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

Competitive Reaction Pathways in Vibrationally Induced Photodissociation of H_2SO_4

Juvenal Yosa Reyes, Tibor Nagy, Markus Meuwly Department of Chemistry, University of Basel, Klingelbergstrasse 80, Basel, Switzerland

Supporting information

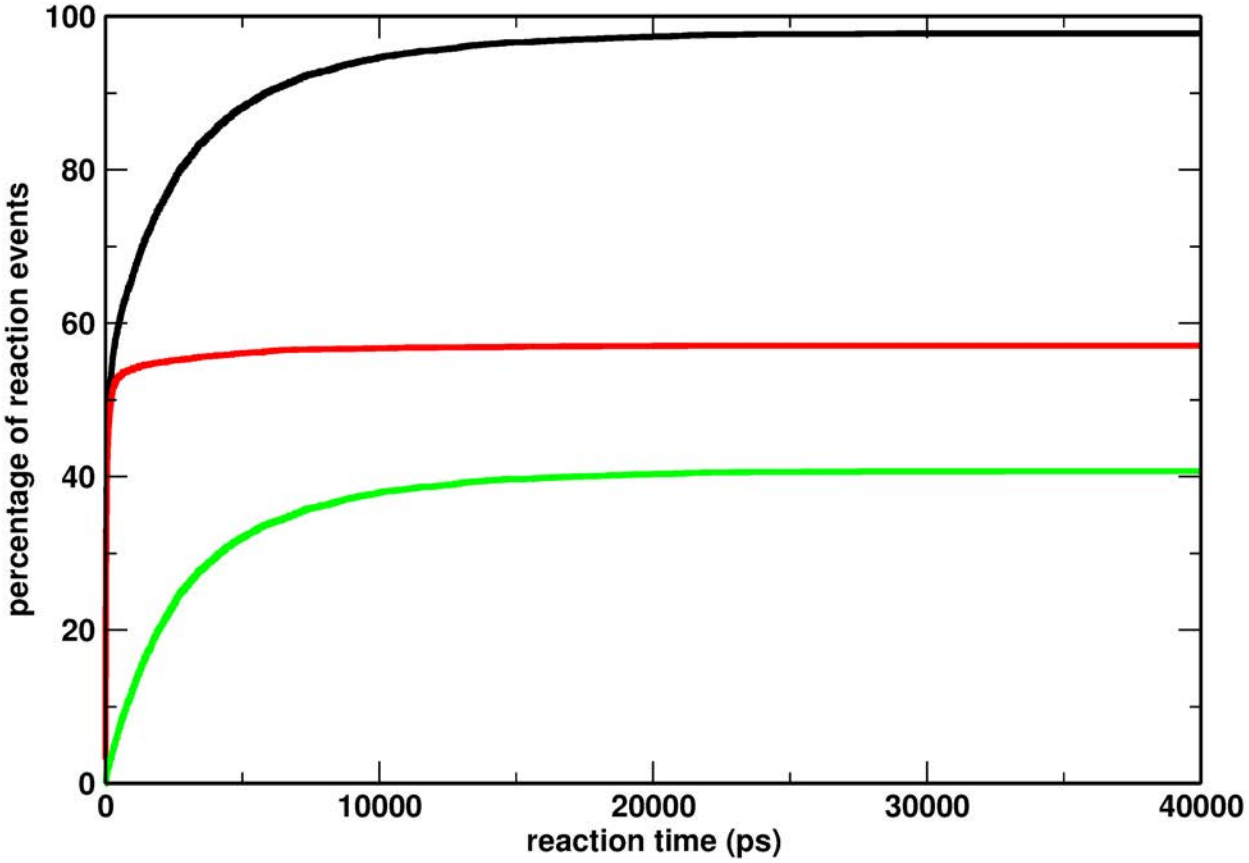

FIG. S-I: Percentage of reactive events for water elimination after excitation of $\nu_9 = 6$. Black, red and green curves correspond to overall, direct water elimination, and water elimination preceded by intramolecular H-transfer, respectively.

TABLE : S-I Optimized Geometry of reactants (H_2SO_4) and products SO_3 + H_2O Calculated with, MP2/6-31G(2d,2p) and Force Field

