

Supporting Information

Theoretical analysis of the reaction mechanism of D₂ gas generation using a Pd/C catalyst

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Table S1. Calculated natural atomic charges for D₂O and H₂/HD in H/D exchange reaction between D₂O and H₂/HD

	D ₂ O-H ₂				D ₂ O-HD			
	Reactant	Int. A	Int. B	Products	Reactant	Int. A	Int. B	Products
O1	-0.921	-0.903	-0.919	-0.937	-0.921	-0.903	-0.920	-0.938
D2	0.552	0.551	0.580	0.549	0.552	0.551	0.580	0.549
D3	0.551	0.556	0.574	0.133	0.551	0.556	0.573	0.138
H4	0.140	0.137	0.592	0.555	0.143	0.137	0.591	0.555
H5/D5	0.118	0.117	0.124	0.100	0.104	0.103	0.114	0.088
Pd ₂₂	-0.440	-0.458	-0.951	-0.400	-0.429	-0.444	-0.938	-0.392

Table S2. Cartesian coordinates of optimized geometries for compounds in H_2 dissociative adsorption reaction on the Pd_{22} cluster model

H_2

Atomic number	x	y	Z
46	-2.145440	2.507624	-0.61214
46	-0.054475	1.201176	-0.844705
46	-0.035646	3.644084	-0.673307
46	-2.237389	-2.465205	-0.597135
46	-0.138909	-3.613689	-0.702600
46	-0.081466	-1.209294	-0.842217
46	-4.249999	-1.202144	-0.597706
46	-4.189345	1.286432	-0.565408
46	-2.157707	0.010156	-0.825228
46	-3.501125	0.004783	1.339825
46	-1.464062	-1.222041	1.237160
46	-1.451202	1.230163	1.230472
46	2.036931	-0.005563	-0.836023
46	4.127179	-1.241823	-0.705962
46	4.164295	1.172247	-0.659156
46	2.085380	2.421709	-0.721004
46	0.595385	2.395411	1.271368
46	2.746778	1.164012	1.263843
46	2.013993	-2.438226	-0.747872
46	0.563736	-2.437663	1.267550
46	2.734452	-1.22502	1.232064
46	0.640370	-0.01665	1.199003
1	-0.476419	0.793942	-2.534587
1	0.396676	1.024005	-2.563166

TS

Atomic number	x	y	z
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46	-2.137956	2.500581	-0.607685
46	-0.044732	1.205168	-0.840505
46	-0.033339	3.643002	-0.67289
46	-2.229906	-2.456545	-0.610646
46	-0.133606	-3.612786	-0.694935
46	-0.076854	-1.204143	-0.839605
46	-4.243815	-1.191735	-0.621964
46	-4.188483	1.289031	-0.573256
46	-2.14559	0.017599	-0.828024
46	-3.506936	-0.002063	1.329765
46	-1.470233	-1.229581	1.235015
46	-1.46046	1.227767	1.238639
46	2.033698	-0.002852	-0.847347
46	4.124474	-1.238108	-0.69271
46	4.160203	1.177178	-0.660332
46	2.081932	2.427525	-0.726076
46	0.587461	2.397405	1.275727
46	2.732917	1.164612	1.254455
46	2.014622	-2.442149	-0.744013
46	0.552172	-2.439357	1.279233
46	2.720634	-1.223563	1.232629
46	0.631718	-0.019503	1.216118
1	0.076579	0.473175	-2.326934
1	1.399144	0.102591	-2.346395

H*H*

Atomic number	x	y	z
46	-2.131094	2.540678	-0.571769
46	-0.010567	1.280465	-0.821788
46	-0.039438	3.707404	-0.615142
46	-2.160443	-2.405754	-0.724200
46	-0.054165	-3.538456	-0.819437

46	-0.022230	-1.123789	-0.895034
46	-4.190000	-1.169575	-0.671632
46	-4.174985	1.314228	-0.580934
46	-2.111197	0.072539	-0.861145
46	-3.477852	-0.002942	1.297738
46	-1.443118	-1.227220	1.168027
46	-1.440945	1.232102	1.249355
46	2.080141	0.095981	-0.833490
46	4.177623	-1.124692	-0.662085
46	4.195391	1.290932	-0.635807
46	2.100260	2.526514	-0.688478
46	0.598622	2.416479	1.301337
46	2.739741	1.202437	1.257051
46	2.083519	-2.350799	-0.786561
46	0.583064	-2.427607	1.204021
46	2.746664	-1.188290	1.248033
46	0.650331	-0.006723	1.206906
1	-0.576687	0.687274	-2.227991
1	1.858586	-0.593576	-2.249288

