Metadynamics-biased ab initio Molecular Dynamics Study of Heterogeneous CO_2 Reduction via Surface Frustrated Lewis Pairs

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1. Background into Metadynamics

In order to investigate the reaction mechanism at finite temperature, we performed ab initio molecular dynamics (AIMD) on the Born Oppenheimer surface. The computationally expensive nature of these simulations restricts them to explore the system's dynamics over short durations only, and therefore AIMD alone is unable to capture full reactions of interest. This limitation is evaded by employing metadynamics (MetaD), a recently developed approach that applies a periodic bias to the system to encourage efficient, self-avoiding exploration of the free energy landscape[25,26]. MetaD has proven to be a useful tool for overcoming the sampling limitations of traditional molecular dynamics on complex molecular processes.[27-30] In this method, a history-dependent potential is added intermittently throughout the simulation to encourage efficient sampling of the associated free energy surface. The latter is defined over a set of collective variables (CVs), carefully selected to provide a complete description of the slow degrees of freedom of the system. The Helmholtz free energy surface corresponds to simulations carried out in the canonical ensemble (N,V,T) and therefore accounts for entropic contributions to the displacement of ions. The history-dependent bias takes the form of Gaussian functions to allow the system to escape beyond high energy barriers, thus allowing for faster sampling of the reaction surface. The sum of the deposited bias potentials may be used to reconstruct the free energy surface as shown here. The free energy surface *F(s)* can be written as

$$F(s) = -T\, lim_{t\to\infty}\, N(s,t) \quad (1)$$

where T is the temperature of the system and $N(s,t) = \int_0^t \delta_{s,s(t')} dt'$ is the histogram of the set of CVs s corresponding to the unbiased simulation. Here we employ well-tempered MetaD which includes an additional tuning parameter to represent the effective sampling temperature of the CV space.[25] In this method, the added Gaussian potentials are rescaled at each step to allow

for the net bias to converge more smoothly, and thus prevent the simulation from overfilling the free energy surface. The bias potential at time *t* takes the form:

$$V(s,t) = \Delta T ln\left[1 + \frac{\omega N(s,t)}{\Delta T}\right] \quad (2)$$

where *V(s,t)* is the bias potential defined over the set of CV coordinates *s*, where ΔT is a tuning parameter and ω is the initial bias deposition rate. The dynamics of the CVs approaches the thermodynamic equilibrium as the simulation proceeds such that their probability distribution in the long time limit ($t \rightarrow \infty$) becomes

$$P(s, t \rightarrow \infty) \propto e^{\frac{-F(s)}{k_B(T+\Delta T)}} \quad (3)$$

and the bias potential converges to

$$V(s, t \rightarrow \infty) = \frac{-T+\Delta T}{\Delta T} F(s) + C \quad (4)$$

where k_B is the Boltzmann constant and *C* is a nonphysical constant.[25] Introducing the tuning parameter ΔT limits the exploration of the free energy surface to physically interesting regions on the order of $T+\Delta T$, avoids the risk of overfilling the free energy surface, and guarantees convergence in the long time limit, making well-tempered MetaD a more effective method, operating between the limiting cases of standard MetaD and nonbiased sampling.[25]

2. Simulation Details

In order to capture the full reaction using a feasible amount of computational resources, separate simulations were carried out for each step of the mechanism; ie. H_2 dissociation, CO_2 reduction, and H_2O desorption. In the parameters described below, Sigma and Height refer to the width and height of the deposited gaussian potentials, and collective variables (CVs) refers to the defined quantities (ie. atomic distances, angles) used to define the free energy surface and/or the constraints on in the MetaD-biased AIMD simulations. The column MetaD refers to the CV(s) that were used to define the free energy surface. Constraints describe the upper and lower walls applied to the simulation, where ARG is the quantity subject to constraint, and KAPPA is the value of the force constant on the walls.

2.1 H_2 Dissocation

Table S1. Parameters for PLUMED plugin used in test simulations

Test #	Temp.	Timestep	CVs	MetaD	Sigma	Height	Constraints
1	400 K	1.25 fs	d1: DISTANCE ATOMS=2,3 d2: DISTANCE ATOMS=3,4	d1	0.02	0.01 eV	UPPER_WALLS ARG=d2 AT=1.1 KAPPA=150.0
2	400 K	1.25 fs	d1: DISTANCE ATOMS=2,3 d2: DISTANCE ATOMS=1,32	d1,d2	0.02, 0.02	0.005 eV	UPPER_WALLS ARG=d1 AT=2.888 KAPPA=150.0
3	293 K	0.8 fs	d1: DISTANCE ATOMS=1,2 c1: CENTER ATOMS=1,2 WEIGHTS=1,1 c2: CENTER ATOMS=3,32 WEIGHTS=1,1 d2: DISTANCE ATOMS=c1,c2	d1, d2	0.1,0.1	0.02 eV	Run 1: LOWER_WALLS ARG=d1 AT=0.74 KAPPA=400 UPPER_WALLS ARG=d2 AT=1 KAPPA=400 Run 2: LOWER_WALLS ARG=d1 AT=0.7 KAPPA=400 UPPER_WALLS ARG=d1 AT=0.76 KAPPA=400 LOWER_WALLS ARG=d2 AT=1.3 KAPPA=400

4	450 K	0.8 fs	d1: DISTANCE ATOMS=1,2 c1: CENTER ATOMS=1,2 WEIGHTS=1,1 c2: CENTER ATOMS=3,32 WEIGHTS=1,1 d2: DISTANCE ATOMS=c1,c2	d1, d2	0.1,0.1	0.02 eV	Run 1: LOWER_WALLS ARG=d1 AT=0.74 KAPPA=400 UPPER_WALLS ARG=d2 AT=1 KAPPA=400 Run 2: LOWER_WALLS ARG=d1 AT=0.7 KAPPA=400 UPPER_WALLS ARG=d1 AT=0.76 KAPPA=400 LOWER_WALLS ARG=d2 AT=1.3 KAPPA=400

After exploring different CV and PLUMED parameter choices (see Table S1), the following variables were selected for simulating the dissociation of H_2 over the $In_2O_{3-x}(OH)_y$ surface. The CVs used to define the free energy surface are shown in Figure S1; CV1 is defined as the distance from the In (In28) to the nearest H on the adsorbate H_2 molecule (H1), while CV2 is the distance from O on the surface hydroxyl group (O1) to H (H2) on the adsorbate H_2 molecule. No constraints were placed on the system in the first simulation, and bias potentials 0.1 eV in height were applied intermittently over the course of 640 fs. Based on the area of the free energy surface explored in the first simulation, three constraints were introduced to ensure exploration of the region relevant to the reaction: an upper wall limiting the distance from O1 to H2 to a maximum of 2 Å, a lower wall limiting the distance from H2 to In28 to a minimum of 1.8 Å, and another lower wall limiting the distance from H1 to H2 to a minimum of 0.74 Å. Gaussian bias potentials of height 0.05 eV were deposited over the course of 640 fs for the latter, at which point dissociation was visibly achieved. The free energy surface was generated by two separate simulations, both employing a tuning parameter of 7000, a bias factor of 6, Gaussian widths of 0.1, and bias potentials placed every 30 iterations. MetaD-biased AIMD simulations

were performed at 20 °C and 180 °C; plots of the simulation temperature over time are shown in Figure S2.

