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SUPPORTING INFORMATION FOR:

Non-Covalent π-π Stacking Interactions Turn off Non-Adiabatic Effects in Proton Coupled Electron Transfer Reactions

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Optimized geometries

- Structure for non-stacked $C_2H_3O^{\bullet}/C_2H_3OH$ model, optimized at M05-2X/6-31+G(d,p) level:

H	-0.00013500	-0.00067700	0.00001000
O	1.06678700	0.51318700	0.00000800
O	-1.06716200	-0.51406200	0.00000700
C	2.04600300	-0.33310300	0.00000300
C	-2.04568900	0.33300400	0.00000300

C	3.35945800	0.05323700	-0.00001000
C	-3.35942300	-0.05226400	-0.00001000
H	3.61310600	1.10409300	-0.00001900
H	-3.61393900	-1.10290200	-0.00001800
H	1.78952000	-1.39447000	0.00001100
H	4.14525800	-0.68738000	-0.00001200
H	-4.14461700	0.68899200	-0.00001200
H	-1.78828700	1.39409900	0.00001100

- Structure for π–π stacked $C_2H_3O^{\bullet}/C_2H_3OH$ model, optimized at M05-2X/6-31+G(d,p) level:

C	2.02526300	0.60602200	0.06455000
C	1.14237900	-0.38952400	0.43705000
O	0.66735400	-1.26786900	-0.37943700
H	-0.52353900	-1.21008600	-0.28250700
O	-1.62768600	-0.80272300	0.00078400
H	2.35081900	0.68089400	-0.96360400
C	-1.53495700	0.45356700	0.26993900
C	-0.70040900	1.33693500	-0.39316900
H	-0.66126100	2.37078100	-0.08150500
H	-0.22522200	1.04780600	-1.31912000
H	-2.13132600	0.81242800	1.11071300
H	0.84879000	-0.45723000	1.48883700
H	2.43074800	1.27815200	0.80619300

- Structure for non-stacked $C_4H_5O^{\bullet}/C_4H_5OH$ model, optimized at M05-2X/6-31+G(d,p) level:

H	0.00000000	-0.00000100	0.00000000
O	1.00571000	-0.63226000	0.00000000
O	-1.00571000	0.63225900	0.00000000
C	2.06511600	0.09572000	0.00000000

C	-2.06511600	-0.09572000	0.00000000
C	3.34537700	-0.42240800	0.00000000
C	-3.34537700	0.42240800	0.00000000
H	3.46582200	-1.49974800	0.00000000
H	-3.46582200	1.49974800	0.00000000
H	1.93343400	1.18222900	0.00000000
H	-1.93343500	-1.18223000	0.00000000
C	-4.49194200	-0.42732200	0.00000000
H	-4.31129200	-1.49926600	0.00000000
C	-5.76979500	0.01848700	0.00000000
H	-5.99040900	1.07912700	-0.00000100
H	-6.60464900	-0.66850800	-0.00000100
C	4.49194200	0.42732300	0.00000000
H	4.31129100	1.49926700	0.00000000
C	5.76979500	-0.01848600	-0.00000100
H	5.99040900	-1.07912500	-0.00000100
H	6.60464800	0.66851000	-0.00000100

- Structure for $\pi-\pi$ stacked $C_4H_5O^{\bullet}/C_4H_5OH$ model, optimized at M05-2X/6-31+G(d,p) level:

C	0.94973600	-1.34050900	-0.25891600
C	-0.34157800	-1.48944800	0.23920900
O	-1.34079200	-1.87249400	-0.47653000
H	-2.22688900	-1.11653100	-0.26584000
O	-2.86118100	-0.13329600	0.09767000
H	1.12004500	-1.55270600	-1.30871800
C	-2.03560000	0.80857500	0.37806500
C	-0.86928400	1.09132600	-0.32696700
H	-0.69906000	0.60694800	-1.28043100
H	-2.25911900	1.40465900	1.26819100

H	-0.50550800	-1.31094200	1.30704800
C	2.00541300	-0.85953700	0.55650700
H	1.77281400	-0.64819500	1.59651400
C	0.06123600	2.07677000	0.14409500
H	-0.19991400	2.60272500	1.05928600
C	1.23699200	2.35146800	-0.45745400
H	1.91089100	3.10006200	-0.06313200
H	1.53356100	1.83508800	-1.36272000
C	3.26175300	-0.61305600	0.10157700
H	3.52813400	-0.80761900	-0.93007400
H	4.02882700	-0.22071200	0.75406200

- Structure for non-stacked phO$^{\bullet}$/phOH model, optimized at M05-2X/6-31+G(d,p) level:

