Supplementary Material to

Molecular Dynamic Simulations of OH-Stretching Overtone Induced Photodissociation of Fluorosulfonic and Chlorosulfonic Acid

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Table S1: Calculated CC-VSCF frequencies (in cm^{-1}) for the OH-stretching SOH-bending and OH-stretching OSOH-torsion combination states in FSO_3H.

OH-stretching state	**OH_{str} + SOH_{bend}**	**OH_{str} + $OSOH_{tors}$**
ν=5	18243	17385
ν=6	22190	21331
ν=7	26928	26069

Table S2: Selected geometric parameters (in Angstroms and degrees) for the dissociative transition state of FSO_3H and $ClSO_3H$.

Parameter	PM3	MP2/TZP	CCSD(T)/AV(T+d)Z
FSO_3H			
$R_{O\text{-}H}$	1.3198	1.1709	1.2379
$\theta_{H\text{-}O\text{-}S}$	91.38	91.96	84.11
$\phi_{H\text{-}O\text{-}S\text{-}O}$	100.21	99.91	99.61
$R_{S\text{-}X}$	1.7951	2.2437	1.9780
$ClSO_3H$			
$R_{O\text{-}H}$	1.3249	1.2142	1.2854
$\theta_{H\text{-}O\text{-}S}$	103.05	98.36	89.13
$\phi_{H\text{-}O\text{-}S\text{-}O}$	98.14	100.26	101.18
$R_{S\text{-}X}$	2.5164	2.8835	2.4146

Table S3: Harmonic frequencies (in cm^{-1}) for the dissociative transition state of FSO_3H and $ClSO_3H$.

Mode	PM3	MP2/TZP	CCSD(T)/AV(D+d)Z
FSO_3H			
1	1408	2044	1951
2	1051	1452	1393
3	942	1260	1228
4	806	999	958
5	793	991	944
6	651	701	686
7	553	630	607
8	402	467	483
9	359	449	458
10	343	326	331
11	219	215	219
12	2306i	1478i	1565i
$ClSO_3H$			
1	1688	2219	1603
2	1134	1373	1374
3	968	1124	1217
4	701	1010	946
5	696	958	749
6	507	692	569
7	394	536	500
8	373	445	445
9	350	391	441
10	137	307	221
11	127	256	167
12	1917i	1857i	1533i

Table S4: Selected geometric parameters (in Angstroms and degrees) for the hydrogen-hopping transition state of FSO_3H and $ClSO_3H$.

Parameter	PM3	MP2/TZP	CCSD(T)/AV(T+d)Z
FSO_3H			
$R_{O\text{-}H}$	1.3518	1.2942	1.2976
$\theta_{H\text{-}O\text{-}S}$	85.37	73.38	73.39
$\phi_{H\text{-}O\text{-}S\text{-}O}$	130.14	134.60	132.99
$R_{S\text{-}X}$	1.5405	1.6017	1.54847
$ClSO_3H$			
$R_{O\text{-}H}$	1.3689	1.2969	1.2933
$\theta_{H\text{-}O\text{-}S}$	85.99	73.64	73.70
$\phi_{H\text{-}O\text{-}S\text{-}O}$	129.26	129.51	129.38
$R_{S\text{-}X}$	2.0664	2.0567	2.0104

Table S5: Harmonic frequencies (in cm^{-1}) for the hydrogen-hopping transition state of FSO_3H and $ClSO_3H$.

Mode	PM3	MP2/TZP	CCSD(T)/AV(D+d)Z
FSO_3H			
1	1152	2231	2138
2	946	1410	1351
3	873	1164	1119
4	808	1039	1004
5	750	971	938
6	640	780	791
7	456	676	654
8	391	493	498
9	353	463	470
10	295	412	402
11	252	307	310
12	2443i	1874i	1928i
$ClSO_3H$			
1	1110	2219	2123
2	931	1373	1319
3	846	1124	1077
4	803	1010	970
5	720	958	931
6	518	692	669
7	450	536	531
8	366	445	452
9	344	391	387
10	248	307	300
11	225	256	258
12	2278i	1857i	1920i

Figure S1: PM3 snapshots of the dissociation of FSO_3H. The simulation is evaluated after excitation to the ν = 5 OH+SOH combination state.

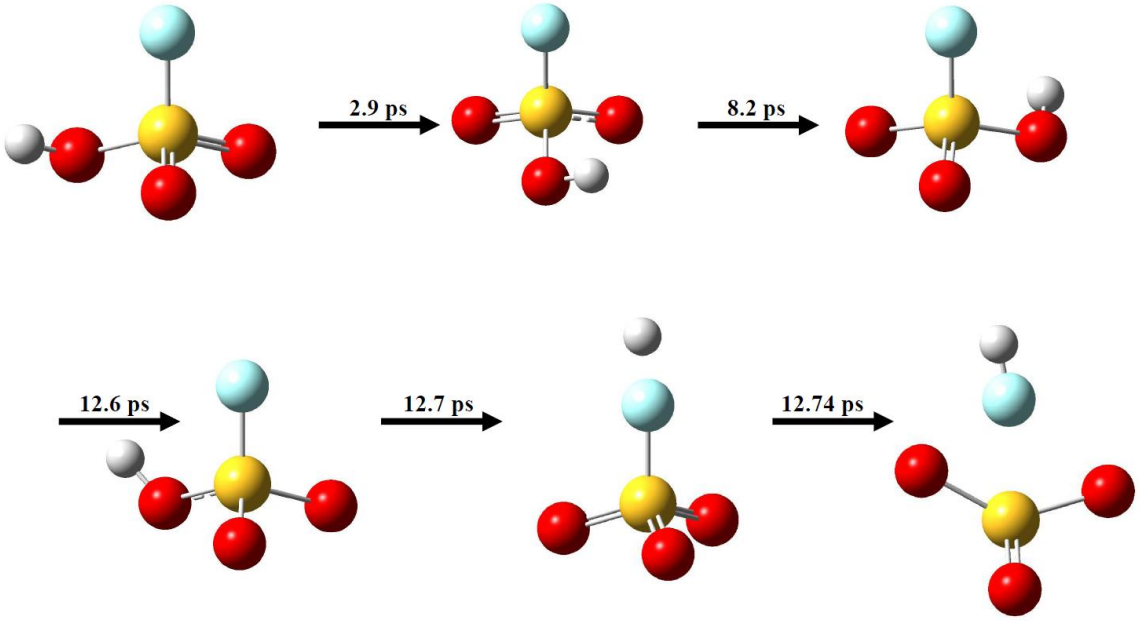

Figure S2: PM3 snapshots of the dissociation of FSO_3H. The simulation is evaluated after excitation to the ν = 5 OH+OSOH combination state.

