

Structures of Seven Molybdenum Surfaces and Their Coverage Dependent Hydrogen Adsorption

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In this method, the surface free energy (γ) of a surface can be described as in Equation 1 (Eq. 1), in which G is the Gibbs free energy of a solid surface, A is total surface area of two equilibrium surfaces (top and bottom sides), $\mu_i(T, p)$ is the chemical potential of the species i , n_i is the number of the i th type species.

$$\gamma(T, p) = \frac{1}{A} [G - \sum_i n_i \mu_i(T, p)] \quad \text{Eq. 1}$$

For describing the adsorption of gas species on surfaces, we define the surface energy of a surface with n_i gas species adsorption as in Equation 2, where $G_{hkl}^{ads}(T, p, \{n_{gas}^{ads}\})$ is the Gibbs free energy of the (hkl) surface with n adsorbed species and $\mu_i(T, p)$ is the chemical potential of all the species in the system (including the adsorbed species).

$$\gamma_{hkl}^{ads}(T, p, n_i) = \frac{1}{A} [G_{hkl}^{ads}(T, p, \{n_{gas}^{ads}\}) - \sum_i n_i \mu_i(T, p)] \quad \text{Eq. 2}$$

For Mo surfaces with nH atoms adsorption, the Eq. 2 can be rewritten as in Equation 3.

$$\gamma_{Mo}^{ads}(T, p, nH) = \frac{1}{A} [G_{Mo}^{ads}(T, p, \{nH\}) - n_{Mo} \mu_{Mo}(T, p) - \frac{1}{2} n_H \mu_{H_2}(T, p)] \quad \text{Eq. 3}$$

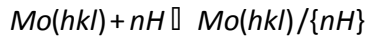
As for the clean Mo surfaces, the surface free energy ($\gamma_{Mo}^{clean}(T, p)$) is given in Equation 4

$$\gamma_{Mo}^{clean}(T, p) = \frac{1}{A} [G_{Mo}^{clean}(T, p) - n_{Mo} \mu_{Mo}(T, p)] \quad \text{Eq. 4}$$

Where $G_{Mo}^{clean}(T, p)$ represents the Gibbs free energy of the clean Mo surface and $\mu_{Fe}(T, p)$ is the chemical potential of bulk Mo. The surface free energy of (hkl) surface with n H atoms by inserting Eq. 4 to Eq. 3 is given in Equation 5.

$$\gamma_{Mo}^{ads}(T, p, nH) = \gamma_{Mo}^{clean}(T, p) + \frac{1}{A} [G_{Mo}^{ads}(T, p, \{nH\}) - G_{Mo}^{clean}(T, p) - \frac{1}{2} n_H \mu_{H_2}(T, p)] \quad \text{Eq. 5}$$

Considering the adsorption process of H atoms on Mo surface as,



the change of Gibbs free energy for those adsorption processes, $\Delta G_{Mo}^{ads}(T, p, nH)$, can be found in Equation 6

$$\Delta G_{Mo}^{ads}(T, p, nH) = G[Mo(hkl)/\{nH\}] - G[Mo(hkl)] - \frac{1}{2} G_{gas}(H_2) \quad \text{Eq. 6}$$

In this equation, $G[Mo(hkl)/\{nH\}]$ is the Gibbs free energy of Mo surface with nH atoms, while $G[Mo(hkl)]$ is the Gibbs free energy of the clean Mo surface. Compared to the large contribution of vibration to the gases, this contribution to

the solid surfaces is negligible because of their large mass differences. Therefore, we apply the DFT calculated total energy to substitute the Gibbs free energies of solid Mo surfaces, and the Equation 6 can be rewritten as

$$\Delta G_{Mo}^{ads}(T, p, nH) = E[Mo(hkl)/\{nH\}] - E[Mo(hkl)] - \frac{1}{2}G_{gas}(H_2)$$

