Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics


# Electronic Supplementary Information for:

# Electronically excited states and photochemical reaction mechanisms of β-glucose

**Deniz Tuna*, Andrzej L. Sobolewski, and Wolfgang Domcke**

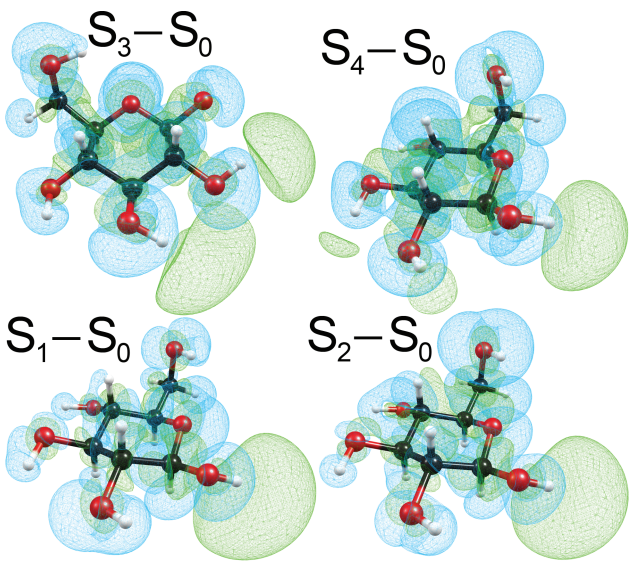


**Figure 1** Differences in the electron densities (computed at the (TD)DFT/aug-cc-pVTZ level) of the first four excited singlet states and the ground state. It is shown that electron density is removed mainly from the $n$ orbitals of several oxygen atoms and relocated mainly to the diffuse $\sigma^*$ orbitals of one OH bond (or two OH bonds in the case of $S_3-S_0$).

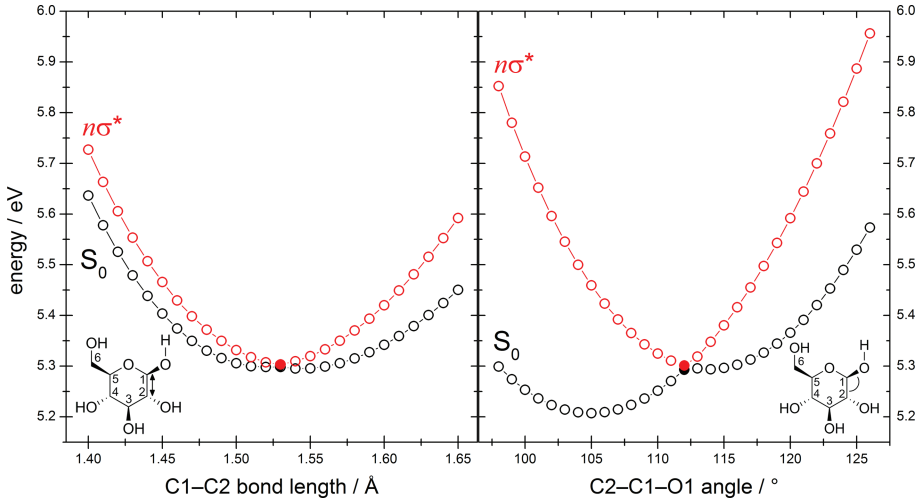


**Figure 2** Comparison of rigid scans along the C1–C2 elongation coordinate and the C2–C1–O1 bending coordinate originating from the conical intersection (full circles) for the hydrogen-detachment reaction of the O–H group located at carbon atom C1 (*cf.* Fig. 3 in the article). It is shown that the splitting of the energy of the ground-state and $n\sigma^*$ potential-energy surfaces is more pronounced for the C2–C1–O1 bending coordinate than for the C1–C2 elongation coordinate. The energies were computed at the SA2-CASSCF(2,2)/cc-pVDZ level.