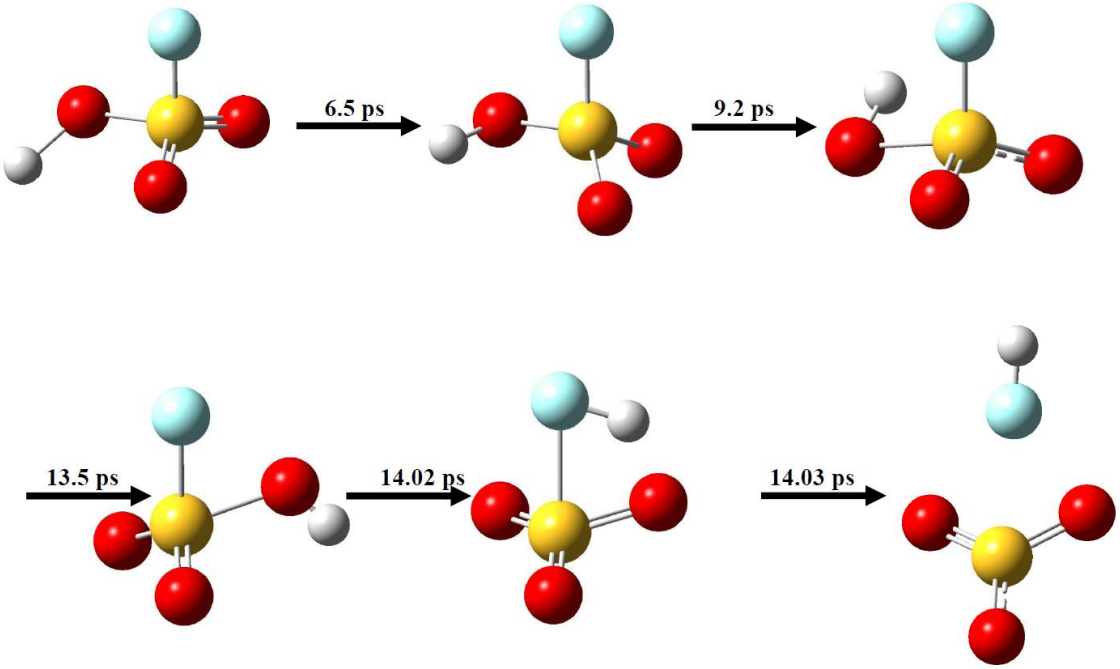

Figure S3: PM3 snapshots of hydrogen-hopping in FSO_3H. The simulation is evaluated after excitation to the ν = 5 OH+SOH combination state.

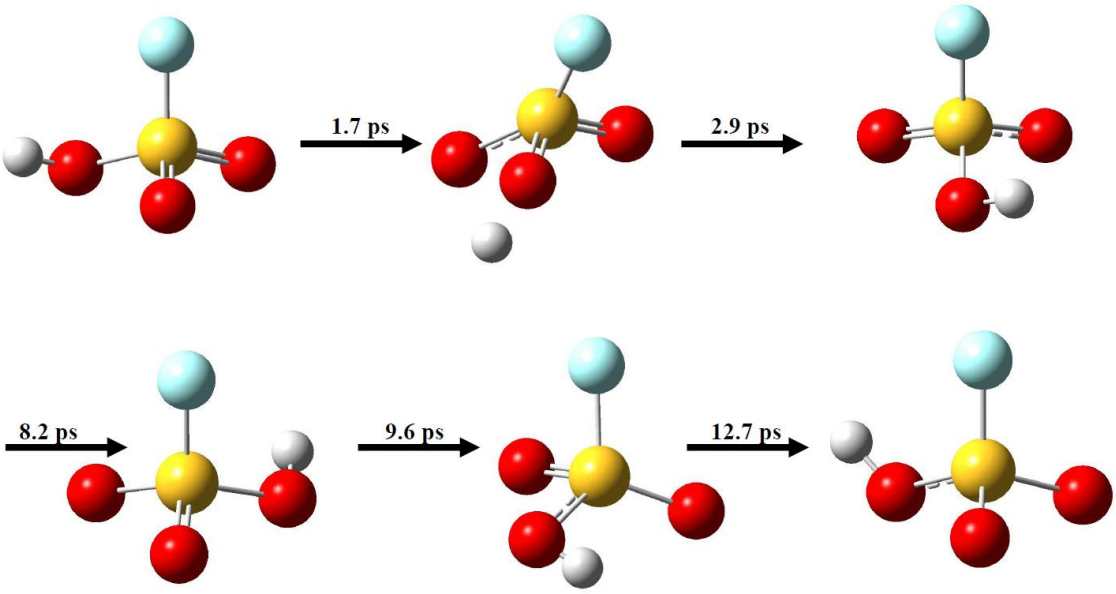

Figure S4: PM3 snapshots of hydrogen-hopping in FSO_3H. The simulation is evaluated after excitation to the ν = 5 OH+OSOH combination state.

