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

Supplementary information for Effect of Microsolvation on the Mode Specificity of $OH^{\bullet}(H_2O)$ + HCl Reaction

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Table S1: Energy barrier (in kcal mol^{-1}) for bare as well as microsolvated reaction obtained using various DFT functionals along with results obtained at CCSD(T)/aug-cc-pVTZ//QCISD/ aug-cc-pVDZ level of theory.

Methods	Bare	Microsolvated
CCSD(T)/aug-cc-pVTZ//QCISD/aug-cc-pVDZ	2.2	-0.5
B3LYP/6-31+g*	-2.0	-4.4
M06-2X/6-31+g*	1.3	-3.0
M05-2X/6-31+g*	1.5	-2.6
PBE1PBE/6-31+g*	-1.7	-5.0
LC-whPBE/6-31+g*	**3.4**	**0.3**

Table S2: Cartesian coordinates, absolute energy and harmonic vibrational frequencies for all the stationary points at LC-whPBE/6-31+g* level of theory

Species	Coordinates (Å)				Frequencies (cm^{-1})			Energy (Hartree)
OH	O	0	0	0.108719	3747.7864			-75.6879114
	H	0	0	-0.869755				
HCl	Cl	0	0	0.07101	3083.6709			-460.6560718
	H	0	0	-1.207169				
Bare RC	O	-2.091406	-0.106648	-0.000001				
	H	-0.151779	-0.129636	0	160.0815	245.2088	379.1286	-536.35009
	H	-2.372106	0.832362	-0.000012	536.3268	2885.9297	3738.721	
	Cl	1.132655	0.008851	0.000001				
Bare TS	Cl	0.909988	0.011069	-0.008845				
	H	-0.41204	-0.306399	0.317687	1383.4559i	320.5479	544.686	-536.3385048
	H	-1.776408	0.870644	0.086315	938.5171	1420.4559	3748.6846	
	O	-1.660169	-0.094052	-0.031704				
Bare PC	O	1.561522	0	-0.115485				
	H	1.766856	-0.773853	0.426935	192.5914	392.2566	405.6577	-536.382731
	H	1.766851	0.773854	0.426934	1665.2483	3814.8742	3937.4699	
	Cl	-0.942699	0	0.004118				
OH-H2O	O	-1.604387	0.000017	0.013823				
	H	-0.61945	-0.000376	-0.048433	144.7924	187.8479	221.3322	
	O	1.246088	-0.000027	-0.064341	459.379	680.5979	1669.1209	-152.0793036
	H	1.742578	0.775349	0.2262	3604.0587	3839.4148	3955.4783	
	H	1.743265	-0.774896	0.226377				
Microsolvated RC	O	-0.985511	1.644424	0.000014				
	H	0.666259	0.729701	0.00003	31.0425	70.1115	171.7024	
	H	-1.529119	0.814567	0.000033	243.9059	271.1023	299.2264	-612.7458657
	Cl	1.557546	-0.219003	0.000008	397.6623	484.3638	501.2706	
	O	-1.783712	-0.984042	-0.000137	841.7526	1666.9163	2748.4197	
	H	-0.953701	-1.482589	-0.000039	3528.401	3818.2564	3944.8694	
	H	-2.50793	-1.621686	0.000825				
Microsolvated TS	O	-0.354293	1.513105	-0.021539				
	H	0.630111	0.757009	0.301242	1398.9688i	50.715	98.5967	
	H	-1.131332	0.886557	-0.027394	252.2599	283.2721	380.5454	-612.7348752
	Cl	1.415044	-0.394565	0.000562	428.5312	552.7073	833.1058	
	O	-2.084863	-0.603482	-0.066864	1024.3258	1313.8229	1681.686	
	H	-1.464673	-1.314006	-0.286477	3377.3163	3817.0737	3932.8559	
	H	-2.576619	-0.898931	0.710301				
Microsolvated PC	Cl	-1.337955	-0.447433	-0.003826				
	H	1.377441	-1.267085	0.062502	75.2645	161.3802	229.5037	
	H	2.664911	-0.737793	-0.619987	254.4138	259.127	369.6079	
	O	2.045226	-0.566436	0.100616	460.5662	509.9298	909.3424	
	H	0.974476	0.871746	-0.009914	1677.0438	1689.0289	3547.6922	
	O	0.170922	1.429287	-0.114764	3813.2281	3883.9817	3932.996	
	H	-0.000778	1.836678	0.745637				

