Electronic Supporting Information (ESI)

Screening Antimonene-Based Single-Atom Catalysts for Nitric Oxide Electroreduction to Ammonia by Density Functional Theory Computations

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Computational Details

The Gibbs reaction free energy change (ΔG) of each elementary step during the NORR to multicarbon products synthesis was computed by using the computational hydrogen electrode (CHE) model. Based on this model, the ΔG value can be obtained by the formula: $\Delta G = \Delta E + \Delta ZPE - T\Delta S + eU$, where ΔE is the reaction energy of reactant and product species adsorbed on the catalyst directly obtained from DFT computations; ΔZPE and ΔS are the changes between the adsorbed species and the gas phase molecules in zero-point energies and entropy at 298.15 K, which can be calculated from the vibrational frequencies, and U represents the applied potential. Moreover, the NORR catalytic activity was estimated using the limiting potential (U_{L}), computed as $U_{\mathrm{L}} = -\Delta G_{\mathrm{max/e}}$, where ΔG_{max} is the free energy change of the most thermodynamically unfavorable elementary step, i.e., the potential–determining step (PDS). The adsorption energy (ΔE_{ads}) of the NO molecule was computed using the equation: $\Delta E_{\mathrm{ads}} = E_{*\mathrm{NO}} - E_{*} - E_{\mathrm{NO}}$, where $E_{*\mathrm{NO}}$, E_{*}, and E_{NO} are the total electronic energies of the adsorbed NO, catalyst, and the free NO molecule, respectively.

Table S1. The distance between the anchored single-atom metals and Sb atoms ($d_{M\text{-}Sb}$, Å), the computed binding energies (E_{bind}, eV), the difference between the calculated binding energies and the cohesive energies of their respective bulk phases, and the band gap derived from the computed band structures.

M/Sb	$d_{M\text{-}Sb}$	E_{bind}	E_{bind} - E_{coh}	*band gap*
V	2.68	-5.77	-0.28	1.10
Cr	2.68	-6.98	-3.20	0.26
Mn	2.67	-4.64	-0.65	0.00
Fe	2.59	-5.60	-0.49	0.45
Co	2.48	-5.14	-0.20	0.00
Ni	2.49	-5.55	-0.39	0.00
Cu	2.56	-4.01	-0.17	0.51
Nb	2.74	-7.04	-7.45	0.00
Mo	2.71	-7.41	-7.03	0.01
Ru	2.56	-7.63	-0.38	0.00
Rh	2.57	-6.96	-0.91	0.15
Pd	2.62	-5.04	-1.34	0.00
Ag	2.73	-3.33	-0.71	0.92
Ta	2.71	-7.29	-7.33	0.22
W	2.69	-6.75	-7.62	0.87
Ir	2.55	-8.09	-0.76	0.00
Pt	2.59	-7.23	-1.70	0.00
Au	2.68	-4.51	-1.43	0.03

Table S2. The distance between the anchored single-atom metals and the N ($d_{\text{N-Metal}}$, Å), the adsorption strength of NO molecule on these M/Sb catalysts (E_{ads}, eV) and the calculated free energies change of $\Delta G_{*\text{NO}}$ and $\Delta G_{*\text{NHO}}$.

M/Sb	$d_{\text{N-Metal}}$	E_{ads}	$\Delta G_{*\text{NO}}$	$\Delta G_{*\text{NHO}}$
V	1.74	-3.08	-2.19	-0.21
Cr	1.66	-2.44	-1.73	0.62
Mn	1.69	-2.37	-1.65	0.42
Fe	1.68	-2.79	-2.13	0.58
Co	1.65	-2.58	-1.92	0.82
Ni	1.70	-2.05	-1.37	0.61
Cu	1.78	-1.29	-0.59	0.34
Nb	1.85	-4.60	-2.90	-0.59
Mo	1.79	-3.51	-2.79	0.54
Ru	1.77	-3.17	-2.45	0.89
Rh	1.84	-1.91	-1.21	0.50
Pd	1.91	-1.34	-0.66	0.42
Ag	2.09	-0.81	-0.13	0.30
Ta	1.86	-3.72	-3.01	-0.88
W	1.79	-4.16	-3.45	0.52
Ir	1.84	-2.23	-1.54	0.44
Pt	1.91	-1.56	-0.88	0.46
Au	2.05	-0.74	-0.06	0.24

Table S3. Computed free energy changes (ΔG, eV) for all potential elementary steps involved in the NORR to NH_3 products on Au/Sb catalysts. Favorable steps are highlighted in red.

Au/Sb	ΔG
$^* + NO \rightarrow {}^*NO$	-0.06
$^*NO + H^+ + e^- \rightarrow {}^*NHO$	0.24
$^*NO + H^+ + e^- \rightarrow {}^*NOH$	1.15
$^*NHO + H^+ + e^- \rightarrow {}^*NH_2O$	-0.32
$^*NHO + H^+ + e^- \rightarrow {}^*NHOH$	0.06
$^*NH_2O + H^+ + e^- \rightarrow {}^*O + NH_3$	-1.69
$^*NH_2O + H^+ + e^- \rightarrow {}^*NH_2OH$	-0.38
$^*O + H^+ + e^- \rightarrow {}^*OH$	-0.56
$^*OH + H^+ + e^- \rightarrow H_2O + ^*$	-1.02