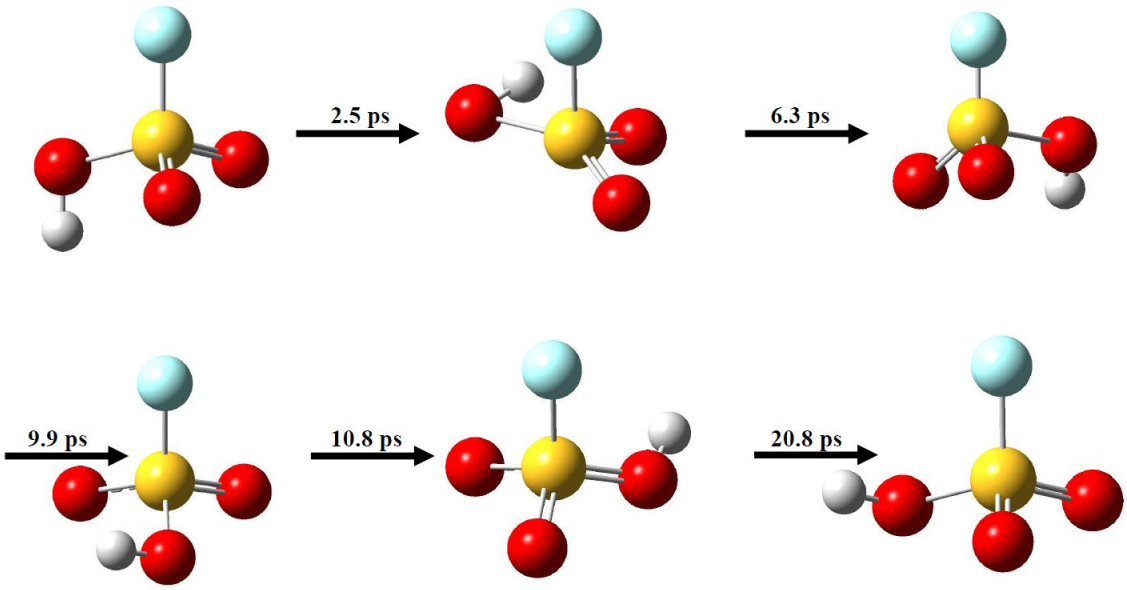

Figure S5: The time distribution of dissociation events for the PM3 ν = 5 OH+SOH and OH+OSOH combination state trajectories of FSO_3H.

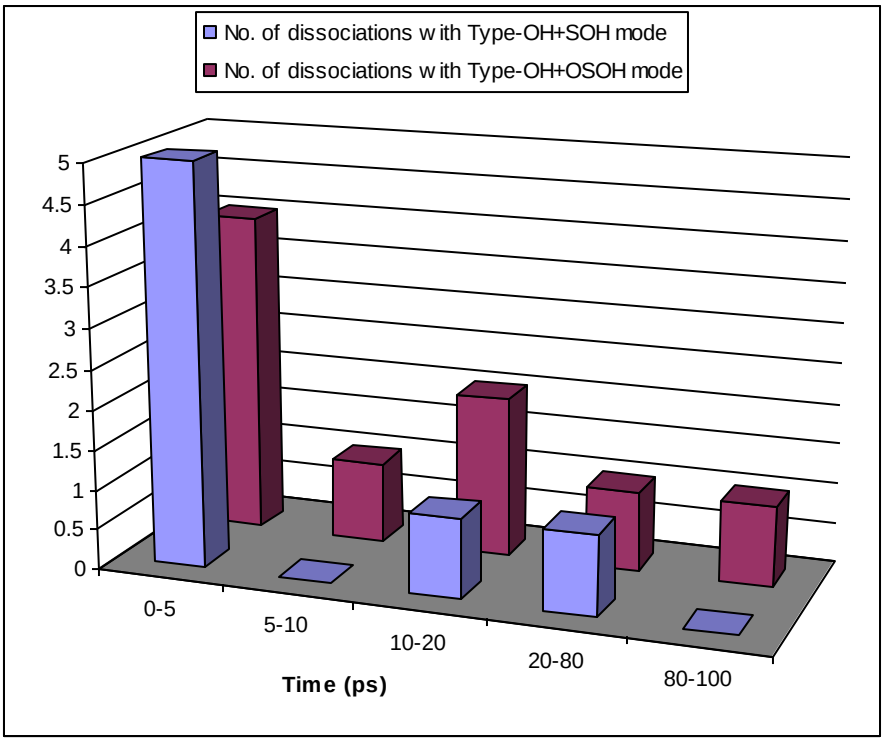

Figure S6: The time distribution of dissociation events for the PM3 ν = 6 OH+SOH and OH+OSOH combination state trajectories of FSO_3H.

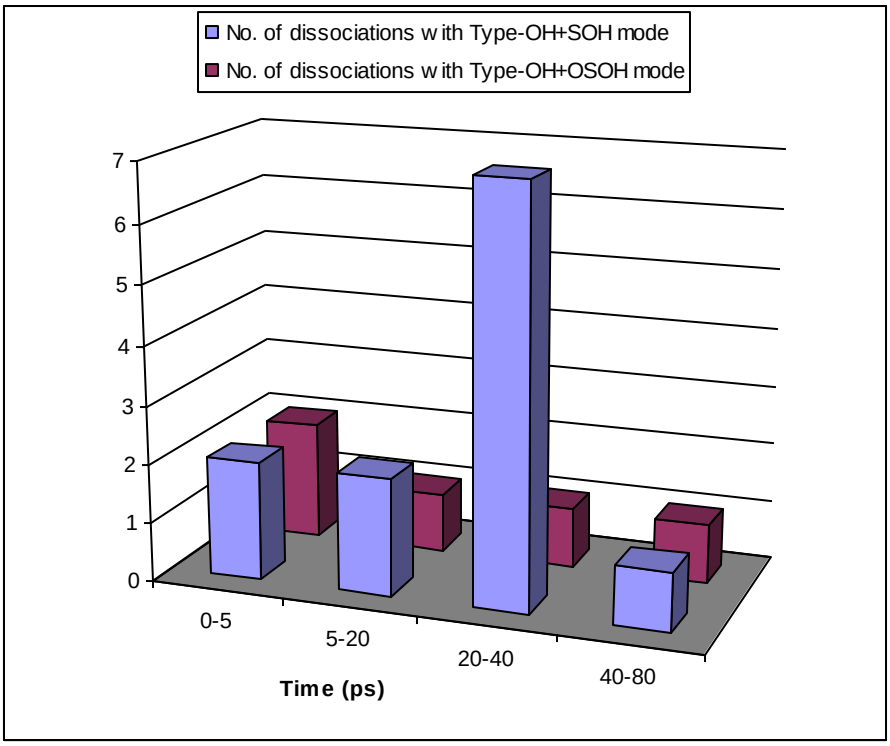

Figure S7: The time distribution of dissociation events for the PM3 ν = 7 OH+SOH and OH+OSOH combination state trajectories of FSO_3H.

