adsorption sites on the Pt load CdS and ZnS (110), please refer to Figure 4(a) and S3(a).

		H*(*M*)	H*(S)	H*(*M*-1)	H*(Pt)	H*(S-1)	H*(S-2)	H*(S-3)	H*(S-4)
CdS	ΔE (eV)	1.97	0.98	0.72	0.07	0.87	0.24	0.68	0.29
	L (Å)	1.82	1.35	1.72	1.58	1.36	1.36	1.35	1.35
	μ (μB)	2	0	2	0	0	0	0	0
ZnS	ΔE (eV)	1.87	1.64	1.05	0.08	1.64	1.11	1.95	0.88
	L (Å)	1.66	1.36	1.56	1.58	1.38	1.37	1.39	1.35
	μ (μB)	2	1.5	2	2	0.6	1.4	0.3	2

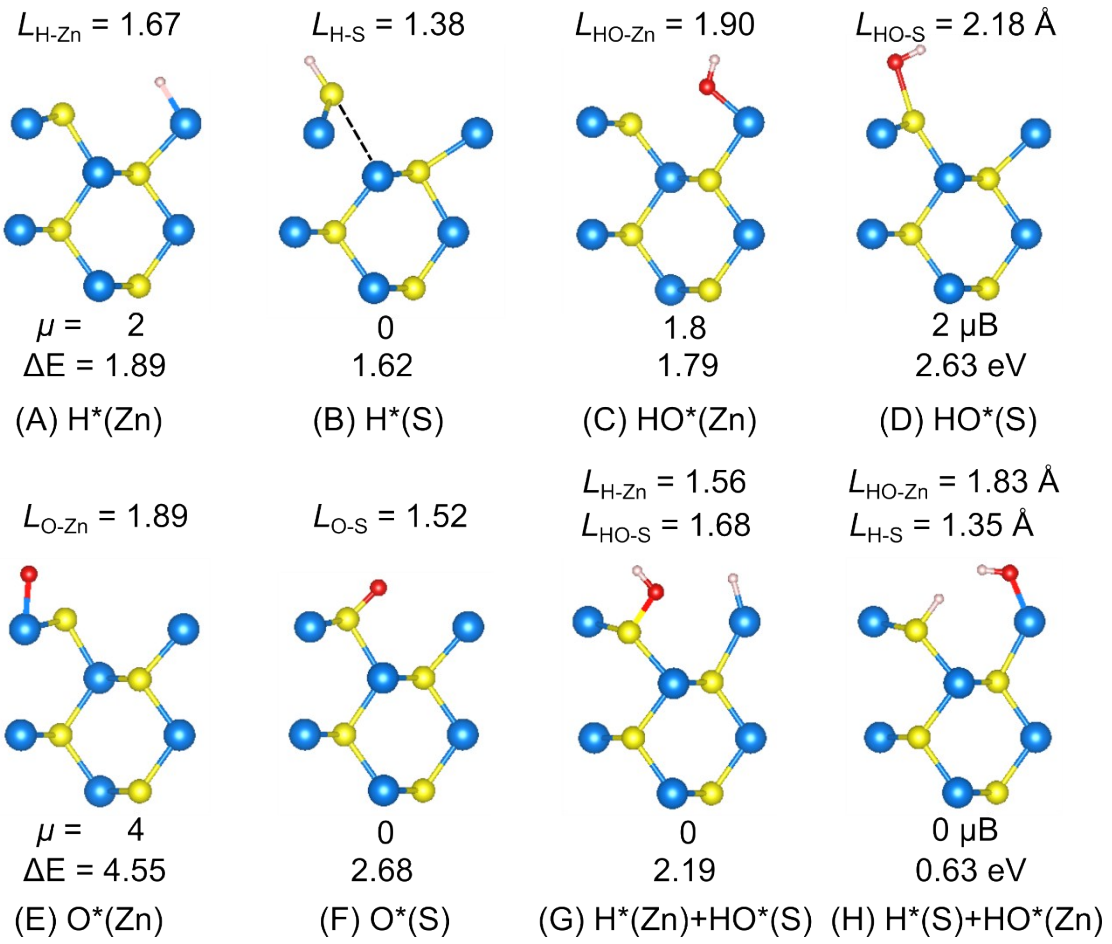

Figure S1. Optimized adsorption geometries for the ZnS (110) with the 1×1 slab: (A) H*(Zn), (B) H*(S), (C) HO*(Zn), (D) HO*(S), (E) O*(Zn), (F) O*(S), (G) H*(Zn)/HO*(S) and (H) H*(S)/HO*(Zn). The bond length (L) of adsorbates with the (110), as well as the total magnetic moment (μ) and the adsorption energy (ΔE), was presented for each geometry. Zn, S, O and H atoms were depicted in blue, yellow, red and white, respectively. Broken Zn-S bonds of which the length exceeded 3 Å were denoted as dashed lines.