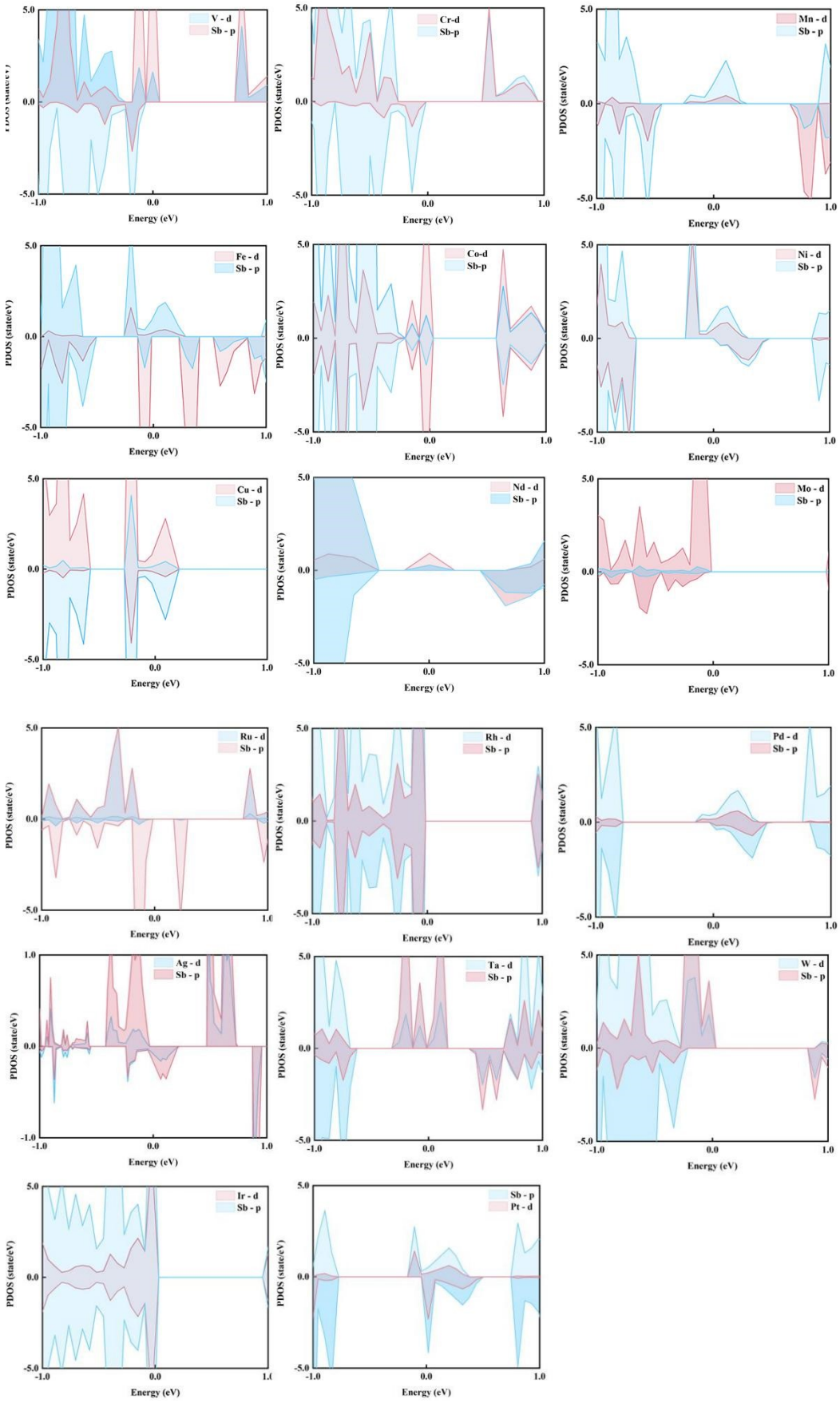

V - d
Sb - p
Cr-d
Sb-p
Mn - d
Sb - p
Fe - d
Sb - p
Co-d
Sb-p
Ni - d
Sb - p
Cu - d
Sb - p
Nd - d
Sb - p
Mo - d
Sb - p
Ru - d
Sb - p
Rh - d
Sb - p
Pd - d
Sb - p
Ag - d
Sb - p
Ta - d
Sb - p
W - d
Sb - p
Ir - d
Sb - p
Sb - p
Pt - d
PDOS (state/eV)
Energy (eV)

Fig. S1. The calculated partial density of states (PDOS) between the metal d-orbitals and Sb p-orbitals in M/Sb catalysts.

