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Hydrogen bond dynamics in the excited states: Photodissociation and ionization of phenol in clusters

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Supporting Information

Cartesian coordinates (in Ångströms) of phenol monomer. The structure was optimized at the MP2/aug-cc-pVDZ level.

C	0.064351	0.000000	-0.064270
C	0.015638	0.000000	1.328295
C	1.200609	0.000000	2.057730
C	2.434686	0.000000	1.407751
C	2.474541	0.000000	0.015592
C	1.292619	0.000000	-0.723168
O	-1.132005	0.000000	-0.731463
H	-0.948496	0.000000	1.818564
H	1.157344	0.000000	3.138991
H	3.352588	0.000000	1.979171
H	3.424569	0.000000	-0.502489
H	1.325459	0.000000	-1.806952
H	-0.956455	0.000000	-1.679337

Cartesian coordinates (in Ångströms) of phenol dimer. The structure was optimized at the MP2/aug-cc-pVDZ level.

C	1.523964	0.540321	0.103083
C	0.948931	-0.215557	1.138481
C	0.450376	0.452841	2.270106
C	0.523312	1.855483	2.369064
C	1.101917	2.595993	1.322565
C	1.604406	1.940417	0.182817
O	2.012322	-0.160414	-1.000397
H	0.897881	-1.304024	1.054586
H	0.000913	-0.132141	3.077527
H	0.132689	2.366711	3.252874
H	1.164150	3.686107	1.386200
H	2.054810	2.515684	-0.633763
H	2.357246	0.476120	-1.644288
C	0.527320	-3.287384	-0.654357
C	1.828071	-3.408373	-0.120598
C	2.128705	-4.474275	0.748663
C	1.145719	-5.423640	1.082640
C	-0.147238	-5.299553	0.537279
C	-0.461097	-4.234709	-0.324554
O	0.166279	-2.267485	-1.502494
H	2.594663	-2.674057	-0.386677
H	3.138754	-4.561196	1.160470
H	1.384012	-6.251460	1.756010
H	-0.920113	-6.032432	0.788052
H	-1.461812	-4.122591	-0.750632
H	0.866155	-1.587712	-1.489080

Cartesian coordinates (in Ångströms) of phenol trimer. The structure was optimized at the MP2/aug-cc-pVDZ level.

O	0.151600	0.388084	-0.358970
O	-0.561584	0.489792	2.461093
O	2.239642	0.339815	1.667919
C	-0.344690	-0.861773	-0.696487
C	-0.707169	-0.755335	3.053155
C	2.719865	-0.949729	1.497511
C	-0.315362	-0.846499	4.402515
C	-0.326953	-2.097664	5.044628
C	-0.733572	-3.252484	4.346791
C	-1.157900	-3.139111	3.009384
C	-1.157212	-1.892513	2.356086
H	0.016010	0.057414	4.921846
H	-0.007505	-2.169693	6.088158
H	-0.730838	-4.225844	4.844788
H	-1.488885	-4.024113	2.457910
H	-1.481191	-1.818131	1.315286
C	3.684304	-1.120036	0.485970
C	4.139821	-2.413368	0.173581
C	3.641209	-3.531766	0.871053
C	2.704995	-3.341398	1.904893
C	2.244583	-2.052325	2.232099
H	4.044738	-0.242091	-0.057959
H	4.877399	-2.546082	-0.623012
H	3.988496	-4.537311	0.618649
H	2.318019	-4.198166	2.464448
H	1.511145	-1.917667	3.030658
C	0.431197	-2.035539	-0.656247
C	-0.190622	-3.274781	-0.897850
C	-1.564864	-3.346146	-1.194392
C	-2.318911	-2.158284	-1.273538
C	-1.711925	-0.913536	-1.028656
H	1.496723	-1.993269	-0.418246
H	0.411342	-4.186811	-0.845505
H	-2.041646	-4.313537	-1.374056
H	-3.384643	-2.198624	-1.515994
H	-2.285490	0.017175	-1.065576
H	1.466777	0.337986	2.266023
H	1.050521	0.306462	0.016080
H	-0.690176	0.423073	1.494462

Cartesian coordinates (in Ångströms) of a phenol dimer minimum with a transferred hydrogen atom. The structure was optimized at the SA5-CASSCF(8/10)/6-31+g* level.