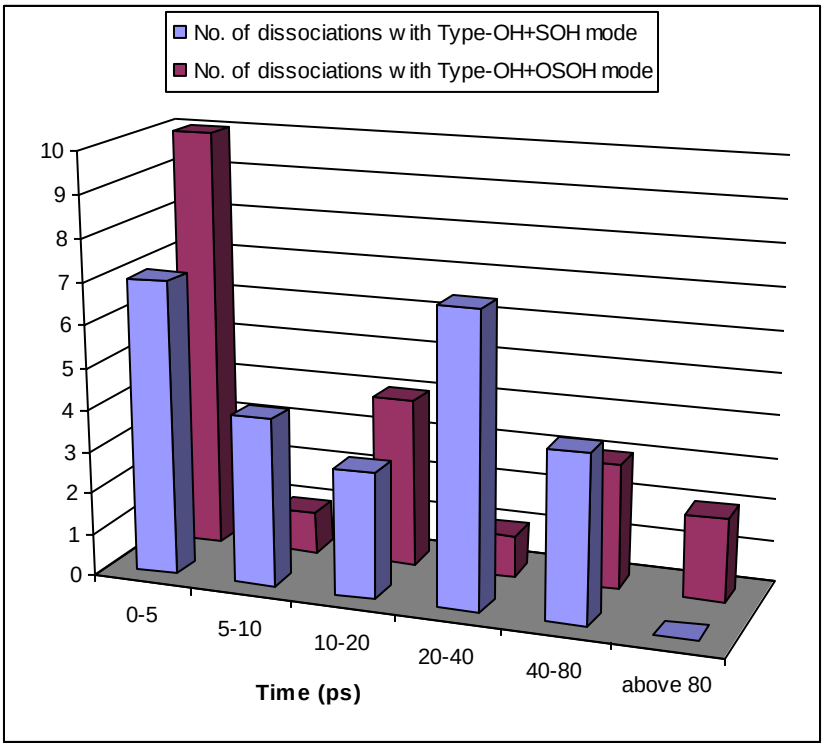

Figure S8: The time distribution of dissociation events for the MP2/TZP ν=5, *v*=6 and *v*=7 OH-stretching trajectories of FSO_3H.

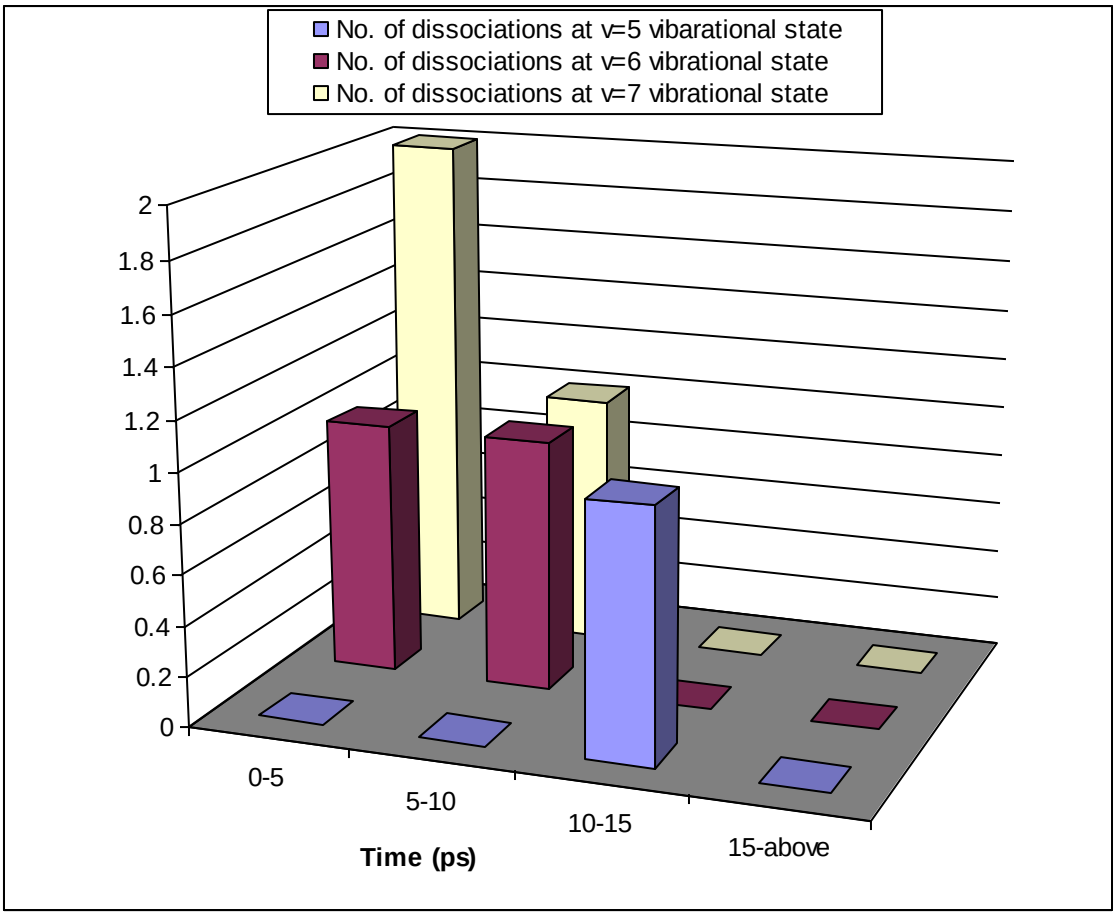

Figure S9: The time distribution of dissociation events for the PM3 ν=4, ν=5 and ν=6 OH-stretching trajectories of $ClSO_3H$.

