Supporting Information

Buffer-assisted proton-coupled electron transfer in a model rhenium-tyrosine complex

Hiroshi Ishikita, Alexander V. Soudackov, and Sharon Hammes-Schiffer*

Department of Chemistry, 104 Chemistry Building,
Pennsylvania State University, University Park, PA 16802, USA;
e-mail: shs@chem.psu.edu

Table S1. Atomic coordinates used for solvent reorganization energy calculation

a) Phosphate-acceptor model (proton acceptor: HPO_4^{2-})

	group	atom	x	y	z		group	atom	x	y	z
1	RE	RE	3.481	-0.271	1.314	6	PHE	H	10.293	-1.736	-1.132
2	PTL	N	3.838	1.557	2.516	6	PHE	C	9.121	0.033	-1.489
2	PTL	N	5.070	-0.828	2.769	6	PHE	H	9.917	0.550	-2.013
2	PTL	C	3.188	2.716	2.407	6	PHE	C	7.888	0.654	-1.328
2	PTL	H	2.453	2.789	1.618	6	PHE	H	7.742	1.647	-1.734
2	PTL	C	3.424	3.802	3.259	6	PHE	C	5.353	2.514	-0.395
2	PTL	H	2.857	4.713	3.121	6	PHE	C	4.404	3.383	-0.952
2	PTL	C	4.370	3.689	4.254	6	PHE	C	6.402	3.052	0.362
2	PTL	H	4.570	4.513	4.928	6	PHE	C	4.522	4.760	-0.781
2	PTL	C	5.078	2.478	4.398	6	PHE	H	3.585	2.992	-1.543
2	PTL	C	4.774	1.431	3.501	6	PHE	C	6.514	4.431	0.532
2	PTL	C	5.433	0.166	3.632	6	PHE	H	7.149	2.402	0.802
2	PTL	C	6.384	-0.026	4.660	6	PHE	C	5.580	5.289	-0.043
2	PTL	C	6.963	-1.304	4.783	6	PHE	H	3.793	5.419	-1.237
2	PTL	H	7.694	-1.492	5.561	6	PHE	H	7.343	4.835	1.103
2	PTL	C	6.572	-2.307	3.923	6	PHE	H	5.678	6.361	0.076
2	PTL	H	6.978	-3.307	4.001	7	BB	C	3.543	-0.232	-6.465
2	PTL	C	5.623	-2.033	2.930	7	BB	O	2.515	-0.845	-6.717
2	PTL	H	5.297	-2.821	2.262	7	BB	N	4.401	0.200	-7.425
2	PTL	C	6.067	2.263	5.414	7	BB	H	5.301	0.598	-7.197
2	PTL	H	6.295	3.076	6.092	7	BB	C	4.167	-0.042	-8.840
2	PTL	C	6.694	1.064	5.538	7	BB	H	3.674	-1.008	-8.958
2	PTL	H	7.430	0.905	6.318	8	CTR	C	5.531	-0.080	-9.510
3	CO	C	3.366	-1.999	0.447	8	CTR	O	6.513	0.468	-9.067
3	CO	O	3.319	-3.051	-0.016	8	CTR	O	5.516	-0.774	-10.653
4	CO	C	2.057	0.442	0.208	9	TYR	C	3.245	1.077	-9.436
4	CO	O	1.203	0.902	-0.410	9	TYR	H	2.357	1.079	-8.829
5	CO	C	2.145	-0.859	2.617	9	TYR	H	3.763	2.026	-9.309
5	CO	O	1.344	-1.203	3.360	9	TYR	C	2.896	0.873	-10.893
6	PHE	P	5.140	0.689	-0.568	9	TYR	C	3.502	1.638	-11.904
6	PHE	C	4.585	0.489	-2.325	9	TYR	H	4.253	2.381	-11.629
6	PHE	C	3.663	-0.496	-2.697	9	TYR	C	1.938	-0.070	-11.289
6	PHE	H	3.194	-1.122	-1.953	9	TYR	H	1.446	-0.684	-10.533