Table S3. Cartesian coordinates of optimized geometries for compounds in H_2 dissociative adsorption reaction on the Pd_{22} cluster model

D₂O

Atomic number	x	y	z
46	-2.131445	2.550336	-0.629926
46	-0.078476	1.154235	-0.855727
46	0.032977	3.566459	-0.741457
46	-2.377883	-2.411154	-0.569063
46	-0.343833	-3.665874	-0.686303
46	-0.203614	-1.244303	-0.836602
46	-4.341909	-1.068928	-0.517147
46	-4.220400	1.417553	-0.569039
46	-2.226695	0.067947	-0.802468
46	-3.559007	0.175627	1.378147
46	-1.586887	-1.170452	1.259382
46	-1.451208	1.281221	1.225308
46	1.958392	-0.160163	-0.851766
46	4.005510	-1.478783	-0.701175
46	4.126275	0.930313	-0.726415
46	2.100211	2.261557	-0.774985
46	0.654659	2.366174	1.241521
46	2.737639	1.012437	1.220807
46	1.847923	-2.587485	-0.744123
46	0.379361	-2.473128	1.265623
46	2.601498	-1.378402	1.229200
46	0.574901	-0.060781	1.185050
8	-0.191374	-0.689881	-3.101351
1	0.645340	-0.173072	-2.990355
1	-0.917666	-0.030686	-2.974696

TS

Atomic number	x	y	z
46	-2.179502	2.477733	-0.725350
46	-0.091973	1.167340	-0.933391
46	-0.070408	3.602320	-0.859374
46	-2.258106	-2.488585	-0.477465
46	-0.184618	-3.666953	-0.615731
46	-0.141661	-1.243639	-0.821914
46	-4.282286	-1.233885	-0.485232
46	-4.222044	1.259152	-0.570110
46	-2.204684	-0.028796	-0.821020
46	-3.516777	0.058905	1.372695
46	-1.483537	-1.175659	1.315235
46	-1.460320	1.255316	1.152345
46	1.980633	-0.057021	-0.900673
46	4.079041	-1.300673	-0.767268
46	4.114845	1.113797	-0.816343
46	2.049219	2.367605	-0.895267
46	0.613554	2.438683	1.109054
46	2.744808	1.173799	1.142500
46	1.961766	-2.489696	-0.762192
46	0.538492	-2.401873	1.270736
46	2.708323	-1.213541	1.178448
46	0.624358	0.015490	1.155355
8	-1.026086	-1.198464	-2.740322
1	-0.251705	-0.972264	-3.299801
1	-0.752732	0.791670	-2.300221

OD*D

Atomic number	x	y	z
46	-2.108467	2.553132	-0.564218
46	-0.035067	1.193192	-0.794576
46	0.016463	3.691103	-0.706761

46	-2.255655	-2.434898	-0.612079
46	-0.182882	-3.626548	-0.674448
46	-0.097803	-1.214870	-0.777324
46	-4.259330	-1.152993	-0.555265
46	-4.157527	1.337599	-0.457611
46	-2.140929	0.043273	-0.747171
46	-3.571646	0.000536	1.433587
46	-1.518197	-1.273764	1.297926
46	-1.492541	1.234028	1.274520
46	2.035555	-0.030816	-0.799189
46	4.108357	-1.284057	-0.681984
46	4.177130	1.133837	-0.663585
46	2.103520	2.400810	-0.702076
46	0.582368	2.417920	1.290168
46	2.767498	1.150133	1.262055
46	1.973040	-2.460698	-0.688668
46	0.536720	-2.508083	1.338533
46	2.742302	-1.280134	1.280077
46	0.631910	-0.038885	1.221916
8	-2.558273	-1.166534	-2.507252
1	-0.115678	2.495095	-1.919190
1	-1.661093	-1.167311	-2.908122

Table S4. Cartesian coordinates of optimized geometries for compounds in H/D exchange reaction between D₂O and H₂/HD