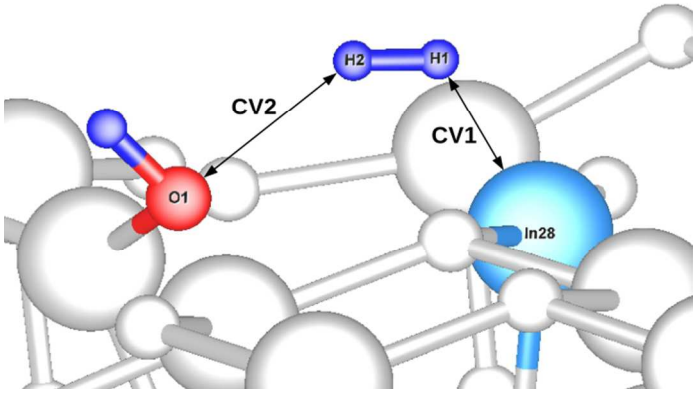

Figure S1: CVs used to define the free energy surface for H_2 dissociation over the $In_2O_{3-x}(OH)_y$ surface.

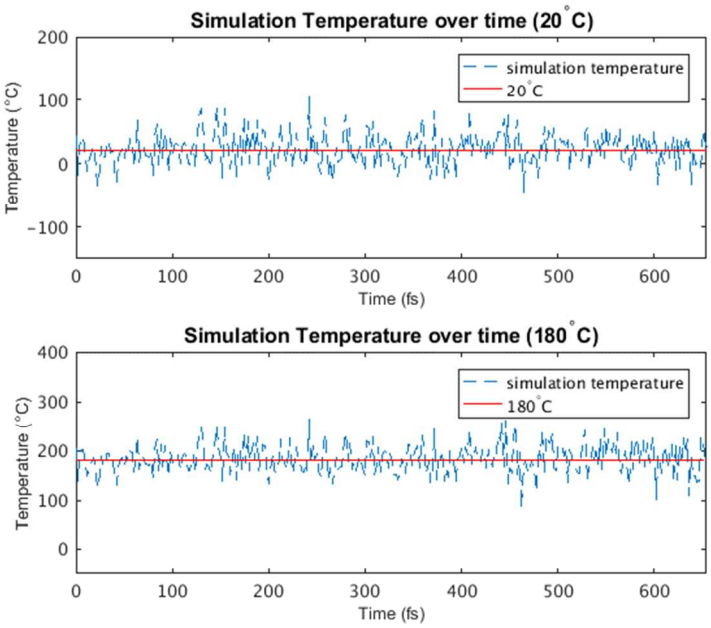

Figure S2: Simulation Temperature over time for of H_2 dissociation over the $In_2O_{3-x}(OH)_y$ surface.

Selecting the In-H1 distance, as well as the O-H2 distance allowed us to capture the H-H bond separation in a more reasonable amount of simulation time by guiding the reaction to the CV space most relevant to the adsorbate-surface interaction. The various H-H distances are still captured by the selected CVs whereas they ensure the molecule will interact with the surface and

adsorb to atoms which have been suggested to very likely participate in any dissociation from previous studies[19] as well as informed conjectures. It should be noted that selecting one set of CVS does not neglect any other possible CVs, some portion of the domain of almost all CVs is explored in the process of exploring other CVs' domain (as ultimately almost all CVs can be reduced to relationships based on atomic positions) and for such a simple variable as H-H distance most of the relevant distances would certainly be sampled. We provide further justification for our choice of CVs by performing the same calculation by taking the H-H distance as CV1, and the distance from the midpoint of the H1 and H2 atoms to the midpoint of the surface In and the O on surface bound hydroxyl group as CV2. PLUMED plugin parameters are provided in Table S1 and correspond to test simulations #3 and #4, for 20 °C and 180 °C, respectively. The collective variable definitions definitions are shown in Figure S3.

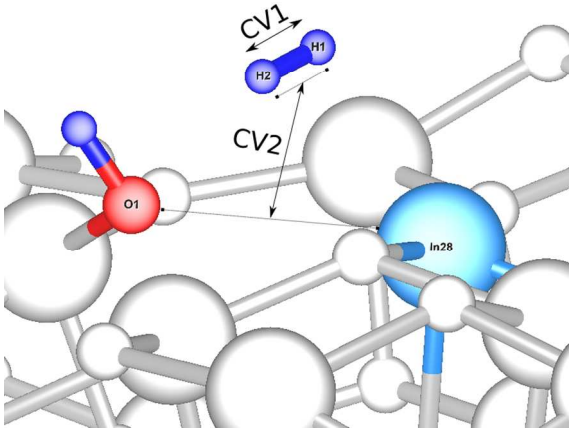

Figure S3: CV1 and CV2 used in MetaD-biased AIMD test simulations #3 and #4.

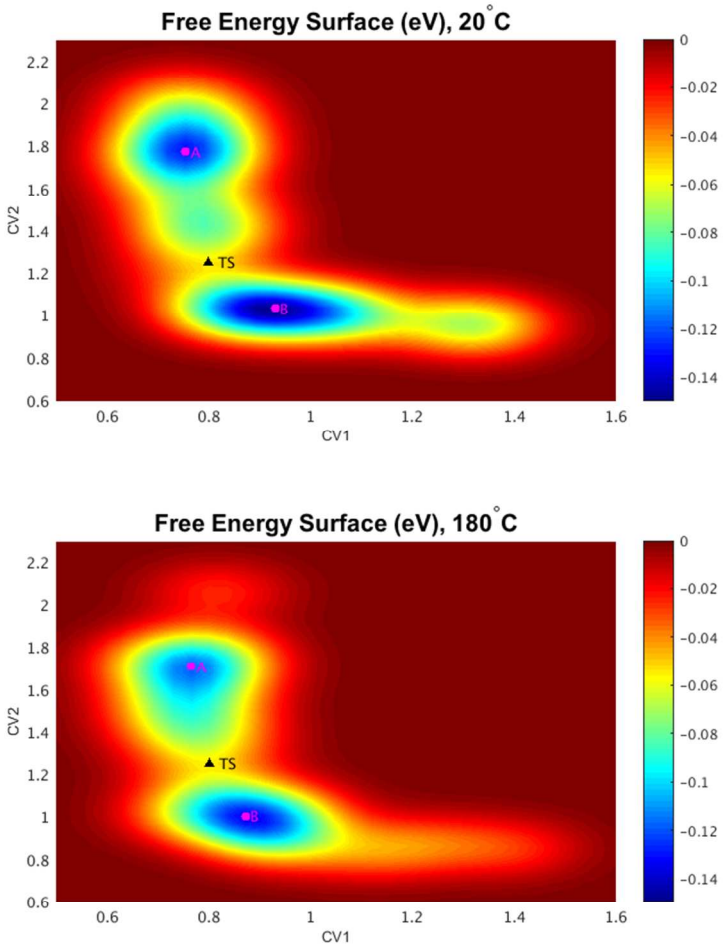

Figure S4: Free Energy surface for hydrogen dissociation over $In_2O_{3-x}(OH)_y$ at 20 °C (top) and 180 °C (bottom) generated from MetaD-biased AIMD test simulations #3 and #4.