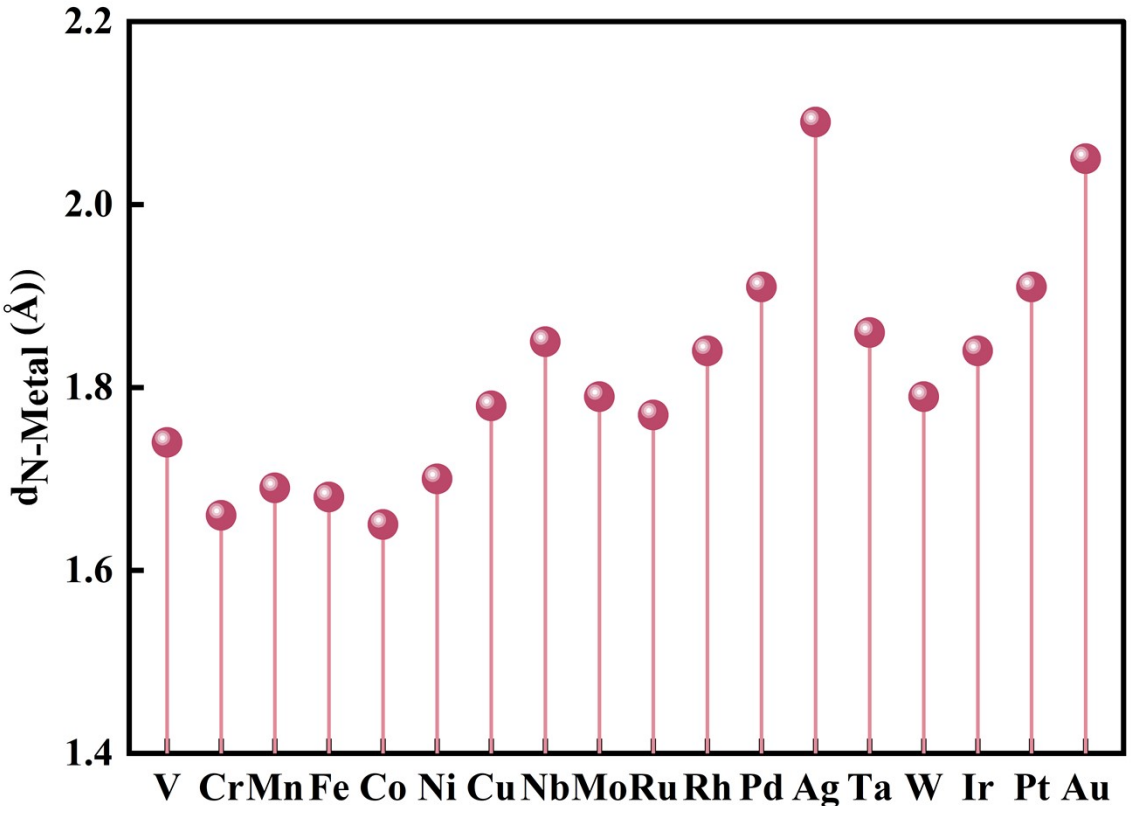


Fig. S2. The distance between the anchored single-atom metals and the N ($d_{N\text{-}Metal}$, Å).

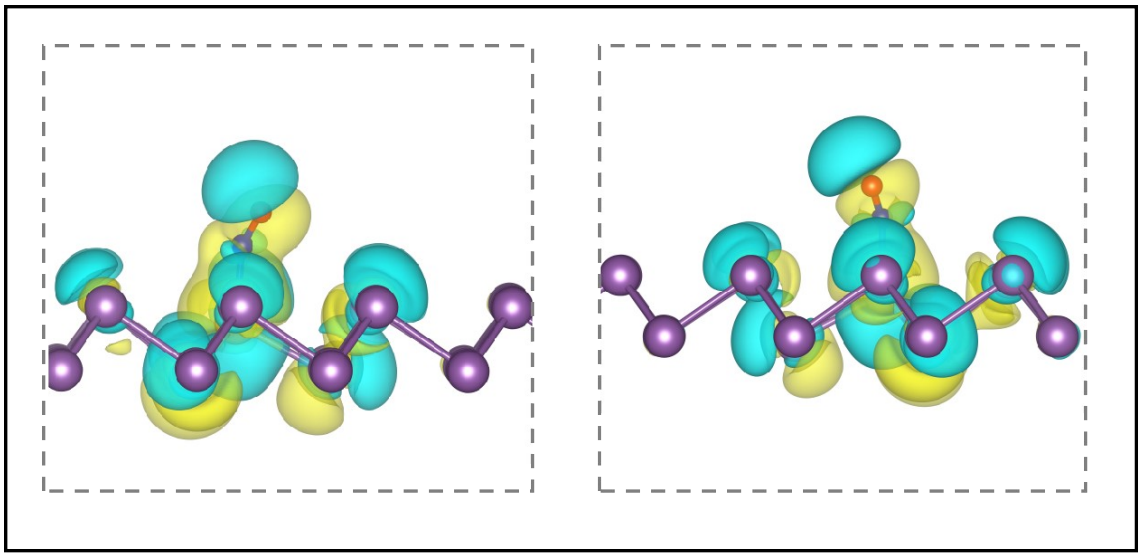


Fig. S3. The charge density difference of the NO molecule on the Au/Sb catalyst, where the isosurface value is set to be 0.005 e Å−3, and cyan and yellow bubbles represent positive and negative charges, respectively.

