Supplementary Information

2D Monolayer Molybdenum (IV) Telluride TMD: An Efficient Electrocatalyst for Hydrogen Evolution Reaction

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S1 Validation of the cluster model:

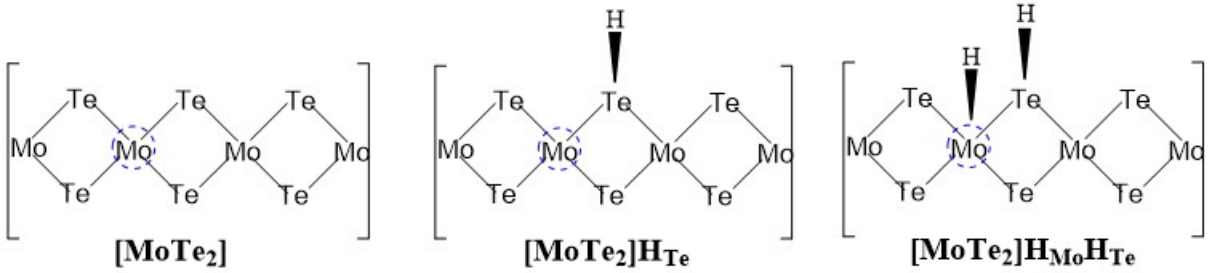

Figure S1: Hydrogen adsorption energies on the 2D monolayer $MoTe_2$ TMD. $E_{cluster}$ represents the relative electronic energy during hydrogen adsorption considering the molecular cluster model system and $E_{periodic}$ is the relative electronic energy obtained from the periodic 2D layer calculations.

S2 Turnover Frequencies calculations:

Different types of technologies correspond to load quality and thus have many differences. Therefore, improved HER performance by turnover frequency (TOF) is an important parameter to evaluate to address such difficulties.[1] The TOF employs the number of catalytic cycles that actually happen per unit of time to determine the catalyst's activity under the reaction circumstances. The higher the TOF value, the better the performance of the electrocatalysts. We have used the following formula for the TOF theoretical calculation:

$$rate = \frac{(k_B T)}{h} \times exp\left(-\frac{\Delta G}{RT}\right)$$

Here k_B means Boltzmann constant (3.298×10^{-27} kcal.mol^{-1}), T is the absolute temperature (298.15 K), h is plank's constant (1.584×10^{-37} kcal S^{-1}), R is the universal ideal gas constant (1.987×10^{-3} kcal K^{-1} mol^{-1}), and ΔG is the energy barrier of the intermediate steps of HER. Using transition state theory (TST)[2], including DFT calculations, we calculated the TOF for both reaction mechanisms (Volmer-Heyrovsky and Volmer-Tafel) for H_2 formation at the edge of the Mo atom.

Another parameter, the Tafel slope is also important for HER calculation to compare with experimental results.[1] The Tafel slope (***m***) demonstrates the effectiveness with which an electrode can generate current in response to a change in applied potential. In other words, if the Tafel slope (mV/decade) is lower, less overpotential is required to get a high current, assuming that the catalyst's reaction rate does not limit the electron transfer from the support to the catalyst. Tafel slope is a theoretical calculation based on the number of electron transfers during the HER steps. The following formula calculates the Tafel slope:

$$m = 2.303\left(\frac{RT}{nF}\right)$$

Hare R= the universal gas constant, T = absolute temperature, F = Faraday constant (96485 C mol^{-1}), and n = the number of electrons in the HER mechanism.[1] This Tafel slope provides information regarding the rate-determining step, kinetics, and energy required to obtain the required activity of the catalyst. Earlier, we discussed two-electron transfer mechanisms in the

HER system as in Figure 3, so the value of n should be taken as 2 for the evolution of one H_2 molecule. So, the Tafel slope calculated for 2D single-layer $MoTe_2$ is found to be 29.58 mV dec^{-1} at T=298.15 K.

Here we calculated the turnover frequency (TOF) for the solvent phase energy barrier of the Heyrovsky reaction barrier. We have calculated the turnover frequency (TOF) of the evolution of H_2 at the edge of each Mo atom in a 2D monolayer $MoTe_2$ catalyst. The turnover frequency is calculated according to the formula mentioned earlier. The TOF of the 2D monolayer MoTe2 obtained from the reaction barrier (ΔG) formed by H_2 in the Heyrovsky TS and Taferl TS in the solvent phase, is about 3.91×10^3 sec^{-1} and 8.22×10^8 sec^{-1}, respectively. The higher the turnover frequency (TOF) value, the more efficient the development of H_2 during HER. The TOF values of other catalysts, such as 2D monolayer MoS_2, WS_2, $W_{0.4}Mo_{0.6}S_2$, and Mn-MoS_2, are mentioned in Table S1 for comparison with 2D monolayer $MoTe_2$ catalysts. The 2D $MoTe_2$ catalyst material shows a reasonably high TOF value, which helps the catalyst material to exhibit significantly superior and efficient performance during HER.