C	0.015591	0.234993	0.095941
C	0.147145	0.466751	1.453831
C	0.100268	1.768006	1.924117
C	-0.081256	2.826936	1.050346
C	-0.207754	2.569490	-0.308737
C	-0.151793	1.276820	-0.795375
C	-0.786277	-3.425390	2.050287
C	-1.571177	-4.039292	3.093879
C	-0.968515	-4.811321	4.074965
C	0.418116	-5.033431	4.050048
C	1.199417	-4.468413	3.005822
C	0.637744	-3.697940	2.045811
O	0.095132	-1.065032	-0.376721
O	-1.325980	-2.663317	1.210960
H	0.300768	-0.356708	2.125913
H	0.206962	1.949151	2.978190
H	-0.129419	3.834919	1.419637
H	-0.339404	3.383784	-0.998372
H	-0.243078	1.080232	-1.845198
H	-0.035167	-1.287351	-1.615865
H	-2.627976	-3.849978	3.098433
H	-1.563495	-5.245838	4.857683
H	0.886487	-5.640429	4.802484
H	2.256638	-4.663236	2.983548
H	1.224355	-3.287167	1.244230
H	-0.450378	-1.712949	0.125785

Cartesian coordinates (in Ångströms) of the $\pi\pi^*/S_0$ conical intersection for phenol monomer. Coordinates of two alternative structures with distorted benzene ring are shown. The structures were optimized at the SA4-CASSCF(4/5)/6-31+g* level.

CI1

C	0.161658	-0.013683	0.163847
C	0.054849	-0.165714	1.581029
C	1.243477	-0.032058	2.228054
C	2.437897	-0.036320	1.393155
C	1.453566	0.135930	-0.467954
C	2.440305	-0.742613	0.110648
H	3.239829	0.655296	1.610120
H	1.317868	0.072670	3.291290
H	-0.895903	-0.297791	2.056846
H	1.578909	0.762341	-1.339142
H	3.027910	-1.554830	-0.267478
H	-0.810914	-0.095963	-1.470828
O	-0.978041	0.018083	-0.545556

CI2

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.463706
C	0.000000	1.250889	2.076618
C	0.202251	2.281178	1.216383
C	0.343574	1.896481	-0.208135
C	-0.714928	1.021820	-0.707008
O	0.422459	-1.154861	-0.587225
H	-0.020230	-0.939893	1.975313
H	-0.162652	1.366108	3.133429
H	0.199493	3.313649	1.507663
H	1.085413	2.352101	-0.843885
H	-0.962189	0.934827	-1.749485
H	-0.243426	-1.438042	-1.201756

Cartesian coordinates (in Ångströms) of the $\pi\pi^*/S_0$ conical intersection for phenol dimer. The structures were optimized at the SA5-CASSCF(8/10)/6-31+g* level.