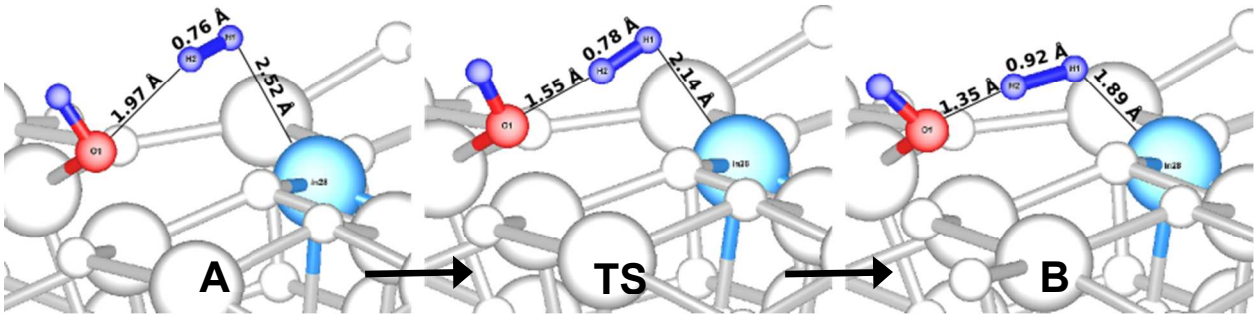

Figure S5: Atomic configurations corresponding to states A, TS, and B shown in the Free Energy surface in Figure S4.

The free energy surfaces are shown in Figure S4, with the reactant, transition, and product states indicated by points A, TS, and B, respectively; the atomic configurations corresponding to these states are shown in Figure S5. We find that this choice of collective variables instead favours exploration of the region of the Free Energy surface corresponding to adsorption of the H_2 molecule immediately prior to splitting. The H_2 molecule begins at a distance relatively far from the surface site, and then approaches the surface almost independently of the H1-H2 bond distance. The product state of the reaction, in which the In-H bond is 1.89 Å appears to coincide with the reactant state of the simulation carried out with our original choice of collective variables, in which H2 is already interacting with the surface In atom (In-H bond is 1.85 Å). These new results offer confirmation of our original choice of collective variables, as the O-H bond distance appears to be a significant quantity in driving the splitting of the H_2 molecule.

2.2 *CO_2 Adsorption and Dissociation*

Table S2: Parameters for PLUMED plugin used in test simulations

Test #	Temp.	Timestep	CVs	MetaD	Sigma	Height	Constraints
1	400 K	1.25 fs	c1: CENTER ATOMS=35,67 WEIGHTS=1,1 d1: DISTANCE ATOMS=c1,3	d1	0.02	0.005 eV	LOWER_WALLS ARG=d1 AT=1.1 KAPPA=150.0
2	400 K	0.766 fs	d1: DISTANCE ATOMS=2,3 d2: DISTANCE ATOMS=3,4	d1	0.02	0.033 eV	UPPER_WALLS ARG=d2 AT=1.1 KAPPA=150.0
3	400 K	0.766 fs	d1: DISTANCE ATOMS=2,3 d2: DISTANCE ATOMS=3,4	d1	0.02	0.01 eV	UPPER_WALLS ARG=d1 AT=2.888 KAPPA=150.0
4	520 K	1.25 fs	d1: DISTANCE ATOMS=2,3 d2: DISTANCE ATOMS=3,4	d1,d2	0.02, 0.02	0.1 eV	UPPER_WALLS ARG=d2 AT=1.0 KAPPA=150.0
5	520 K	0.8 fs	d1: DISTANCE ATOMS=2,3 d2: DISTANCE	d1,d2	0.02, 0.02	0.05 eV	UPPER_WALLS ARG=d2 AT=1.0 KAPPA=150.0

			ATOMS=3,4				
6	520 K	0.8 fs	d1: DISTANCE ATOMS=2,3 d2: DISTANCE ATOMS=3,4	d1,d2	0.02, 0.02	0.005 eV	UPPER_WALLS ARG=d1 AT=2.888 KAPPA=150.0

After exploring different CVs and PLUMED parameter choices (see Table S2), the following variables were selected for simulating the dissociation of CO_2 adsorption and dissociation over the $In_2O_{3-x}(OH)_y$ surface. The CVs used to define the free energy surface are shown in Figure S6. CV1 is defined as the angle formed by O1, C1, and O2, and CV2 is the distance from C1 to the midpoint between In28 and In60. In the first simulation, bias potentials of height 0.3 eV were deposited with the distances from O2 to H1 constrained to a maximum of 1.2 Å. In the second, bias potentials of height 0.1 eV were deposited with an additional constraint forcing the distance from O2 to the surface to a maximum of 3.2 Å. In the third and fourth simulations, Gaussian bias potentials of height 0.1 eV were also deposited; however, the constraint on the distance from O2 to the surface was decreased to 2.8 Å. A final run was performed with no constraints placed on the system using 0.1 eV bias potentials. The combination of the various simulations modeled the reaction over a total of 1520 fs at both 20 °C and 180 °C. Bias potentials were placed every 30 iterations for all runs. Gaussian widths of 0.1, a bias factor of 6.0, and a tuning parameter of 10,000 were employed for all simulations. MetaD-biased AIMD simulations were performed at 20 °C and 180 °C; plots of the simulation temperature over time are shown in Figure S7.

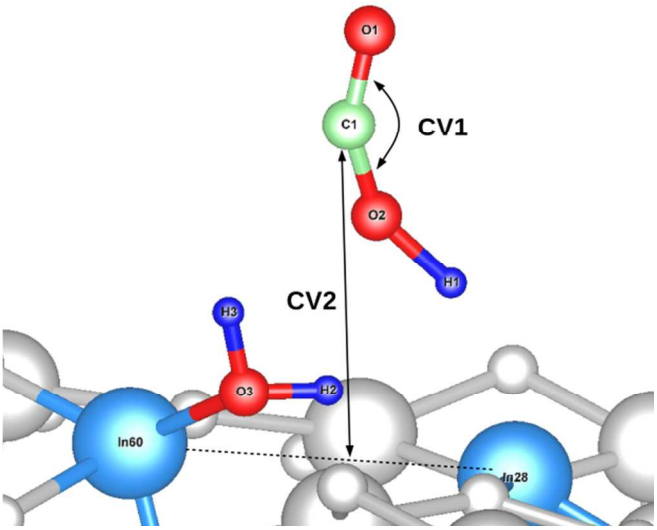

Figure S6: CVs used to define the free energy surface of the adsorption and reduction of CO_2 over the $In_2O_{3-x}(OH)_y$ surface.