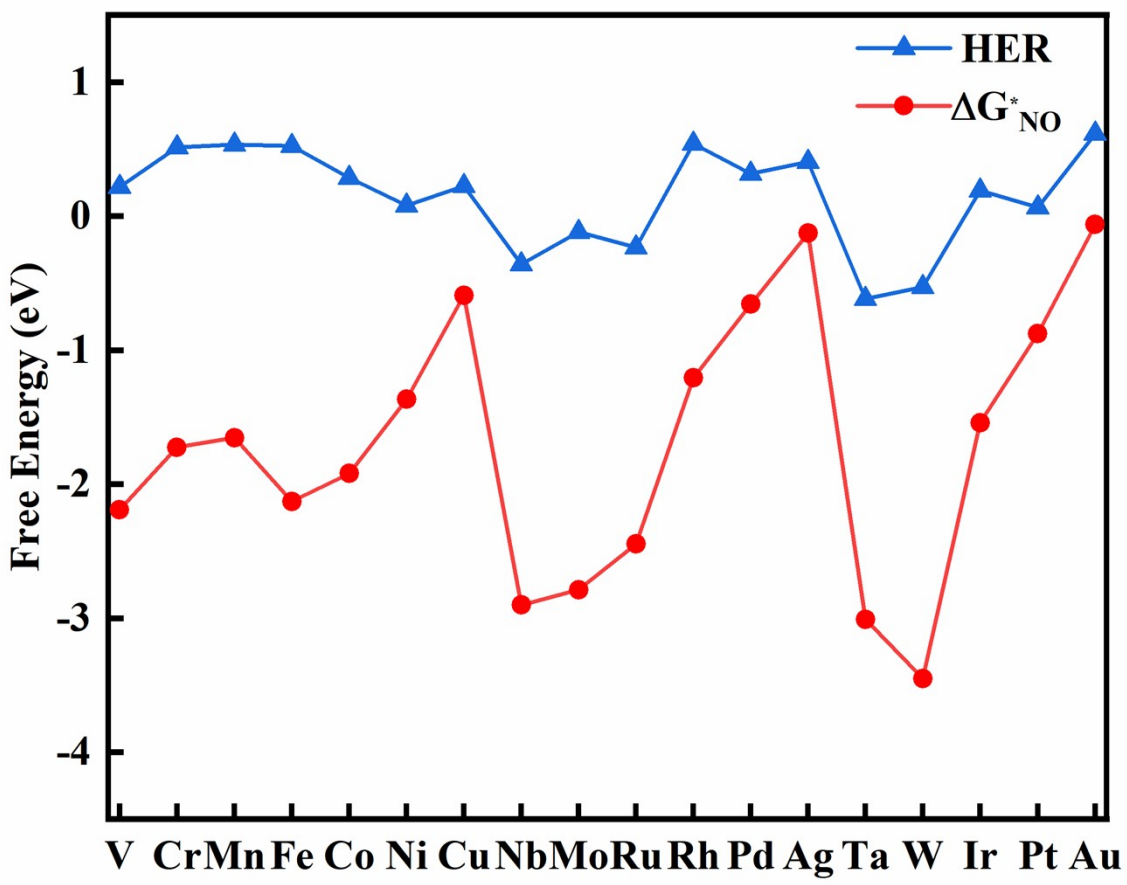


Fig. S4. The calculated Gibbs free energy changes of ΔG_{*NO} and HER.

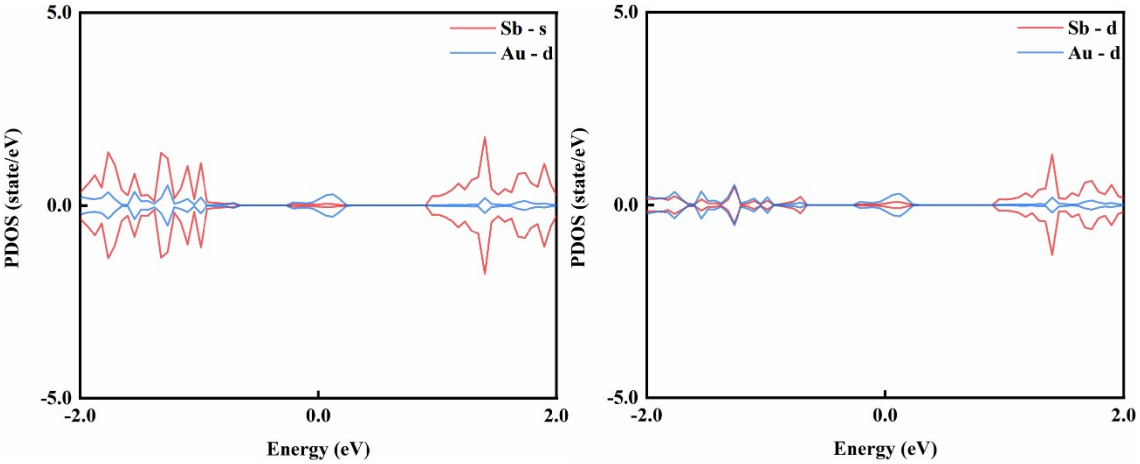


Fig. S5. Electronic partial density of states (PDOS) of Sb-s and Sb-d for the Au/Sb system.