Where $E[Mo(hkl)/\{nH\}]$ and $E[Mo(hkl)]$ are the total energies of corresponding systems. The $G_{gas(H_2)}$ term equals to $n\mu_{H_2}(T, p)$. Then, the chemical potential of H_2 (μ_{H_2}) can be described as:

$$\mu_{H_2}(T, p) = E_{H_2}^{total} + \tilde{\mu}_{H_2}(T, p^0) + k_B T \ln \frac{p_{H_2}}{p^0}$$

At 0 K, the chemical potential of H_2 can be regarded as the total energy of isolated H_2 molecule which can be calculated directly with VASP. The $\tilde{\mu}_{H_2}(T, p^0)$ term includes the contributions from vibration and rotation of H_2 molecule. It can be calculated or got from thermodynamic tables. In this paper we calculate these data by Gaussian software (Gaussian 09, Revision D.01, Frisch, M. J. et al.; Gaussian, Inc., Wallingford CT, 2009). The last term of the formula is the contributions of temperature and H_2 partial pressure to the chemical potential. Finally, the change in the Gibbs free energy of the Mo surfaces after the adsorption of n H atoms can be expressed as in equation 7

$$\Delta G_{Mo}^{ads}(T, p, nH) = E[Mo(hkl)/\{nH\}] - E[Mo(hkl)] - \frac{1}{2}nE_{H_2}^{total} - \frac{1}{2}n\tilde{\mu}_{H_2}(T, p^0) - \frac{1}{2}nk_B T \ln \frac{p_{H_2}}{p^0} \quad \text{Eq. 7}$$

In this respect, we can plot $\Delta G(T, p)$ as a function of T and p. The system (surface with nH atoms adsorption) with the lowest value of $\Delta G(T, p)$ will be most stable under the given condition, and this also provides information about the H_2 equilibrium coverage on the Mo surface under fixed conditions. Furthermore, the $\Delta G_{Mo}^{ads}(T, p, nH)$ part is equal to the second part of Equation 5. Finally, we can get the value of surface free energy of a surface with nH atoms adsorption under different temperatures and pressures by adding the contribution of hydrogen adsorption by using the Equation 8

$$\gamma_{Mo}^{ads}(T, p, nH) = \gamma_{Mo}^{clean}(T, p) + \frac{1}{A}[\Delta G_{Mo}^{ads}(T, p, \{nH\})] \quad \text{Eq. 8}$$

The surface energy of clean Mo surface (γ_{Mo}) can be written as

$$\gamma_{Mo}^{clean}(T, p) = \frac{1}{A}[E_{Mo(hkl)} - n_{Mo}E_{Mo\ bulk}] \quad \text{Eq. 9}$$

where $E_{Mo(hkl)}$ was the total energy of Mo(hkl) surface and $E_{Mo-bulk}$ was the total energy of bulk Mo.

Table S1: Effects of spin polarization on the energies (eV) and lattice parameters of Mo bulk.

	spin polarization	non spin polarization	error
E[Mo bulk]	-10.860775	-10.860768	0.0000070
E[Mo(100)-7L]	-73.476276	-73.476779	0.0005
E[Mo(100)-1H]	-454.3845665	-454.384663	0.0001
E[Mo(100)-2H]	-458.4873819	-458.4872051	0.00018
E[Mo(100)-3H]	-462.5708096	-462.5704939	0.0003
E[Mo(100)-4H]	-466.6421875	-466.6421546	0.00003
E[Mo(100)-5H]	-470.6944407	-470.694382	0.00006
E[Mo(100)-6H]	-474.8610805	-474.8612434	0.00016
lattice parameters of Mo bulk	a=b=c=3.17 Å	a=b=c=3.17 Å	0

Table S2: Surfaces energies (J/m^2) of Mo surfaces at different layers.