6	PHE	C	3.338	-0.696	-4.035	9	TYR	C	3.178	1.468	-13.248
6	PHE	H	2.617	-1.448	-4.327	9	TYR	H	3.664	2.065	-14.017
6	PHE	C	3.935	0.069	-5.037	9	TYR	C	1.596	-0.249	-12.629
6	PHE	C	4.845	1.064	-4.668	9	TYR	H	0.862	-0.978	-12.954
6	PHE	H	5.302	1.706	-5.413	9	TYR	C	2.217	0.510	-13.638
6	PHE	C	5.165	1.273	-3.332	9	TYR	O	1.931	0.365	-14.938
6	PHE	H	5.865	2.061	-3.085	9	TYR	H	1.273	-0.435	-15.112
6	PHE	C	6.850	-0.001	-0.651	10	POS	O	0.324	-1.519	-15.314
6	PHE	C	7.079	-1.284	-0.144	10	POS	O	2.258	-2.349	-16.785
6	PHE	H	6.294	-1.773	0.413	10	POS	O	-0.125	-2.183	-17.784
6	PHE	C	8.311	-1.910	-0.316	10	POS	P	0.752	-2.386	-16.547
6	PHE	H	8.470	-2.908	0.075	10	POS	O	0.360	-3.953	-16.051
6	PHE	C	9.333	-1.253	-0.993	10	POS	H	0.790	-4.102	-15.184

b) Water-acceptor model (proton acceptor: H_2O)

	group	atom	x	y	z		group	atom	x	y	z
1	RE	RE	3.481	-0.271	1.314	6	PHE	H	9.917	0.550	-2.013
2	PTL	N	3.838	1.557	2.516	6	PHE	C	7.888	0.654	-1.328
2	PTL	N	5.070	-0.828	2.769	6	PHE	H	7.742	1.647	-1.734
2	PTL	C	3.188	2.716	2.407	6	PHE	C	5.353	2.514	-0.395
2	PTL	H	2.453	2.789	1.618	6	PHE	C	4.404	3.383	-0.952
2	PTL	C	3.424	3.802	3.259	6	PHE	C	6.402	3.052	0.362
2	PTL	H	2.857	4.713	3.121	6	PHE	C	4.522	4.760	-0.781
2	PTL	C	4.370	3.689	4.254	6	PHE	H	3.585	2.992	-1.543
2	PTL	H	4.570	4.513	4.928	6	PHE	C	6.514	4.431	0.532
2	PTL	C	5.078	2.478	4.398	6	PHE	H	7.149	2.402	0.802
2	PTL	C	4.774	1.431	3.501	6	PHE	C	5.580	5.289	-0.043
2	PTL	C	5.433	0.166	3.632	6	PHE	H	3.793	5.419	-1.237
2	PTL	C	6.384	-0.026	4.660	6	PHE	H	7.343	4.835	1.103
2	PTL	C	6.963	-1.304	4.783	6	PHE	H	5.678	6.361	0.076
2	PTL	H	7.694	-1.492	5.561	7	BB	C	3.543	-0.232	-6.465
2	PTL	C	6.572	-2.307	3.923	7	BB	O	2.515	-0.845	-6.717
2	PTL	H	6.978	-3.307	4.001	7	BB	N	4.401	0.200	-7.425
2	PTL	C	5.623	-2.033	2.930	7	BB	H	5.301	0.598	-7.197
2	PTL	H	5.297	-2.821	2.262	7	BB	C	4.167	-0.042	-8.840
2	PTL	C	6.067	2.263	5.414	7	BB	H	3.674	-1.008	-8.958