Table S1: The Heyrovsky reaction barrier (ΔG) and turnover frequency (TOF) of the 2D monolayer MoS_2, WS_2, $W_{0.4}Mo_{0.6}S_2$, Mn-MoS_2, and $MoTe_2$ TMD in the solvent phase are listed here.

Materials	**Barrier in gas phase (ΔG) (in kcal.mol^{-1})**	**Barrier in solvent phase (ΔG) (in kcal.mol^{-1})**	**Turnover frequency (TOF) in solvent phase Sec^{-1}**	**References**
MoS_2	16.0	23.8	2.1×10^{-5}	[3]
WS_2	14.5	21.3	1.5×10^{-3}	[3]
$W_{0.4}Mo_{0.6}S_2$	11.5	13.3	1.1×10^3	[3]
Mn-MoS_2	10.6	10.8	7.74×10^4	[4]
$MoTe_2$	6.07	5.29	8.22×10^8	This work

S3 HOMO-LUMO Calculations

Our present calculations using 2D single-layer $MoTe_2$ reveal the low energy barriers of the Vollmer-Heyrovsky phases in HER, which are expected to be a good candidate as electrocatalysts in HER. To further support the development of our $MoTe_2$ molecular cluster model system, we apply natural bond orbital (NBO), HOMO, and LUMO calculations by the same DFT analysis. HOMO-LUMO energy is the most famous quantum mechanics parameter, and it plays an essential role in controlling a wide range of chemical interactions. NBO calculations can detect the structure with the largest electron charge in the Lewis orbital. This NBO study explains the wave function's density of interaction or overlaps. The wave function calculated from the NBO is a linear combination of the atomic orbitals of the Te, Mo, and H atoms of the Volmer energy barrier and the atomic orbitals of the Te, Mo, H, and O atoms of the Heyrovsky energy barrier. Understanding the Highest Occupied Molecular Orbitals (HOMO) and Lowest Unoccupied Molecular Orbitals (LUMO) computation for the Vollmer and Heyrovsky transition state has been performed using the same DFT method as shown in Figure S2, where the red color indicates the in-phase bonding and blue color represents the out-of-phase bonding of the orbital. These calculations of the Heyrovsky transition TS2 can better explain the Heyrovsky mechanism of effective HER from the perspective of the charge cloud and molecular orbital overlap during the formation of H_2.

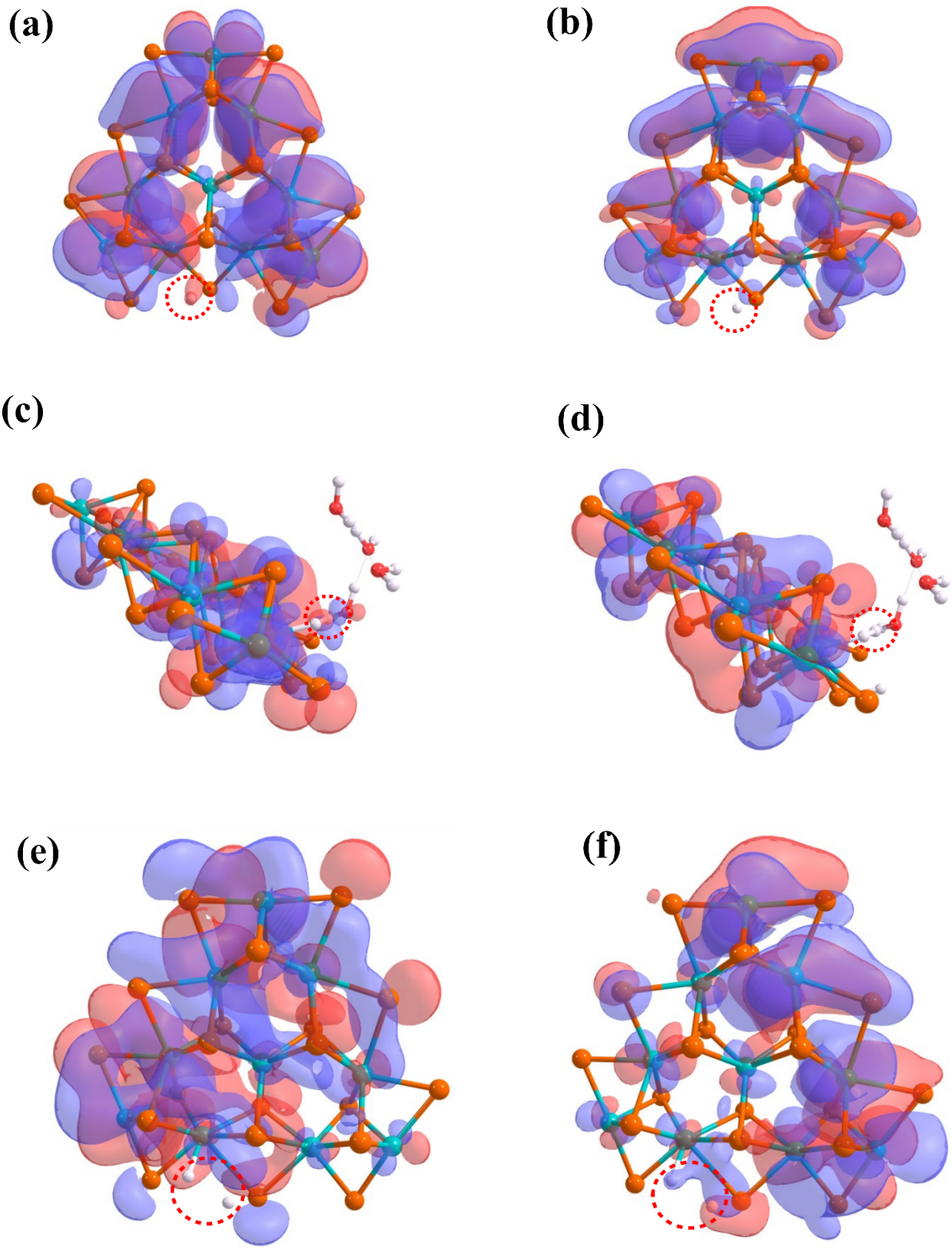
(a)
(b)
(c)
(d)
(e)
(f)