	MP2/6-311G++(2d,2p)	**Force field**	**Experimental**	
H_2SO_4				
Distances (Å)			**X-ray**	**Microwave**
S1-O2	1.42	1.43	1.43	1.42
S1-O3	1.42	1.43	1.43	1.42
S1-O4	1.59	1.59	1.54	1.57
S1-O6	1.59	1.59	1.54	1.57
O4-H5	0.96	0.97		0.97
O6-H7	0.96	0.97		0.97
Angles (°)				
O3-S1-O2	124.51	125.86		123.30
O4-S1-O2	105.52	107.11		106.40
O4-S1-O3	108.65	107.17		108.60
O4-S1-O6	101.78	99.26		101.30
H5-O4-S1	107.98	106.31		108.50
O6-S1-O3	105.52	107.05		106.40
O6-S1-O2	108.65	107.23		108.40
H7-O6-S1	107.98	106.25		108.50
Dihedrals (°)				
H5-O4-S1-O2	163.83	162.73		
H5-O4-S1-O3	28.25	25.28		
H5-O4-S1-O6	-82.78	-85.91		
H7-O6-S1-O2	28.26	25.29		
H7-O6-S1-O3	163.85	162.75		
H7-O6-S1-H4	-82.77	-85.97		

TABLE : S-I Optimized Geometry of reactants (H_2SO_4) and products SO_3 + H_2O Calculated with, MP2/6-31G(2d,2p) and Force Field

	MP2/6-311G++(2d,2p)	**Force field**	**Experimental**	
SO_3				
Distances (Å)			**X-ray**	**Microwave**
S1-O2	1.44	1.44		
S1-O3	1.44	1.44		
S1-O4	1.44	1.44		
Angles (°)				
O2-S1-O3	120.00	120.00		
O4-S1-O2	120.00	120.00		
O4-S1-O3	120.00	120.00		
H_2O				
Distances (Å)			**X-ray**	**Microwave**
O6-H7	0.96	0.96		
O6-H5	0.96	0.96		
Angles (°)				
H7-O6-H5	104.26	104.32		
$SO_3 \cdots H_2O$				
Distances (Å)			**X-ray**	**Microwave**
S1-O2	1.44	1.45		
S1-O3	1.44	1.45		
S1-O4	1.44	1.45		
O6-H7	0.96	0.96		
O6-H5	0.96	0.96		
O6-S1	2.44	2.29		

TABLE : S-I Optimized Geometry of reactants (H_2SO_4) and products SO_3 + H_2O Calculated with, MP2/6-31G(2d,2p) and Force Field

	MP2/6-311G++(2d,2p)	**Force field**	**Experimental**	
$SO_3 \cdots H_2O$				
Angles (°)			**X-ray**	**Microwave**
O3-S1-O2	119.90	119.70		
O3-S1-O4	119.50	119.80		
O3-S1-O6	91.30	92.40		
O4-S1-O2	119.90	119.70		
O4-S1O6	91.30	92.40		
O2-S1-O6	93.90	93.30		
H5-O6-H7	105.10	103.17		
H5-O6-S1	106.80	128.30		
H7-O6-S1	106.80	128.30		

TABLE : S-II Experimental and calculated (Force Field and MP2/6-311G(2d,2p)) frequencies (Experimental frequencies are found in the bibliographic reference 51-53 from the main text.)

mode	**MP2/6-311G++(2d,2p) cm^{-1}**	**Force field cm^{-1}**	**Exp. cm^{-1}**
H2SO4			
1	177.5	274.8	
2	260.9	295.4	
3	346.2	413.4	281.1
4	398.1	432.3	
5	455.9	449.7	
6	502.1	490.1	550.0
7	510.8	510.4	568.0
8	770.5	740.1	834.1
9	818.9	820.3	891.4
10	1096.9	1227.7	1138.0
11	1112.0	1232.9	1157.1
12	1159.3	1289.0	1220.1
13	1397.3	1567.2	1464.7
14	3614.1	3740.7	
15	3618.1	3742.2	3609.2
SO3			
1	460.2	461.7	488.1
2	494.3	491.3	
3	494.5	491.4	532.1
4	990.0	1038.1	
5	1325.4	1294.3	1395.3
6	1326.3	1294.4	1397.7

TABLE : S-II Experimental and calculated (Force Field and MP2/6-311G(2d,2p)) frequencies, (Experimental frequencies are found in the bibliographic reference 51-53 from the main text.).

mode	**MP2/6-311G++(2d,2p) cm^{-1}**	**Force field cm^{-1}**	**Exp. cm^{-1}**
	H_2O		
1	1610.8	1607.2	1597.6
2	3746.0	3723.0	3634.5
3	3862.4	3824.1	3726.9
	$SO_3 \cdots H_2O$		
1	71.3	50.2	
2	147.6	74.6	
3	154.7	144.6	
4	165.0	167.1	
5	395.2	200.4	
6	438.5	292.3	
7	459.4	463.5	488.5
8	507.8	489.2	545.8
9	516.0	490.7	549.4
10	1006.0	1050.1	1079.3
11	1331.2	1303.5	1397.0
12	1343.0	1313.9	1399.1
13	1607.1	1605.8	1591.4
14	3702.3	3698.0	3562.8
15	3816.4	3798.4	3678.2