Layers	Mo(100)	Mo(110)	Mo(111)	Mo(210)	Mo(211)	Mo(310)	Mo(321)
8L		2.76				3.11	3.10
9L	3.22	2.76				3.13	3.09
10L	3.17	2.77			2.91	3.07	3.01
11L	3.17	2.76		3.15	2.91	3.09	2.98
12L	3.20	2.78	2.96	3.12	2.88	3.12	2.97
13L	3.18	2.76	2.99	3.13	2.89	3.09	3.00
14L	3.21	2.75	3.04	3.10	2.91	3.11	3.00
15L	3.16	2.76	3.01	3.13	2.90	3.10	3.01
16L	3.19	2.77	2.98	3.11	2.89	3.10	3.01
17L	3.16	2.76	2.96	3.12	2.89	3.09	3.02
18L	3.19	2.74	2.97	3.10	2.89	3.08	
19L	3.14	2.76	2.95	3.12	2.90	3.09	
20L	3.18	2.75	2.98	3.10	2.90	3.09	
21L	3.15	2.75	3.00	3.11	2.89	3.08	
22L	3.17	2.76	3.00	3.11	2.88		
23L	3.14	2.75	2.96	3.11	2.89		
24L	3.15		2.97	3.11	2.90		
25L			2.97	3.11	2.89		
26L			2.96	3.10			
27L			2.95				

Table S3: The values of H₂ chemical potential (eV) from our Gaussian 09 (BP86/6-311G) calculation and NIST database.

	100K	200K	300K	400K	500K	600K	700K	800K	900K	1000K
NIST	-0.073	-0.189	-0.319	-0.459	-0.607	-0.760	-0.919	-1.083	-1.250	-1.421
our results	-0.072	-0.186	-0.315	-0.455	-0.602	-0.755	-0.914	-1.077	-1.243	-1.413

Table S4 Charge transfer from the surface to each H atom at different H coverage using Bader charge analysis

	Mo(100)	Mo(110)		Mo(111)	Mo(210)	Mo(211)	Mo(310)	Mo(321)
1H (1/9ML)	0.44/H	0.45/H	1H (1/6 ML)	0.44/H	0.45/H	0.45/H	0.45/H	0.45/H
3H (1/3 ML)	0.45/H	0.45/H	3H (1/2 ML)	0.43/H	0.45/H	0.45/H	0.45/H	0.44/H
9H (1ML)	0.40/H	0.43/H	6H (1 ML)	0.43/H	0.46/H	0.45/H	0.44/H	0.43/H
18H (2ML)	0.34/H		12H (2 ML)	0.40/H	0.45/H	0.40/H	0.44/H	0.43/H

Fig. S1: Structures and stepwise adsorption energies (eV) of H atoms on Mo(100) surface

