Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Reaction Selectivity in Ionized Water Dimer studied by Nonadiabatic *Ab Initio* Dynamics Simulations

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Supporting information

I.) Molecular geometries

Optimal geometry of **neutral water dimer** (optimized at CCSD/6-31++g**)

O	-0.117337	0.018102	-1.416772
O	0.407777	-0.038298	1.471928
H	0.243984	0.774134	-1.891318
H	0.197823	-0.760369	-1.888020
H	0.185916	-0.011587	0.531035
H	-0.432580	0.017480	1.935858

Proton transferred structure (optimized at MRCI(11,6)/6-31++g**)

O	1.595258	0.786663	-0.447275
O	-0.801431	0.331809	-0.963408
H	-0.900665	-0.551039	-1.348290
H	-1.316070	0.994151	-1.445494
H	2.039004	1.474725	0.079097
H	0.166240	0.592972	-0.751612

Hydrazine-like structure (optimized at MRCI(11,6)/6-31++g**)

O	-0.015891	0.067031	-1.007846
O	-0.015890	-0.067030	1.007847
H	0.874037	-0.241145	-1.252109
H	-0.621812	-0.685857	-1.123274
H	-0.621803	0.685860	1.123297
H	0.874047	0.241138	1.252084

Transition state structure (optimized at MRCI(11,6)/6-31++g**)

O	0.018678	-0.010033	-0.034969
O	-0.067724	0.056560	2.248847
H	0.899811	0.012037	-0.468843
H	-0.373935	-0.869279	-0.298392
H	-0.317588	0.581614	1.451194
H	0.826789	0.312616	2.562752

II.) Active space used

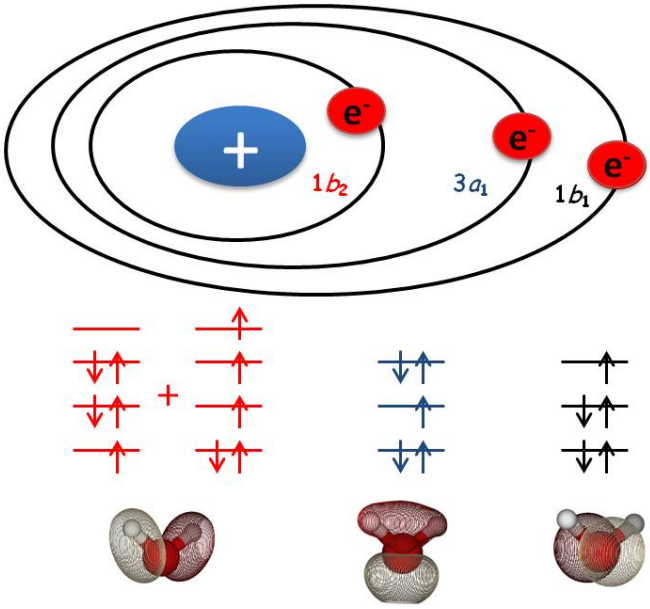

Fig. 1: Schematic description of electronic configurations considered in our study. For $1b_1$ and $3a_1$ electron ionizations our active space was restricted to excitations to the SOMO orbital. However for ionization of $1b_2$ electron we were obliged to insert virtual orbitals to account for tri-radical states.

III.) Conical intersections between Active space used D_1 and D_2, respectively D_2 and D_3 states

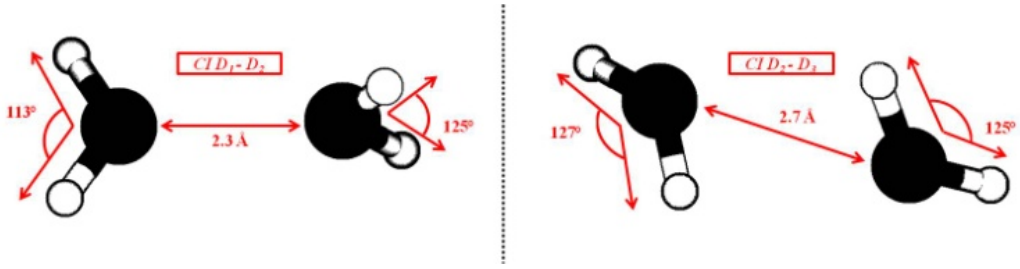

Fig. 2: Conical intersections between D_1 and D_2 states, respectively D_2 and D_3 states. Calculated at the SA4-CASSCF(7,4)/6-31++g** level.