Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information: Transfer Learned Potential Energy Surfaces: Accurate Anharmonic Vibrational Dynamics and Dissociation Energies for the Formic Acid Monomer and Dimer

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1 Molecular Geometries

Table S1: Coordinates and energy (in E_h) of FAM optimized at the MP2/AVTZ level of theory.

FAM	MP2/AVTZ	ENERGY=-189.48676129	
	x	y	z
C	1.4520860701	0.2420155948	-0.0706270260
H	0.3886055057	-0.0022636281	-0.0180112547
O	1.7795679729	0.5699513997	-1.3349111851
O	2.2170078996	0.2215156425	0.8605086772
H	2.7281099589	0.7770183078	-1.3284469693

Table S2: Coordinates and energy (in E_h) of FAD optimized at the MP2/AVTZ level of theory.

FAD	MP2/AVTZ	ENERGY=-379.00025498	
	x	y	z
C	-1.9764324596	-0.1494375270	0.1666266080
H	-3.0549779301	-0.2186023083	0.3193894061
O	-1.6825757966	0.2969079440	-1.0328347642
O	-1.1776513399	-0.4610563717	1.0396060847
H	-0.6892121927	0.3479665039	-1.1351578367
C	1.7585514984	0.1213186293	-0.4302037094
H	2.8370616671	0.1933717275	-0.5818836749
O	1.4647336363	-0.3267641096	0.7686141982
O	0.9597539040	0.4336624956	-1.3028922022
H	0.4714710032	-0.3780585438	0.8709677203

Table S3: Coordinates and energy (in E_h) of the TS for double proton transfer optimized at the MP2/AVTZ level of theory.

FAD TS	MP2/AVTZ	ENERGY=-378.98955690	
	x	y	z
C	1.7580863319	0.0022963293	0.0961466133
H	2.8483449275	0.0047147133	0.1321411491
O	1.1960765375	-1.1283848924	0.0522983349
O	1.1894021598	1.1304667771	0.1026492092
H	-0.0079795935	-1.0950129011	0.0132873913
O	-1.2118222166	-1.1337245552	-0.0273401908
O	-1.2185020156	1.1251240211	0.0231035418
C	-1.7805078142	-0.0055548519	-0.0208134067
H	-0.0144445979	1.0917544630	0.0620743374
H	-2.8707647037	-0.0079727954	-0.0568725511

2 Harmonic Frequencies

Table S4: Comparison of the normal mode frequencies of FAM calculated from PhysNet trained on MP2 data (PES_{MP2}) and transfer learned to CCSD(T) quality (PES_{TL}), the corresponding reference values (MP2 and CCSD(T)) and experimental fundamental vibration frequencies from Ref. 2 and Refs. therein. PhysNet reproduces its reference frequencies with a MAE of 0.2 cm^{-1}. Largest deviations to experiments are found for the O–H and C–H modes having high frequencies. MAEs with respec to experiment are given for modes below 2000 cm^{-1} ($MAE_{exp}^{<2000}$) and for all modes (MAE_{exp}). All frequencies are given in cm^{-1}.

Mode	**PES_{MP2}**	**MP2**	**PES_{TL}**	**CCSD(T)**	**Exp**[1]
1	625.9	625.9	626.2	626.5	626.2
2	675.2	675.1	664.5	664.9	640.7
3	1058.6	1058.7	1050.9	1051.0	1033.5
4	1130.6	1130.8	1131.8	1131.3	1104.9
5	1301.5	1301.7	1310.7	1310.8	1306.2
6	1409.0	1409.0	1404.8	1404.7	1380.0
7	1793.0	1793.2	1802.7	1802.6	1776.8
8	3123.6	3124.2	3087.7	3087.6	2942.0
9	3741.0	3740.8	3741.7	3741.8	3570.5
MAE_{ref}	**0.2**		**0.2**		
MAE_{exp}	**53.3**	**53.4**	**48.1**	**48.2**	
$MAE_{exp}^{<2000}$	**19.4**	**19.4**	**17.6**	**17.7**	

Table S5: Comparison of the normal mode frequencies of dimeric FA calculated from PhysNet trained on MP2 data (PES_{MP2}) and transfer learned to CCSD(T) quality (PES_{TL}), the corresponding reference values (MP2 and CCSD(T), the latter taken from Ref. 3) and experimental fundamental vibration frequencies ([b]Ref. 4; [c]Ref. 5; [d]Ref. 6; [e]Ref. 7; [f]Ref. 8 [g]Ref. 9; [h]Ref. 10 [i]Ref. 11; [j]Ref. 12; [k]Ref. 13; [l]Ref. 14). The PhysNet frequencies reproduce their MP2 reference values with and MAE of 2.1 cm^{-1} and the CCSD(T) with a MAE of 10.7 cm^{-1}. MAEs with respec to experiment are given for modes below 2000 cm^{-1} ($MAE_{exp}^{<2000}$) and for all modes (MAE_{exp}). All frequencies are given in cm^{-1}.