2	PTL	H	6.295	3.076	6.092	8	CTR	C	5.531	-0.080	-9.510
2	PTL	C	6.694	1.064	5.538	8	CTR	O	6.513	0.468	-9.067
2	PTL	H	7.430	0.905	6.318	8	CTR	O	5.516	-0.774	-10.653
3	CO	C	3.366	-1.999	0.447	9	TYR	C	3.254	1.066	-9.441
3	CO	O	3.319	-3.051	-0.016	9	TYR	H	2.357	1.079	-8.829
4	CO	C	2.057	0.442	0.208	9	TYR	H	3.763	2.026	-9.309
4	CO	O	1.203	0.902	-0.410	9	TYR	C	2.885	0.885	-10.896
5	CO	C	2.145	-0.859	2.617	9	TYR	C	3.497	1.642	-11.904
5	CO	O	1.344	-1.203	3.360	9	TYR	H	4.241	2.391	-11.633
6	PHE	P	5.140	0.689	-0.568	9	TYR	C	1.930	-0.064	-11.287
6	PHE	C	4.585	0.489	-2.325	9	TYR	H	1.430	-0.667	-10.529
6	PHE	C	3.663	-0.496	-2.697	9	TYR	C	3.182	1.465	-13.252
6	PHE	H	3.194	-1.122	-1.953	9	TYR	H	3.669	2.063	-14.020
6	PHE	C	3.338	-0.696	-4.035	9	TYR	C	1.599	-0.259	-12.629
6	PHE	H	2.617	-1.448	-4.327	9	TYR	H	0.854	-0.998	-12.912
6	PHE	C	3.935	0.069	-5.037	9	TYR	C	2.227	0.509	-13.618
6	PHE	C	4.845	1.064	-4.668	9	TYR	O	1.929	0.368	-14.947
6	PHE	H	5.302	1.706	-5.413	9	TYR	H	1.266	-0.361	-15.095
6	PHE	C	5.165	1.273	-3.332	10	HOH	O	0.154	-1.574	-15.391
6	PHE	H	5.865	2.061	-3.085	10	HOH	H	-0.614	-1.204	-15.871
6	PHE	C	6.850	-0.001	-0.651	10	HOH	H	0.531	-2.231	-16.008
6	PHE	C	7.079	-1.284	-0.144	11	HOH	O	4.646	3.382	-15.828
6	PHE	H	6.294	-1.773	0.413	11	HOH	H	3.815	3.889	-15.834
6	PHE	C	8.311	-1.910	-0.316	11	HOH	H	4.393	2.536	-16.263
6	PHE	H	8.470	-2.908	0.075	12	HOH	O	3.850	0.929	-16.901
6	PHE	C	9.333	-1.253	-0.993	12	HOH	H	4.589	0.323	-16.707
6	PHE	H	10.293	-1.736	-1.132	12	HOH	H	3.168	0.689	-16.240
6	PHE	C	9.121	0.033	-1.489						

Table S2. Atomic partial charges used for solvent reorganization energy calculation

a) Phosphate-acceptor model (proton acceptor: HPO_4^{2-})