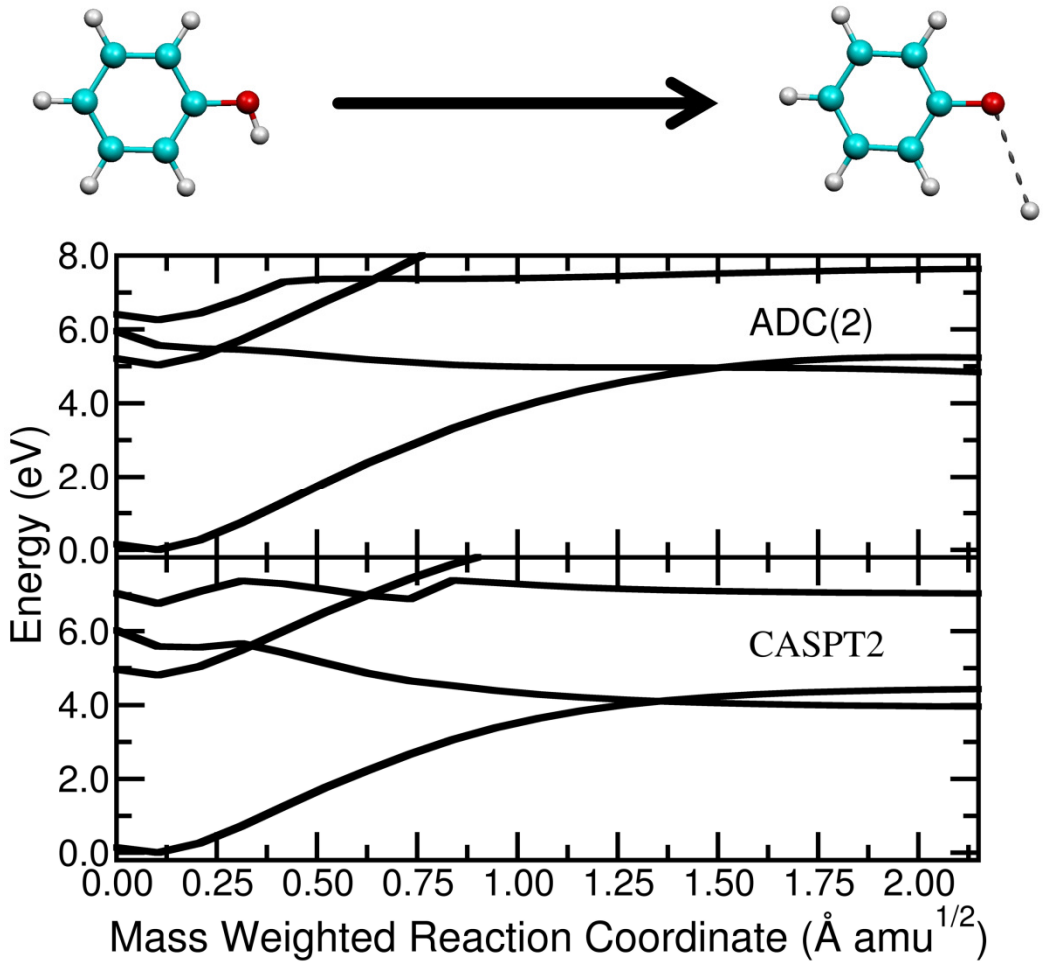
CI with ring-distorted donor phenol

C	0.095372	-0.212477	0.108186
C	0.057452	0.086911	1.462492
C	1.294018	-0.065053	2.076485
C	2.313447	-0.711865	1.272319
C	2.039217	-1.765767	0.345908
C	1.335802	-0.775066	-0.419854
C	-0.402115	1.475984	-3.921143
C	0.297608	2.365440	-3.111872
C	0.685305	3.589809	-3.618650
C	0.369999	3.946090	-4.927343
C	-0.341123	3.061926	-5.719572
C	-0.732267	1.821523	-5.223069
O	-0.974091	0.094419	-0.640538
O	-0.733179	0.259790	-3.397784
H	-0.818786	0.483132	1.932225
H	1.499375	0.333028	3.049847
H	3.344255	-0.431870	1.446775
H	2.865495	-2.283674	-0.095681
H	1.666958	-0.487090	-1.416287
H	-0.846193	-0.054217	-1.567689
H	0.526787	2.103463	-2.097438
H	1.233394	4.267329	-2.986825
H	0.676924	4.898245	-5.305442
H	-0.594137	3.323640	-6.727609
H	-1.280816	1.129388	-5.838001
H	-1.247316	-0.250187	-4.006550