D₂O-H₂ system

Reactants

Atomic number	x	y	z
46	-2.291443	2.520508	-0.459381
46	-0.159816	1.276056	-0.784725
46	-0.196799	3.679514	-0.513123
46	-2.259500	-2.435760	-0.679711
46	-0.147095	-3.545427	-0.870728
46	-0.147561	-1.121342	-0.890321
46	-4.298602	-1.216929	-0.554667
46	-4.311709	1.262287	-0.446105
46	-2.240566	0.053449	-0.765781
46	-3.550664	-0.057577	1.414388
46	-1.501355	-1.265376	1.212617
46	-1.518383	1.190935	1.315827
46	1.958338	0.094987	-0.864437
46	4.077918	-1.100239	-0.780702
46	4.061684	1.314106	-0.686610
46	1.947021	2.513491	-0.644756
46	0.518810	2.397390	1.384360
46	2.674415	1.178207	1.263170
46	1.980328	-2.337306	-0.879931
46	0.537195	-2.445620	1.146464
46	2.684929	-1.202469	1.154529
46	0.587092	-0.020108	1.182174
1	2.067966	0.555851	-2.803272
1	1.681964	-0.186009	-2.838482
8	-0.800247	-0.681789	-3.161640
1	-1.649457	-1.127970	-2.921028
1	-0.950288	0.268389	-2.929689

TS (Step 1)

Atomic number	x	y	z
46	-2.268795	2.533038	-0.503788
46	-0.146604	1.285374	-0.835754
46	-0.175569	3.692443	-0.554002
46	-2.269728	-2.419708	-0.695890
46	-0.160385	-3.530991	-0.872286
46	-0.138525	-1.115119	-0.919783
46	-4.302801	-1.188006	-0.600273
46	-4.292542	1.283445	-0.468995
46	-2.225151	0.063344	-0.803291
46	-3.528085	-0.055683	1.377554
46	-1.478100	-1.257922	1.183980
46	-1.500415	1.200839	1.269094
46	1.975032	0.107740	-0.915552
46	4.097272	-1.108189	-0.852072
46	4.078919	1.311771	-0.697944
46	1.964664	2.527740	-0.671275
46	0.524186	2.413648	1.353755
46	2.675667	1.193123	1.243660
46	1.974413	-2.339757	-0.927600
46	0.557813	-2.441338	1.134088
46	2.698417	-1.181714	1.082936
46	0.602571	-0.006607	1.145584
1	1.481615	0.747009	-2.331751
1	2.184897	-0.525299	-2.379659
8	-0.905038	-0.774387	-3.219565
1	-1.810739	-1.044384	-2.930216
1	-0.858817	0.190842	-3.012515

Int. A

Atomic number	x	y	z
46	-2.108630	2.517169	-0.753346
46	-0.013151	1.180755	-0.882637
46	0.009990	3.654651	-0.809760
46	-2.237528	-2.436104	-0.702412
46	-0.176599	-3.637213	-0.735925
46	-0.071220	-1.215573	-0.863878
46	-4.240991	-1.158624	-0.694484
46	-4.172363	1.333321	-0.718127
46	-2.136809	0.040753	-0.907293
46	-3.546404	0.089975	1.233770
46	-1.544520	-1.193922	1.167430
46	-1.490204	1.272242	1.150106
46	2.054521	-0.046296	-0.826427
46	4.187484	-1.328603	-0.591022
46	4.158644	1.098967	-0.515353
46	2.117154	2.386013	-0.686364
46	0.565184	2.420722	1.226134
46	2.673275	1.145200	1.347604
46	1.990763	-2.516245	-0.723497
46	0.459287	-2.440626	1.253865
46	2.647231	-1.250781	1.244719
46	0.574795	-0.018688	1.179401
1	-0.133838	2.440473	-2.068966
1	2.917893	-1.345339	-1.799662
8	-0.388050	-0.838393	-3.148717
1	-1.368336	-0.881840	-3.024316
1	-0.169495	0.122281	-3.038761

TS (Step 2)

Atomic number	x	y	z
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46	-2.165439	2.491613	-0.590425
46	-0.044620	1.204291	-0.792859
46	-0.071717	3.684345	-0.692790
46	-2.168931	-2.462596	-0.638967
46	-0.065288	-3.596148	-0.728326
46	-0.043855	-1.180409	-0.791280
46	-4.198526	-1.225943	-0.613680
46	-4.201379	1.260117	-0.581571
46	-2.128730	0.017323	-0.817350
46	-3.513741	-0.000186	1.336761
46	-1.482432	-1.235235	1.240628
46	-1.478842	1.227907	1.268135
46	2.055934	0.031394	-0.761582
46	4.156456	-1.190238	-0.605593
46	4.158026	1.225954	-0.560580
46	2.063359	2.454653	-0.668761
46	0.547853	2.427407	1.298673
46	2.701302	1.214679	1.332878
46	2.057892	-2.400695	-0.705257
46	0.558442	-2.426504	1.287553
46	2.719144	-1.185665	1.307549
46	0.613756	0.000493	1.278581
1	-0.108338	2.462622	-1.958398
1	1.851067	-0.358153	-2.307765
8	0.757620	-0.449247	-3.419436
1	0.338404	-1.293703	-3.106439
1	0.202416	0.258812	-2.985646