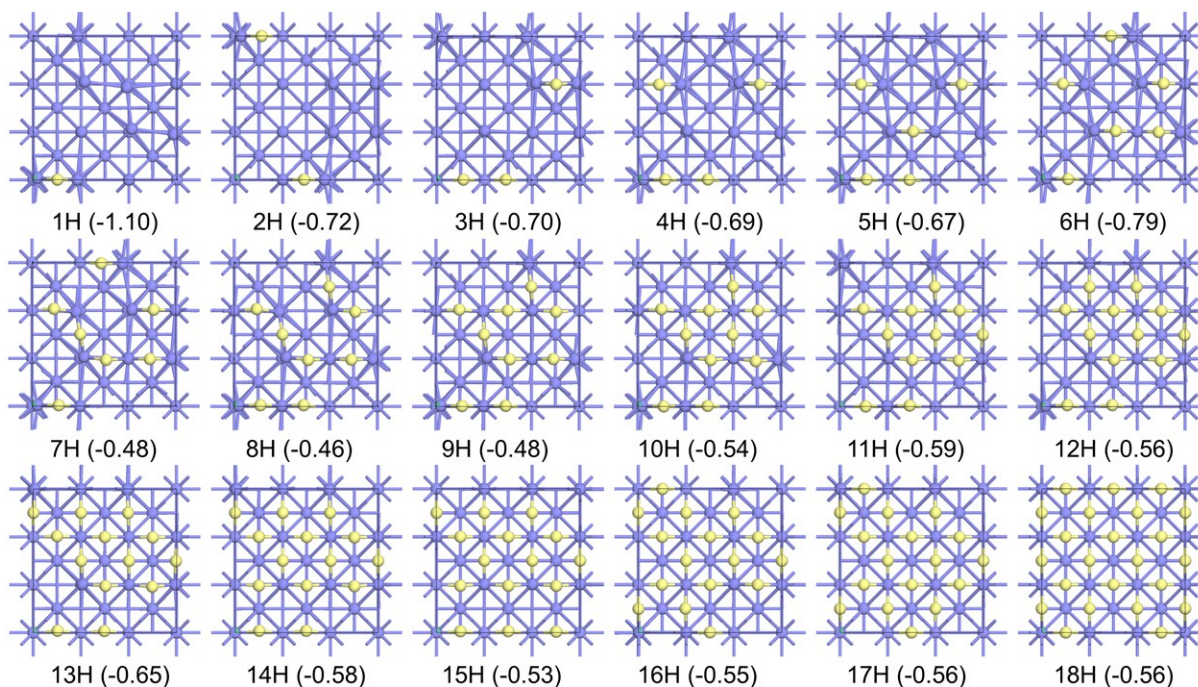


Fig. S2: Structures and stepwise adsorption energies (eV) of H atoms on Mo(110) surface

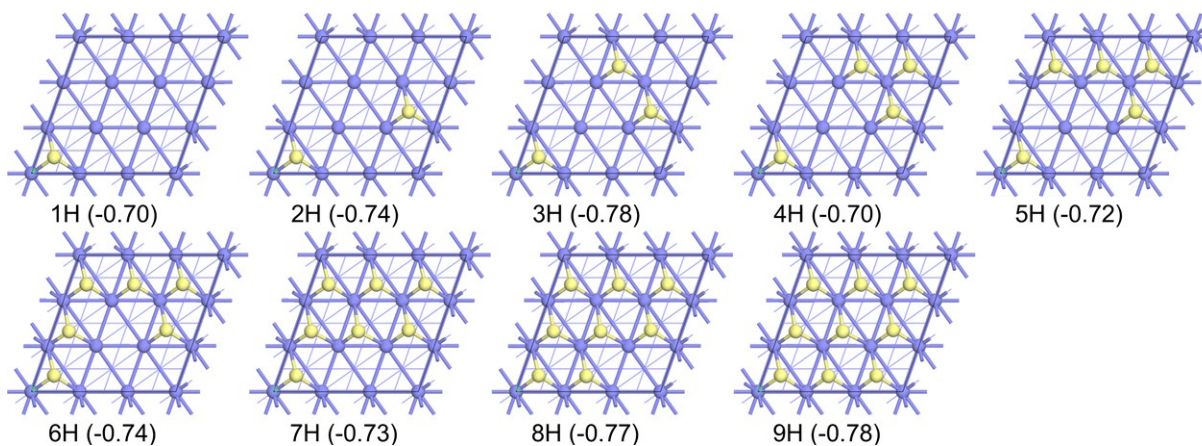


Fig. S3: Structures and stepwise adsorption energies (eV) of H atoms on Mo(111) surface