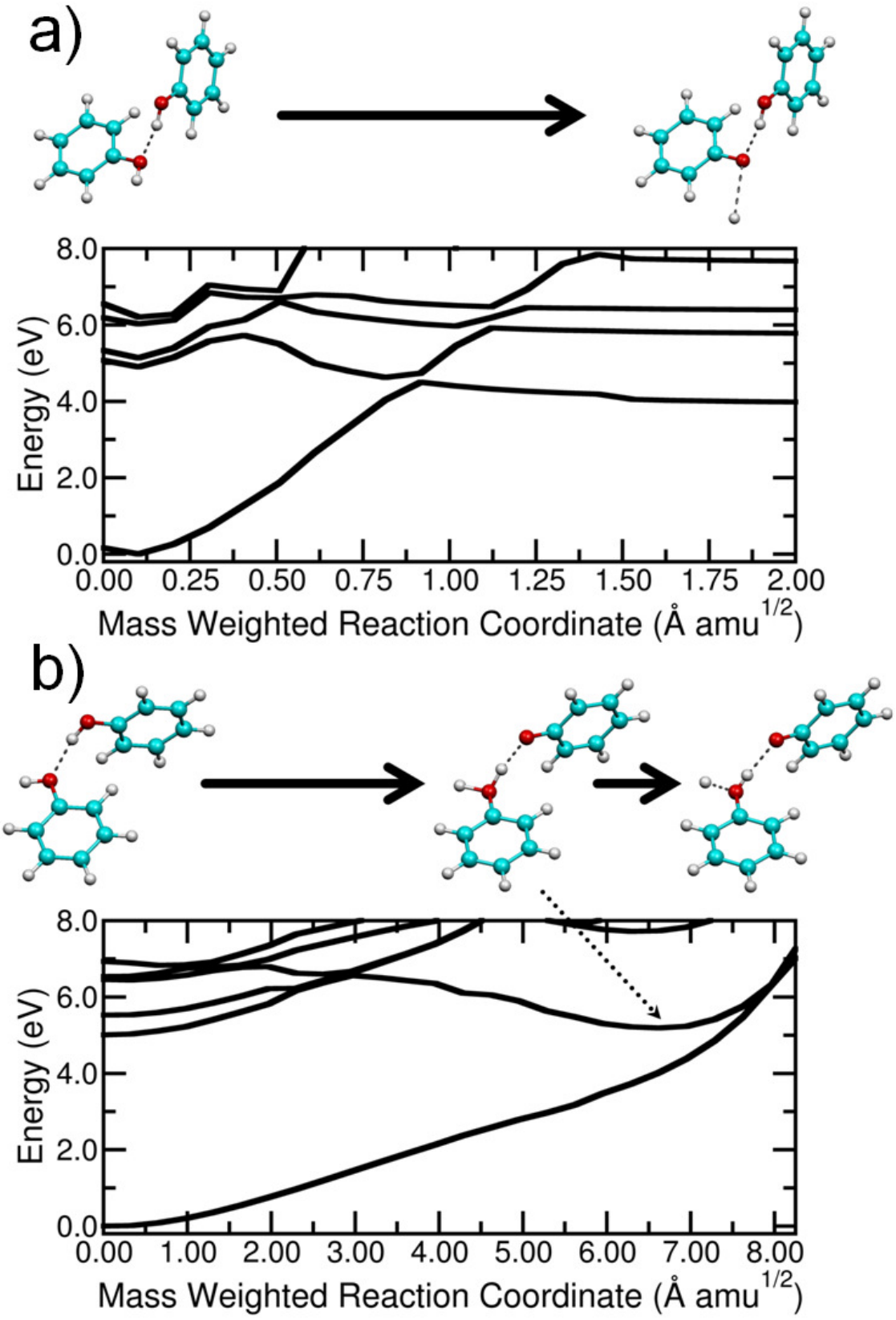
Cartesian coordinates (in Ångströms) of the $\pi\pi^*/S_0$ conical intersection for phenol dimer. The structures were optimized at the SA5-CASSCF(8/10)/6-31+g* level.

CI with ring-distorted acceptor phenol

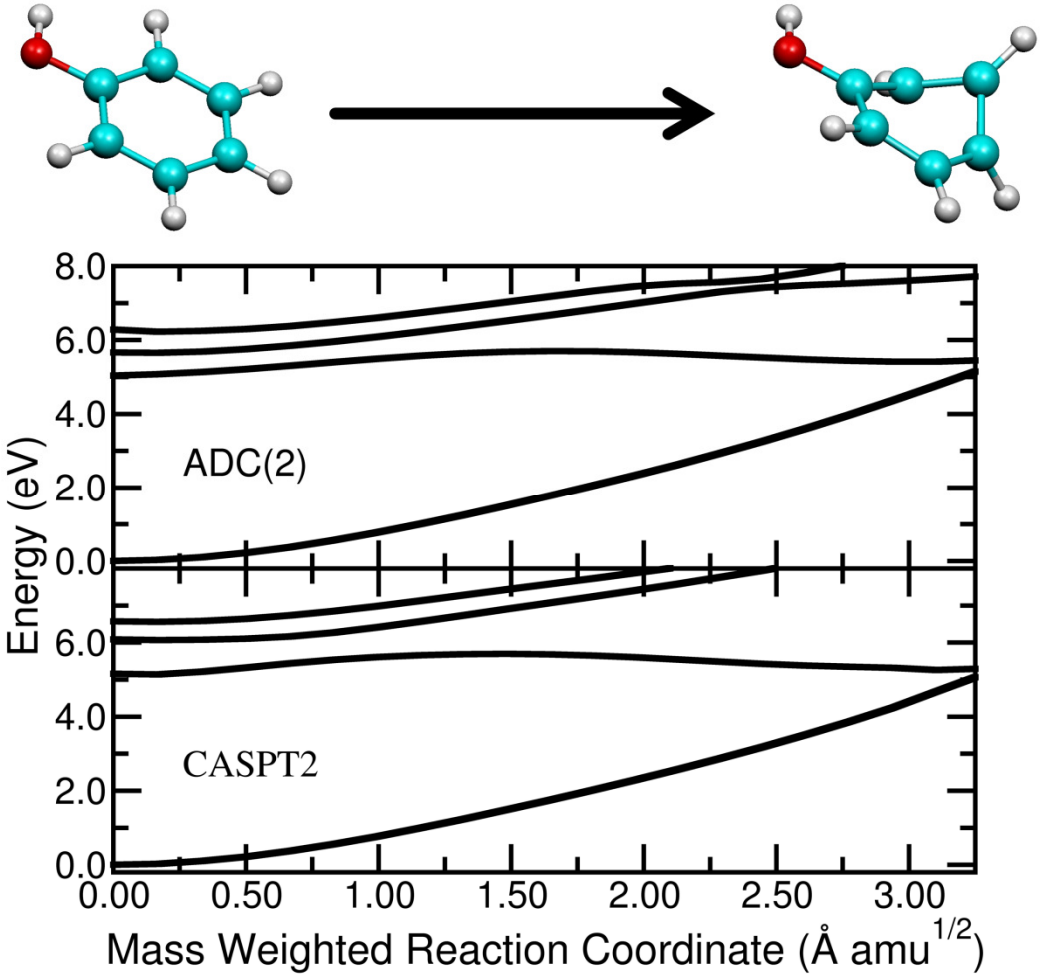
C	0.132391	-0.019546	-0.173811
C	0.056324	0.068886	1.207878
C	1.299042	0.016899	1.823131
C	2.400650	-0.368318	0.946150
C	2.237256	-1.323045	-0.098713
C	1.435319	-0.328085	-0.748251
C	-3.534335	1.230908	2.134075
C	-3.647410	-0.153450	2.054205
C	-4.100704	-0.875332	3.157190
C	-4.451283	-0.230136	4.327494
C	-4.352467	1.160929	4.399662
C	-3.895379	1.892498	3.308505
O	-0.979668	0.240846	-0.915896
O	-3.076667	1.988245	1.104662
H	-0.865653	0.217320	1.723492
H	1.449745	0.305370	2.846699
H	3.377092	0.056635	1.135306
H	2.996892	-1.938915	-0.535326
H	1.748293	0.165496	-1.665350
H	-0.866320	0.006981	-1.824878
H	-3.375811	-0.662432	1.145497
H	-4.170283	-1.946419	3.086746
H	-4.794333	-0.792732	5.177683
H	-4.620972	1.675488	5.305229
H	-3.803456	2.961960	3.352021
H	-2.650596	1.461105	0.438969