Table S3: The values of N_{total} and N_r for each initial condition of bare and microsolvated channels

BARE			Microsolvated		
GS					
E_{trans} (kcal mol^{-1})	N_{total}	N_r	E_{trans} (kcal mol^{-1})	N_{total}	N_r
1	500	14	1	500	94
4	500	14	4	500	74
8	500	22	8	500	66
12	500	38	12	500	54
HCl-1					
1	500	137	1	500	196
4	500	90	4	500	157
8	500	57	8	500	124
12	500	52	12	500	113
HCl-2					
1	500	172	1	500	208
4	500	105	4	500	170
8	500	76	8	500	142
12	500	77	12	500	135
OH-1					
1	500	13	1	500	105
4	500	12	4	500	66
8	500	25	8	500	68
12	500	41	12	500	65

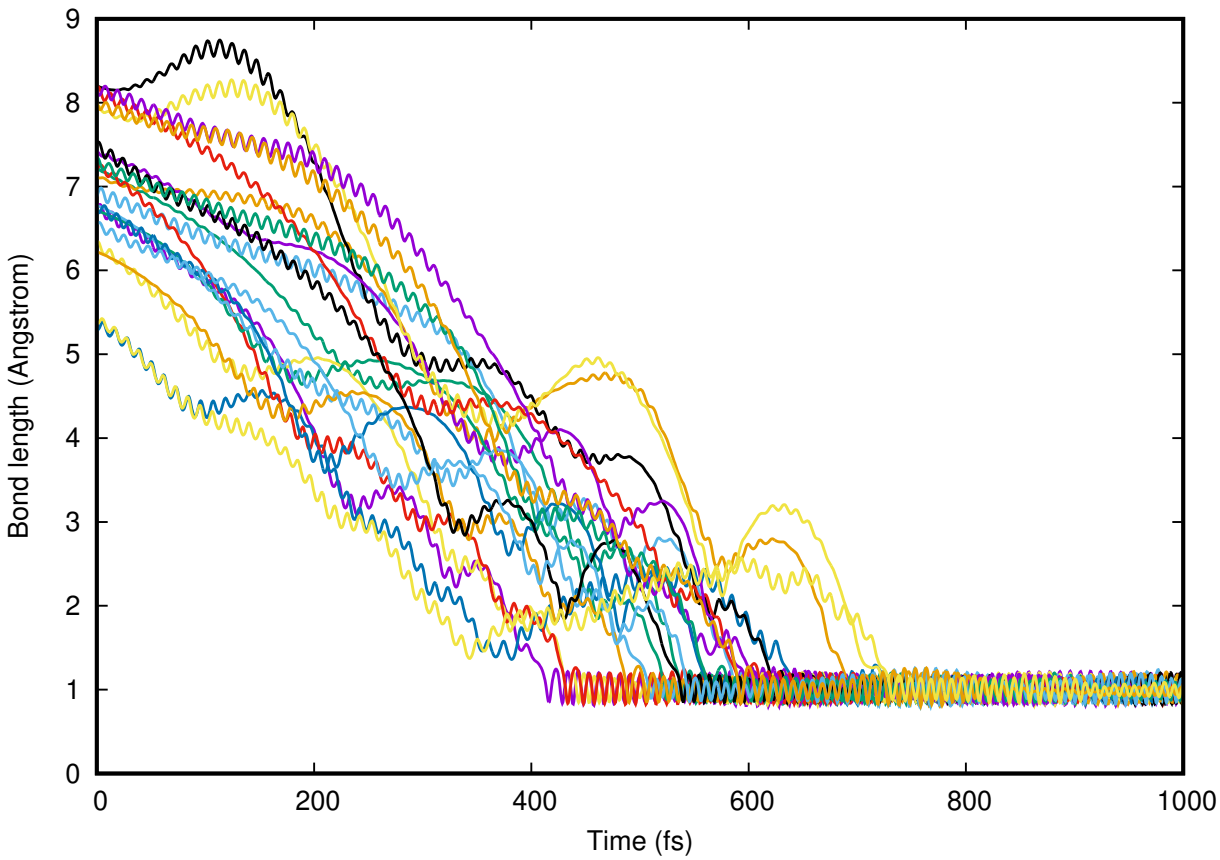

Figure S1: The O-H bond distance with time for trajectories that are passing through a hydrogen bonded pre-reactive complex for the ground state of the $OH^{\bullet}(H_2O)$ + HCl reaction at E_{trans} = 1 kcal mol^{-1}.