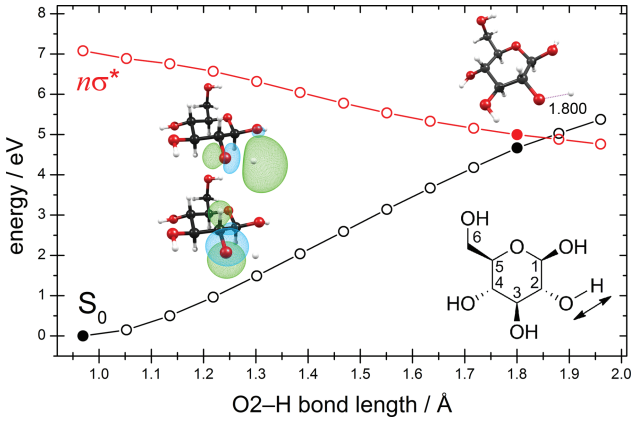


**Figure 3** Energy profiles of the ground state and the $n\sigma^*$ state along the stretching coordinate of the O–H group located at carbon atom C2. The profiles were obtained by linear interpolation between the ground-state equilibrium geometry (full black circle at the lower left) and the conical intersection (full black and red circles at the right). The last two geometries were obtained by rigid scan originating from the conical intersection. The insets show the lone-pair orbital of the oxygen atom and the $\sigma^*$ orbital of the O–H bond. Also shown is the structure of the conical intersection with the value of the O–H internuclear distance and the structural formula with the numbering of the C atoms. (For details, consult the section on Computational methods in the article.)

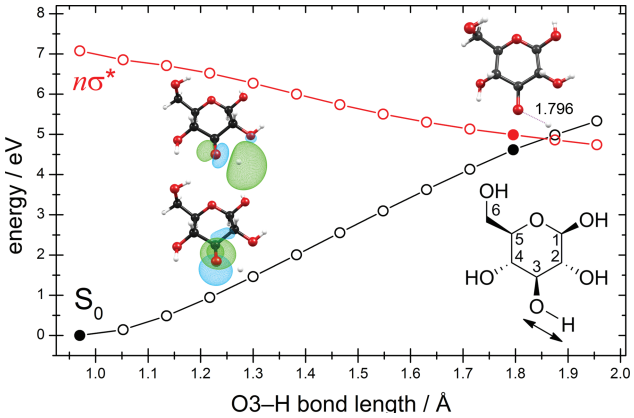


**Figure 4** Energy profiles of the ground state and the $n\sigma^*$ state along the stretching coordinate of the O–H group located at carbon atom C3. The profiles were obtained by linear interpolation between the ground-state equilibrium geometry (full black circle at the lower left) and the conical intersection (full black and red circles at the right). The last two geometries were obtained by rigid scan originating from the conical intersection. The insets show the lone-pair orbital of the oxygen atom and the $\sigma^*$ orbital of the O–H bond. Also shown is the structure of the conical intersection with the value of the O–H internuclear distance and the structural formula with the numbering of the C atoms. (For details, consult the section on Computational methods in the article.)

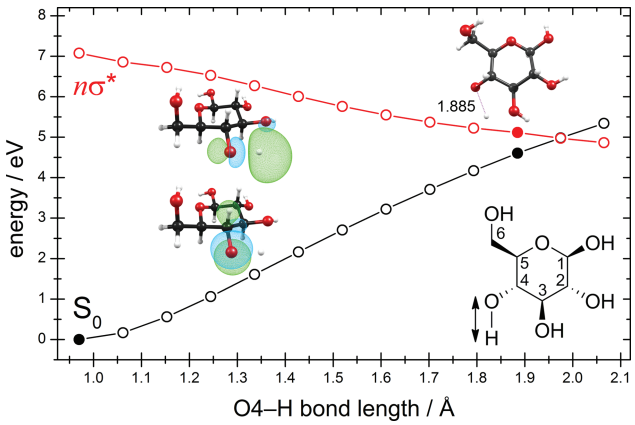


**Figure 5** Energy profiles of the ground state and the $n\sigma^*$ state along the stretching coordinate of the O–H group located at carbon atom C4. The profiles were obtained by linear interpolation between the ground-state equilibrium geometry (full black circle at the lower left) and the conical intersection (full black and red circles at the right). The last two geometries were obtained by rigid scan originating from the conical intersection. The insets show the lone-pair orbital of the oxygen atom and the $\sigma^*$ orbital of the O–H bond. Also shown is the structure of the conical intersection with the value of the O–H internuclear distance and the structural formula with the numbering of the C atoms. (For details, consult the section on Computational methods in the article.)