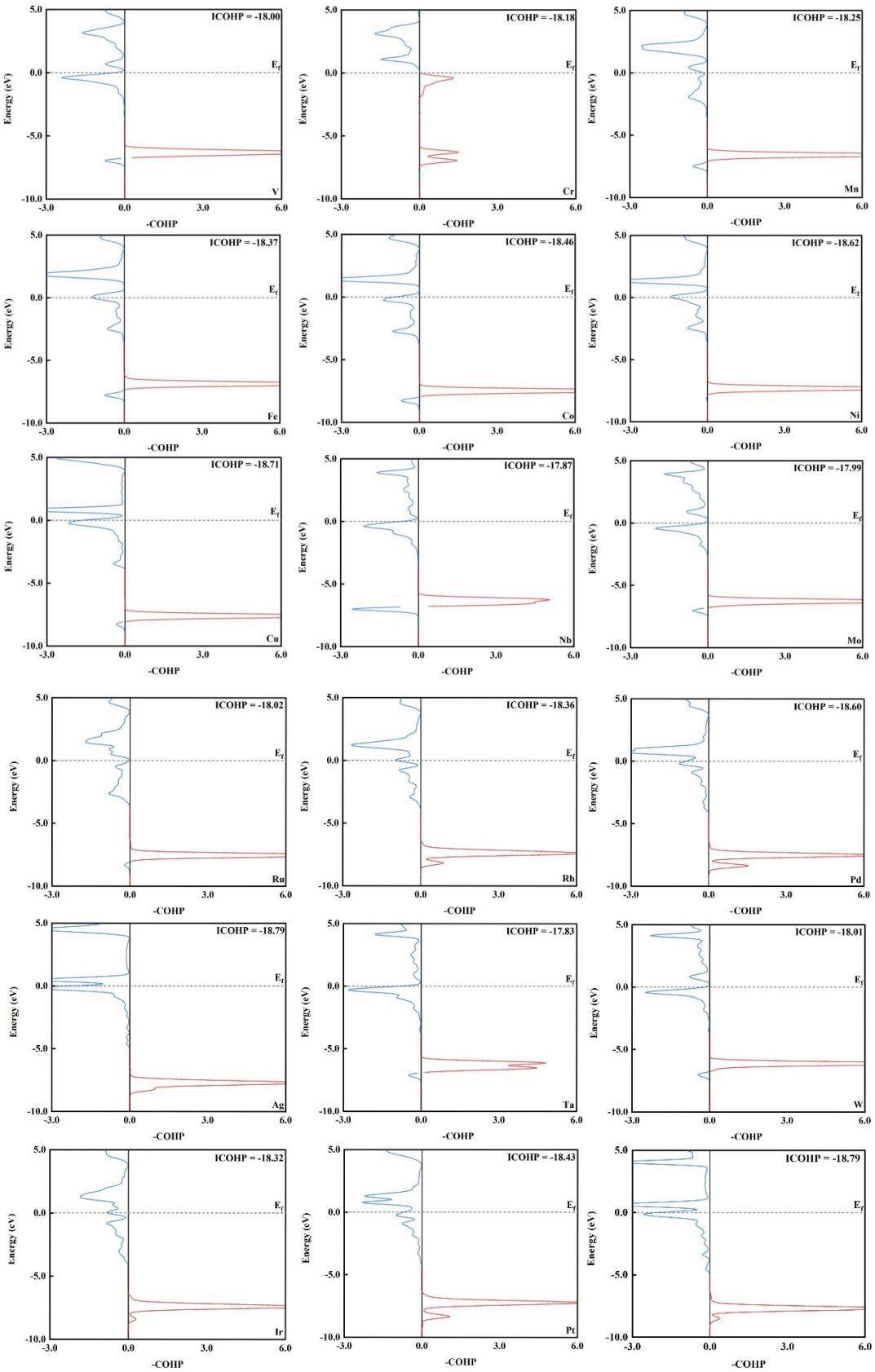


Fig. S6. Integrated crystal orbital Hamilton population (ICOHP) of M/Sb.