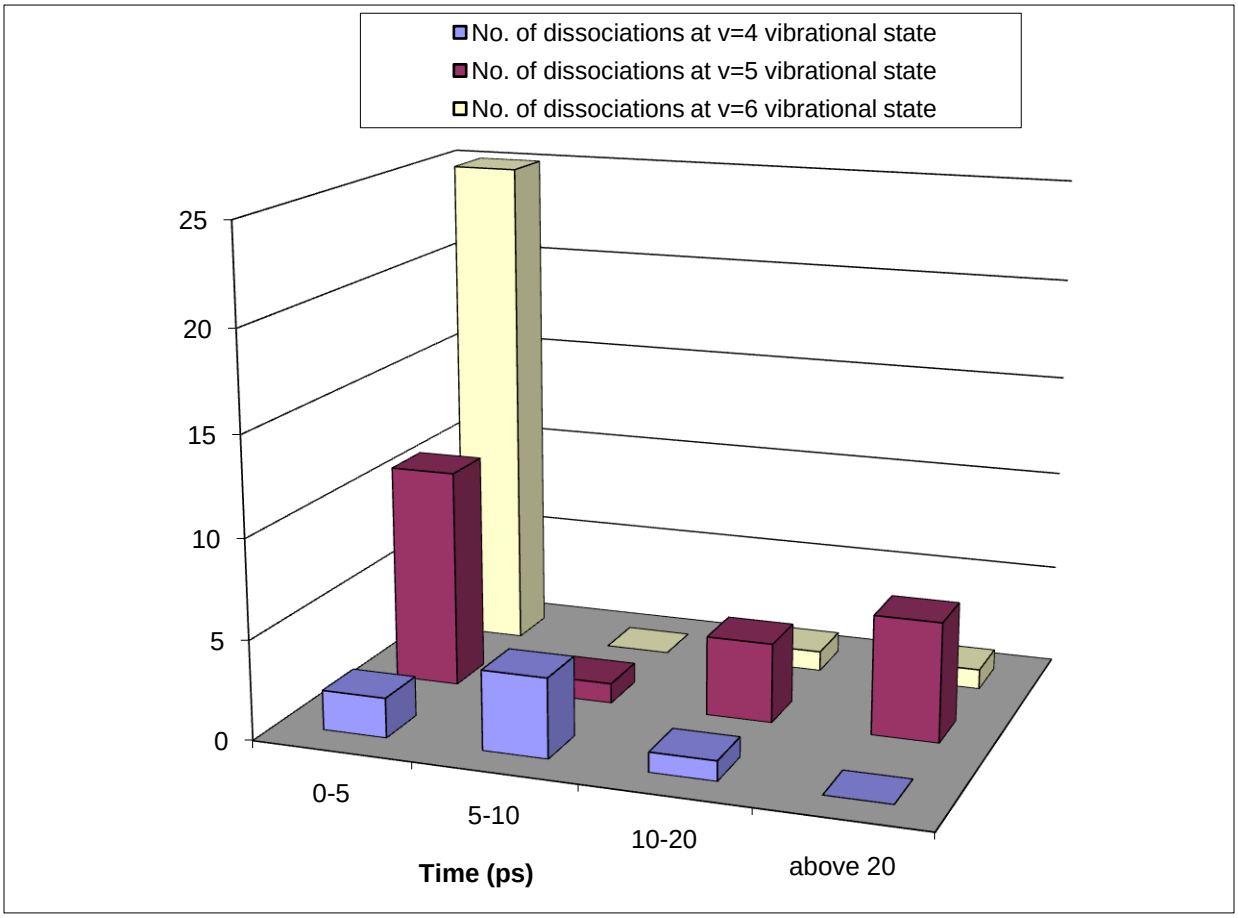

Figure S10: The time distribution of dissociation events for the MP2/TZP ν=4, *v*=5 and *v*=6 OH-stretching trajectories of $ClSO_3H$.