Int.B

Atomic number	x	y	z
46	-2.129268	2.404590	-0.719566
46	-0.015127	1.127191	-0.857784

46	-0.049246	3.592155	-0.818565
46	-2.128600	-2.541327	-0.575592
46	-0.021482	-3.673402	-0.593358
46	-0.003514	-1.267812	-0.752265
46	-4.165488	-1.323936	-0.590880
46	-4.161681	1.168926	-0.643547
46	-2.100066	-0.074361	-0.819947
46	-3.491423	-0.027738	1.320052
46	-1.446179	-1.242360	1.274761
46	-1.462552	1.223729	1.209558
46	2.080512	-0.030391	-0.771117
46	4.190414	-1.227948	-0.568110
46	4.185549	1.185231	-0.584846
46	2.090887	2.395026	-0.750505
46	0.558158	2.433633	1.209060
46	2.721666	1.228472	1.300127
46	2.103055	-2.460842	-0.616567
46	0.603203	-2.425018	1.372191
46	2.749892	-1.159549	1.340149
46	0.637954	0.008944	1.249327
1	-0.090293	2.001230	-2.233889
1	-0.032955	-1.226345	-2.903156
8	-0.670683	-0.543277	-3.351225
1	-1.534343	-0.709676	-2.795085
1	-0.353509	0.342886	-2.879994

TS (Step 3)

Atomic number	x	y	z
46	-2.170463	2.409814	-0.673955
46	-0.058490	1.134731	-0.855892
46	-0.085513	3.577506	-0.787459
46	-2.170244	-2.547243	-0.531984

46	-0.057843	-3.673640	-0.572536
46	-0.045325	-1.268743	-0.744164
46	-4.204632	-1.322528	-0.542603
46	-4.199482	1.168796	-0.591731
46	-2.140733	-0.076737	-0.794179
46	-3.504157	-0.032990	1.361018
46	-1.454230	-1.242330	1.297189
46	-1.470616	1.216048	1.228904
46	2.041494	-0.032416	-0.798969
46	4.153501	-1.227717	-0.622395
46	4.150427	1.184819	-0.645872
46	2.054330	2.395502	-0.772617
46	0.550654	2.423369	1.219611
46	2.715465	1.225282	1.261847
46	2.065666	-2.461187	-0.637057
46	0.599288	-2.424449	1.379672
46	2.745141	-1.164178	1.309845
46	0.632991	0.004797	1.238388
1	-0.056136	1.504553	-2.488938
1	0.185800	-1.266088	-3.009207
8	-0.55504	-0.676824	-3.358511
1	-1.352315	-0.965865	-2.811761
1	-0.282772	0.470465	-2.758362

Products

Atomic number	x	y	z
46	-2.118199	2.678408	-0.308908
46	-0.031799	1.380931	-0.667830
46	0.005629	3.785510	-0.322225
46	-2.228139	-2.278660	-0.739271
46	-0.143456	-3.436289	-0.982447
46	-0.081969	-1.014315	-0.866243

46	-4.231211	-1.004866	-0.592307
46	-4.173031	1.477232	-0.369865
46	-2.145153	0.217920	-0.724008
46	-3.492682	0.050224	1.434878
46	-1.475310	-1.199736	1.208967
46	-1.427573	1.247615	1.421044
46	2.045450	0.150307	-0.771994
46	4.129739	-1.110686	-0.736376
46	4.181533	1.287543	-0.498008
46	2.115716	2.556034	-0.447455
46	0.631251	2.393551	1.540643
46	2.762066	1.131823	1.421740
46	2.010431	-2.279276	-0.905563
46	0.539870	-2.426622	1.101943
46	2.716217	-1.249481	1.184813
46	0.642381	-0.008924	1.248134
1	-0.120944	2.125939	-2.552597
1	-0.386941	-1.889707	-3.120556
8	-0.657553	-0.934265	-3.173011
1	-1.594555	-0.927469	-2.847684
1	-0.071854	1.318467	-2.712424

D₂O-HD system

Reactants

Atomic number	x	y	z
46	-2.291437	2.520937	-0.458073
46	-0.159572	1.276711	-0.782814
46	-0.196778	3.680015	-0.510973
46	-2.258603	-2.435258	-0.680323
46	-0.146054	-3.544709	-0.870740
46	-0.146848	-1.120530	-0.889451
46	-4.297938	-1.216703	-0.556165