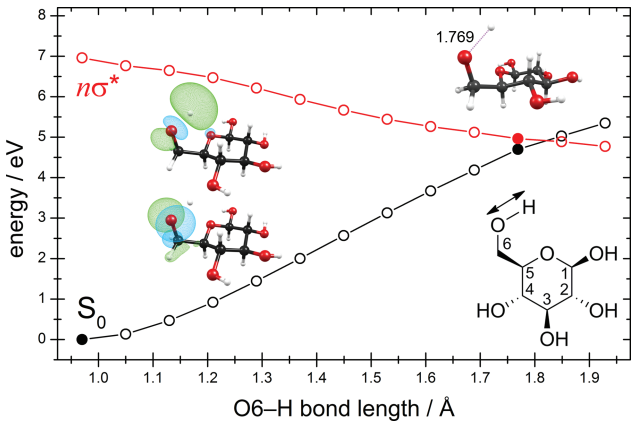


**Figure 6** Energy profiles of the ground state and the $n\sigma^*$ state along the stretching coordinate of the O–H group located at carbon atom C6. The profiles were obtained by linear interpolation between the ground-state equilibrium geometry (full black circle at the lower left) and the conical intersection (full black and red circles at the right). The last two geometries were obtained by rigid scan originating from the conical intersection. The insets show the lone-pair orbital of the oxygen atom and the $\sigma^*$ orbital of the O–H bond. Also shown is the structure of the conical intersection with the value of the O–H internuclear distance and the structural formula with the numbering of the C atoms. (For details, consult the section on Computational methods in the article.)

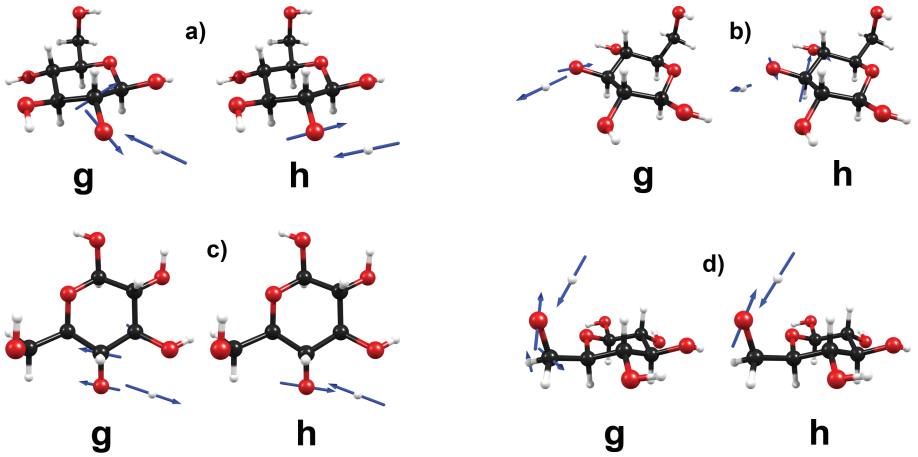


**Figure 7** Nuclear-displacement vectors of the gradient-difference vector **g** and the non-adiabatic-coupling vector **h** of the conical intersection for the O2–H hydrogen-detachment reaction shown in Figure 3 (a), the conical intersection for the O3–H hydrogen-detachment reaction shown in Figure 4 (b), the conical intersection for the O4–H hydrogen-detachment reaction shown in Figure 5 (c), the conical intersection for the O6–H hydrogen-detachment reaction shown in Figure 6 (d). (For details, consult the section on Computational methods in the article.)