group [a]	atom	charge				group	atom	charge			
		diabatic state						diabatic state			
		1a	1b	2a	2b			1a	1b	2a	2b
RE	RE	1.000	1.000	0.000	0.000	PHE	H	0.089	0.089	0.089	0.089
PTL	N	-0.556	-0.556	-0.556	-0.556	PHE	C	-0.233	-0.233	-0.233	-0.233
PTL	N	-0.556	-0.556	-0.556	-0.556	PHE	H	0.125	0.125	0.125	0.125
PTL	C	0.382	0.382	0.382	0.382	PHE	C	0.359	0.359	0.359	0.359
PTL	H	0.008	0.008	0.008	0.008	PHE	C	-0.187	-0.187	-0.187	-0.187
PTL	C	-0.318	-0.318	-0.318	-0.318	PHE	C	-0.228	-0.228	-0.228	-0.228
PTL	H	0.127	0.127	0.127	0.127	PHE	C	-0.066	-0.066	-0.066	-0.066
PTL	C	0.059	0.059	0.059	0.059	PHE	H	0.073	0.073	0.073	0.073
PTL	H	0.074	0.074	0.074	0.074	PHE	C	-0.052	-0.052	-0.052	-0.052
PTL	C	-0.073	-0.073	-0.073	-0.073	PHE	H	0.121	0.121	0.121	0.121
PTL	C	0.335	0.335	0.335	0.335	PHE	C	-0.126	-0.126	-0.126	-0.126
PTL	C	0.335	0.335	0.335	0.335	PHE	H	0.093	0.093	0.093	0.093
PTL	C	-0.073	-0.073	-0.073	-0.073	PHE	H	0.088	0.088	0.088	0.088
PTL	C	0.059	0.059	0.059	0.059	PHE	H	0.095	0.095	0.095	0.095
PTL	H	0.074	0.074	0.074	0.074	BB	C	0.510	0.510	0.510	0.510
PTL	C	-0.318	-0.318	-0.318	-0.318	BB	O	-0.510	-0.510	-0.510	-0.510
PTL	H	0.127	0.127	0.127	0.127	BB	N	-0.470	-0.470	-0.470	-0.470
PTL	C	0.382	0.382	0.382	0.382	BB	H	0.310	0.310	0.310	0.310
PTL	H	0.008	0.008	0.008	0.008	BB	C	0.070	0.070	0.070	0.070
PTL	C	-0.151	-0.151	-0.151	-0.151	BB	H	0.090	0.090	0.090	0.090
PTL	H	0.115	0.115	0.115	0.115	CTR	C	0.340	0.340	0.340	0.340
PTL	C	-0.151	-0.151	-0.151	-0.151	CTR	O	-0.670	-0.670	-0.670	-0.670
PTL	H	0.115	0.115	0.115	0.115	CTR	O	-0.670	-0.670	-0.670	-0.670
CO	C	0.510	0.510	0.510	0.510	TYR	C	-0.132	-0.082	-0.247	-0.197
CO	O	-0.510	-0.510	-0.510	-0.510	TYR	H	0.054	0.000	0.142	0.088
CO	C	0.510	0.510	0.510	0.510	TYR	H	0.054	0.000	0.142	0.088
CO	O	-0.510	-0.510	-0.510	-0.510	TYR	C	0.133	-0.024	0.414	0.257
CO	C	0.510	0.510	0.510	0.510	TYR	C	-0.181	-0.172	-0.230	-0.221
CO	O	-0.510	-0.510	-0.510	-0.510	TYR	H	0.108	0.061	0.177	0.130
PHE	P	-0.512	-0.512	-0.512	-0.512	TYR	C	-0.151	-0.151	-0.217	-0.217
PHE	C	0.372	0.372	0.372	0.372	TYR	H	0.117	0.058	0.190	0.132
PHE	C	-0.195	-0.195	-0.195	-0.195	TYR	C	-0.171	-0.298	-0.033	-0.160
PHE	H	0.075	0.075	0.075	0.075	TYR	H	0.133	0.059	0.193	0.118
PHE	C	-0.064	-0.064	-0.064	-0.064	TYR	C	-0.244	-0.300	-0.105	-0.161
PHE	H	0.093	0.093	0.093	0.093	TYR	H	0.110	0.060	0.167	0.117
PHE	C	-0.031	-0.031	-0.031	-0.031	TYR	C	0.326	0.506	0.319	0.499
PHE	C	-0.041	-0.041	-0.041	-0.041	TYR	O	-0.559	-0.718	-0.315	-0.473
PHE	H	0.086	0.086	0.086	0.086	TYR	H	0.404	0.355	0.404	0.355
PHE	C	-0.248	-0.248	-0.248	-0.248	POS	O	-0.898	-0.645	-0.898	-0.645
PHE	H	0.127	0.127	0.127	0.127	POS	O	-0.898	-0.759	-0.898	-0.759
PHE	C	0.353	0.353	0.353	0.353	POS	O	-0.898	-0.759	-0.898	-0.759
PHE	C	-0.177	-0.177	-0.177	-0.177	POS	P	1.150	1.099	1.150	1.099

PHE	H	0.070	0.070	0.070	0.070	POS	O	-0.757	-0.645	-0.757	-0.645
PHE	C	-0.075	-0.075	-0.075	-0.075	POS	H	0.301	0.355	0.301	0.355
PHE	H	0.094	0.094	0.094	0.094						
PHE	C	-0.114	-0.114	-0.114	-0.114						
PHE	H	0.092	0.092	0.092	0.092						
PHE	C	-0.056	-0.056	-0.056	-0.056						

b) Water-acceptor model (proton acceptor: H_2O)