Figure S2 The equilibrium structure of $MoTe_2$ (a) The HOMO of Volmer TS; (b) The LUMO of Volmer TS; (c) The HOMO of Heyrovsky TS; (d) The LUMO of Heyrovsky TS; (e) The HOMO of Tafel TS; (f) The LUMO of Tafel TS is shown here.

The energy difference between the HOMO and LUMO studies provides stability to the molecule. The potentials of the electron donor and acceptor units are explained by the HOMO energy and the LUMO energy, respectively. This study found that TS1 and TS2 in the case of 2D $MoTe_2$ are reduced by the overlap of ***s*** orbitals of H and ***d*** orbitals of Mo metal atoms, as shown in Figure S2(a-d). Figure S2(a-b) indicates the HOMO and LUMO of the Volmer transition state of 2D $MoTe_2$, respectively. The electron cloud between the H atom and Mo metal atom in the Volmer transition state structure highlighted by the red dotted circle is the 2D $MoTe_2$ TMD structure in the Volmer step of H* migration. The electron cloud between the H atom and Mo metal atom in the Volmer transition state structure highlighted by the red dotted circle is the 2D $MoTe_2$ TMD structure in the Volmer step of H* migration. The energy values of HOMO and LUMO of Volmer TS are found to be E_{HOMO}=-2.18 eV and E_{LUMO}=-2.10 eV, respectively. So, the energy difference between HOMO and LUMO of Volmer TS is found to be E_{GAP}= E_{LUMO} - E_{HOMO}= 0.075 eV, so it means this is the energy required for an electron to transition from HOMO to LUMO. The electron cloud between two H atoms in the Heyrovsky transition state structure highlighted by the red dotted circle is the 2D $MoTe_2$ TMD structure in the presence of four water molecules in the Heyrovsky step of H_2 evolution, as shown in Figures S2 c and d. So, the Heyrovsky reaction is performed by overlapping the atomic orbitals of two H atoms with adjacent hydrated hydrogen (H_3O^+) in the water cluster to form H_2 molecules during the HER process. Figure S2 c-d indicates the HOMO and LUMO of the Heyrovsky transition state of 2D $MoTe_2$, respectively. The energy difference between HOMO and LUMO, also known as the HOMO–LUMO gap, is used to predict the HER's stability of transition metal-based electrocatalysts. The energy values of HOMO and LUMO of Heyrovsky TS are found to be E_{HOMO}=-6.90 eV and E_{LUMO}=-6.74 eV, respectively. So, the energy difference between HOMO and LUMO of Heyrovsky TS is found to be E_{GAP}= E_{LUMO} - E_{HOMO}= 0.16 eV, so it means this is the energy required for an electron to transition from HOMO to LUMO. This is also another reason why the two-dimensional monolayer $MoTe_2$ shows excellent HER activity. To better visualize the Tafel reaction mechanism, a HOMO-LUMO calculation was also performed, shown in Figures S2(b) and S2(c). The electron cloud uses red and blue to represent the positive

and negative parts of the wave function. A red dotted circle highlights the electron cloud around hydrogen in the HOMO-LUMO. The phase or orbit is the direct result of the wave-like characteristics of electrons. Usually, in-phase mixing indicates a low energy state, and out-of-phase mixing indicates an anti-bonding orbital or higher energy state. The HOMO and LUMO of Heyrovsky TS energy values are E_{HOMO}=-4.80 eV and E_{LUMO}=-4.66 eV, respectively. So, the energy difference between HOMO and LUMO of Tafel TS is found to be E_{GAP}= E_{LUMO} - E_{HOMO}= 0.14 eV, so it means this is the energy required for an electron to transition from HOMO to LUMO. The gentle orbital overlaps of the molecular orbitals during the H migration in the H*-migration reaction step and the H_2 formation in the Heyrovsky and Tafel reaction steps reveal the excellent electrocatalytic activity of the 2D monolayer $MoTe_2$ TMD for HER.