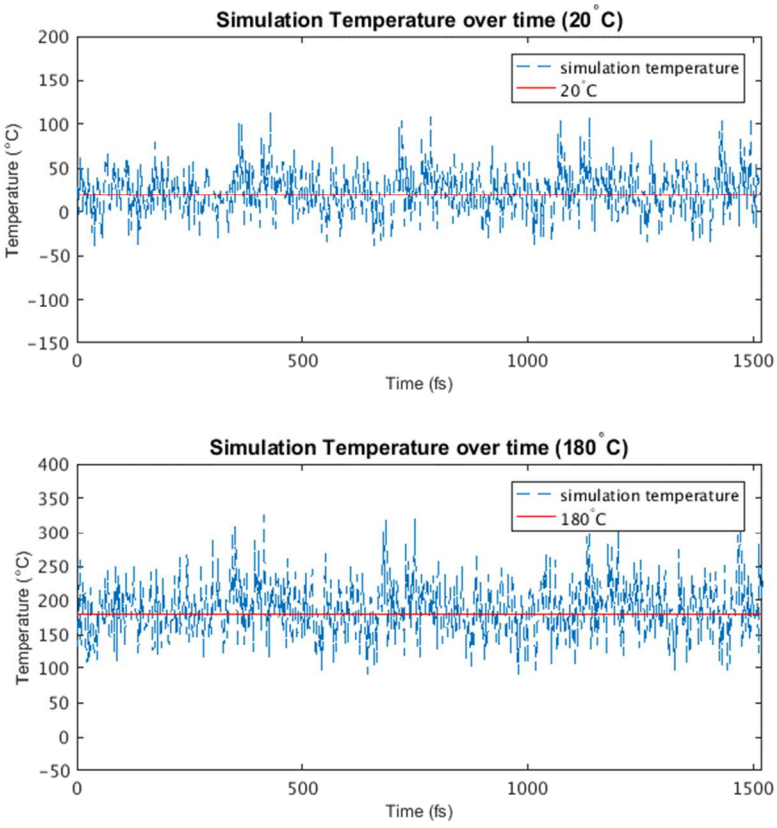

Figure S7: Simulation Temperature over time for the adsorption and reduction of CO_2 over the $In_2O_{3-x}(OH)_y$ surface.

2.3 *Dissociative adsorption of H_2O*

Table S3: Parameters for PLUMED plugin used in test simulation

Test #	Temp.	Timestep	CVs	MetaD	Sigma	Height	Constraints
1	520 K	1.75 fs	d1: DISTANCE ATOMS=67,6	d1	0.07	0.15	LOWER_WALLS ARG=d1 AT=2.25 KAPPA=150.0

After exploring different CVs and PLUMED parameter choices (see Table S3), the following variables were selected for simulating the dissociation of CO_2 adsorption and dissociation over the $In_2O_{3-x}(OH)_y$ surface. The CVs used to define the free energy surface are shown in Figure S8. CV1 is defined as the distance from In60 on the surface to O2, while CV2 is the distance from In28 to O1. Four simulations were performed to capture the diffusive behavior of H_2O at the surface. In the first simulation, Gaussian bias potentials of height 0.3 eV were deposited, with no force constraints applied to the system. In the second, forces limiting the distance from O1 to In28 to 2.08 Å, and the distance from O1 to H2 to 1.22 Å, were introduced. In the third and fourth simulations, the height of the Gaussian potentials was reduced to 0.1 eV, and the constraint on the distance between O1 and H2 was increased to 2.75 Å. The combination of the simulations modeled the reaction over the course of 2075 fs at both 20 °C and 180 °C. Gaussian bias potentials of width 0.1 were deposited every 30 iterations and a bias factor of 6 and a tuning parameter of 10,000 were applied in all simulations. MetaD-biased AIMD simulations were performed at 20 °C and 180 °C; plots of the simulation temperature over time are shown in Figure S9.

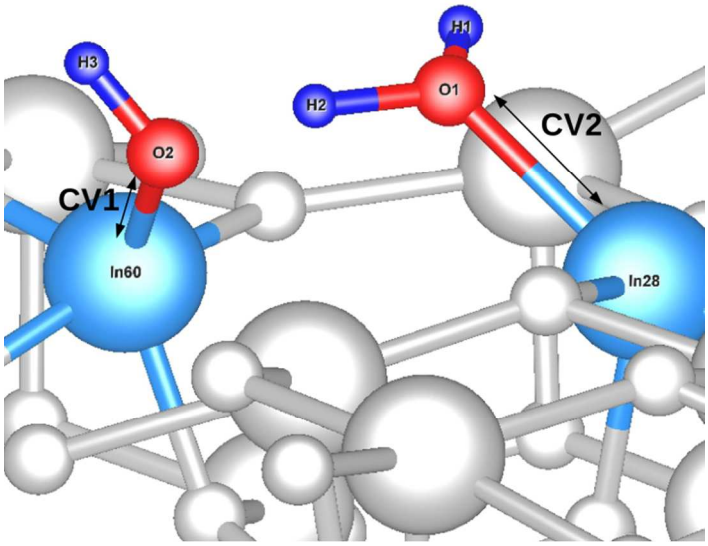

Figure S8: CVs used to define the free energy surface.