group [a]	**atom**	**charge**				**group**	**atom**	**charge**			
		diabatic state						**diabatic state**			
		1a	**1b**	**2a**	**2b**			**1a**	**1b**	**2a**	**2b**
RE	RE	1.000	1.000	0.000	0.000	PHE	H	0.089	0.089	0.089	0.089
PTL	N	-0.556	-0.556	-0.556	-0.556	PHE	C	-0.233	-0.233	-0.233	-0.233
PTL	N	-0.556	-0.556	-0.556	-0.556	PHE	H	0.125	0.125	0.125	0.125
PTL	C	0.382	0.382	0.382	0.382	PHE	C	0.359	0.359	0.359	0.359
PTL	H	0.008	0.008	0.008	0.008	PHE	C	-0.187	-0.187	-0.187	-0.187
PTL	C	-0.318	-0.318	-0.318	-0.318	PHE	C	-0.228	-0.228	-0.228	-0.228
PTL	H	0.127	0.127	0.127	0.127	PHE	C	-0.066	-0.066	-0.066	-0.066
PTL	C	0.059	0.059	0.059	0.059	PHE	H	0.073	0.073	0.073	0.073
PTL	H	0.074	0.074	0.074	0.074	PHE	C	-0.052	-0.052	-0.052	-0.052
PTL	C	-0.073	-0.073	-0.073	-0.073	PHE	H	0.121	0.121	0.121	0.121
PTL	C	0.335	0.335	0.335	0.335	PHE	C	-0.126	-0.126	-0.126	-0.126
PTL	C	0.335	0.335	0.335	0.335	PHE	H	0.093	0.093	0.093	0.093
PTL	C	-0.073	-0.073	-0.073	-0.073	PHE	H	0.088	0.088	0.088	0.088
PTL	C	0.059	0.059	0.059	0.059	PHE	H	0.095	0.095	0.095	0.095
PTL	H	0.074	0.074	0.074	0.074	BB	C	0.510	0.510	0.510	0.510
PTL	C	-0.318	-0.318	-0.318	-0.318	BB	O	-0.510	-0.510	-0.510	-0.510
PTL	H	0.127	0.127	0.127	0.127	BB	N	-0.470	-0.470	-0.470	-0.470
PTL	C	0.382	0.382	0.382	0.382	BB	H	0.310	0.310	0.310	0.310
PTL	H	0.008	0.008	0.008	0.008	BB	C	0.070	0.070	0.070	0.070
PTL	C	-0.151	-0.151	-0.151	-0.151	BB	H	0.090	0.090	0.090	0.090
PTL	H	0.115	0.115	0.115	0.115	CTR	C	0.340	0.340	0.340	0.340
PTL	C	-0.151	-0.151	-0.151	-0.151	CTR	O	-0.670	-0.670	-0.670	-0.670
PTL	H	0.115	0.115	0.115	0.115	CTR	O	-0.670	-0.670	-0.670	-0.670
CO	C	0.510	0.510	0.510	0.510	TYR	C	-0.132	-0.082	-0.247	-0.197
CO	O	-0.510	-0.510	-0.510	-0.510	TYR	H	0.054	0.000	0.142	0.088
CO	C	0.510	0.510	0.510	0.510	TYR	H	0.054	0.000	0.142	0.088
CO	O	-0.510	-0.510	-0.510	-0.510	TYR	C	0.133	-0.024	0.414	0.257
CO	C	0.510	0.510	0.510	0.510	TYR	C	-0.181	-0.172	-0.230	-0.221
CO	O	-0.510	-0.510	-0.510	-0.510	TYR	H	0.108	0.061	0.177	0.130
PHE	P	-0.512	-0.512	-0.512	-0.512	TYR	C	-0.151	-0.151	-0.217	-0.217
PHE	C	0.372	0.372	0.372	0.372	TYR	H	0.117	0.058	0.190	0.132
PHE	C	-0.195	-0.195	-0.195	-0.195	TYR	C	-0.171	-0.298	-0.033	-0.160
PHE	H	0.075	0.075	0.075	0.075	TYR	H	0.133	0.059	0.193	0.118
PHE	C	-0.064	-0.064	-0.064	-0.064	TYR	C	-0.244	-0.300	-0.105	-0.161
PHE	H	0.093	0.093	0.093	0.093	TYR	H	0.110	0.060	0.167	0.117
PHE	C	-0.031	-0.031	-0.031	-0.031	TYR	C	0.326	0.506	0.319	0.499