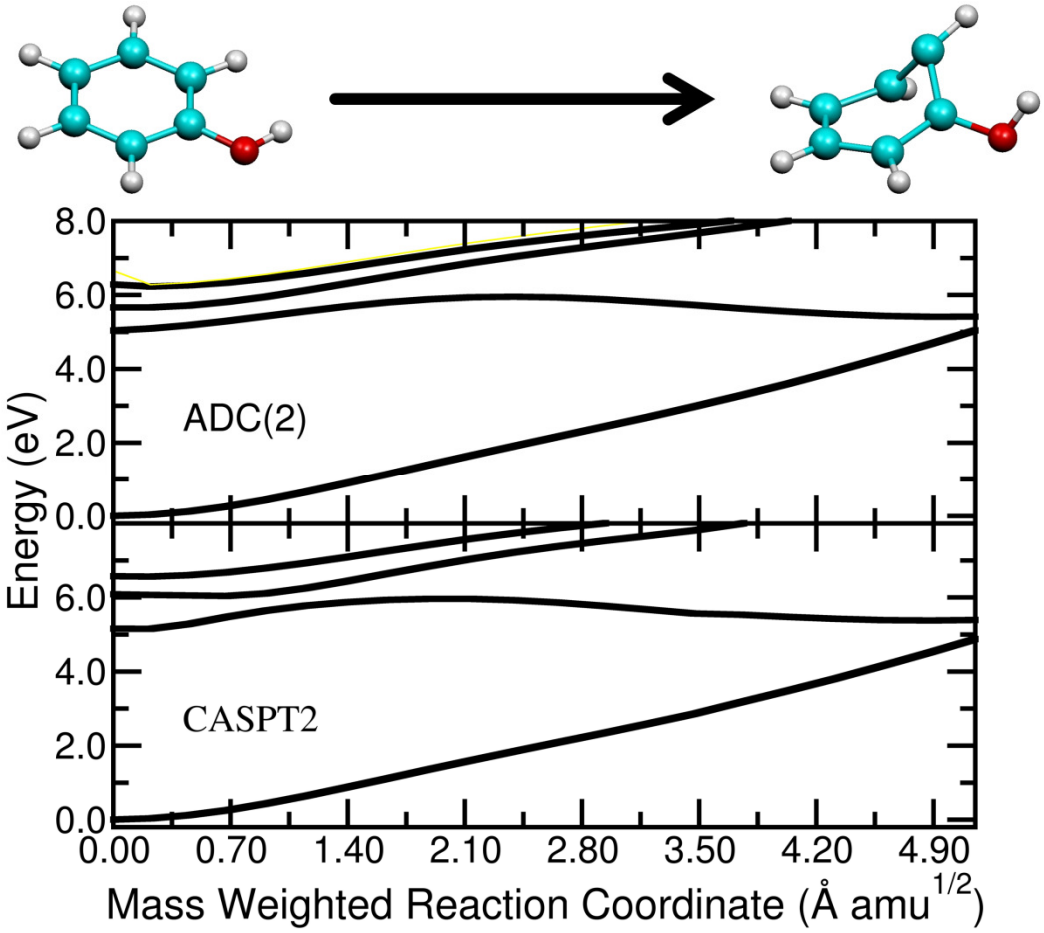
Cut through potential energy surface of phenol monomer along O–H dissociation coordinate. All remaining degrees of freedom are kept frozen. The molecule keeps C_s symmetry for all geometries. Energies are calculated at the ADC(2)/6-61+g* level (top panel) and at the SA6-CASSCF(10/9)/CASPT2/6-31+g* level (bottom panel).