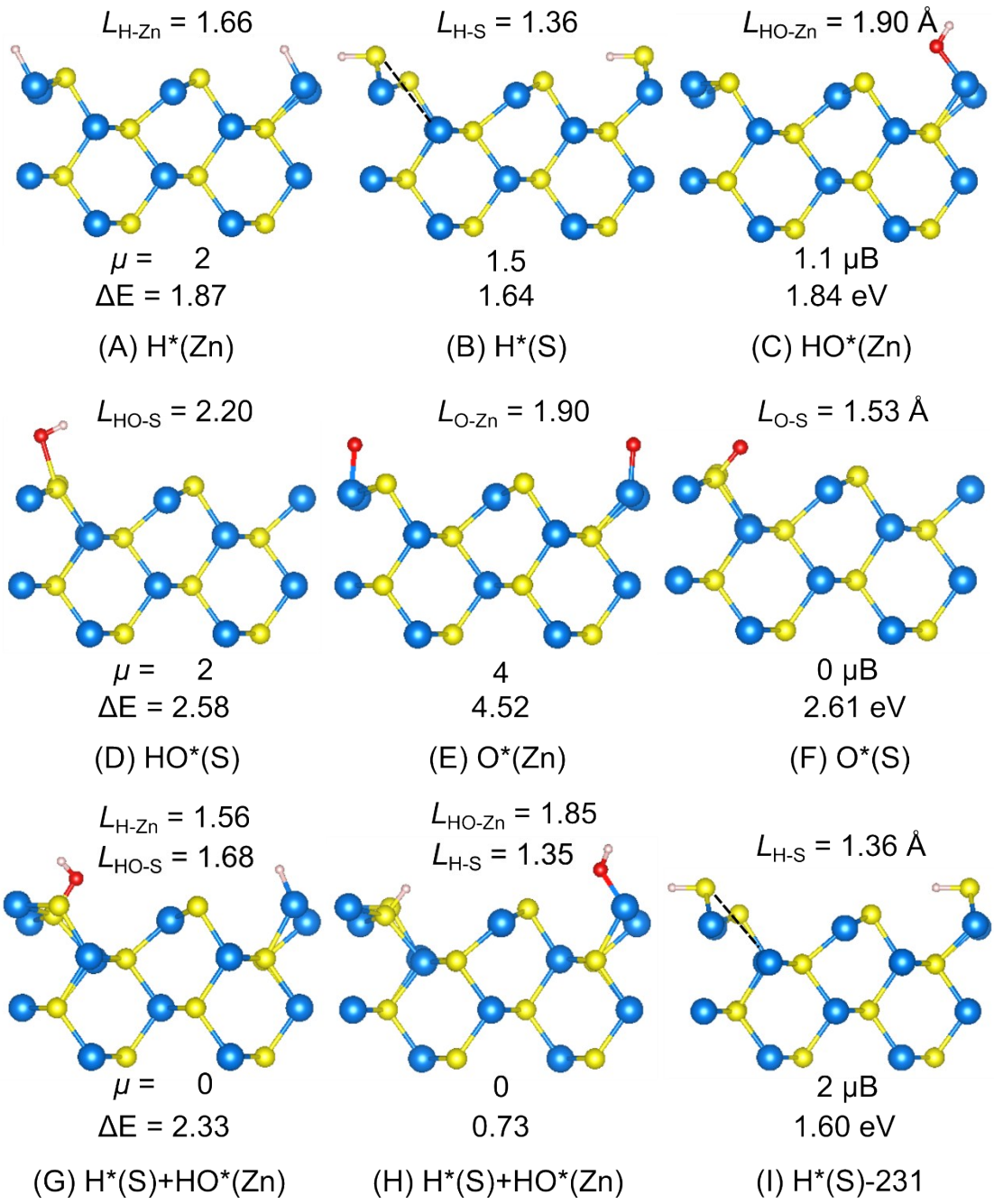

Figure S2. Optimized adsorption geometries for the ZnS (110) with the 2×2 slab: (A) H*(Zn), (B) H*(S), (C) HO*(Zn), (D) HO*(S), (E) O*(Zn), (F) O*(S), (G) H*(Zn)/HO*(S) and (H) H*(S)/HO*(Zn); Optimized adsorption geometry with the 2×3 slab: (I) H*(S).

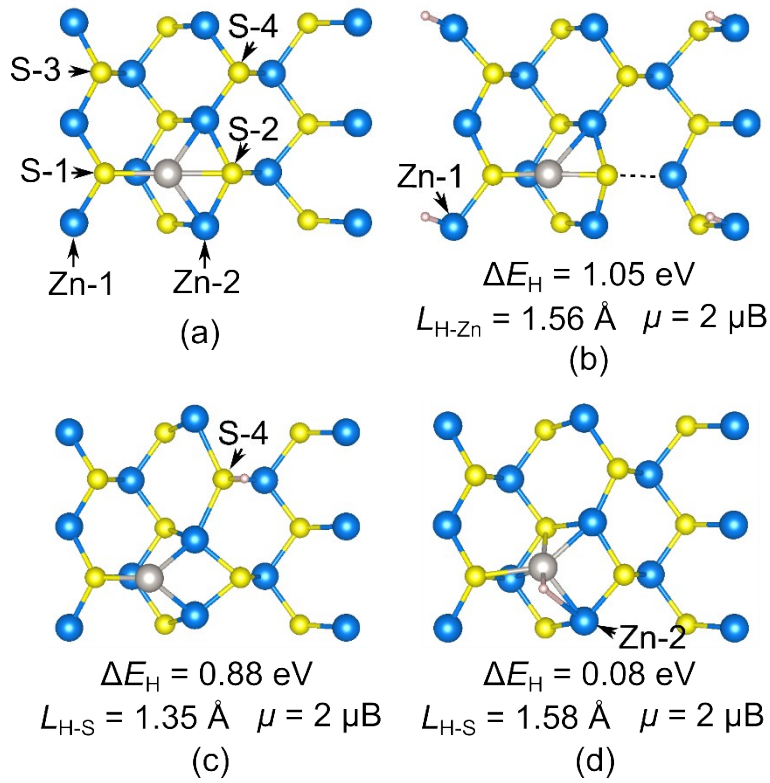

Figure S3. Top views of the geometries for (a) Pt loaded ZnS (110) and H* adsorbed at (b) Zn-1, (c) S-4 and (d) Pt site with the 2×2 slab. Two types of surface Zn atoms and four types of surface S atoms were distinguished on the Pt loaded (110). The adsorption energy, bond length and magnetic moment were presented for each geometry.