S4- Optimized Structure of Symmetric 2D $MoTe_2$ TMD (.cif format)

```
_cell_length_a                    3.403393
_cell_length_b                    3.403393
_cell_length_c                    20.000000
_cell_angle_alpha                  90.000000
_cell_angle_beta                   90.000000
_cell_angle_gamma                  120.000000
_symmetry_space_group_name_H-M        'P 1'
_symmetry_Int_Tables_number           1

loop_
_symmetry_equiv_pos_as_xyz
  'x, y, z'
```

loop_

_atom_site_label

_atom_site_type_symbol

_atom_site_fract_x

_atom_site_fract_y

_atom_site_fract_z

MO001 MO -0.333333 0.333333 0.000000

TE002 TE 0.333333 -0.333333 -0.089661

TE003 TE 0.333333 -0.333333 0.089661

S5- Optimized Geometries of Non-periodic Relevant Structures in gas phase

The optimized geometries of various intermediates and the transition structure resulting in the proposed HER mechanism are listed below in .xyz file format.

- **[MoTe2]**

E= -845.885106 Hartree, G= -845.965044 Hartree, H= -845.794640 Hartree

Mo -0.52821 -0.01321 0.08021

Te -0.49452 -0.01846 2.69606

Mo 2.10842 -0.03243 1.53369

Te 2.60985 -0.91272 4.07291

Mo 5.02354 -0.02323 3.14735

Te 5.42300 -0.00361 5.96962

Mo 7.65677 0.01300 4.60772

Te	- 0.90158	0.46261	-2.48648
Te	0.94394	2.15927	0.21899
Te	1.18146	-1.98217	-0.17468
Mo	1.73582	0.29901	-1.64580
Te	3.90983	1.97224	1.70702
Te	4.18116	-1.81274	1.23863
Mo	4.97664	0.33120	-0.21331
Te	6.74365	2.17828	3.43122
Te	6.97353	-1.96271	3.02863
Mo	7.91302	0.32119	1.77237
Te	2.39195	0.54368	-4.37100
Te	3.78587	2.17765	-1.83420
Te	3.99147	-1.26543	-2.20251
Mo	5.12865	0.73100	-3.80749
Te	6.97170	2.18906	-0.06951
Te	7.19487	-1.25319	-0.42999
Mo	7.93921	0.74123	-2.25230
Te	10.02633	0.50053	3.55686
Te	5.45863	1.11890	-6.53044
Te	6.77285	2.89615	-3.47349
Te	7.02629	-1.24010	-3.90631
Mo	7.68386	1.02668	-5.11028
Te	9.87097	0.57485	-0.23428

Te 10.06905 1.13087 -3.98108

- **$[MoTe2]^{-1}$**

E= -846.015966 Hartree, G= -846.097228 Hartree, H= -845.925586 Hartree

Mo 0.01473 -0.01213 0.01045

Te 0.01456 0.01548 2.62884

Mo 2.62315 0.01167 1.47318

Te 3.12010 -0.91042 4.01327

Mo 5.53220 0.05053 3.13472

Te 5.84981 0.09137 5.98154

Mo 8.09169 0.09872 4.63086

Te -0.38459 0.39151 -2.55448

Te 1.44954 2.19133 0.13513

Te 1.73995 -1.96777 -0.23398

Mo 2.28780 0.32334 -1.70360

Te 4.41473 2.02351 1.67020

Te 4.73198 -1.74405 1.21094

Mo 5.51887 0.39311 -0.23755

Te 7.24495 2.29110 3.44764

Te 7.50141 -1.91625 3.06272

Mo 8.38557 0.39683 1.79699

Te	2.93397	0.59665	-4.40421
Te	4.32750	2.22141	-1.87627
Te	4.56892	-1.21337	-2.23352
Mo	5.70500	0.78088	-3.83708
Te	7.49024	2.27718	-0.05777
Te	7.74063	-1.19366	-0.41198
Mo	8.47850	0.80774	-2.22070
Te	10.49698	0.44248	3.65130
Te	6.03640	1.13889	-6.55233
Te	7.34189	2.96289	-3.46338
Te	7.63005	-1.18285	-3.89313
Mo	8.26250	1.09327	-5.09816
Te	10.37965	0.69214	-0.13876
Te	10.63155	1.14919	-3.90980

- **[MoTe2]H_{Te}**

E= -846.457231 Hartree, G= -846.532156 Hartree, H= -846.359593 Hartree

Mo	0.00338	0.06559	0.01866
Te	0.06305	0.29105	2.64107
Mo	2.58770	0.04943	1.40416
Te	3.12392	-1.21479	3.90235