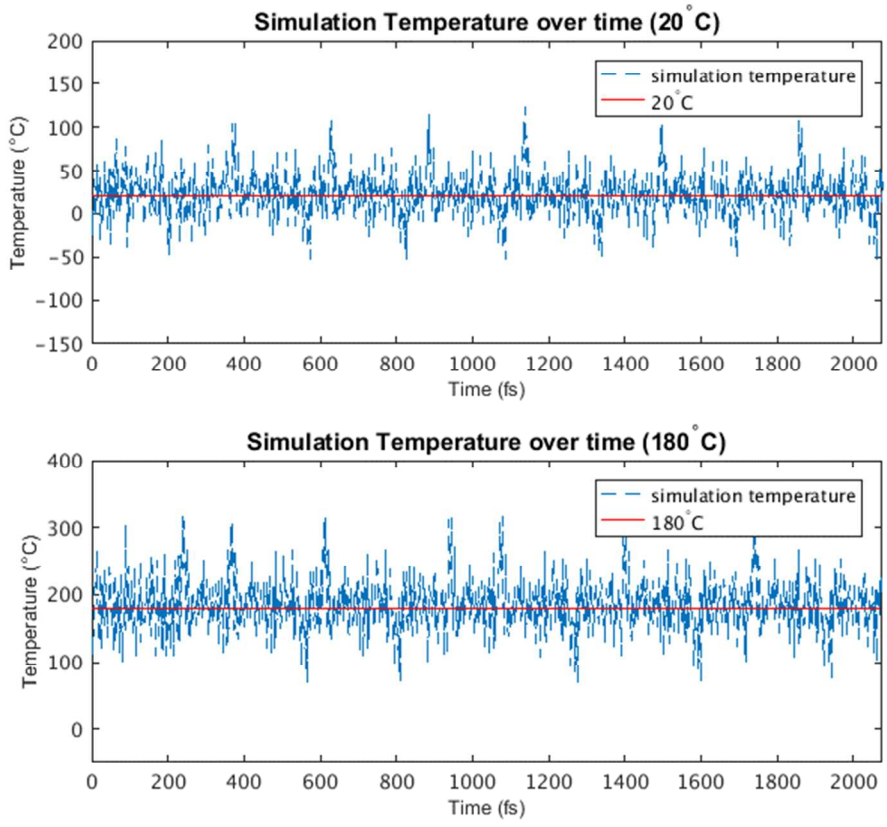

Figure S9: Simulation Temperature over time for the dissociative adsorption of H_2O over the $In_2O_{3-x}(OH)_y$ surface.

3. Atomic Coordinates

3.1 Input atomic coordinates for MetaD-biased AIMD simulations of H_2 dissociation (for simulations at both 20 °C and 180 °C):

CELL_PARAMETERS (alat= 26.78406211)

-0.922748620 0.157823829 -0.502741902

-0.345208088 2.054489671 -1.201278795

-0.025295741 -0.000637859 -1.078012610

ATOMIC_POSITIONS angstrom

H -10.188485242 13.207720920 -19.283391982

H -10.879234553 12.969651902 -19.121758861

O -12.491577047 12.569287308 -18.968883089

H -12.914241361 13.440511188 -18.721991736

In -11.771183192 5.573262603 -20.552699676 0 0 0

In -6.284017449 10.986155825 -13.109526899

In -7.832691312 1.658769572 -13.089699001 0 0 0

In -2.233732176 7.229688591 -5.626871199

In -5.277608283 4.549171863 -17.001291284 0 0 0

In -12.749558141 11.941756810 -16.459674020

In -1.330101442 0.732454039 -9.611562897 0 0 0

In -8.779362866 8.233259987 -9.215407669

In -5.058634278 4.534626705 -9.370182048 0 0 0

In -13.087135147 11.979690904 -24.364361146

In -0.999296297 0.728332776 -1.845390710 0 0 0

In -8.975893183 8.244764181 -16.854177305

In -11.573458092 5.680990059 -12.883913036 0 0 0

In -6.353286455 10.776227417 -20.990640666

In -7.667132506 1.852178138 -5.331100424 0 0 0

In -2.534693572 7.108794336 -13.291684964

In -8.374893138 4.891557016 -7.043313209 0 0 0

In -3.271085074 10.202548804 -14.887400141

In -10.871323034 2.445345257 -11.260941211 0 0 0

In -5.657055435 7.919105669 -19.141953532

In -8.263197777 5.248749221 -15.223186962 0 0 0

In -2.781552508 10.435782264 -7.761099167

In -11.280457587 2.187067504 -18.443143605 0 0 0

In -5.817705150 7.510048125 -10.999655576

In -4.241522937 1.469818337 -7.708617368 0 0 0

In -12.179869629 8.943219100 -22.709234725

In -1.839490586 3.967614726 -3.514977892 0 0 0

In -9.530026419 11.247970749 -18.450423807

In -4.791727194 1.175080008 -14.774903478 0 0 0

In -12.259364765 8.685603132 -14.572679873

In -1.721019562 4.109747331 -11.601660392 0 0 0

In -9.249998149 11.334853979 -11.490292452

In -1.758986480 3.693117313 -15.182107172 0 0 0

In -9.248114627 11.238246744 -14.950619209

In -4.778956619 1.352812579 -11.229922714 0 0 0

In -12.237287038 9.030666040 -10.891768579

In -8.547354280 5.347195103 -11.116113630 0 0 0

In -3.369645159 10.568434500 -18.955270519

In -10.731166930 2.050350167 -7.220813743 0 0 0

In -5.515147203 7.397157141 -15.105998161

In -4.675009674 1.619268526 -3.664806617 0 0 0

In -12.516137455 8.983226558 -18.627081549

In -1.535264283 3.815911506 -7.557168728 0 0 0

In -9.401999623 11.136245432 -22.633999382

In -10.743520888 2.322390136 -14.860306595 0 0 0

In -5.307812726 7.522841844 -7.551734041

In -8.691072083 5.333637598 -18.755270593 0 0 0

In -3.356822590 10.346117011 -11.325230948

In -11.832074931 5.481274217 -16.953578985 0 0 0

In -6.357915587 10.762897035 -9.584559874

In -7.748427322 1.800858113 -16.671887306 0 0 0

In -2.196555650 7.308936507 -9.238613504

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In -12.561578221 12.142773753 -12.629844685

In -1.494425253 0.434016182 -13.509859213 0 0 0

In -9.054051395 8.077323758 -13.275819469

In -1.032814090 0.963851006 -5.287791267 0 0 0

In -8.927833339 8.396870767 -20.440216370

In -5.036991874 4.537653214 -5.793903276 0 0 0

In -13.125053081 11.848543746 -20.955678696

In -7.956370018 1.648911354 -9.576394988 0 0 0

In	-2.707229724	7.015570685	-17.296045746			
In	-11.294635563	5.801434031	-8.848120675	0	0	0
In	-6.123842954	10.837220313	-16.637843210			
O	-9.529631251	6.328871488	-20.667109685	0	0	0
O	-4.091889052	11.348365357	-13.201291357			
O	-10.065461546	1.232652489	-13.077728936	0	0	0
O	-4.373100949	6.630367319	-5.542772321			
O	-5.980565645	5.212810583	-14.922764698	0	0	0
O	-13.640092114	12.699295020	-14.609195717			
O	-0.503012232	-0.160119362	-11.609532150	0	0	0
O	-8.105086218	7.543890889	-11.289744627			
O	-5.746483777	2.325299798	-9.298467064	0	0	0
O	-13.601700336	9.783951172	-24.219393037			
O	-0.413790333	2.936590034	-1.947263486	0	0	0
O	-8.190062758	10.297896430	-17.078720202			
O	-12.356604376	6.479059527	-14.971333875	0	0	0
O	-7.301106413	11.409505489	-22.892389070			
O	-6.776422656	1.101586000	-3.480616756	0	0	0
O	-1.646979568	6.366060222	-11.274159374			
O	-12.684930931	6.849508870	-22.241836533	0	0	0
O	-7.176816520	11.819874185	-14.897317596			
O	-7.007951113	0.554399896	-11.230652169	0	0	0
O	-1.314409263	6.005879454	-3.890044459			
O	-9.285241402	5.894339149	-13.293527996	0	0	0
O	-4.197037083	11.048251860	-21.092267598			
O	-9.946269808	1.625432933	-5.063719075	0	0	0
O	-4.735324767	6.969212168	-12.905492978			
O	-5.418162234	2.264265424	-16.677324922	0	0	0
O	-12.826481908	9.745859099	-16.477487386			
O	-1.109883429	3.006012086	-9.717286858	0	0	0
O	-8.640432724	10.328099396	-9.574170835			
O	-6.205215219	5.440055568	-7.571508470	0	0	0
O	-14.247827905	12.565219156	-22.594081133			
O	0.003830080	-0.098716240	-3.554385664	0	0	0
O	-7.786168230	7.441984377	-18.680865964			
O	-12.418064540	6.873783880	-18.740683825	0	0	0
O	-7.131266305	11.947007677	-11.329641691			
O	-6.890973414	0.570031313	-14.909196015	0	0	0