H	0.55570500	-0.10717500	0.00727800
O	0.59899200	0.01456100	1.19053100
O	0.61058400	-0.24984700	-1.17329900
C	0.57476500	1.25077700	1.60054200
C	0.09859300	-1.36936100	-1.59926800
C	0.54525700	3.89441000	2.53904700
C	-0.97259300	-3.77339000	-2.57072100
C	0.97034100	1.54922000	2.93267600
C	0.40838700	-1.82081100	-2.91091300
C	0.15289100	2.31371200	0.75278600
C	-0.77257300	-2.15146200	-0.78945000
C	0.94969900	2.85258600	3.38675700
C	-0.12577300	-3.00336000	-3.38163800
C	0.15242300	3.61347500	1.22509300
C	-1.28600800	-3.33928200	-1.27726500
H	0.53232100	4.91377900	2.90234800

H	-1.38699900	-4.69974400	-2.94675000
H	1.28827100	0.72654400	3.55969800
H	1.07310200	-1.21149900	-3.50917400
H	-0.16109500	2.07868900	-0.25647000
H	-1.01649300	-1.79547700	0.20362800
H	1.25197800	3.07353800	4.40291800
H	0.11394900	-3.34180500	-4.38202100
H	-0.16541400	4.41910500	0.57499000
H	-1.94491900	-3.93294200	-0.65589400

- Structure for π–π stacked phO$^{\bullet}$/phOH model, optimized at M05-2X/6-31+G(d,p) level:

H	0.23733300	-0.04224700	0.00583600
O	-0.02299800	-0.29684000	1.14783700
O	0.20512100	0.27546700	-1.14960600
C	-1.26298000	0.02342400	1.38482800
C	-1.03072900	0.49203700	-1.49887400
C	-3.96675200	0.66709200	1.78508100
C	-3.71306600	1.01617100	-2.14350600
C	-1.73156400	1.35590500	1.19377100
C	-2.02256500	-0.52413900	-1.37541000
C	-2.18798300	-0.96713700	1.82649100
C	-1.42177200	1.76826600	-1.99919300
C	-3.06989800	1.65839700	1.37859700
C	-3.34477100	-0.24972300	-1.68083600
C	-3.51196900	-0.64021100	2.02875100
C	-2.73955200	2.01415500	-2.32124000
H	-5.01172700	0.90970300	1.92988000
H	-4.74808000	1.22464700	-2.38245700
H	-1.01273800	2.11013400	0.90042000

H	-1.70805300	-1.50268900	-1.03611100
H	-1.81070300	-1.96936700	1.98534800
H	-0.65186700	2.52197700	-2.10518200
H	-3.42200300	2.66784200	1.20675200
H	-4.09590200	-1.02024000	-1.55988500
H	-4.21040800	-1.39742600	2.36332100
H	-3.03085200	2.98622800	-2.69984500

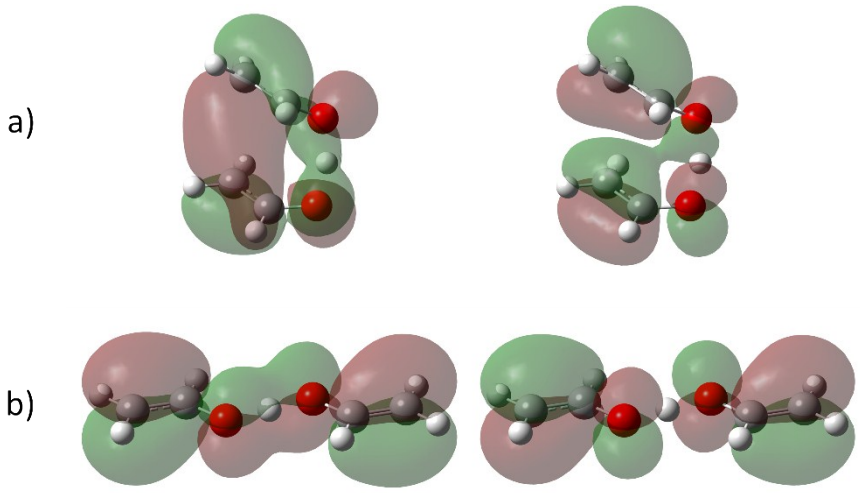

Figure S1. SOMO-1 (left) and SOMO (right) orbitals at transition state geometries for the $C_2H_3O^{\bullet}/C_2H_3OH$ model systems calculated at restricted open-shell M05-2X/6-31+G(d,p) level. a) π-π stacking and (b) non-stacked systems.