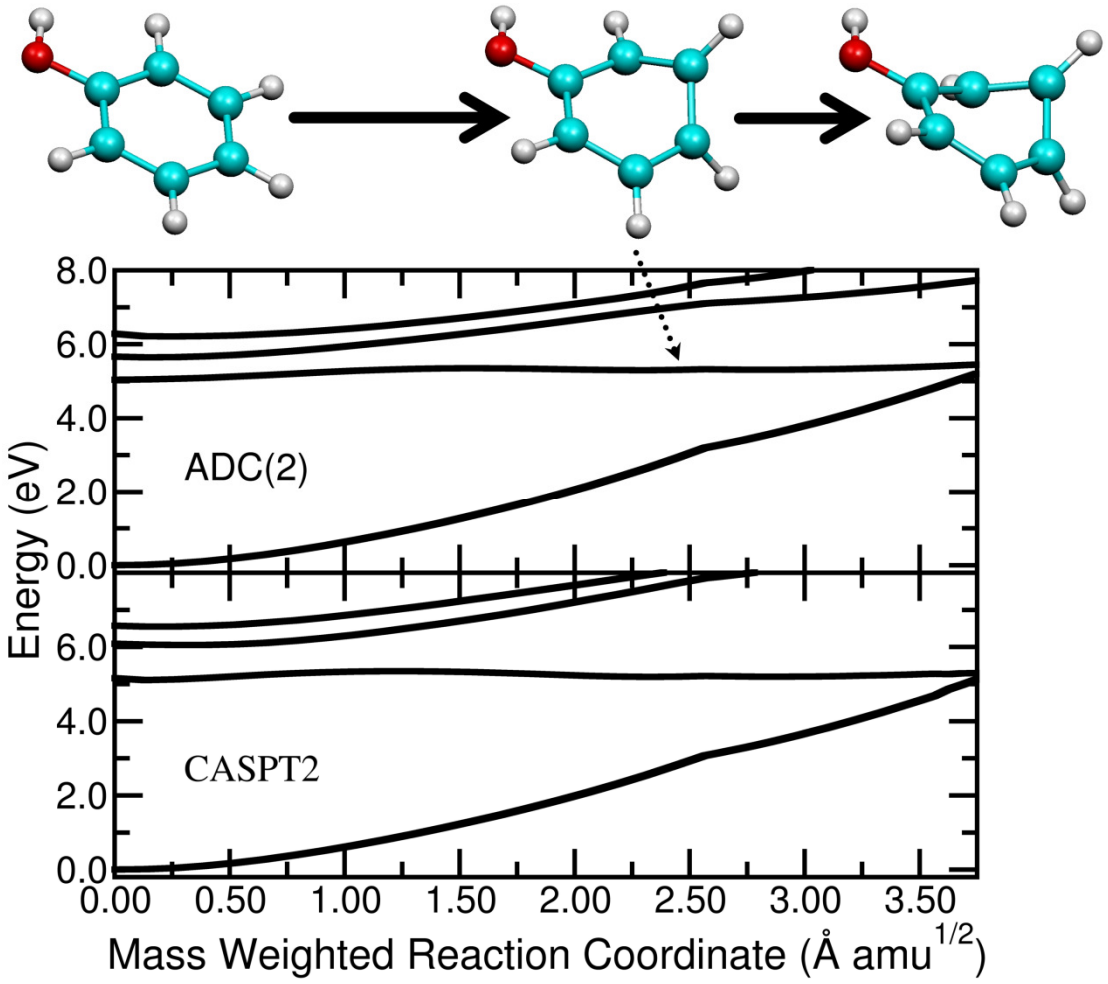
Potential energy curves along hydrogen dissociation (part **a**) and excited state hydrogen transfer (part **b**) reaction coordinate for phenol dimer. The energies were calculated at the SA5-CASSCF(8/10)/CASPT2/6-31+g* level. The minimum with a transferred hydrogen was optimized with the CASSCF method.