Mo	5.56555	0.05298	3.11057
Te	5.71313	0.38390	5.89833
Mo	8.02276	0.10667	4.63720
Te	-0.39043	0.46144	-2.55108
Te	1.46884	2.25476	0.05494
Te	1.68677	-1.93083	-0.29988
Mo	2.27571	0.35740	-1.72620
Te	4.38350	2.02913	1.70694
Te	4.72235	-1.74938	1.15637
Mo	5.51613	0.38834	-0.22721
Te	7.28383	2.29512	3.37268
Te	7.51434	-1.93598	3.04776
Mo	8.36960	0.36534	1.78741
Te	2.91741	0.65249	-4.40773
Te	4.34873	2.22924	-1.87401
Te	4.55497	-1.18072	-2.26220
Mo	5.70888	0.80448	-3.85025
Te	7.49536	2.26070	-0.06974
Te	7.73139	-1.20562	-0.44301
Mo	8.47088	0.79722	-2.23345

Te	10.44149	0.43115	3.63197
Te	6.01768	1.18972	-6.54108
Te	7.36130	2.97109	-3.46976
Te	7.61134	-1.17687	-3.91891
Mo	8.26712	1.09972	-5.10906
Te	10.36957	0.63928	-0.16001
Te	10.62641	1.13406	-3.90915
H	2.46268	-0.14005	4.99512

- **$[MoTe2]H_{Te}^{-1}$**

E= -846.577657 Hartree, G= -846.651782 Hartree, H= -846.480228 Hartree

Mo	0.01845	-0.00155	0.04124
Te	0.02158	0.07292	2.67785
Mo	2.55201	0.01832	1.40401
Te	3.13419	-1.45541	3.79544
Mo	5.50836	0.03230	3.17880
Te	5.56923	0.10722	6.01023
Mo	7.89959	0.03650	4.77549
Te	-0.34770	0.52551	-2.51715
Te	1.32237	2.29013	0.23112
Te	1.76302	-1.90701	-0.47017

Mo	2.29403	0.55394	-1.62464
Te	4.23044	2.06280	1.94076
Te	4.78009	-1.64447	1.05584
Mo	5.46946	0.64009	-0.10851
Te	7.10574	2.31762	3.70037
Te	7.54690	-1.88116	3.00504
Mo	8.29788	0.57977	1.98056
Te	2.96705	1.12319	-4.28120
Te	4.23733	2.56486	-1.60529
Te	4.64857	-0.81328	-2.28529
Mo	5.70506	1.37131	-3.64196
Te	7.35668	2.57926	0.26610
Te	7.78428	-0.80131	-0.40253
Mo	8.47031	1.38162	-1.98168
Te	10.32669	0.57529	3.89301
Te	6.10453	1.95194	-6.30591
Te	7.22348	3.58200	-3.05292
Te	7.71828	-0.47553	-3.85050
Mo	8.29288	1.92508	-4.82223
Te	10.32269	1.15290	0.13502

Te	10.63067	1.96816	-3.58818
H	2.40874	-0.53530	4.98848

- **H*-Migration Transition state from [MoTe2]H_{Te}^{-1} to [MoTe2]H_{Mo}^{-1}**

E= -846.562517 Hartree, G= -846.638289 Hartree, H= -846.467192 Hartree

Mo	-0.00366	0.00637	-0.09740
Te	-0.14420	-0.26392	2.49340
Mo	2.54554	0.00108	1.43121
Te	3.13551	-1.37808	3.85202
Mo	5.49955	0.02313	3.09397
Te	5.55798	0.03742	5.95460
Mo	7.88690	-0.01605	4.72080
Te	-0.33744	0.63888	-2.61095
Te	1.27422	2.27829	0.32077
Te	1.78846	-1.85521	-0.53375
Mo	2.29691	0.65284	-1.63661
Te	4.19978	2.08416	1.94958
Te	4.76099	-1.61800	0.98110
Mo	5.46225	0.70434	-0.11844
Te	7.09279	2.28641	3.69180
Te	7.52721	-1.91138	2.92880

Mo	8.27890	0.57158	1.94146
Te	2.96014	1.29488	-4.27553
Te	4.22027	2.67263	-1.55837
Te	4.64570	-0.69260	-2.33538
Mo	5.68824	1.53700	-3.63650
Te	7.35286	2.62749	0.29178
Te	7.76232	-0.75031	-0.47112
Mo	8.44807	1.48046	-1.99078
Te	10.31477	0.52605	3.85433
Te	6.07385	2.19664	-6.28450
Te	7.21160	3.72360	-2.98522
Te	7.69317	-0.31124	-3.91861
Mo	8.26891	2.12064	-4.81071
Te	10.30419	1.17111	0.10964
Te	10.60793	2.12015	-3.57867
H	2.29688	0.13540	3.77774