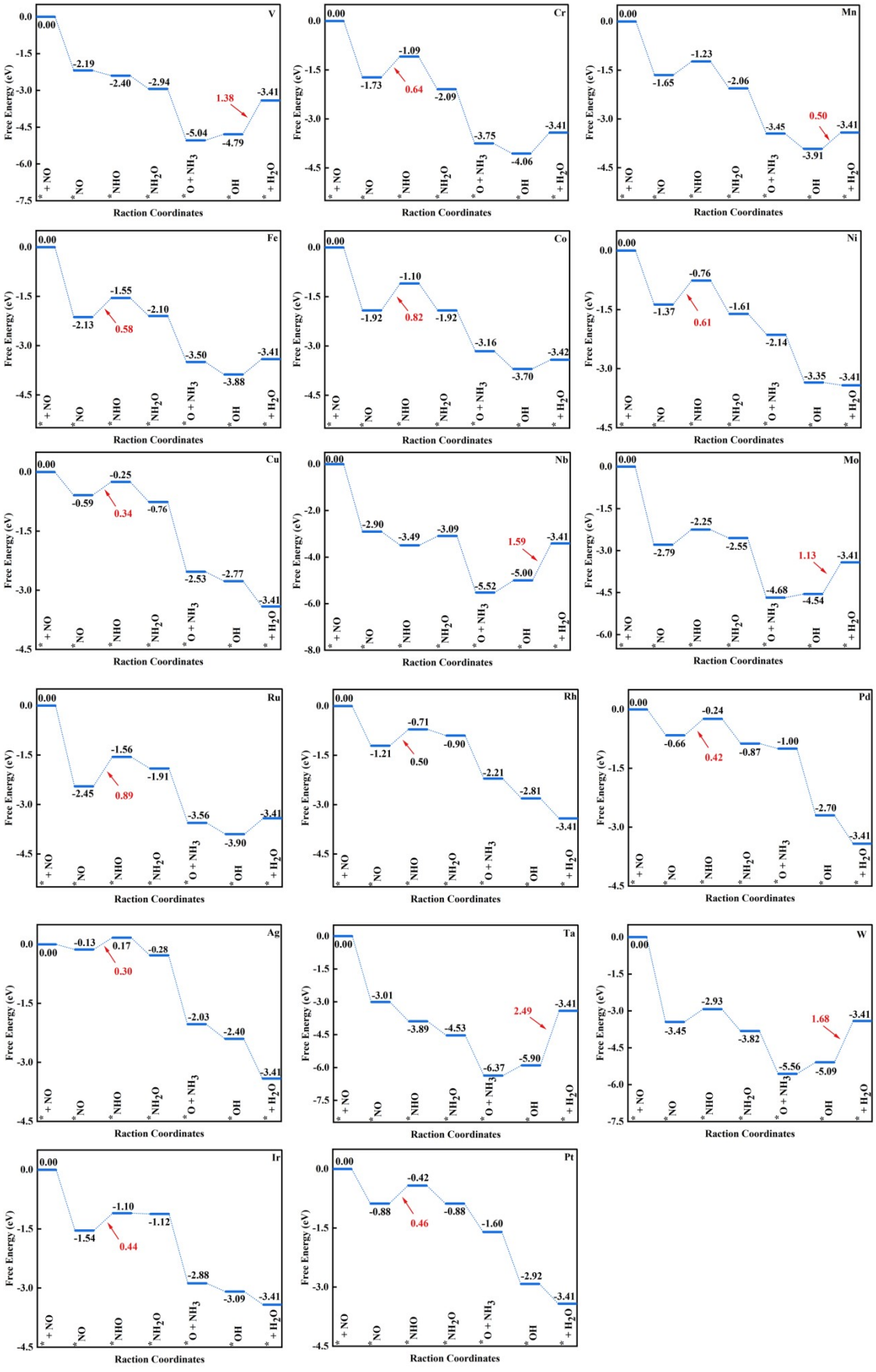

V
0.00
-2.19
-2.40
-2.94
-5.04
-4.79
-3.41
1.38
Cr
0.00
-1.73
-1.09
-2.09
-3.75
-4.06
-3.41
0.64
Mn
0.00
-1.65
-1.23
-2.06
-3.45
-3.91
-3.41
0.50
Fe
0.00
-2.13
-1.55
-2.10
-3.50
-3.88
-3.41
0.58
Co
0.00
-1.92
-1.10
-1.92
-3.16
-3.70
-3.42
0.82
Ni
0.00
-1.37
-0.76
-1.61
-2.14
-3.35
-3.41
0.61
Cu
0.00
-0.59
-0.25
-0.76
-2.53
-2.77
-3.41
0.34
Nb
0.00
-2.90
-3.49
-3.09
-5.52
-5.00
-3.41
1.59
Mo
0.00
-2.79
-2.25
-2.55
-4.68
-4.54
-3.41
1.13
Ru
0.00
-2.45
-1.56
-1.91
-3.56
-3.90
-3.41
0.89
Rh
0.00
-1.21
-0.71
-0.90
-2.21
-2.81
-3.41
0.50
Pd
0.00
-0.66
-0.24
-0.87
-1.00
-2.70
-3.41
0.42
Ag
0.00
-0.13
0.17
-0.28
-2.03
-2.40
-3.41
0.30
Ta
0.00
-3.01
-3.89
-4.53
-6.37
-5.90
-3.41
2.49
W
0.00
-3.45
-2.93
-3.82
-5.56
-5.09
-3.41
1.68
Ir
0.00
-1.54
-1.10
-1.12
-2.88
-3.09
-3.41
0.44
Pt
0.00
-0.88
-0.42
-0.88
-1.60
-2.92
-3.41
0.46
Free Energy (eV)
Raction Coordinates
* + NO
*NO
*NHO
*NH2O
O + NH3
*OH
* + H2O

Fig. S7. The reaction pathways of NORR to NH_3 products are considered along possible mechanisms.