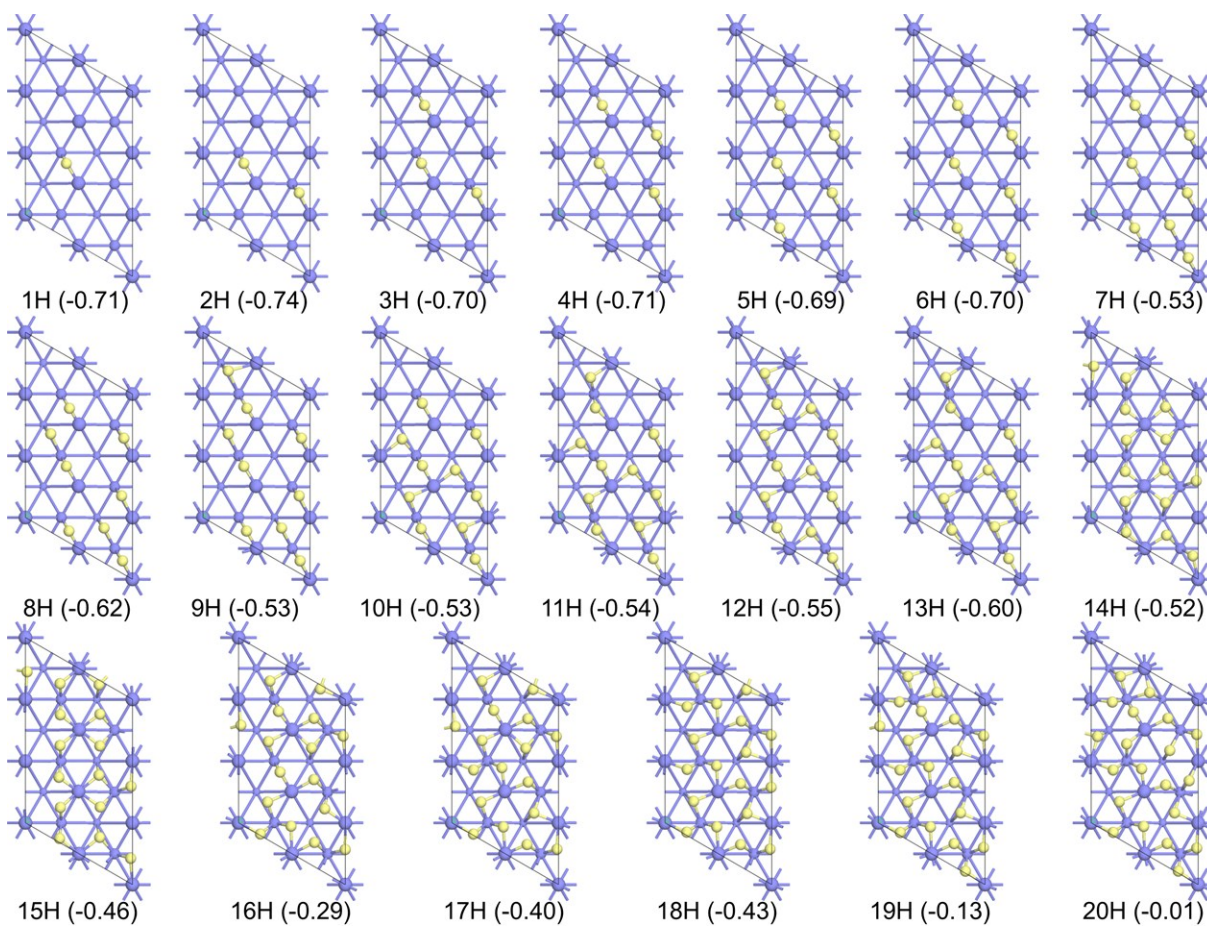


Fig. S4: Structures and stepwise adsorption energies (eV) of H atoms on Mo(210) surface