O -1.491000985 6.009177393 -7.293369565
O -6.270328279 5.361963119 -11.075229831 0 0 0
O -14.222849085 12.712800060 -26.114989813
O 0.102290662 -0.245889622 -0.088369248 0 0 0
O -7.701785483 7.478513642 -15.195337573
O -11.894775367 3.486632379 -13.184453274 0 0 0
O -6.819760542 8.611577100 -21.192691227
O -7.225998250 4.162867641 -5.146057291 0 0 0
O -2.263441836 9.289246933 -12.885038898
O -2.969455844 4.835871242 -16.791665422 0 0 0
O -10.513946753 12.007903594 -16.600505745
O -3.475921688 0.460792490 -9.528558084 0 0 0
O -11.084987337 7.978016525 -9.395091757
O -5.593061634 2.521530545 -13.129837967 0 0 0
O -13.089191192 10.027470397 -12.882464434
O -0.909869703 2.658162070 -13.170826729 0 0 0
O -8.379673566 10.066009083 -13.024597606
O -1.989402838 1.185512104 -7.199809201 0 0 0
O -10.014958516 9.090816215 -22.313185662
O -4.176283651 3.902575003 -3.878819849 0 0 0
O -9.714515786 6.189310879 -16.764038383 0 0 0
O -4.132120845 11.103500483 -9.391442856
O -9.937991728 1.356056406 -16.815297943 0 0 0
O -4.376294732 6.650076991 -9.461966183
O -8.326082936 2.319105061 -7.407710756 0 0 0
O -3.267222019 7.784414369 -15.291619865
O -10.783841120 4.839587635 -10.820009223 0 0 0
O -5.707300957 10.042048058 -18.861185244
O -8.616246390 3.126493715 -14.843910034 0 0 0
O -3.177421893 8.379386074 -7.301876193
O -10.839340297 4.376053074 -18.818810696 0 0 0
O -5.487961737 9.593798468 -11.427947552
O -5.407974117 1.663100668 -5.926568783 0 0 0
O -13.055626216 9.662869814 -20.648975043
O -0.845099985 3.274787454 -5.340368459 0 0 0
O -8.627535148 10.947561770 -20.458142152
O -8.927752724 6.092294050 -8.861996870 0 0 0
O -4.030719962 11.084040339 -16.856938023

O -10.244006213 1.393149114 -9.341319319 0 0 0

O -5.056637566 6.674652169 -17.431346050

O -2.623957132 1.463694767 -15.419826172 0 0 0

O -10.116841030 9.066474121 -15.049047517

O -3.843742857 3.633417422 -11.087242404 0 0 0

O -11.392923402 11.097148262 -10.746651124

O -8.542019701 3.053665919 -11.339096881 0 0 0

O -3.300050920 8.328120964 -19.048362536

O -10.718563850 4.359825974 -7.078277839 0 0 0

O -5.439245239 9.596496172 -14.957100684

O -2.589637501 1.200931738 -3.564083321 0 0 0

O -10.309404091 9.271467963 -18.779604883

O -3.769692432 3.766201778 -7.617397399 0 0 0

O -11.591314579 11.535392295 -22.733742640

O -2.751091136 4.956940817 -13.538675936 0 0 0

O -10.436033697 11.962508912 -13.323528806

O -3.696054091 0.290591877 -12.961741688 0 0 0

O -11.277404561 7.805986851 -12.590188838

O -12.189270137 3.151527802 -16.373051587 0 0 0

O -6.548523527 8.443913180 -9.075995756

O -7.527577281 4.270570133 -17.272318673 0 0 0

O -1.831932071 9.426280320 -9.832232703

3.2 Input coordinates for MetaD-biased AIMD simulations of CO_2 reduction (for simulations at both 20 °C and 180 °C)

CELL_PARAMETERS (alat= 26.78406211)