46	-4.311615	1.262621	-0.446825
46	-2.240197	0.054022	-0.765310
46	-3.551517	-0.057733	1.413701
46	-1.501819	-1.265331	1.212931
46	-1.519242	1.190924	1.317236
46	1.958580	0.095814	-0.861699
46	4.078307	-1.099302	-0.778596
46	4.061656	1.314681	-0.682482
46	1.947343	2.514100	-0.641207
46	0.517912	2.397574	1.386651
46	2.673968	1.178727	1.266818
46	1.981232	-2.336356	-0.878663
46	0.537186	-2.445025	1.146978
46	2.684939	-1.202129	1.156397
46	0.586514	-0.019794	1.183785
1	2.060732	0.544371	-2.819001
1	1.678753	-0.187578	-2.856946
8	-0.797196	-0.680455	-3.160175
1	-1.645852	-1.127736	-2.919338
1	-0.948278	0.269391	-2.927274

TS (Step 1)

Atomic number	x	y	z
46	-2.283664	2.535579	-0.493199
46	-0.162741	1.288695	-0.833396
46	-0.189247	3.694365	-0.554916
46	-2.285567	-2.416558	-0.690931
46	-0.177342	-3.529412	-0.871210
46	-0.155726	-1.111822	-0.922587
46	-4.318718	-1.184836	-0.583681
46	-4.307452	1.285429	-0.445145
46	-2.241513	0.066305	-0.794556

46	-3.534210	-0.058837	1.393982
46	-1.482715	-1.256796	1.186921
46	-1.509737	1.201051	1.276307
46	1.956290	0.111152	-0.924184
46	4.086646	-1.107947	-0.880455
46	4.062142	1.311200	-0.696914
46	1.949580	2.525174	-0.669856
46	0.514971	2.416513	1.353325
46	2.668611	1.196637	1.250539
46	1.956531	-2.335299	-0.941566
46	0.555539	-2.436867	1.127078
46	2.694641	-1.175409	1.063881
46	0.596837	-0.003002	1.140001
1	1.523409	0.629312	-2.385069
1	2.426410	-0.489970	-2.352008
8	-0.907263	-0.760674	-3.215638
1	-1.810927	-1.038241	-2.926816
1	-0.870612	0.205512	-3.011468

Int. A

Atomic number	x	y	z
46	-2.109835	2.516839	-0.753739
46	-0.013855	1.180680	-0.883504
46	0.009047	3.654247	-0.812557
46	-2.237645	-2.436339	-0.701571
46	-0.176689	-3.637392	-0.734862
46	-0.071773	-1.215508	-0.862922
46	-4.241478	-1.159413	-0.694539
46	-4.173292	1.332685	-0.717268
46	-2.137556	0.040339	-0.907067
46	-3.546517	0.088826	1.233998
46	-1.544310	-1.194006	1.168154

46	-1.490780	1.272255	1.149547
46	2.053994	-0.046209	-0.826271
46	4.186267	-1.328313	-0.592809
46	4.158328	1.099175	-0.515599
46	2.116948	2.386085	-0.686620
46	0.564415	2.421406	1.224795
46	2.673046	1.145841	1.347428
46	1.990128	-2.515988	-0.723656
46	0.459699	-2.440242	1.254670
46	2.647305	-1.250261	1.244521
46	0.574606	-0.017873	1.179332
1	-0.127643	2.441215	-2.060945
1	2.917128	-1.348678	-1.801279
8	-0.386938	-0.838021	-3.148030
1	-1.367577	-0.879659	-3.026066
1	-0.166939	0.122583	-3.041059

TS (Step 2)

Atomic number	x	y	z
46	-2.165378	2.491540	-0.590420
46	-0.044517	1.203890	-0.794058
46	-0.071260	3.683863	-0.696675
46	-2.168926	-2.462853	-0.639004
46	-0.065296	-3.596442	-0.727698
46	-0.043808	-1.180724	-0.791348
46	-4.198566	-1.226188	-0.614002
46	-4.201222	1.259909	-0.581230
46	-2.128714	0.016998	-0.817470
46	-3.513760	-0.000814	1.336754
46	-1.482363	-1.235530	1.240617
46	-1.478972	1.227558	1.267756
46	2.056142	0.031021	-0.761486