PHE	C	-0.041	-0.041	-0.041	-0.041	TYR	O	-0.559	-0.718	-0.315	-0.473
PHE	H	0.086	0.086	0.086	0.086	TYR	H	0.404	0.631	0.404	0.631
PHE	C	-0.248	-0.248	-0.248	-0.248	HOH	O	-0.730	-0.894	-0.730	-0.894
PHE	H	0.127	0.127	0.127	0.127	HOH	H	0.365	0.631	0.365	0.631
PHE	C	0.353	0.353	0.353	0.353	HOH	H	0.365	0.631	0.365	0.631
PHE	C	-0.177	-0.177	-0.177	-0.177	HOH	O	-0.730	-0.730	-0.730	-0.730
PHE	H	0.070	0.070	0.070	0.070	HOH	H	0.365	0.365	0.365	0.365
PHE	C	-0.075	-0.075	-0.075	-0.075	HOH	H	0.365	0.365	0.365	0.365
PHE	H	0.094	0.094	0.094	0.094	HOH	O	-0.730	-0.730	-0.730	-0.730
PHE	C	-0.114	-0.114	-0.114	-0.114	HOH	H	0.365	0.365	0.365	0.365
PHE	H	0.092	0.092	0.092	0.092	HOH	H	0.365	0.365	0.365	0.365
PHE	C	-0.056	-0.056	-0.056	-0.056						

Abbreviations: RE, rhenium ion; PTL, phenanthroline ligand; CO, carbon monoxide ligand; PHE, triphenyl-phosphine ligand; BB, peptide backbone; CTR, peptide C-terminus carboxylic group; TYR, tyrosine side chain; POS, phosphate ion; HOH, water.

Total energy of the optimized ReYOH structure: –2769.78423409861 Hartrees
Calculated at the DFT B3LYP/LACV3P** level with Jaguar

Reference 35:

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.03; Gaussian, Inc.: Pittsburgh, PA, 2003.
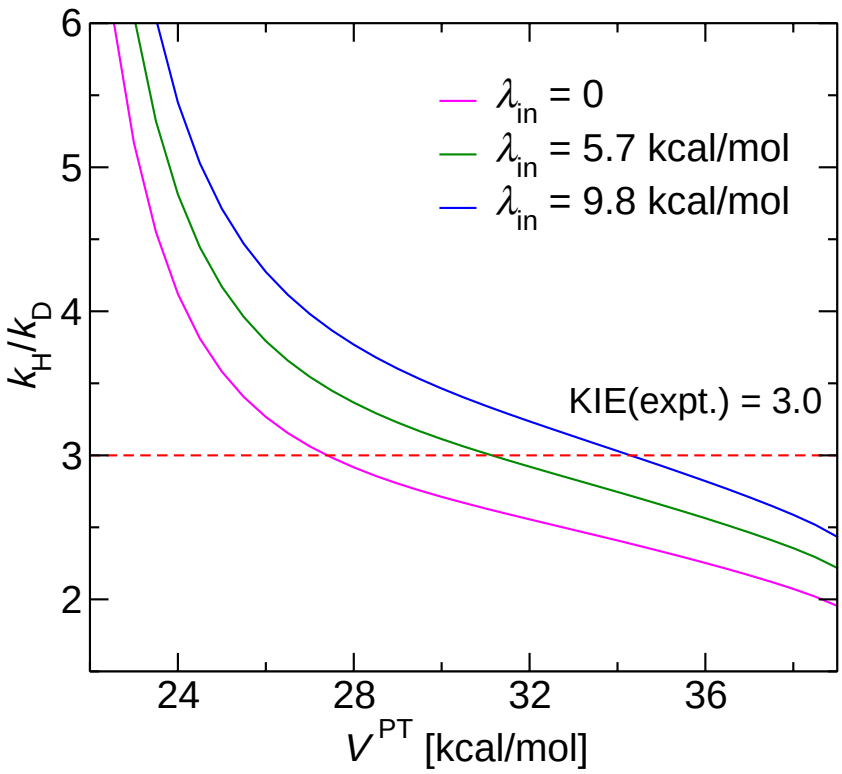
Figure S1. Sensitivity of the KIE (k_H/k_D) for the unimolecular PCET rate constant k_{PCET}^{uni} to the coupling parameter V^{PT} and the inner-sphere reorganization energy λ_{in} for the phosphate-acceptor model.