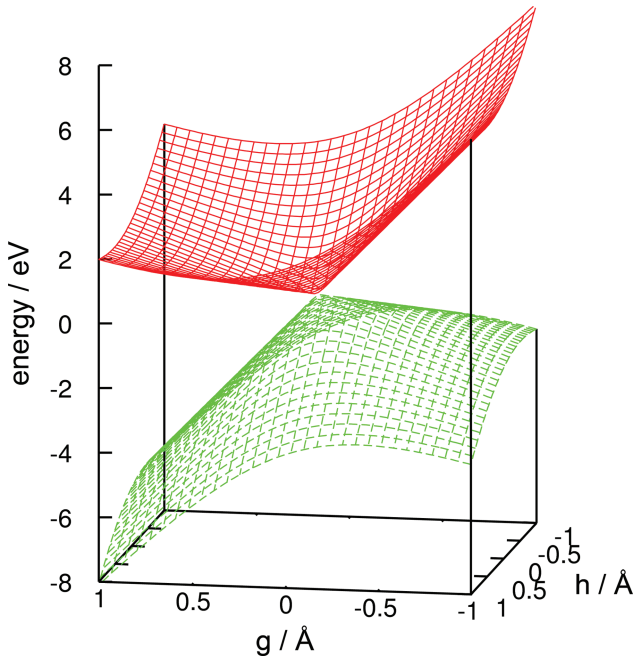


**Figure 8** Linear approximation of the potential-energy surfaces of the ground state and the $n\sigma^*$ state in the branching space of the conical intersection for the C1–O5 ring-opening process shown in Figure 7 of the article. (For details, consult the section on Computational methods in the article.)

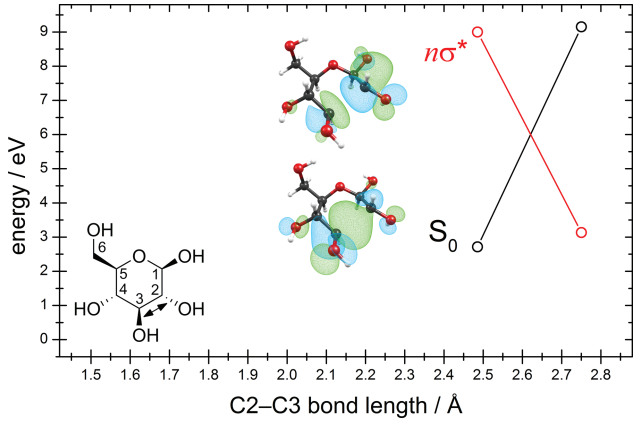


**Figure 9** Potential energies of the ground state and the $n\sigma^*$ state in the vicinity of a conical intersection along the C2–C3 ring-opening coordinate. The insets show the bonding σ orbital (mixed with some lone-pair contributions) and the $\sigma^*$ orbital (also mixed with some lone-pair contributions) of the C2–C3 bond. (For details, consult the section on Computational methods in the article.)

**Table 1** Cartesian coordinates of the MP2/cc-pVDZ optimized ground-state equilibrium geometry (energy: $-685.342209\ E_h$)

```
24

C   -0.035725  -0.066553   0.068441
C    1.146615  -0.279914   2.115256
C    1.666428  -1.662952   1.751249
C    1.786270  -1.767113   0.243595
C    0.461202  -1.428117  -0.417188
C   -1.448660   0.234515  -0.413916
O   -0.114470  -0.048670   1.502720
O    2.957518  -1.901743   2.292045
O    2.148700  -3.074036  -0.179539
O    0.604755  -1.347410  -1.826872
O   -2.373259  -0.700471   0.112382
O    0.989995  -0.253049   3.500502
H   -2.203399  -0.693474   1.067386
H   -1.706306   1.273566  -0.127530
H   -1.476814   0.150031  -1.510342
H    0.663950   0.716770  -0.293897
H   -0.289238  -2.189960  -0.129558
H    1.024931  -2.184245  -2.080233
H    2.963046  -3.283388   0.303572
H    2.540616  -1.025142  -0.095825
H    2.857153  -1.813535   3.252090
H    0.924634  -2.402177   2.115117
H    1.867785   0.493733   1.766999
H    0.772156   0.659022   3.741468
```