- **[MoTe2]H_{Mo}^{-1}**

E= -846.562517 Hartree, G= -846.668079 Hartree, H= -846.497697 Hartree

Mo	-0.01730	0.05088	-0.15589
Te	-0.15168	-0.56785	2.36033

Mo	2.55556	0.07301	1.47680
Te	3.06649	-1.02821	3.99305
Mo	5.37533	0.02450	3.15955
Te	5.75328	-0.35118	6.04141
Mo	7.95505	-0.00692	4.70015
Te	-0.33136	0.50276	-2.69437
Te	1.26361	2.28179	0.32704
Te	1.78552	-1.82493	-0.53245
Mo	2.29939	0.65693	-1.67255
Te	4.23276	2.14198	1.91620
Te	4.70319	-1.58870	1.04644
Mo	5.44312	0.72957	-0.10762
Te	7.02993	2.25315	3.74414
Te	7.45018	-1.86535	2.91585
Mo	8.26957	0.60170	1.92587
Te	2.97208	1.30434	-4.29345
Te	4.21186	2.68713	-1.58212
Te	4.64277	-0.69403	-2.32128
Mo	5.69692	1.52422	-3.64252
Te	7.34878	2.65550	0.28419

Te	7.73388	-0.73667	-0.46133
Mo	8.44393	1.48460	-1.99537
Te	10.35675	0.47214	3.80236
Te	6.08598	2.16692	-6.29431
Te	7.21012	3.71567	-3.00573
Te	7.70084	-0.32662	-3.91165
Mo	8.27886	2.09974	-4.81793
Te	10.28946	1.19150	0.10757
Te	10.61298	2.10765	-3.57562
H	1.92538	1.03512	2.76433

- **[MoTe2]$H_{Mo}H_{Te}$**

E= -847.043392 Hartree, G= -847.109235 Hartree, H= -846.937694 Hartree

Mo	-0.06905	0.12979	-0.17070
Te	-0.23570	-0.59305	2.31499
Mo	2.48703	0.03251	1.49677
Te	3.07517	-1.39217	3.88815
Mo	5.42143	0.00605	3.17914
Te	5.67471	-0.08744	5.99913
Mo	7.97862	-0.06853	4.73571
Te	-0.28626	0.43377	-2.75872

Te	1.28690	2.28126	0.41110
Te	1.73619	-1.75923	-0.52398
Mo	2.26937	0.70177	-1.66428
Te	4.24570	2.05729	1.93485
Te	4.67166	-1.61645	1.03010
Mo	5.41975	0.70088	-0.13428
Te	7.07865	2.20831	3.74484
Te	7.41487	-1.86598	2.91414
Mo	8.31418	0.56685	1.95081
Te	2.99912	1.41393	-4.29844
Te	4.21094	2.70461	-1.54344
Te	4.59837	-0.68090	-2.33962
Mo	5.69317	1.54740	-3.62402
Te	7.32961	2.59710	0.30959
Te	7.73009	-0.75447	-0.44966
Mo	8.43869	1.47881	-1.99021
Te	10.35464	0.62375	3.81323
Te	6.10026	2.16577	-6.30066
Te	7.22769	3.73509	-2.99165
Te	7.67971	-0.32858	-3.90331

Mo	8.26183	2.09739	-4.79039
Te	10.30752	1.22117	0.05932
Te	10.61684	2.09070	-3.60367
H	1.90454	0.93896	2.83356
H	2.46884	-0.39186	5.07934

- **[MoTe2]$H_{Mo}H_{Te}$+3H_2O+H_3O^+**

E= -1153.159169 Hartree, G= -1153.127269 Hartree, H= -1152.931995 Hartree

Mo	0.60738	1.80036	-0.61734
Te	0.55613	2.27275	1.95213
Mo	3.16079	1.32457	0.99894
Te	3.48852	0.72942	3.76532
Mo	6.04052	0.74062	2.58038
Te	6.66355	1.62155	5.22847
Mo	8.59029	0.22378	4.10686
Te	0.14606	1.24795	-3.11694
Te	2.76294	3.22854	-0.97520
Te	1.46166	-0.63175	-0.09659
Mo	2.72517	0.70986	-2.16410
Te	5.62031	2.38103	0.50962
Te	4.43215	-1.13690	1.28946

Mo	5.82897	-0.02341	-0.72867
Te	8.48174	2.09542	2.24507
Te	7.07829	-1.71911	3.22437
Mo	8.69824	-0.48717	1.33679
Te	3.21142	-0.07939	-4.80758
Te	5.28621	1.56575	-2.88305
Te	4.18615	-1.67657	-2.14128
Mo	5.85585	-0.83139	-4.21967
Te	8.37300	0.91588	-1.05444
Te	7.30924	-2.29664	-0.29032
Mo	8.57679	-1.38280	-2.61772
Te	10.86966	-0.55114	3.03117
Te	6.02880	-1.54387	-6.87144
Te	8.20403	0.55267	-4.51966
Te	6.88738	-3.29399	-3.59416
Mo	8.22205	-1.93043	-5.42756
Te	10.48471	-1.53849	-0.59343
Te	10.53615	-2.43820	-4.26487
H	3.25463	2.82613	1.83921
H	3.42627	2.24525	4.49498

O	2.45658	4.98866	3.36616
H	1.88629	4.22020	3.15033
H	3.38758	4.64779	3.48939
O	2.58983	6.47309	1.46860
H	2.34805	7.39450	1.61714
H	2.46531	5.72462	2.46787
O	5.05061	4.36713	3.43565
H	5.53373	4.56708	4.24942
H	5.40236	5.46194	1.83708
O	5.14230	6.09682	1.14720
H	5.60178	5.83587	0.34305
H	3.55546	6.43121	1.20041
H	5.26574	3.42332	3.26316