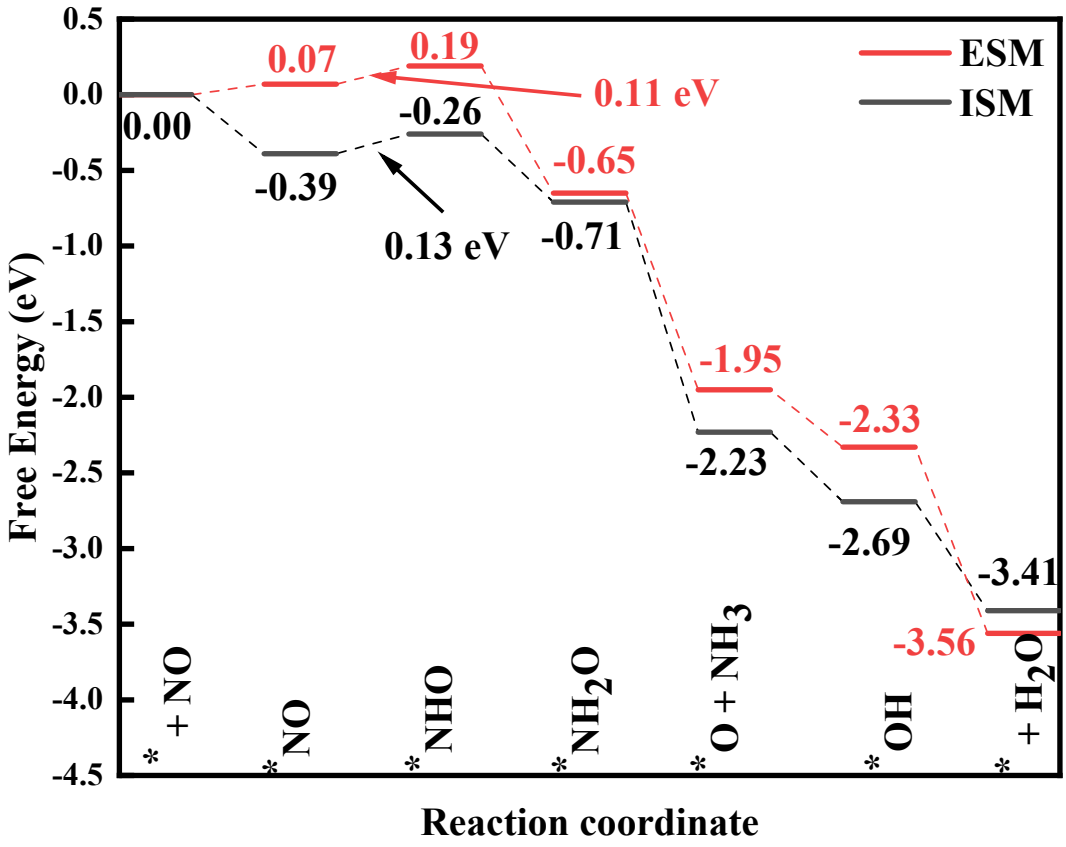
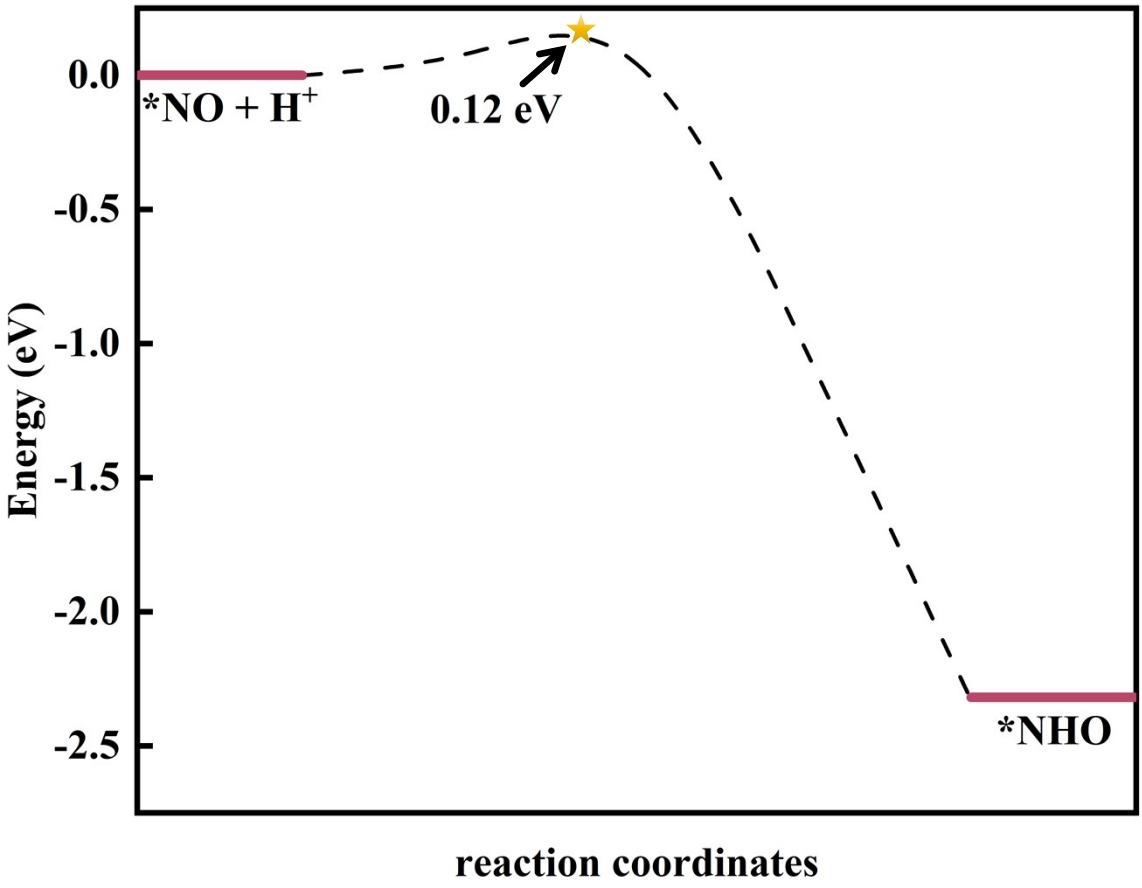


Fig. S8. Free energy diagrams for NORR on Au/Sb under implicit solvation (ISM) and explicit solvation (ESM) conditions


0.0
-0.5
-1.0
-1.5
-2.0
-2.5
Energy (eV)
*NO + H+
0.12 eV
*NHO
reaction coordinates