**Table 2** Cartesian coordinates of the SA2-CASSCF(2,2)/cc-pVDZ optimized minimum-energy conical intersection for the hydrogen detachment channel of the O1–H group (energy: −683.189144 $E_h$)

```
24

C    2.27197289  -0.90531301  -0.00256700
C    0.86894202  -1.11484694  -0.56121999
C   -0.01826500  -0.01215900  -0.02354700
C    0.01811000   0.01286600   1.49451804
C    1.45408702   0.04897300   2.01317501
C    1.54389799  -0.20125601   3.50888205
O    2.23550010  -0.95313400   1.39028704
O    3.15160894  -1.79228997  -0.48927301
O    0.86055201  -1.03834403  -1.95394599
O   -1.35191298  -0.16717499  -0.41321999
O   -0.62349302   1.15344799   1.98686504
O    1.06664300  -1.46582794   3.86093807
H    2.64954996   0.07337500  -0.34702301
H    0.50188702  -2.08702302  -0.21557400
H    0.37157100   0.94284397  -0.39588299
H   -0.46460399  -0.89380902   1.86708403
H    1.87818801   1.03575301   1.79426301
H    0.93260300   0.53258401   4.02817917
H    2.58415890  -0.07186700   3.82295895
H    4.15206385  -2.56701589   0.74416399
H    1.45908904  -1.68606400  -2.29982710
H   -1.38657606  -0.20028900  -1.35924196
H   -1.50864899   1.16430795   1.65048397
H    1.58130300  -2.11317396   3.40014601
```

**Table 3** Cartesian coordinates of the SA2-CASSCF(2,2)/cc-pVDZ optimized minimum-energy conical intersection for the hydrogen detachment channel of the O2–H group (energy: −683.184296 $E_h$)

```
24

C    2.20811200  -1.12275398   0.08023500
C    0.80589902  -1.18929899  -0.50566399
C   -0.03304900  -0.02404300  -0.00352300
C   -0.01024600   0.03781800   1.50997603
C    1.42839301   0.03337400   2.01641512
C    1.53041506  -0.12058500   3.52312112
O    2.12923288  -1.06742704   1.47238004
O    2.89126992  -2.25940704  -0.27454600
O    0.78090298  -1.22043002  -1.87343395
O   -1.35998297  -0.13639900  -0.42210001
O   -0.61924303   1.20815504   1.96931696
O    1.04019701  -1.35631299   3.94802594
H    2.72697806  -0.22427200  -0.28366399
H    0.35047299  -2.13216591  -0.17308500
H    0.40329599   0.90609199  -0.39026600
H   -0.51951802  -0.84705198   1.90032899
H    1.90927899   0.97239900   1.71685195
H    0.93768698   0.65276003   4.00451183
H    2.57757306   0.00991500   3.81452990
H    3.77902293  -2.20484805   0.05044300
H    2.35442400  -1.63947499  -2.64097500
H   -1.36333001  -0.28721401  -1.35809600
H   -1.49871898   1.23993003   1.61896396
H    1.50292504  -2.03040195   3.46947098
```

**Table 4** Cartesian coordinates of the SA2-CASSCF(2,2)/cc-pVDZ optimized minimum-energy conical intersection for the hydrogen detachment channel of the O3–H group (energy: −683.185281 $E_h$)

```
24

C    2.24785709  -1.04217899   0.08194000
C    0.88747698  -1.05301094  -0.58432198
C    0.02087700   0.06184500  -0.02694400
C    0.01769900   0.07263400   1.50389194
C    1.43823504  -0.01833800   2.05487609
C    1.48602295  -0.25147900   3.55488992
O    2.11283398  -1.11212003   1.46728003
O    2.93311405  -2.14985800  -0.36125901
O    1.00471604  -0.86718100  -1.96287704
O   -1.26607096   0.00860400  -0.50868303
O   -0.54698300   1.25413406   1.98914695
O    0.90522200  -1.47001004   3.91066408
H    2.78022790  -0.11949900  -0.18424700
H    0.42073700  -2.01654696  -0.35224500
H    0.42325899   1.02754295  -0.36606300
H   -0.54035401  -0.79739302   1.85965097
H    1.96276700   0.91671097   1.82336998
H    0.93282300   0.53577602   4.06071091
H    2.53114200  -0.20405200   3.87776089
H    3.81392193  -2.13753295  -0.01593700
H    1.49243999  -1.59280503  -2.32592797
H   -1.48159897  -0.89200199  -2.04717588
H   -1.42310703   1.33374596   1.63819396
H    1.34750605  -2.15490508   3.42849207
```

