Supplementary Material

Tunneling in H loss from energy selected ethanol ions

Andras Bodi,[a*] M. Daniel Brannock,[b] Bálint Sztáray,[c] and Tomas Baer[b*]

[a]Molecular Dynamics Group, Paul Scherrer Institut, 5232 Villigen, Switzerland

[b]Department of Chemistry, University of North Carolina, Chapel Hill, NC 27517

[c]Department of Chemistry, University of the Pacific, Stockton, CA 95211

[*] Authors to whom correspondence should be addressed. E-mail: andras.boedi@psi.ch and baer@unc.edu.

Neutral				Parent ion				H/D-loss transition state				Me-loss product		
C_2H_5OH	C_2D_5OD	CD_3CH_2OH	CH_3CD_2OH	$C_2H_5OH^+$	$C_2D_5OD^+$	$CD_3CH_2OH^+$	$CH_3CD_2OH^+$	$C_2H_5OH^{+‡}$	$C_2D_5OD^{+‡}$	$CD_3CH_2OH^{+‡}$	$CH_3CD_2OH^{+‡}$	CH_2OH^+	CD_2OD^+	CD_2OH^+
239	179	189	237	226	166	173	222	-800	-599	-799	-601	1053	771	922
287	207	274	284	314	276	300	308	216	156	167	208	1123	810	976
416	360	372	411	438	346	434	401	454	357	411	380	1265	1005	1005
825	600	681	691	708	605	631	653	513	387	478	409	1395	1102	1112
912	753	773	873	853	627	636	765	557	428	550	485	1508	1118	1313
1054	829	939	929	863	644	679	857	687	524	620	653	1690	1609	1618
1114	928	1073	982	945	706	933	882	927	720	806	863	3149	2300	2302
1188	934	1080	1030	1126	805	1057	898	997	776	879	904	3300	2477	2477
1271	1007	1100	1136	1268	987	1067	1047	1090	874	962	1028	3605	2630	3605
1312	1045	1127	1152	1295	1051	1074	1085	1181	940	1029	1064			
1409	1082	1160	1197	1374	1059	1126	1276	1277	998	1044	1106	CH_3	CD_3	
1457	1092	1255	1333	1440	1073	1275	1334	1392	1033	1166	1336	486	377	
1504	1102	1286	1421	1470	1077	1371	1440	1427	1044	1174	1398	1445	1063	
1521	1163	1451	1503	1506	1183	1480	1470	1456	1104	1258	1438	1445	1063	
1546	1263	1544	1522	1684	1490	1618	1593	1489	1211	1439	1485	3178	2248	
3045	2209	2213	2213	3094	2203	2203	2249	1588	1541	1572	1563	3369	2511	
3079	2217	2349	2297	3103	2247	2417	2408	3027	2183	2183	2359	3369	2511	
3089	2296	2353	3079	3221	2405	2439	3096	3142	2314	2314	3027			
3171	2349	3045	3171	3251	2418	3101	3251	3183	2358	2378	3142			
3177	2354	3091	3175	3278	2441	3223	3276	3205	2378	3185	3203			
3846	2801	3846	3846	3684	2683	3684	3683	3638	2651	3638	3638			

Table S1. Harmonic MP2 frequencies in cm^{-1} used in the statistical model to calculate densities and numbers of states.

	ΔE / eV	B3LYP	B3LYP/anharm	M06-2X	MP2	MP2/anharm	CCSD	$\overline{\Delta E}$	2 x σ
		6-311++G(d,p)				cc-pVTZ			
H/D loss	C_2D_5OD	0.097	0.096	0.097	0.099	0.097	0.097	**0.097**	0.002
	CD_3CH_2OH	0.009	0.008	0.007	0.008	0.013	0.006	**0.008**	0.005
	CH_3CD_2OH	0.094	0.089	0.096	0.096	0.096	0.096	**0.095**	0.005
CH_3/CD_3 loss	C_2D_5OD	0.058	0.057	0.059	0.057	0.054	0.059	**0.057**	0.003
	CD_3CH_2OH	0.047	0.044	0.047	0.046	0.046	0.048	**0.046**	0.002
	CH_3CD_2OH	0.014	0.012	0.015	0.014	0.015	0.014	**0.014**	0.002

Table S2. Dissociative photoionization energy shifts in meV with respect to light ethanol thanks to zero point energy differences of the different isotopologues. The error bar is taken as twice the standard deviation of the ZPE shift values.

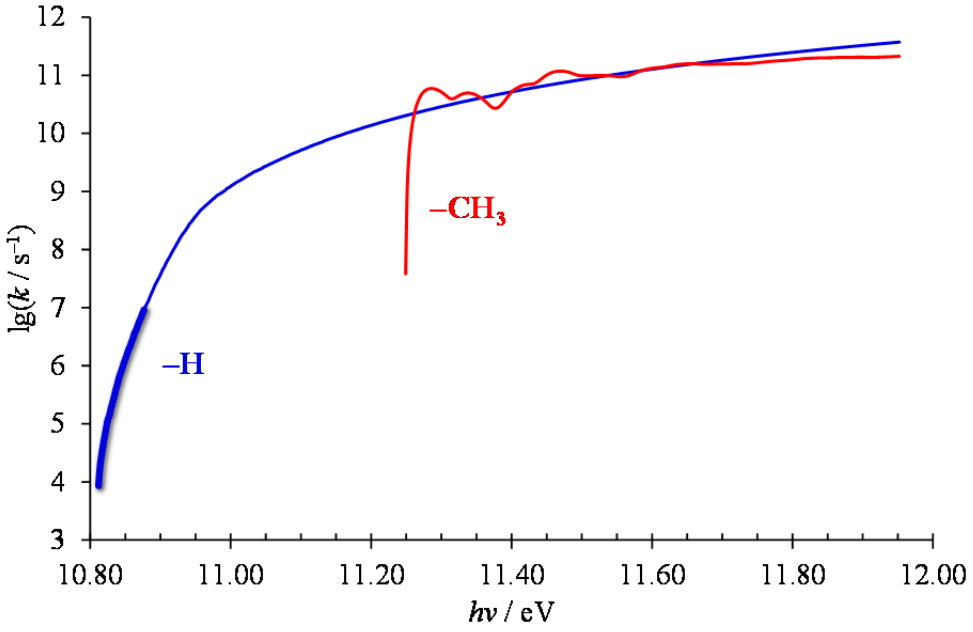

Figure S1. SSACM unimolecular rate constants for H and CH_3 loss from $C_2H_5OH^+$ with the energy referenced to ground state C_2H_5OH. The bold portion of the H-loss rate curve is where there is experimental rate information. The dissociation is only slow because of tunneling. The oscillations in the methyl-loss rate curve are due to the sparsely spaced vibrational levels of the product ion CH_2OH^+.