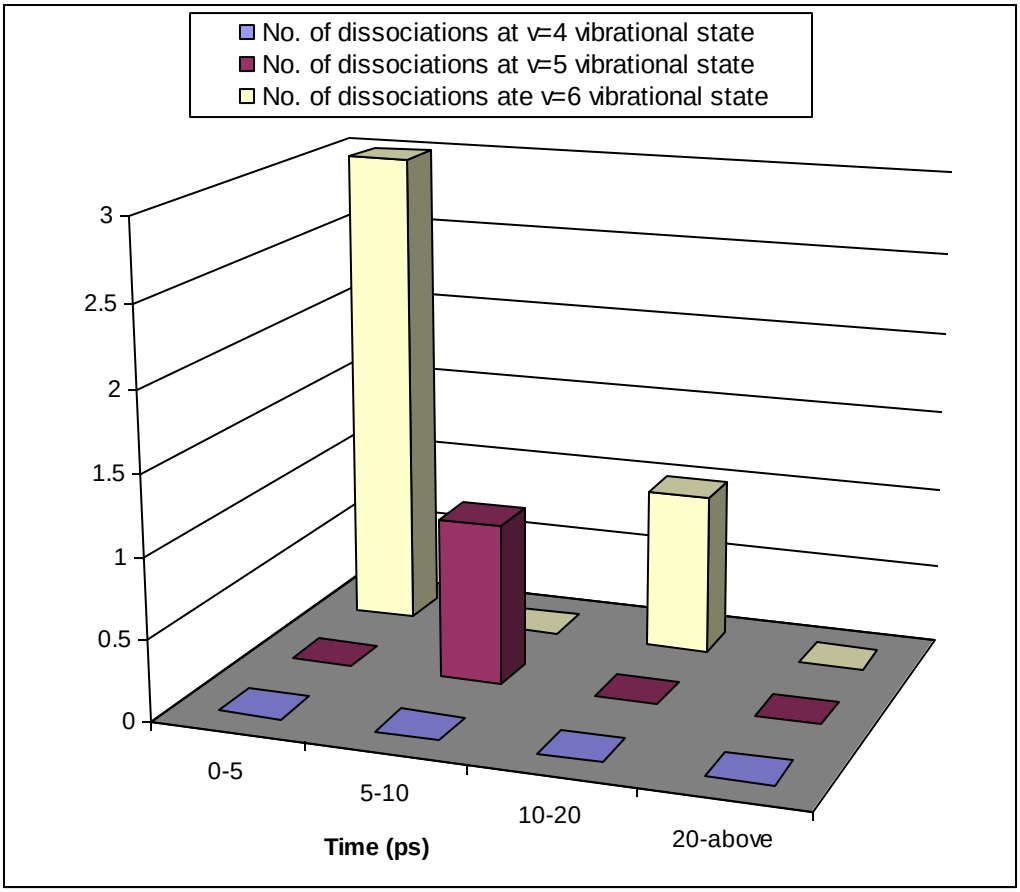

Figure S11: The time distribution of the first hydrogen-hopping event exhibited in PM3 trajectories for the $\nu = 5$, $\nu = 6$ and $\nu = 7$ OH-stretching states of FSO_3H.

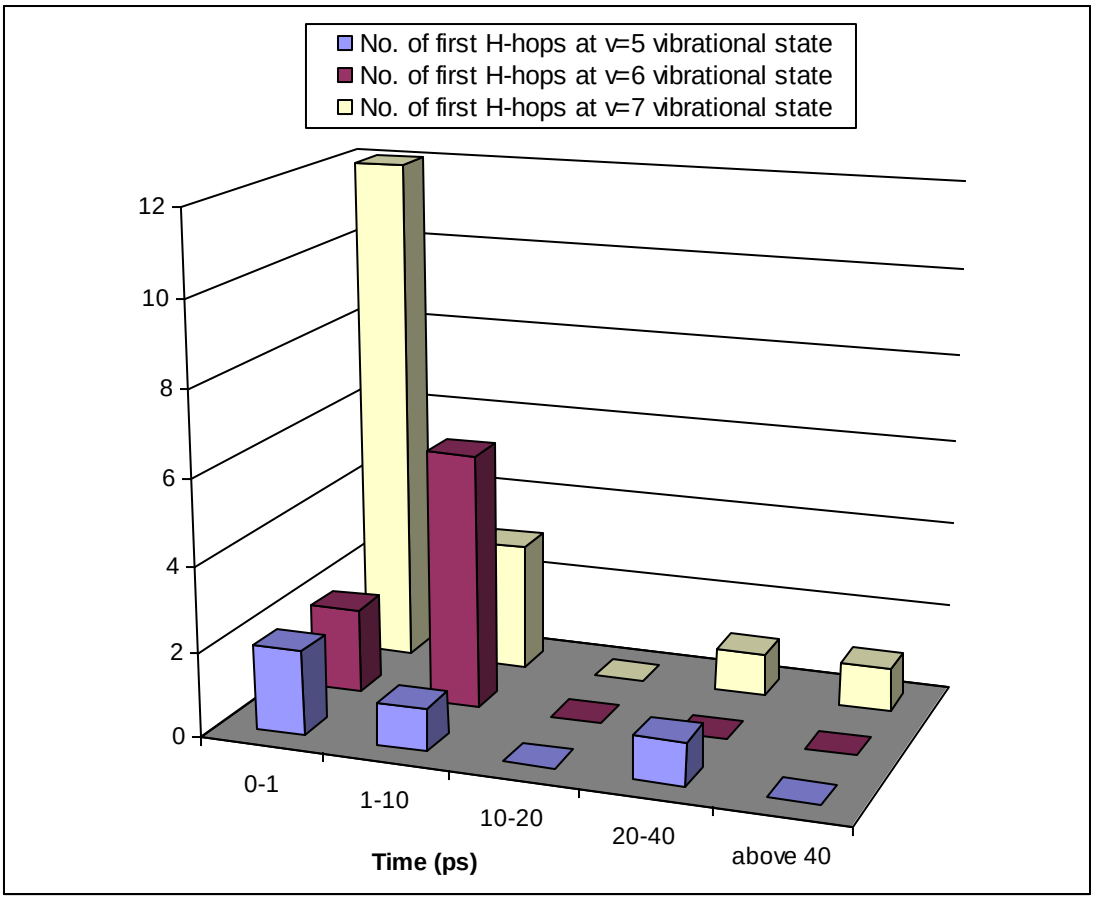

Figure S12: The time distribution of the first hydrogen-hopping event exhibited in PM3 trajectories for the ν = 5 OH+SOH and OH+OSOH combination states of FSO_3H.