-0.922748620 0.157823829 -0.502741902

-0.345208088 2.054489671 -1.201278795

-0.025295741 -0.000637859 -1.078012610

ATOMIC_POSITIONS angstrom

O -10.975311475 17.165362086 -18.756632599

C -10.892773998 15.978856671 -18.826882191

O -10.837657421 14.799119262 -19.020746276

H -10.222942754 12.795311077 -19.343036622

H -11.488620810 12.919712351 -18.935347456

O -12.517210014 12.939276762 -18.955715972

H -12.813088330 13.896749295 -18.982319548

In -11.771183192 5.573262603 -20.552699676 0 0 0

In -6.159814915 11.010082457 -13.174379881

In -7.832691312 1.658769572 -13.089699001 0 0 0

In -2.368492265 6.945182832 -5.669723036

In -5.277608283 4.549171863 -17.001291284 0 0 0

In -12.799948639 11.867754043 -16.170050347

In -1.330101442 0.732454039 -9.611562897 0 0 0

In -9.067410180 8.324805227 -9.071404711

In -5.058634278 4.534626705 -9.370182048 0 0 0

In -13.128737323 12.017611701 -24.303510648

In -0.999296297 0.728332776 -1.845390710 0 0 0

In -9.082496748 8.247127955 -16.905420122

In -11.573458092 5.680990059 -12.883913036 0 0 0

In -6.390932133 10.882537666 -21.031847106

In -7.667132506 1.852178138 -5.331100424 0 0 0

In -2.482025822 7.072056273 -13.254104090

In -8.374893138 4.891557016 -7.043313209 0 0 0

In -3.289514996 10.219900257 -14.864277634

In -10.871323034 2.445345257 -11.260941211 0 0 0

In -5.622968167 7.995893946 -19.277347867

In -8.263197777 5.248749221 -15.223186962 0 0 0

In -2.918037860 10.359847093 -7.737395143

In -11.280457587 2.187067504 -18.443143605 0 0 0

In -5.794627693 7.637199919 -11.006627934

In -4.241522937 1.469818337 -7.708617368 0 0 0

In -12.223597736 8.951212230 -22.599211769

In -1.839490586 3.967614726 -3.514977892 0 0 0

In -9.401774522 11.460299606 -18.488658179

In -4.791727194 1.175080008 -14.774903478 0 0 0

In -12.204065896 8.619942507 -14.503106132

In -1.721019562 4.109747331 -11.601660392 0 0 0

In -9.096107497 11.075199736 -11.571836501

In -1.758986480 3.693117313 -15.182107172 0 0 0

In -9.205144541 11.165078203 -14.907362525

In -4.778956619 1.352812579 -11.229922714 0 0 0

In -12.323822341 9.041002735 -10.965644426

In -8.547354280 5.347195103 -11.116113630 0 0 0

In -3.365956357 10.505457098 -19.030592517

In -10.731166930 2.050350167 -7.220813743 0 0 0

In -5.438339526 7.321638028 -15.114131805

In -4.675009674 1.619268526 -3.664806617 0 0 0

In -12.533692957 8.986667285 -18.637752617

In -1.535264283 3.815911506 -7.557168728 0 0 0

In -9.422014975 11.213445231 -22.571878494

In -10.743520888 2.322390136 -14.860306595 0 0 0

In -5.175492400 7.374943628 -7.507829180

In -8.691072083 5.333637598 -18.755270593 0 0 0

In -3.240694249 10.217733076 -11.335884324

In -11.832074931 5.481274217 -16.953578985 0 0 0

In -6.310294053 10.745134979 -9.538573440

In -7.748427322 1.800858113 -16.671887306 0 0 0

In -2.139866740 7.250957096 -9.170883625

In -5.002134368 4.686428017 -12.912571208 0 0 0

In -12.562439285 12.005669869 -12.618990315

In -1.494425253 0.434016182 -13.509859213 0 0 0

In -9.051909832 8.090531608 -13.309491583

In -1.032814090 0.963851006 -5.287791267 0 0 0

In -8.840292336 8.455799982 -20.329233006

In -5.036991874 4.537653214 -5.793903276 0 0 0

In -13.098038131 11.966777684 -21.013160144

In -7.956370018 1.648911354 -9.576394988 0 0 0

In -2.833657774 7.020301773 -17.385434782

In -11.294635563 5.801434031 -8.848120675 0 0 0

In -6.143116062 10.796096990 -16.580151476

O -9.529631251 6.328871488 -20.667109685 0 0 0

O -3.960710813 11.390570114 -12.968981870

O -10.065461546 1.232652489 -13.077728936 0 0 0

O -4.549950708 6.521346946 -5.474381129

O -5.980565645 5.212810583 -14.922764698 0 0 0

O -13.442912202 12.729503079 -14.382078182

O -0.503012232 -0.160119362 -11.609532150 0 0 0

O -8.229310616 7.580076280 -11.303762964

O -5.746483777 2.325299798 -9.298467064 0 0 0

O -13.617344309 9.882051850 -24.284876954

O -0.413790333 2.936590034 -1.947263486 0 0 0

O -8.183228528 10.547912696 -16.999679288
O -12.356604376 6.479059527 -14.971333875 0 0 0
O -7.296878848 11.655590498 -22.810524006
O -6.776422656 1.101586000 -3.480616756 0 0 0
O -1.840979650 6.343392502 -11.196300738
O -12.684930931 6.849508870 -22.241836533 0 0 0
O -7.239806753 11.899741234 -14.899618176
O -7.007951113 0.554399896 -11.230652169 0 0 0
O -1.480547095 6.085861946 -3.952937919
O -9.285241402 5.894339149 -13.293527996 0 0 0
O -4.035079373 11.053194990 -21.219415293
O -9.946269808 1.625432933 -5.063719075 0 0 0
O -4.804335324 6.913532642 -12.972122420
O -5.418162234 2.264265424 -16.677324922 0 0 0
O -12.900364924 9.714273804 -16.292249637
O -1.109883429 3.006012086 -9.717286858 0 0 0
O -8.675141018 10.491815638 -9.509576760
O -6.205215219 5.440055568 -7.571508470 0 0 0
O -14.263173083 12.819141234 -22.561898351
O 0.003830080 -0.098716240 -3.554385664 0 0 0
O -7.734276053 7.409858127 -18.628756655
O -12.418064540 6.873783880 -18.740683825 0 0 0
O -7.119672243 11.845831989 -11.292053084
O -6.890973414 0.570031313 -14.909196015 0 0 0
O -1.562309891 5.930239968 -7.397846433
O -6.270328279 5.361963119 -11.075229831 0 0 0
O -14.235168368 12.723434862 -26.032583338
O 0.102290662 -0.245889622 -0.088369248 0 0 0
O -7.678371596 7.562900007 -15.215195485
O -11.894775367 3.486632379 -13.184453274 0 0 0
O -6.707445108 8.653096598 -21.263056384
O -7.225998250 4.162867641 -5.146057291 0 0 0
O -2.177837328 9.295922380 -13.169258195
O -2.969455844 4.835871242 -16.791665422 0 0 0
O -10.684489775 11.696750898 -16.636940484
O -3.475921688 0.460792490 -9.528558084 0 0 0
O -11.177992790 8.036819199 -9.491579379
O -5.593061634 2.521530545 -13.129837967 0 0 0

O -13.295478893 10.039996720 -12.913141436

O -0.909869703 2.658162070 -13.170826729 0 0 0

O -8.125657002 9.891677405 -12.987181791

O -1.989402838 1.185512104 -7.199809201 0 0 0

O -9.895215373 9.006185739 -22.241878827

O -4.176283651 3.902575003 -3.878819849 0 0 0

O -9.714515786 6.189310879 -16.764038383 0 0 0

O -4.214294156 11.012778404 -9.415823518

O -9.937991728 1.356056406 -16.815297943 0 0 0

O -4.264727026 6.646716817 -9.341815413

O -8.326082936 2.319105061 -7.407710756 0 0 0

O -3.183713211 7.755046571 -15.225787561

O -10.783841120 4.839587635 -10.820009223 0 0 0

O -5.656059941 10.276604893 -19.008069112

O -8.616246390 3.126493715 -14.843910034 0 0 0

O -3.139003475 8.243379313 -7.401073337

O -10.839340297 4.376053074 -18.818810696 0 0 0

O -5.357565133 9.611535445 -11.420946406

O -5.407974117 1.663100668 -5.926568783 0 0 0

O -12.713323212 9.824362370 -20.669168247

O -0.845099985 3.274787454 -5.340368459 0 0 0

O -8.653059650 10.815838127 -20.416379505

O -8.927752724 6.092294050 -8.861996870 0 0 0

O -3.955548079 10.561556468 -16.838621058

O -10.244006213 1.393149114 -9.341319319 0 0 0

O -5.094797994 6.764604151 -17.228160495

O -2.623957132 1.463694767 -15.419826172 0 0 0

O -10.094799280 9.036124125 -15.137000217

O -3.843742857 3.633417422 -11.087242404 0 0 0

O -11.415325052 11.281615815 -10.891705254

O -8.542019701 3.053665919 -11.339096881 0 0 0

O -3.450467234 8.322104347 -19.012347798

O -10.718563850 4.359825974 -7.078277839 0 0 0

O -5.466704899 9.586273531 -14.838547273

O -2.589637501 1.200931738 -3.564083321 0 0 0

O -10.149521461 9.249534443 -18.665258417

O -3.769692432 3.766201778 -7.617397399 0 0 0

O -11.523127452 11.756863517 -22.536492823

O -2.751091136 4.956940817 -13.538675936 0 0 0

O -10.362702378 11.725898359 -13.275829281

O -3.696054091 0.290591877 -12.961741688 0 0 0

O -11.365389898 7.844749840 -12.576571663

O -12.189270137 3.151527802 -16.373051587 0 0 0

O -6.726158442 8.510695803 -9.108884798

O -7.527577281 4.270570133 -17.272318673 0 0 0

O -1.948453706 9.432143824 -9.917511458

3.3 Input coordinates for MetaD-biased AIMD simulations for the motion of product H_2O (for simulations at both 20 °C and 180 °C):