- **Hydronium water cluster ($3H_2O\_H_3O^+$)**

E= -306.0813535 Hartree, G= -306.008336 Hartree, H= -305.961126 Hartree

O	-0.00143	0.00246	0.00670
H	-0.00357	0.01087	0.96979
H	0.92276	-0.00206	-0.26268
O	-2.05417	0.91395	-1.31507
H	-1.90028	1.79847	-1.66583
H	-1.23663	0.58941	-0.83408
O	-2.05143	-2.44733	-4.05789

H	-2.03667	-2.46012	-5.02082
H	-2.82698	-1.29537	-3.25258
O	-3.27466	-0.52471	-2.79352
H	-4.13495	-0.79766	-2.45516
H	-2.62970	0.16437	-2.05357
H	-1.92529	-3.35800	-3.77241

- **Heyrovsky TS2 from [MoTe2]$H_{Mo}H_{Te}$+3H_2O+H_3O^+**

E= -1153.141429 Hartree, G= -1153.113174 Hartree, H= -1152.917149 Hartree

Mo	0.04018	0.12665	-0.58706
Te	-0.13720	0.45071	1.98402
Mo	2.62114	0.27087	1.02133
Te	3.17980	-0.45250	3.75225
Mo	5.62485	0.34415	2.54396
Te	6.02398	1.29472	5.19906
Mo	8.21764	0.43672	4.02663
Te	-0.27996	-0.54287	-3.09037
Te	1.77919	2.03472	-0.95723
Te	1.49779	-2.01549	-0.13787
Mo	2.35554	-0.37431	-2.18733
Te	4.78970	1.87718	0.50281
Te	4.51723	-1.78866	1.15668
Mo	5.57343	-0.34102	-0.83382

Te	7.64139	2.27779	2.21925
Te	7.24606	-1.80311	3.07886
Mo	8.47699	-0.14039	1.22942
Te	2.97626	-0.94113	-4.86218
Te	4.60742	1.12600	-2.92029
Te	4.36926	-2.32221	-2.26064
Mo	5.73474	-1.02256	-4.32191
Te	7.79914	1.21307	-1.12211
Te	7.56890	-2.19357	-0.45290
Mo	8.53472	-0.92305	-2.75389
Te	10.60902	0.29040	2.91699
Te	6.04710	-1.59041	-6.99607
Te	7.65794	0.91118	-4.59002
Te	7.36136	-3.16487	-3.78498
Mo	8.28709	-1.45707	-5.57951
Te	10.44663	-0.65991	-0.73445
Te	10.67159	-1.39636	-4.44506
H	2.19726	1.83606	1.88569
H	2.72489	0.91546	4.59844
O	1.22252	4.59725	1.47937

H	0.28342	4.43115	1.60736
H	1.48678	5.18699	2.19680
O	3.23434	5.30903	-0.28615
H	3.21585	5.98129	-0.97283
H	2.31034	5.14512	-0.02980
O	3.28123	3.08853	3.38542
H	4.12653	2.66073	3.63648
H	3.51385	3.97292	2.98209
O	3.78689	5.47117	2.35179
H	4.45217	6.06807	2.70436
H	3.81636	5.53645	1.37064
H	2.72957	2.29843	2.48868

- **$[MoTe2]H_{Te}^{+1}$**

E= -846.238742 Hartree, G= -846.312637 Hartree, H= -846.140974 Hartree

Mo	0.01445	-0.08630	0.10053
Te	0.26752	0.53720	2.65206
Mo	2.66777	-0.11373	1.35812
Te	3.29921	-0.95254	4.01588
Mo	5.77341	-0.08471	2.88037
Te	6.20991	0.59358	5.56533

Mo	8.39089	-0.00936	4.20788
Te	-0.46471	-0.00587	-2.49460
Te	1.65119	1.93985	-0.26551
Te	1.53149	-2.23889	0.02579
Mo	2.19431	-0.26315	-1.77398
Te	4.63625	1.72409	1.23692
Te	4.64602	-2.08529	1.28858
Mo	5.49803	-0.26937	-0.48345
Te	7.64907	1.99486	2.67426
Te	7.55397	-2.18339	2.97701
Mo	8.54161	-0.20452	1.33718
Te	2.70243	-0.52782	-4.51183
Te	4.37045	1.39128	-2.33394
Te	4.30538	-2.06342	-2.17451
Mo	5.49436	-0.43546	-4.11245
Te	7.62594	1.42172	-0.73788
Te	7.59236	-2.03247	-0.56491
Mo	8.37097	-0.40837	-2.70332
Te	10.73490	0.09510	2.99761
Te	5.67925	-0.42222	-6.85590

Te	7.30084	1.61825	-4.19794
Te	7.23468	-2.54484	-3.98451
Mo	7.98600	-0.54828	-5.55475
Te	10.39742	-0.45176	-0.73933
Te	10.42576	-0.37852	-4.52945
H	2.83924	0.37138	4.91588