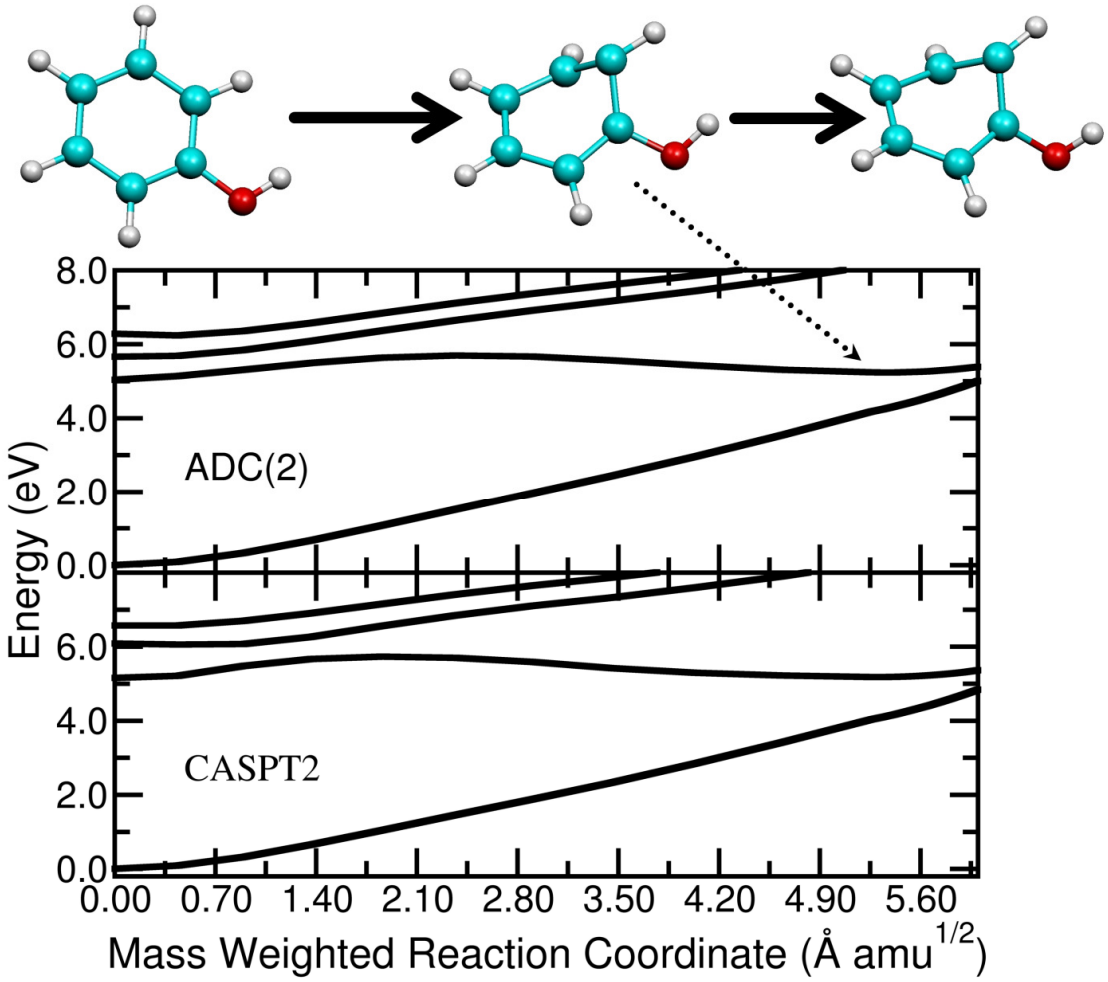
Interpolation curve between Franck-Condon point and ring-puckering $\pi\pi^*/S_0$ conical intersection CI1 calculated at the ADC(2) level (top panel) and at the SA4-CASSCF(4/7)/CASPT2/6-31+g* level (bottom panel).