46	4.156544	-1.19081	-0.605089
46	4.158512	1.225271	-0.559758
46	2.064221	2.454227	-0.669337
46	0.547353	2.427843	1.296336
46	2.701000	1.214935	1.333113
46	2.057901	-2.400944	-0.704867
46	0.558635	-2.426268	1.287798
46	2.719085	-1.185379	1.307924
46	0.613611	0.000711	1.278240
1	-0.105540	2.463524	-1.950737
1	1.849576	-0.354611	-2.308406
8	0.756592	-0.448487	-3.419859
1	0.339521	-1.293788	-3.106232
1	0.199461	0.258434	-2.986808

Int. B

Atomic number	x	y	z
46	-2.130209	2.406722	-0.716560
46	-0.015271	1.130998	-0.856700
46	-0.050131	3.591962	-0.810797
46	-2.127679	-2.539288	-0.578153
46	-0.020219	-3.670646	-0.595407
46	-0.002809	-1.265108	-0.752987
46	-4.164660	-1.322309	-0.592597
46	-4.162203	1.170372	-0.643706
46	-2.099611	-0.071884	-0.820087
46	-3.491598	-0.027373	1.319235
46	-1.445916	-1.241755	1.273596
46	-1.462246	1.224180	1.210997
46	2.080671	-0.027163	-0.770602
46	4.190890	-1.224339	-0.568345
46	4.185280	1.188808	-0.582492

46	2.090548	2.398542	-0.745796
46	0.558149	2.434911	1.215237
46	2.721586	1.229459	1.302579
46	2.104085	-2.457870	-0.617957
46	0.603870	-2.424203	1.371239
46	2.750095	-1.158441	1.339939
46	0.638028	0.010185	1.249044
1	-0.090285	1.958192	-2.247087
1	-0.029353	-1.222075	-2.903333
8	-0.672269	-0.544220	-3.351835
1	-1.533839	-0.715655	-2.794627
1	-0.360025	0.346031	-2.883573

TS (Step 3)

Atomic number	x	y	z
46	-2.165378	2.491540	-0.590420
46	-0.044517	1.203890	-0.794058
46	-0.071260	3.683863	-0.696675
46	-2.168926	-2.462853	-0.639004
46	-0.065296	-3.596442	-0.727698
46	-0.043808	-1.180724	-0.791348
46	-4.198566	-1.226188	-0.614002
46	-4.201222	1.259909	-0.581230
46	-2.128714	0.016998	-0.817470
46	-3.513760	-0.000814	1.336754
46	-1.482363	-1.235530	1.240617
46	-1.478972	1.227558	1.267756
46	2.056142	0.031021	-0.761486
46	4.156544	-1.190810	-0.605089
46	4.158512	1.225271	-0.559758
46	2.064221	2.454227	-0.669337
46	0.547353	2.427843	1.296336

46	2.701000	1.214935	1.333113
46	2.057901	-2.400944	-0.704867
46	0.558635	-2.426268	1.287798
46	2.719085	-1.185379	1.307924
46	0.613611	0.000711	1.278240
1	-0.105540	2.463524	-1.950737
1	1.849576	-0.354611	-2.308406
8	0.756592	-0.448487	-3.419859
1	0.339521	-1.293788	-3.106232
1	0.199461	0.258434	-2.986808

Products

Atomic number	x	y	z
46	-2.122147	2.679865	-0.305835
46	-0.034654	1.384086	-0.666119
46	0.001354	3.787569	-0.316877
46	-2.229210	-2.277084	-0.73615
46	-0.144032	-3.433209	-0.981964
46	-0.084039	-1.010934	-0.864177
46	-4.232928	-1.004443	-0.587939
46	-4.176407	1.477823	-0.367643
46	-2.147752	0.219683	-0.722047
46	-3.493309	0.052592	1.437830
46	-1.475838	-1.197551	1.211388
46	-1.427958	1.249286	1.422505
46	2.043177	0.153892	-0.772021
46	4.128236	-1.106036	-0.737475
46	4.178881	1.292308	-0.500325
46	2.112162	2.559460	-0.446636
46	0.630850	2.395615	1.543527
46	2.762063	1.134717	1.421197
46	2.009147	-2.275467	-0.905641

46	0.539555	-2.424258	1.102692
46	2.715848	-1.246477	1.184345
46	0.642247	-0.006442	1.249518
1	-0.092284	2.099545	-2.575066
1	-0.378587	-1.887080	-3.119715
8	-0.661908	-0.935248	-3.171138
1	-1.598562	-0.940554	-2.844674
1	-0.063988	1.299549	-2.728168

Table S5. Cartesian coordinates of optimized geometries for compounds in D/H exchange reaction between HDO and D₂