Mode	**PES_{MP2}**	**MP2**	**PES_{TL}**	**CCSD(T)[3]**	**Exp**
1	66.5	68.8	69.5	72.3	69.2 [b]
2	166.0	168.8	167.5	166.5	161.0 [c]
3	175.4	180.3	175.6	189.9	168.5 [b]
4	214.0	212.9	210.5	214.1	194.0 [c]
5	256.5	258.4	253.0	259.4	242.0 [c]
6	286.4	282.5	277.2	279.6	264.0 [d]
7	682.3	684.6	682.1	688.4	682.0 [c]
8	715.3	715.1	710.7	716.2	698.0 [b]
9	978.9	979.8	963.5	994.1	911.0 [e]
10	991.4	997.7	986.7	1017.6	942 [f]
11	1089.6	1089.1	1079.9	1105.0	1050 [g]
12	1113.8	1116.3	1101.5	1131.2	1060 [h]
13	1261.0	1261.4	1250.2	1260.0	1214 [h]
14	1265.9	1265.9	1254.9	1265.0	1233.9 [i]
15	1406.2	1404.0	1401.5	1405.7	1371.78 [j]
16	1407.5	1408.1	1404.1	1408.7	1375 [h]
17	1455.6	1455.5	1458.3	1466.0	1415 [g]
18	1481.8	1482.7	1487.3	1497.2	1454 [b]
19	1701.6	1702.2	1708.0	1718.5	1666 [k]
20	1769.1	1769.9	1772.2	1784.9	1741 [k]
21	3103.1	3109.7	3094.4	3095.1	2900 [d]
22	3128.9	3128.6	3098.4	3098.1	2939.7 [l]
23	3137.4	3138.4	3189.2	3202.3	2949 [h]
24	3223.3	3230.3	3293.1	3308.5	3050 [b]
MAE_{ref}	**2.1**		**10.7**		
MAE_{exp}	**55.5**	**56.7**	**55.8**	**66.4**	
$MAE_{exp}^{<2000}$	**28.9**	**29.6**	**25.1**	**36.4**	

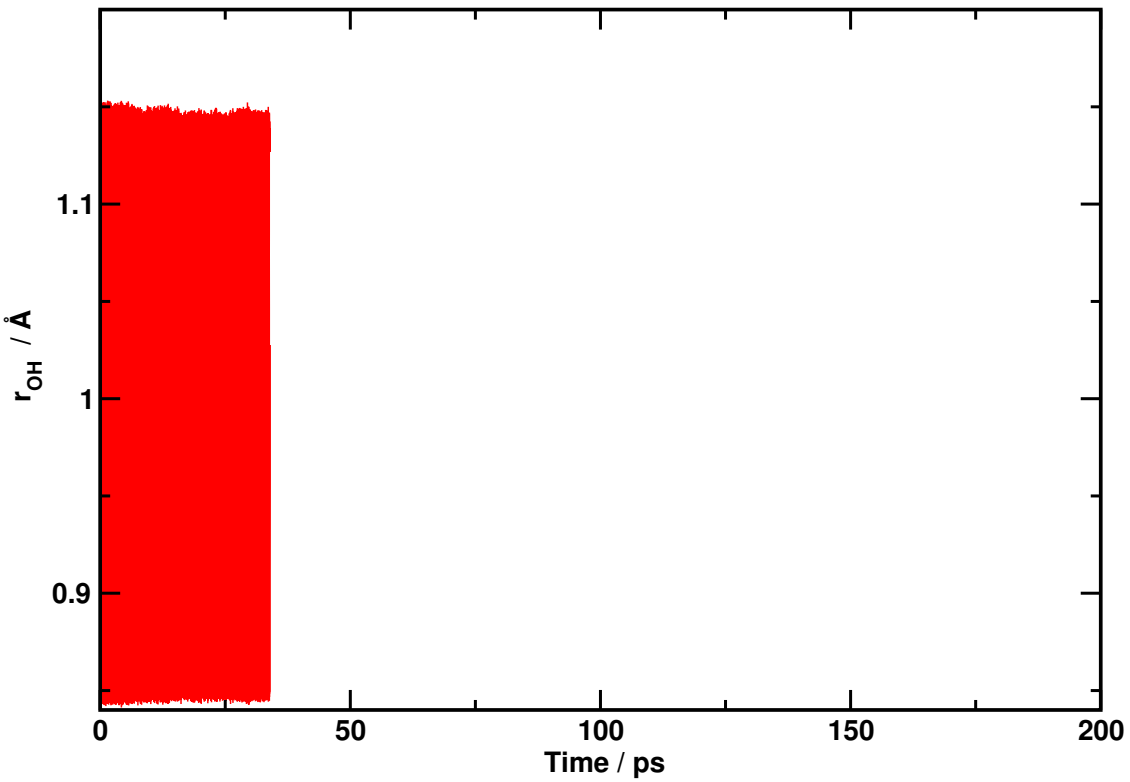

Figure S1: MD simulation, 200 ps in length, of FAM run with PES_{TL}. The simulation is initialized with a kinetic energy of 0.5 eV in the O–H stretch mode and is used to asses the amount of vibrational energy redistribution.

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