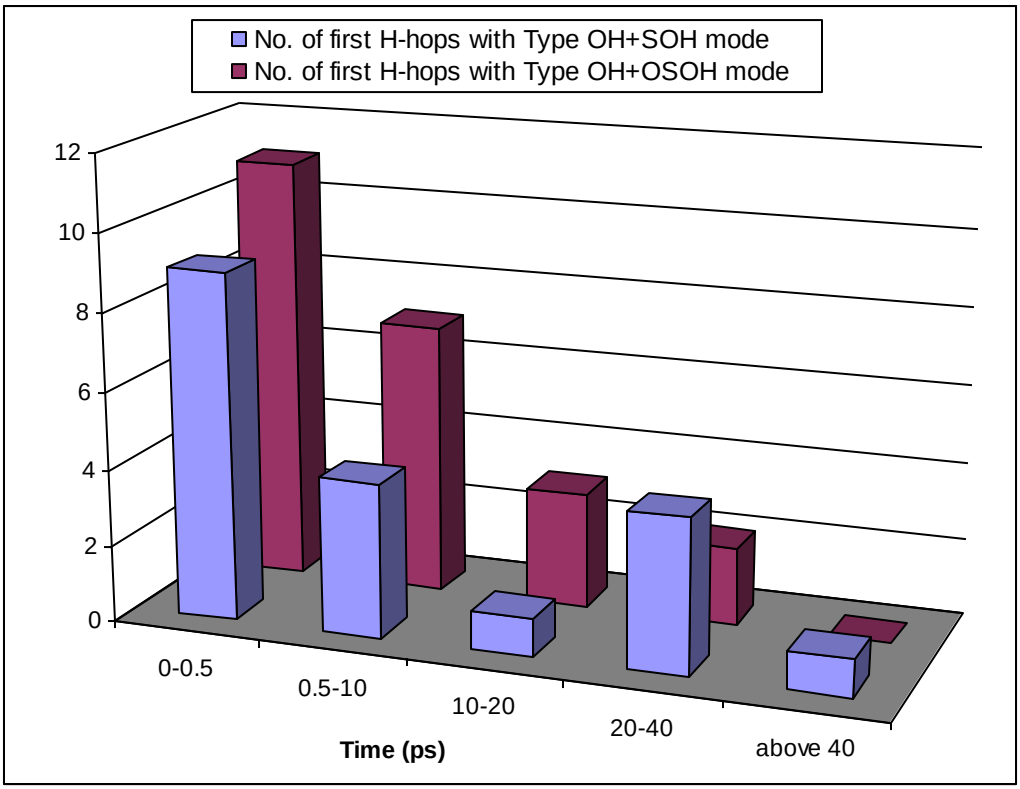

Figure S13: The time distribution of the first hydrogen-hopping event exhibited in PM3 trajectories for the ν = 6 OH+SOH and OH+OSOH combination states of FSO_3H.

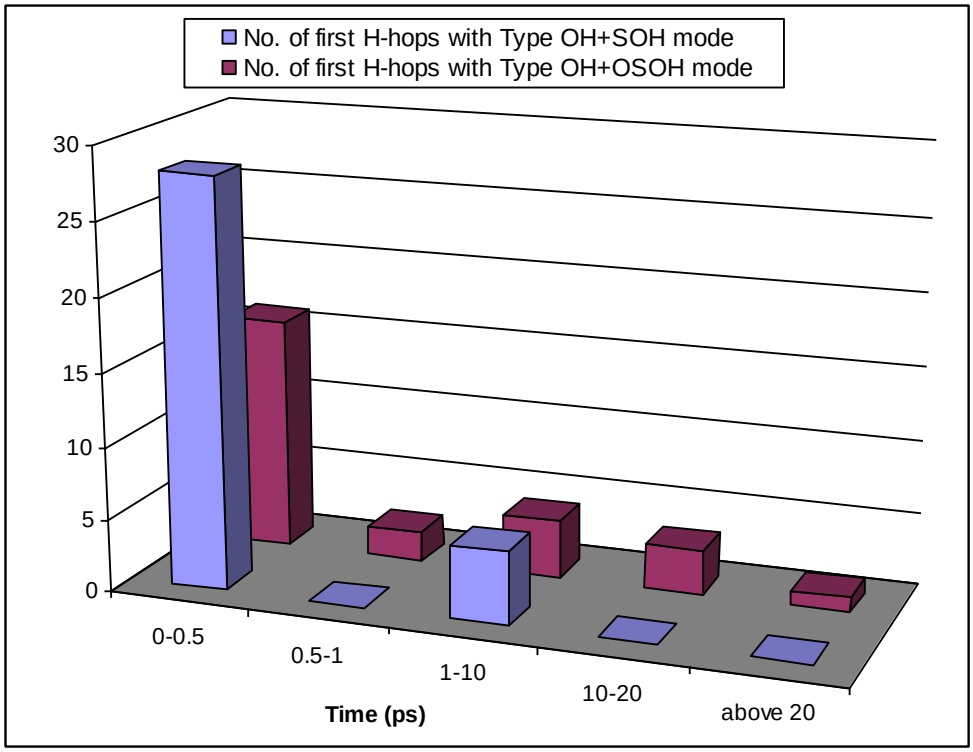

Figure S14: The time distribution of the first hydrogen-hopping event exhibited in PM3 trajectories for the ν = 7 OH+SOH and OH+OSOH combination states of FSO_3H.

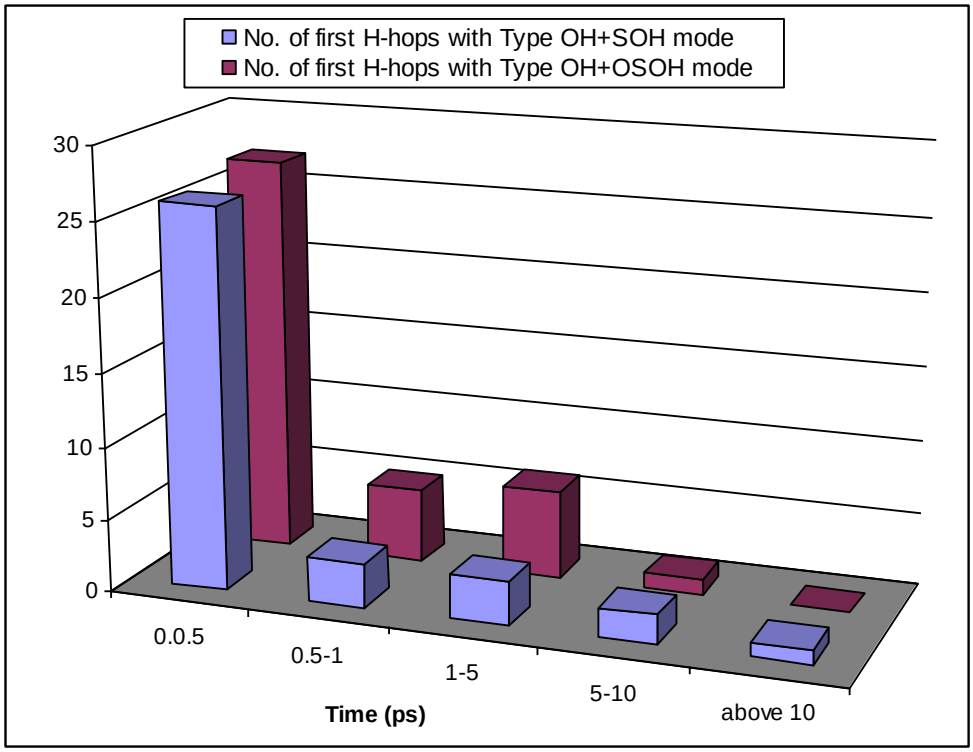

Figure S15: The time distribution of the first hydrogen-hopping event exhibited in MP2/TZP trajectories for the ν = 5, ν = 6 and ν = 7 OH-stretching states of FSO_3H.