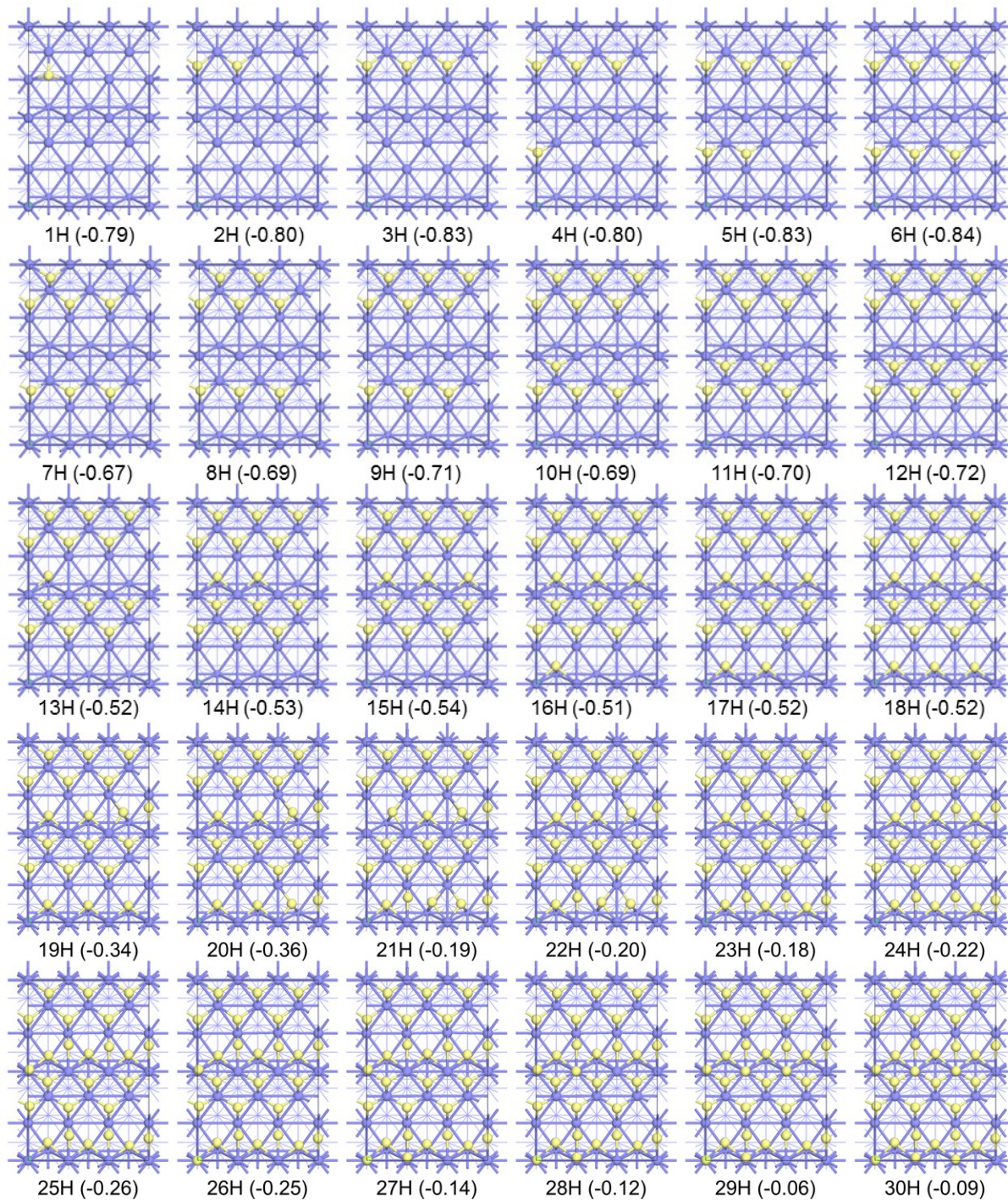


Fig. S5: Structures and stepwise adsorption energies (eV) of H atoms on Mo(211) surface