- **Water cluster with hydrogen molecule ($4H_2O+H_2$)**

E= -306.901172 Hartree, G= -306.824977 Hartree, H= -306.775177 Hartree

O	-0.02286	-0.01018	0.06509
H	-0.11845	-0.24446	0.99090
H	0.95055	-0.03786	-0.09213
O	-0.69946	-2.00565	-1.64931
H	-1.23066	-1.58515	-2.32928
H	-0.56138	-1.29590	-0.97736
O	2.61292	-0.38408	-0.50015
H	3.00011	0.32153	-1.02329
H	2.48073	-1.11504	-1.14623
O	1.90444	-2.25396	-2.35249
H	2.15614	-3.16767	-2.20327
H	0.93085	-2.22841	-2.18726
H	2.90305	0.19516	-4.06357
H	2.67994	-0.44985	-3.75829

- **Tafel TS3**

E= -847.032343 Hartree, G= -847.099563 Hartree, H= -846.928387 Hartree

Mo	0.02661	-0.18385	-0.32294
Te	-0.19663	-0.21818	2.27563
Mo	2.44128	0.01173	1.29207
Te	3.37240	-0.00629	4.33030
Mo	6.00411	-0.01817	3.20907
Te	6.67408	-0.22984	5.90039
Mo	8.70596	0.01490	4.23389
Te	-0.09255	-0.77282	-2.86591
Te	1.55738	1.93325	-0.44518
Te	1.58197	-2.29172	-0.06132
Mo	2.51453	-0.27610	-1.84271
Te	4.64295	1.70477	1.44909
Te	4.57799	-1.77852	1.60251
Mo	5.55149	-0.16731	-0.35738
Te	7.77445	2.02831	2.80702
Te	7.76020	-2.12036	2.97817
Mo	8.68020	-0.11685	1.36045
Te	2.73913	0.34067	-4.52146
Te	4.47021	1.64488	-2.03036
Te	4.42625	-2.15478	-1.90333

Mo	5.27816	-0.35488	-3.74649
Te	7.66645	1.54226	-0.64598
Te	7.62423	-1.93199	-0.47150
Mo	8.27726	-0.32356	-2.64822
Te	10.97420	-0.22386	2.92293
Te	5.38163	-0.80154	-6.55113
Te	7.07016	1.69174	-4.11698
Te	7.09872	-2.47714	-3.88592
Mo	7.73454	-0.46381	-5.45496
Te	10.42312	-0.19162	-0.80899
Te	10.22203	-0.68032	-4.57693
H	1.78612	1.42472	2.05205
H	2.65543	1.29293	3.54991

- **H_2**

E= -1.170264 Hartree, G= -1.171713 Hartree, H= -1.156918 Hartree

H	0.00000	0.00000	0.06943
H	0.00000	0.00000	0.81331

Table S2: Energy (E), Enthalpy (H) and Gibbs free energy (G) for different steps and transition states (TSs) during HER mechanism in the gas phase calculations are tabulated here.

Systems	Energy (E)	Enthalpy (H)	Gibbs free

	(in Hartree)	(in Hartree)	energy (G) (in Hartree)
$[MoTe_2]$	-845.855288	-845.794640	-845.965044
$[MoTe_2]^{-1}$	-845.986444	-845.925586	-846.097228
$[MoTe_2]H_{Te}$	-846.421000	-846.359593	-846.532156
$[MoTe_2]H_{Te}^{-1}$	-846.541708	-846.480228	-846.651782
TS1	-846.528370	-846.467192	-846.638289
$[MoTe_2]H_{Mo}^{-1}$	-846.558610	-846.497697	-846.668079
$[MoTe_2]H_{Mo}H_{Te}$	-846.999057	-846.937694	-847.109235
$[MoTe_2]H_{Mo}H_{Te}$+ $3H_2O$+H_3O^+	-1153.003936	-1152.931995	-1153.127269
TS2	-1152.989854	-1152.917149	-1153.113174
$[MoTe_2]H_{Te}^{+1}$	-846.202217	-846.140974	-846.312637
TS3	-846.989468	-846.928387	-847.099563

Tabel S3: Charge distribution and imaginary frequency count across intermediates and TSs in the HER mechanism.

Systems	Charge	No. of imaginary frequencies
$[MoTe_2]$	0	0
$[MoTe_2]^{-1}$	-1	0
$[MoTe_2]H_{Te}$	0	0
$[MoTe_2]H_{Te}^{-1}$	-1	0
TS1	-1	1 (-648.14 cm^{-1})
$[MoTe_2]H_{Mo}^{-1}$	-1	0
$[MoTe_2]H_{Mo}H_{Te}$	0	0
$[MoTe_2]H_{Mo}H_{Te}$+ $3H_2O$+H_3O^+	+1	0
TS2	+1	1 (-787.08 cm^{-1})
$[MoTe_2]H_{Te}^{+1}$	+1	0
TS3	0	1 (-516.07 cm^{-1})

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