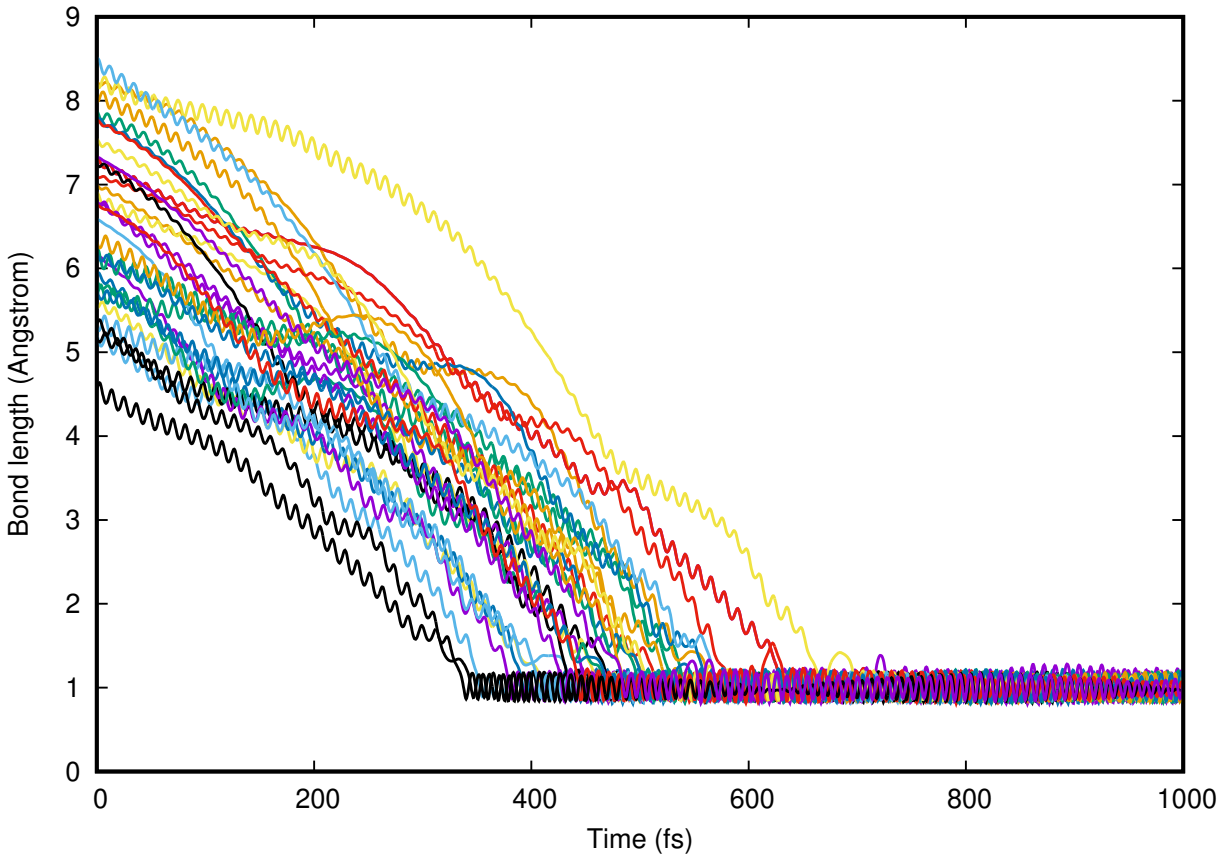

Figure S2: The O-H bond distance with time for trajectories that are passing through a direct hydrogen abstraction path for the ground state of the $OH^{\bullet}(H_2O)$ + HCl reaction at E_{trans} = 1 kcal mol^{-1}.

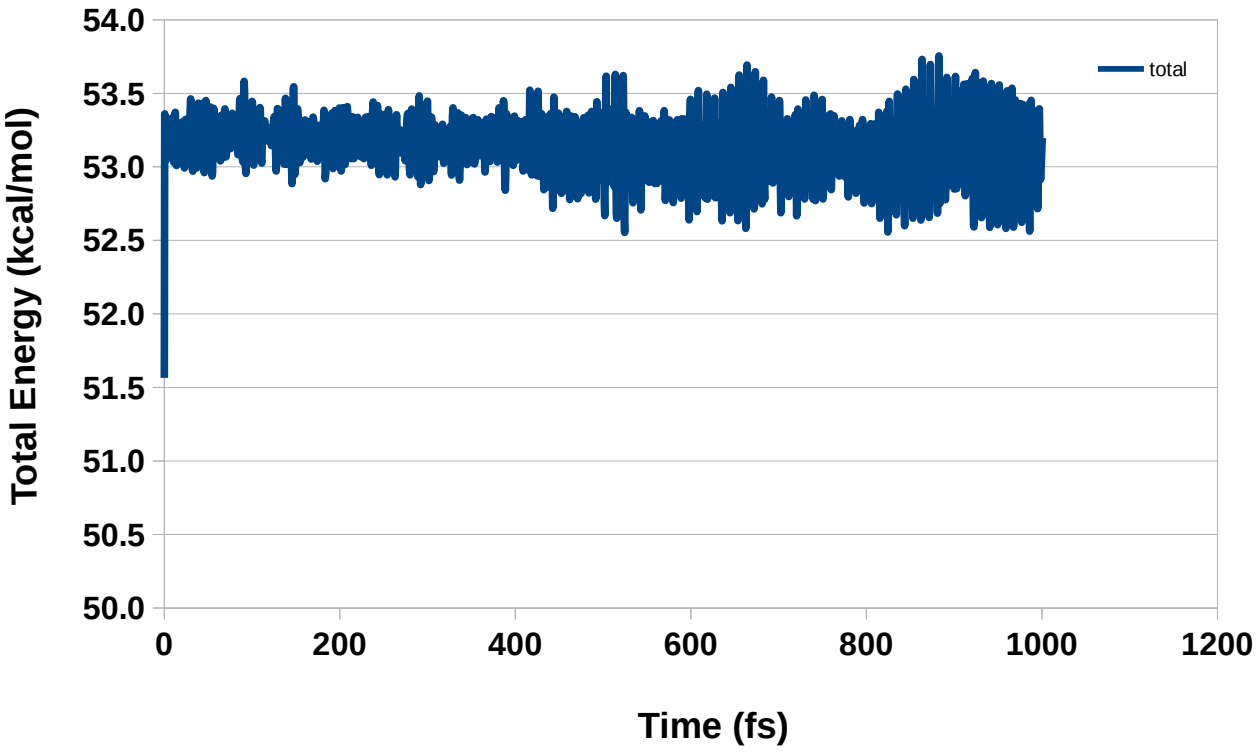

Figure S3: Evolution of total energy for a representative trajectory of $OH^{\bullet}(H_2O)$ + HCl reaction.