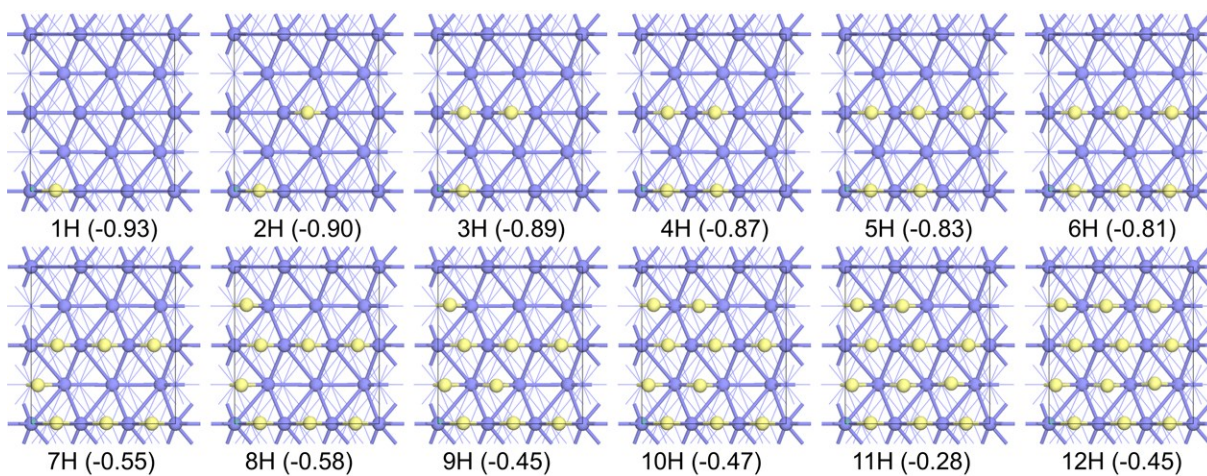


Fig. S6: Structures and stepwise adsorption energies (eV) of H atoms on Mo(310) surface

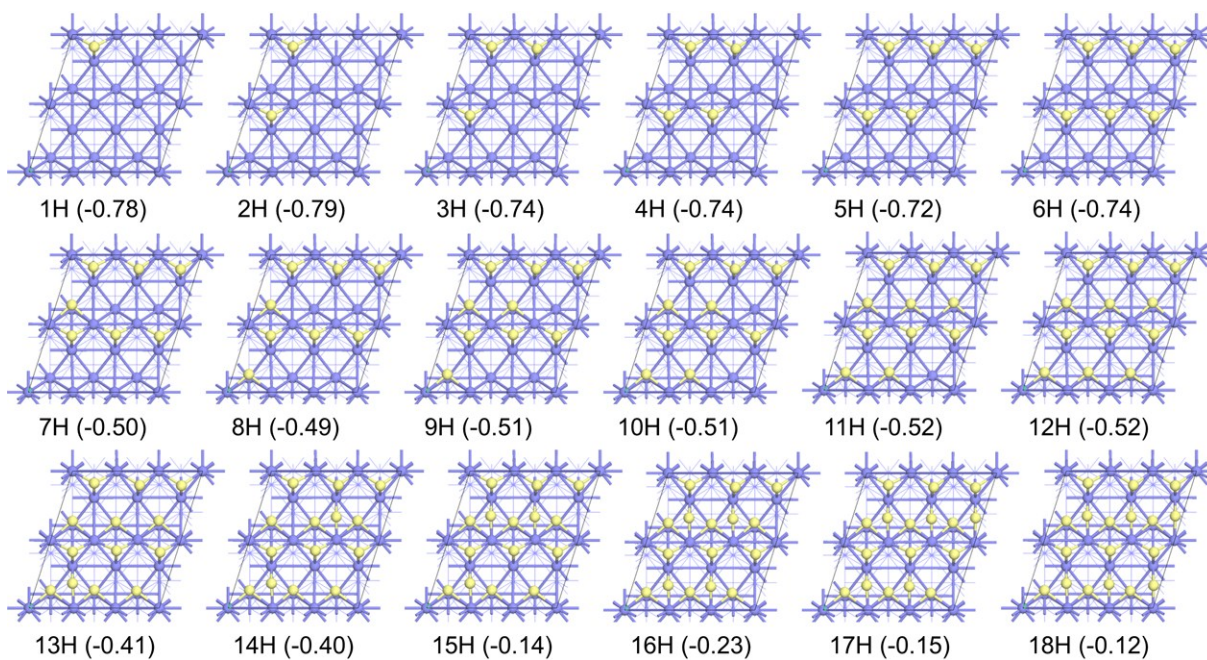


Fig. S7: Structures and stepwise adsorption energies (eV) of H atoms on Mo(321) surface