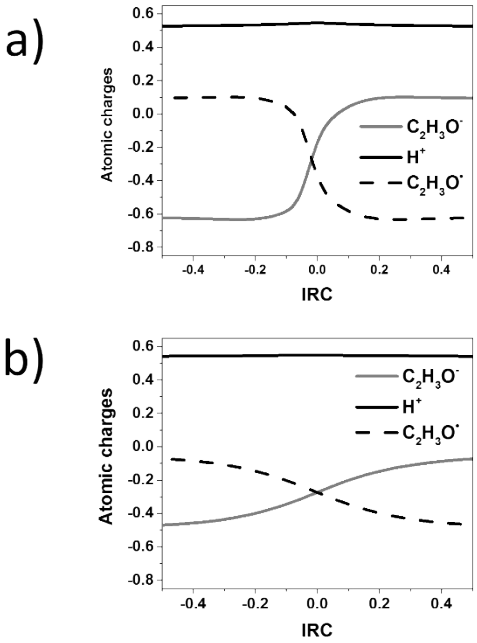

Figure S2. NPA atomic charges and spin densities for the H-acceptor, H-transferred and H-donor as a function of the intrinsic reaction coordinate (IRC). (a) non-stacked $C_2H_3O^\bullet/C_2H_3OH$ and (b) $C_2H_3O^\bullet/C_2H_3OH$ with π-π stacking interactions.

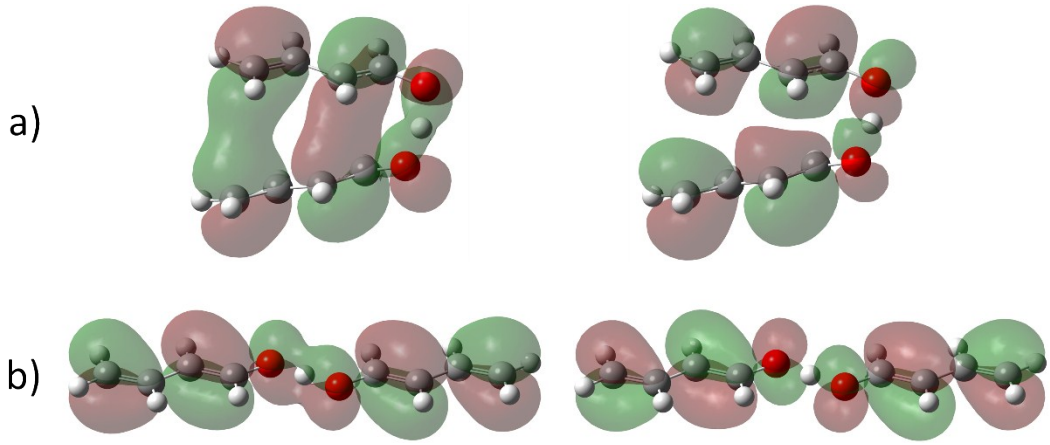

Figure S3. SOMO-1 (left) and SOMO (right) orbitals at transition state geometries for the $C_4H_5O^\bullet/C_4H_5OH$ model systems calculated at restricted open-shell M05-2X/6-31+G(d,p) level. a) π-π stacking and (b) non-stacked systems.

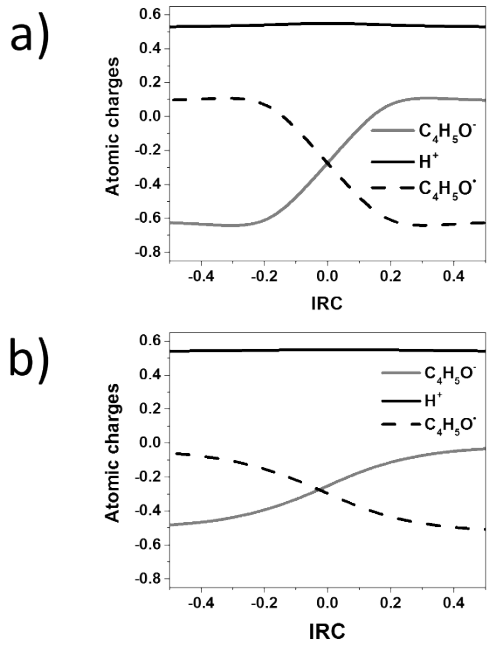

Figure S4. NPA atomic charges and spin densities for the H-acceptor, H-transferred and H-donor as a function of the intrinsic reaction coordinate (IRC). (a) non-stacked $C_4H_5O^\bullet/C_4H_5OH$ and (b) $C_4H_5O^\bullet/C_4H_5OH$ with π-π stacking interactions.