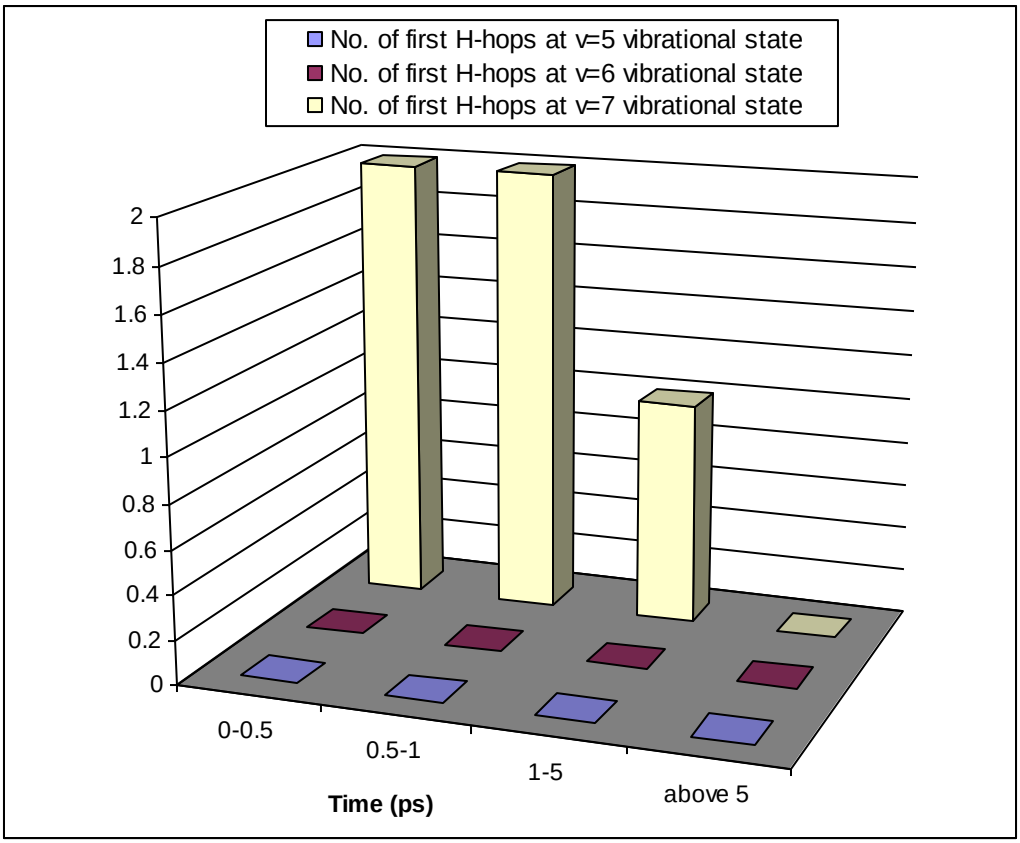

Figure S16: The time distribution of the first hydrogen-hopping event exhibited in PM3 trajectories for the $\nu = 4$, $\nu = 5$ and $\nu = 6$ OH-stretching states of $ClSO_3H$.

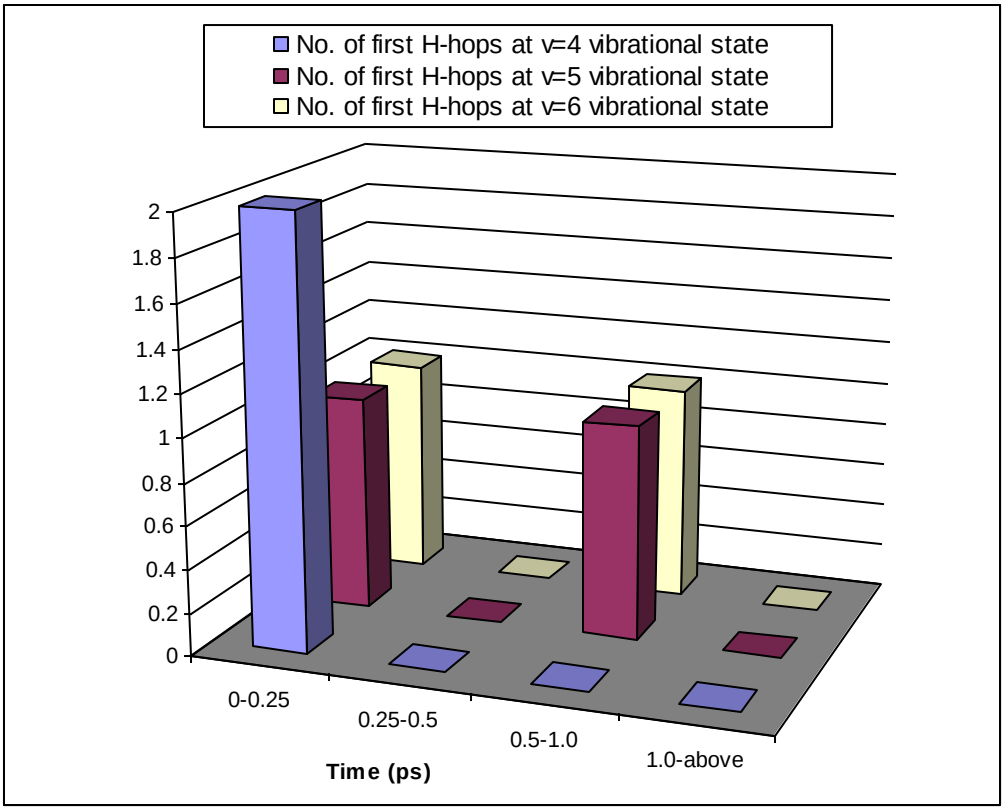

Figure S17: The time distribution of the first hydrogen-hopping event exhibited in MP2/TZP trajectories for the ν = 4, ν = 5 and ν = 6 OH-stretching states of $ClSO_3H$.