CELL_PARAMETERS (alat= 26.78406211)

-0.922748620 0.157823829 -0.502741902

-0.345208088 2.054489671 -1.201278795

-0.025295741 -0.000637859 -1.078012610

ATOMIC_POSITIONS angstrom

O -10.240679875 13.472527001 -20.194621038

H -9.651718340 14.185235492 -19.827382222

H -11.117277487 13.497032589 -19.722349266

O -12.609791488 12.975329058 -19.421982376

H -13.352500939 13.401999033 -19.083978296

In -11.771183192 5.573262603 -20.552699676 0 0 0

In -6.295351078 11.195146173 -13.144513527

In -7.832691312 1.658769572 -13.089699001 0 0 0

In -2.248308679 7.112889048 -5.672262111

In -5.277608283 4.549171863 -17.001291284 0 0 0

In -12.634565659 11.850619266 -15.997269253

In -1.330101442 0.732454039 -9.611562897 0 0 0

In -8.925320268 8.223327558 -9.185084731

In -5.058634278 4.534626705 -9.370182048 0 0 0

In -13.007086403 11.997658454 -24.364088714

In -0.999296297 0.728332776 -1.845390710 0 0 0

In -8.869971370 8.177169154 -16.929921913

In -11.573458092 5.680990059 -12.883913036 0 0 0

In -6.449588118 10.714993077 -21.249024283

In -7.667132506 1.852178138 -5.331100424 0 0 0

In -2.486679232 7.047965168 -13.371359249

In -8.374893138 4.891557016 -7.043313209 0 0 0

In -3.209413131 10.227302819 -14.843137139

In -10.871323034 2.445345257 -11.260941211 0 0 0

In -5.529326397 7.995140939 -19.013350262

In -8.263197777 5.248749221 -15.223186962 0 0 0

In -2.900152109 10.243307546 -7.950872038

In -11.280457587 2.187067504 -18.443143605 0 0 0

In -5.878885481 7.581862750 -10.938197324

In -4.241522937 1.469818337 -7.708617368 0 0 0

In -12.294818484 9.024546933 -22.638134218

In -1.839490586 3.967614726 -3.514977892 0 0 0

In -9.423885948 11.086631922 -18.299821124

In -4.791727194 1.175080008 -14.774903478 0 0 0

In -12.259530166 8.527890791 -14.633261920

In -1.721019562 4.109747331 -11.601660392 0 0 0

In -9.276021519 11.125232437 -11.455924310

In -1.758986480 3.693117313 -15.182107172 0 0 0

In -9.358086164 11.086648766 -14.847244787

In -4.778956619 1.352812579 -11.229922714 0 0 0

In -12.342322280 9.189019610 -10.843032695

In -8.547354280 5.347195103 -11.116113630 0 0 0

In -3.476363077 10.501545579 -19.096446161

In -10.731166930 2.050350167 -7.220813743 0 0 0

In -5.588185138 7.445522967 -15.019714869

In -4.675009674 1.619268526 -3.664806617 0 0 0

In -12.616518509 9.040989593 -18.593535103

In -1.535264283 3.815911506 -7.557168728 0 0 0

In -9.463627253 11.033947444 -22.501718750

In -10.743520888 2.322390136 -14.860306595 0 0 0

In -5.293388917 7.414408194 -7.359826147

In -8.691072083 5.333637598 -18.755270593 0 0 0

In -3.477596388 10.465980523 -11.568707248

In -11.832074931 5.481274217 -16.953578985 0 0 0

In -6.418538715 10.697552460 -9.619005659

In -7.748427322 1.800858113 -16.671887306 0 0 0

In -2.091545290 7.281633017 -9.243658817

In -5.002134368 4.686428017 -12.912571208 0 0 0

In -12.535317938 11.972866292 -12.623075272

In -1.494425253 0.434016182 -13.509859213 0 0 0

In -9.188758122 8.036195575 -13.338378847

In -1.032814090 0.963851006 -5.287791267 0 0 0

In -8.832884275 8.406478462 -20.490482432

In -5.036991874 4.537653214 -5.793903276 0 0 0

In -13.132153439 11.952040474 -21.061685351

In -7.956370018 1.648911354 -9.576394988 0 0 0

In -2.775728076 6.971817116 -17.377736623

In -11.294635563 5.801434031 -8.848120675 0 0 0

In -5.976602788 10.876404402 -16.540151260

O -9.529631251 6.328871488 -20.667109685 0 0 0

O -4.138180437 11.529760060 -13.324042111

O -10.065461546 1.232652489 -13.077728936 0 0 0

O -4.394960002 6.487961676 -5.409012584

O -5.980565645 5.212810583 -14.922764698 0 0 0

O -13.647339393 12.619238155 -14.365356562

O -0.503012232 -0.160119362 -11.609532150 0 0 0

O -8.149525973 7.476499134 -11.332438219

O -5.746483777 2.325299798 -9.298467064 0 0 0

O -13.744707540 9.788295354 -24.234406102

O -0.413790333 2.936590034 -1.947263486 0 0 0

O -8.097129603 10.213445490 -16.894991061

O -12.356604376 6.479059527 -14.971333875 0 0 0

O -7.441319189 11.427196037 -22.986811523

O -6.776422656 1.101586000 -3.480616756 0 0 0

O -1.599781884 6.459602122 -11.260108579

O -12.684930931 6.849508870 -22.241836533 0 0 0

O -7.229055500 11.771926658 -14.907537706

O -7.007951113 0.554399896 -11.230652169 0 0 0

O -1.487315079 5.983815049 -3.909767000

O -9.285241402 5.894339149 -13.293527996 0 0 0

O -4.198267164 10.814882117 -21.255926129

O -9.946269808 1.625432933 -5.063719075 0 0 0

O -4.747385411 6.985097393 -12.956788030

O -5.418162234 2.264265424 -16.677324922 0 0 0

O -12.759503327 9.681466453 -16.451744604

O -1.109883429 3.006012086 -9.717286858 0 0 0

O -8.705320835 10.322481878 -9.578401640

O -6.205215219 5.440055568 -7.571508470 0 0 0

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