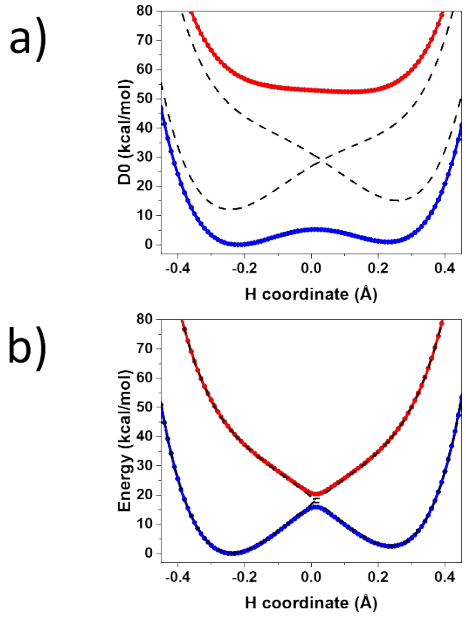

Figure S5. State-averaged CASSCF for the ground and excited state electronically adiabatic (lines in colors) and diabatic (black dashed lines) potential energy curves along the transferring hydrogen coordinate for (a) $C_2H_3O^\bullet/C_2H_3OH$ system with π-π stacking interactions [CASSCF(3,6)/ 6-31+G(d,p)] and (b) non-stacked $C_2H_3O^\bullet/C_2H_3OH$ system [CASSCF(3,6)/ 6-31+G(d,p)].

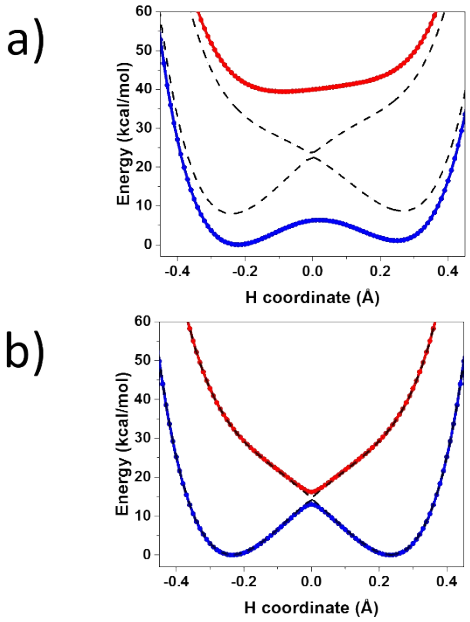

Figure S6. State-averaged CASSCF for the ground and excited state electronically adiabatic (lines in colors) and diabatic (black dashed lines) potential energy curves along the transferring hydrogen coordinate for (a) $C_4H_5O^{\bullet}/C_4H_5OH$ system with π-π stacking interactions [CASSCF(5,6)/ 6-31+G(d,p)] and (b) non-stacked $C_5H_4O^{\bullet}/C_4H_5OH$ system [CASSCF(3,6)/ 6-31+G(d,p)].

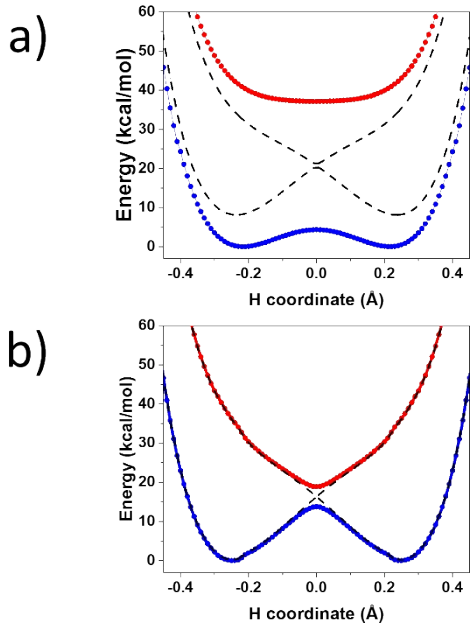

Figure S7. State-averaged CASSCF for the ground and excited state electronically adiabatic (lines in colors) and diabatic (black dashed lines) potential energy curves along the transferring hydrogen coordinate for (a) phO•/phOH system with π-π stacking interactions [CASSCF(7,8)/ 6-31+G(d,p)] and (b) non-stacked phO•/phOH system [CASSCF(3,6)/ 6-31+G(d,p)].

Table S1. Electronic Coupling V^{ET} (kcal/mol), Proton Tunneling Time τ_p (fs), Electronic Transition τ_e (fs) and Adiabaticity Parameter *p* for the studied systems.

	Model[a]	V^{ET}	τ_p	τ_e	*p*
$\pi-\pi$stacked	A	23.82	0.324	0.637	0.509
	B	16.84	0.685	0.901	0.760
	C	16.40	1.242	0.925	1.342
non-stacked	A	2.19	0.080	6.924	0.012
	B	1.60	0.095	9.505	0.010
	C	2.54	0.153	5.975	0.026

[a] Models A=$C_2H_3O^{\bullet}/C_2H_3OH$, B=$C_4H_5O^{\bullet}/C_4H_5OH$, C=$phO^{\bullet}$/phO.