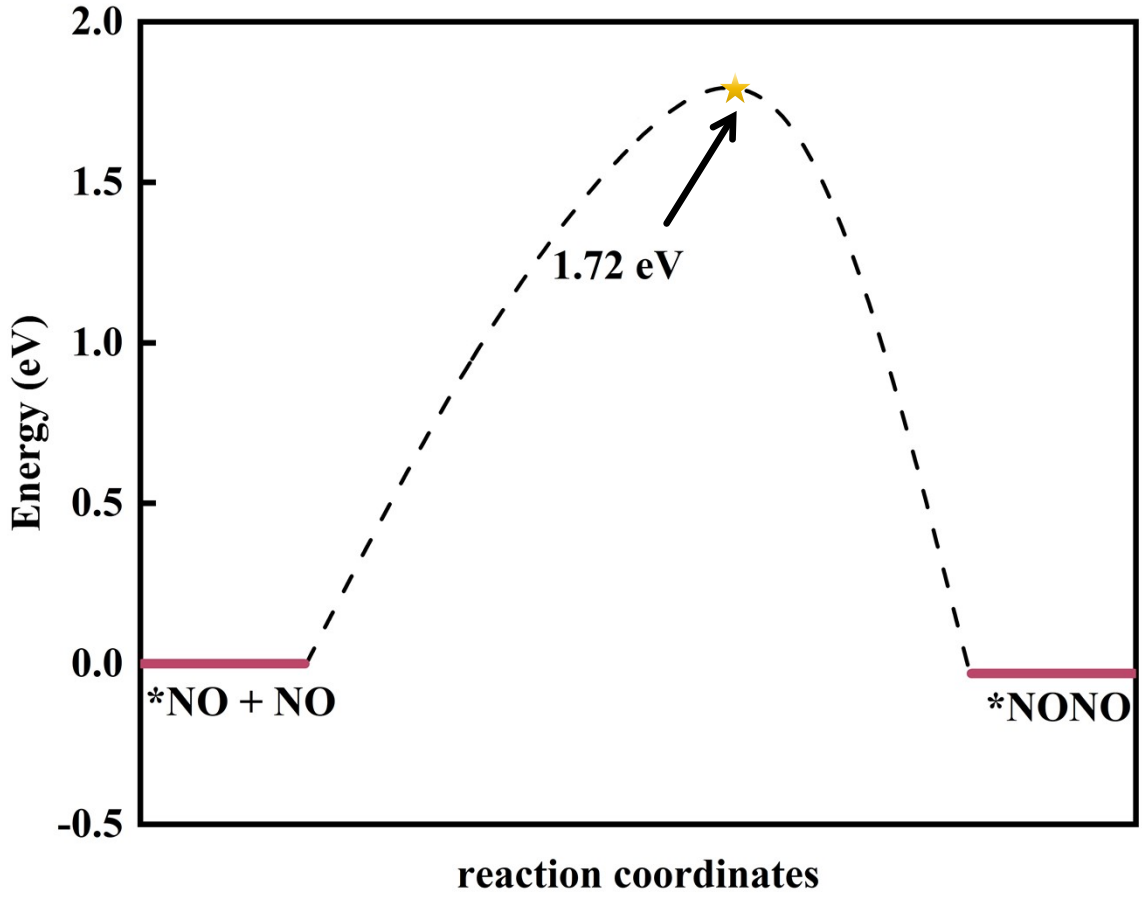

2.0
1.5
1.0
0.5
0.0
-0.5
Energy (eV)
1.72 eV
*NO + NO
*NONO
reaction coordinates

Fig. S9. The Kinetic barriers for NO hydrogenation reaction and $^{*}N_2O_2$ formation on Au/Sb surfaces.

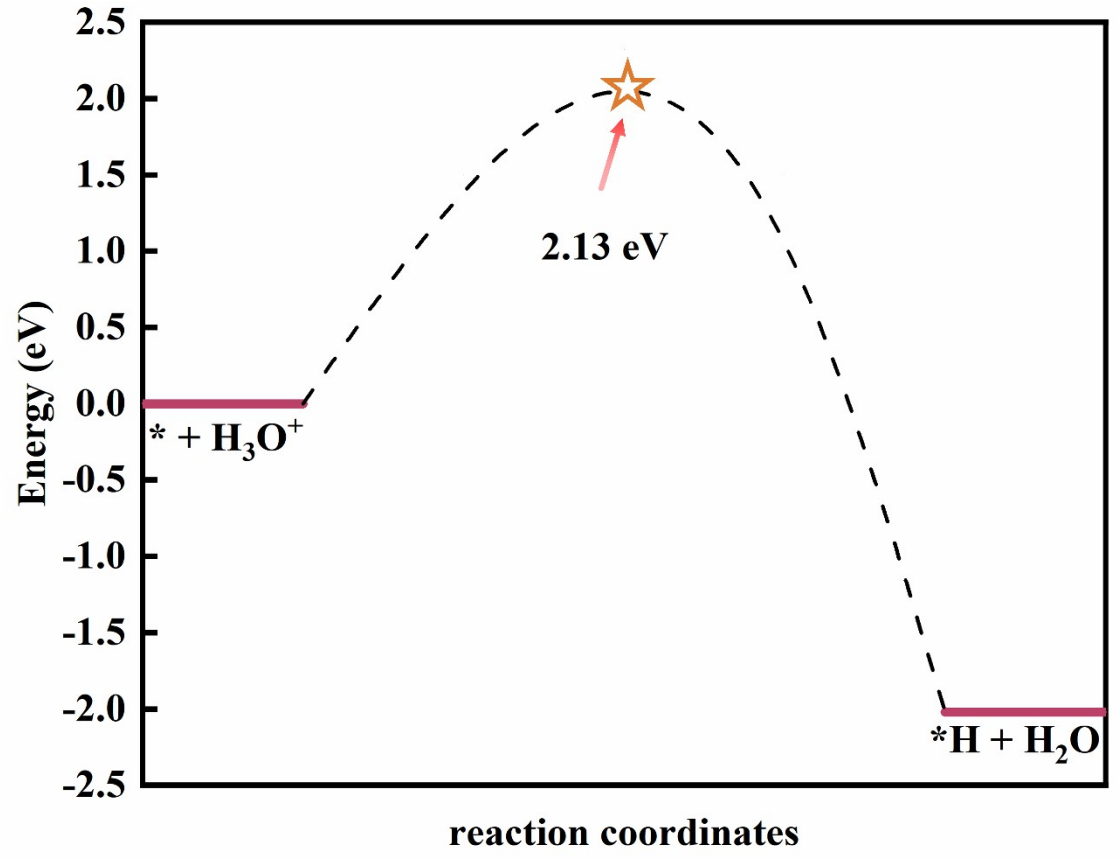


Fig. S10. Kinetic energy barrier for $^{*}H$ adsorption supplied by H_3O^+ on the Au/Sb surface.