HDO-D₂ system

Reactants

Atomic number	x	y	z
46	-2.293751	2.520315	-0.457465
46	-0.162283	1.275947	-0.782068
46	-0.199025	3.679298	-0.511175
46	-2.261176	-2.436094	-0.676596
46	-0.149046	-3.545980	-0.868556
46	-0.149774	-1.121681	-0.887438
46	-4.300516	-1.217672	-0.551526
46	-4.313832	1.262001	-0.444399
46	-2.243057	0.052973	-0.763381
46	-3.553345	-0.056976	1.416803
46	-1.503934	-1.265087	1.215904
46	-1.520825	1.191002	1.318172
46	1.955282	0.094702	-0.861592
46	4.074926	-1.100545	-0.779707
46	4.058475	1.313307	-0.685065
46	1.944908	2.513063	-0.642225
46	0.516929	2.397385	1.386409
46	2.672795	1.178154	1.265934
46	1.978201	-2.337553	-0.877779
46	0.534837	-2.445094	1.148381
46	2.683108	-1.203000	1.156422
46	0.584754	-0.020031	1.184478
1	2.076184	0.543212	-2.835306
1	1.690731	-0.175464	-2.872938
8	-0.787351	-0.681295	-3.154233
1	-1.639645	-1.128056	-2.926810
1	-0.939395	0.274417	-2.915803

TS (Step 1)

Atomic number	x	y	z
46	-2.272391	2.532187	-0.503081
46	-0.150468	1.284928	-0.836603
46	-0.179321	3.691918	-0.556374
46	-2.273622	-2.420294	-0.693158
46	-0.164741	-3.532123	-0.870105
46	-0.142565	-1.116094	0.919842
46	-4.306758	-1.188684	-0.595519
46	-4.296006	1.282456	-0.464371
46	-2.228932	0.062360	-0.801601
46	-3.529301	-0.056566	1.381330
46	-1.479149	-1.258126	1.185576
46	-1.502281	1.200493	1.269579
46	1.970879	0.106871	-0.920411
46	4.094517	-1.109665	-0.858314
46	4.074746	1.310546	-0.702053
46	1.960635	2.526639	-0.674129
46	0.522277	2.414226	1.351845
46	2.673848	1.193911	1.241376
46	1.970085	-2.340947	-0.929803
46	0.557059	-2.440997	1.133847
46	2.697075	-1.180469	1.078005
46	0.601274	-0.006082	1.143272
1	1.490493	0.732067	-2.334952
1	2.224260	-0.519233	-2.372110
8	-0.899302	-0.770314	-3.216051
1	-1.808173	-1.038241	-2.935327
1	-0.849967	0.200485	-3.002588

Int. A

Atomic number	x	y	z
46	-2.131304	2.410809	-0.712067
46	-0.017712	1.134191	-0.855823
46	-0.050194	3.592841	-0.806894
46	-2.132152	-2.536162	-0.577615
46	-0.025142	-3.668945	-0.596534
46	-0.006557	-1.263354	-0.752991
46	-4.168135	-1.317369	-0.589343
46	-4.164133	1.175591	-0.639033
46	-2.102666	-0.068074	-0.817928
46	-3.493004	-0.024095	1.322617
46	-1.447978	-1.239538	1.274068
46	-1.462669	1.226232	1.213822
46	2.077805	-0.026098	-0.772597
46	4.187461	-1.224909	-0.572828
46	4.183112	1.188272	-0.584443
46	2.089340	2.399515	-0.745288
46	0.558557	2.435462	1.218115
46	2.720943	1.228940	1.301916
46	2.099690	-2.457022	-0.620757
46	0.601337	-2.423290	1.370312
46	2.748528	-1.159236	1.336943
46	0.637011	0.010777	1.247461
1	-0.094172	1.928524	-2.262810
1	-0.005016	-1.210793	-2.936645
8	-0.663622	-0.545026	-3.349093
1	-1.513319	-0.745765	-2.785114
1	-0.361126	0.356553	-2.858228

TS (Step 2)

Atomic number	x	y	z
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46	-2.165957	2.490490	-0.591089
46	-0.046303	1.201688	-0.795422
46	-0.071414	3.681858	-0.700649
46	-2.172534	-2.464029	-0.635310
46	-0.069570	-3.598657	-0.724325
46	-0.046568	-1.183225	-0.790906
46	-4.201430	-1.226319	-0.610744
46	-4.202365	1.259834	-0.579153
46	-2.130853	0.015563	-0.816260
46	-3.514409	-0.000285	1.338926
46	-1.483382	-1.235357	1.242405
46	-1.479284	1.227669	1.267706
46	2.054029	0.027670	-0.764434
46	4.153780	-1.194706	-0.607912
46	4.156962	1.221384	-0.564127
46	2.063212	2.450856	-0.673729
46	0.547600	2.427237	1.293245
46	2.700846	1.213834	1.329754
46	2.054298	-2.404026	-0.704514
46	0.557054	-2.426862	1.289416
46	2.717895	-1.186674	1.306114
46	0.613033	0.000167	1.277052
1	-0.106028	2.460331	-1.953550
1	1.852097	-0.331517	-2.310137
8	0.767316	-0.439142	-3.417129
1	0.366570	-1.292731	-3.104664
1	0.195236	0.261836	-2.976512