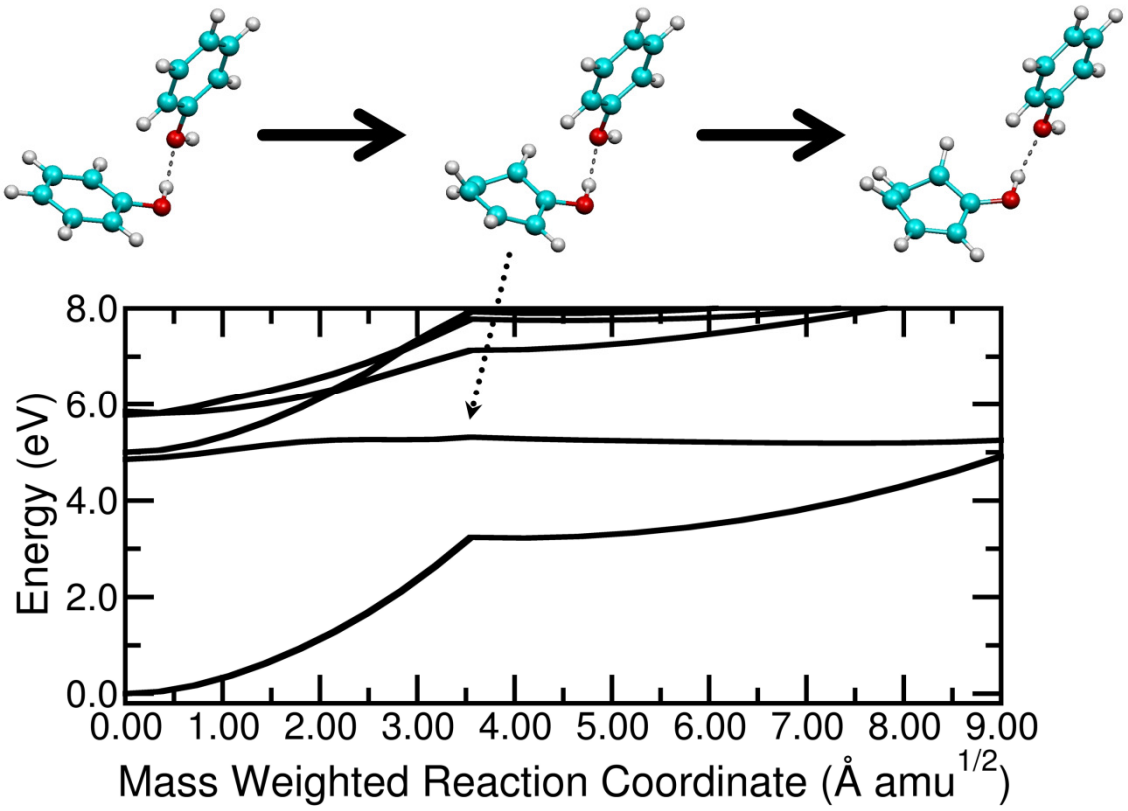
Interpolation curve between Franck-Condon point and ring-puckering $\pi\pi^*/S_0$ conical intersection CI2 calculated at the ADC(2) level (top panel) and at the SA4-CASSCF(4/7)/CASPT2/6-31+g* level (bottom panel).



Two–step interpolation curve between Franck-Condon point and ring-puckering $\pi\pi^*/S_0$ conical intersection CI1 calculated at the ADC(2) level (top panel) and at the SA4-CASSCF(4/7)/CASPT2/6-31+g* (bottom panel). The intermediate structure is an optimized transition state separating the S_1 minimum and $\pi\pi^*/S_0$ intersection. The transition state optimization was performed at the TDDFT/BHandHLYP/6-31+g* level.



Two–step interpolation curve between Franck-Condon point and ring-puckering $\pi\pi^*/S_0$ conical intersection CI2 calculated at the ADC(2) level (top panel) and at the SA4-CASSCF(4/7)/CASPT2/6-31+g* (bottom panel). The intermediate structure is an optimized transition state separating the S_1 minimum and $\pi\pi^*/S_0$ intersection. The transition state optimization was performed at the TDDFT/BHandHLYP/6-31+g* level.



Two–step interpolation curve between Franck-Condon point and $\pi\pi^*/S_0$ conical intersection calculated at the ADC(2) level for phenol dimer with distorted H-bond donor molecule (analogical curve for phenol dimer with distorted H-bond acceptor molecule is presented in Fig. 4c in the main body of the text).