Int. B

Atomic number	x	y	z
46	-2.131304	2.410809	-0.712067
46	-0.017712	1.134191	-0.855823

46	-0.050194	3.592841	-0.806894
46	-2.132152	-2.536162	-0.577615
46	-0.025142	-3.668945	-0.596534
46	-0.006557	-1.263354	-0.752991
46	-4.168135	-1.317369	-0.589343
46	-4.164133	1.175591	-0.639033
46	-2.102666	-0.068074	-0.817928
46	-3.493004	-0.024095	1.322617
46	-1.447978	-1.239538	1.274068
46	-1.462669	1.226232	1.213822
46	2.077805	-0.026098	-0.772597
46	4.187461	-1.224909	-0.572828
46	4.183112	1.188272	-0.584443
46	2.089340	2.399515	-0.745288
46	0.558557	2.435462	1.218115
46	2.720943	1.228940	1.301916
46	2.099690	-2.457022	-0.620757
46	0.601337	-2.423290	1.370312
46	2.748528	-1.159236	1.336943
46	0.637011	0.010777	1.247461
1	-0.094172	1.928524	-2.26281
1	-0.005016	-1.210793	-2.936645
8	-0.663622	-0.545026	-3.349093
1	-1.513319	-0.745765	-2.785114
1	-0.361126	0.356553	-2.858228

TS (Step 3)

Atomic number	x	y	z
46	-2.163338	2.414686	-0.672183
46	-0.049967	1.141194	-0.854583
46	-0.078860	3.583444	-0.779741
46	-2.158433	-2.542594	-0.547834

46	-0.044856	-3.666969	-0.583589
46	-0.034225	-1.261774	-0.748549
46	-4.194132	-1.319774	-0.559301
46	-4.192007	1.172154	-0.598742
46	-2.131570	-0.070792	-0.798424
46	-3.501962	-0.036529	1.351905
46	-1.450491	-1.243515	1.289162
46	-1.469008	1.215309	1.229088
46	2.051268	-0.024044	-0.790185
46	4.164198	-1.217139	-0.608429
46	4.158781	1.195185	-0.626557
46	2.062062	2.403745	-0.759528
46	0.550747	2.424638	1.225689
46	2.716533	1.229248	1.275656
46	2.078326	-2.452963	-0.634809
46	0.60389	-2.423168	1.374802
46	2.748408	-1.160164	1.318688
46	0.635334	0.006291	1.241118
1	-0.024560	1.468294	-2.487655
1	0.116576	-1.296546	-3.030628
8	-0.606377	-0.686562	-3.359643
1	-1.403576	-0.959865	-2.801395
1	-0.295998	0.440960	-2.766050

Products

Atomic number	x	y	z
46	-2.118795	2.680991	-0.302512
46	-0.032441	1.384392	-0.664252
46	0.004827	3.788302	-0.312337
46	-2.229711	-2.275749	-0.742131
46	-0.144608	-3.432124	-0.986023
46	-0.083032	-1.010720	-0.867296

46	-4.232410	-1.001620	-0.594300
46	-4.173703	1.480153	-0.366946
46	-2.146140	0.221224	-0.723083
46	-3.493346	0.049473	1.434987
46	-1.475660	-1.199874	1.207234
46	-1.428000	1.246714	1.424116
46	2.044477	0.153919	-0.770958
46	4.128775	-1.106652	-0.738216
46	4.180865	1.290961	-0.495116
46	2.115047	2.559239	-0.441643
46	0.630812	2.392423	1.546517
46	2.761670	1.131142	1.424368
46	2.009483	-2.275502	-0.908629
46	0.539637	-2.426766	1.099267
46	2.715972	-1.249577	1.183141
46	0.641973	-0.009376	1.249258
1	-0.102792	2.097153	-2.555318
1	-0.376055	-1.867261	-3.144100
8	-0.667499	-0.924678	-3.177286
1	-1.600502	-0.944005	-2.840352
1	-0.068929	1.289023	-2.715000