**Table 5** Cartesian coordinates of the SA2-CASSCF(2,2)/cc-pVDZ optimized minimum-energy conical intersection for the hydrogen detachment channel of the O4–H group (energy: −683.176693 $E_h$)

```
24

C    0.44667855   0.22944556  -1.77279687
C    1.01492536  -0.81247467  -0.83486760
C   -0.07543109  -1.75127065  -0.38592348
C   -1.30177617  -1.00452828   0.13470779
C   -1.71074307   0.12803738  -0.80746913
C   -2.73976135   1.04784691  -0.17683464
O   -0.58883667   0.92113465  -1.14248121
O    1.45823359   1.10827279  -2.07806087
O    1.99646449  -1.59928215  -1.44631672
O    0.40123659  -2.58101296   0.63974130
O   -2.34157634  -1.86193419   0.34884971
O   -2.24504471   1.67547178   0.96828413
H    0.05872086  -0.25580746  -2.67835093
H    1.41281593  -0.29245126   0.04103369
H   -0.38502070  -2.35979533  -1.24335599
H   -1.04966986  -0.57409608   1.11273515
H   -2.14131474  -0.31133738  -1.71631432
H   -3.60222936   0.45698744   0.12268607
H   -3.06340504   1.78068054  -0.92223275
H    1.14256024   1.74800229  -2.69930100
H    2.73403931  -1.05265403  -1.67453408
H    1.06179261  -3.16254997   0.28680429
H   -1.27356672  -3.32726789   0.86359626
H   -1.46049917   2.14805365   0.72807574
```

**Table 6** Cartesian coordinates of the SA2-CASSCF(2,2)/cc-pVDZ optimized minimum-energy conical intersection for the hydrogen detachment channel of the O6–H group (energy: −683.183921 $E_h$)

```
24

C    2.29712510  -1.02946401   0.03778500
C    0.92154002  -1.07971597  -0.60479897
C    0.00863100  -0.03892900   0.01308100
C    0.02623300  -0.14444900   1.52840400
C    1.47270799  -0.04501800   2.00779700
C    1.65945899  -0.07948800   3.51584411
O    2.20355511  -1.10407996   1.42806804
O    3.00629306  -2.11331105  -0.42862999
O    0.98974299  -0.81382102  -1.97871304
O   -1.31561303  -0.18919501  -0.41553700
O   -0.71456099   0.88164800   2.11645699
O    1.18920898  -1.19843400   4.13447285
H    2.79558611  -0.09048000  -0.23699300
H    0.50689799  -2.07516789  -0.42132899
H    0.37737301   0.95566303  -0.26210400
H   -0.37720701  -1.12183404   1.81018996
H    1.87931395   0.91464102   1.66415596
H    1.21642900   0.80952197   3.97074509
H    2.73460197  -0.04402400   3.73793697
H    3.86630607  -2.12093711  -0.03321400
H    1.52053297  -1.47847998  -2.39461493
H   -1.33483696  -0.12121000  -1.36017704
H   -1.58898306   0.85683399   1.75230098
H    0.49264899  -2.54276991   3.21966696
```

**Table 7** Cartesian coordinates of the SA2-CASSCF(2,2)/cc-pVDZ optimized minimum-energy conical intersection for the C1–O5 ring-opening channel (energy: −683.228090 $E_h$)

```
24

C   -0.763542  -0.067772  -0.868966
C   -1.414513   0.591777   0.353832
C    1.659347   0.537116   1.241554
C    1.673849  -0.288411   0.007810
C    0.723717   0.235494  -1.072992
C   -2.900268   0.262945   0.468997
O   -0.759799   0.210818   1.500449
O   -3.086256  -1.083506   0.800991
O    2.097300  -0.060209   2.344219
O    2.966805  -0.275027  -0.581894
O    1.036831  -0.374768  -2.297088
O   -1.461899   0.402017  -1.987650
H   -2.574990  -1.250712   1.581094
H   -3.337039   0.915144   1.234108
H   -3.412708   0.444017  -0.471414
H   -1.297588   1.680596   0.229598
H   -0.878122  -1.151862  -0.777379
H   -1.046252   0.045080  -2.760231
H    1.978256  -0.371890  -2.400046
H    0.853894   1.321269  -1.161241
H    3.573116  -0.736036  -0.020773
H    1.404552  -1.311774   0.277575
H    1.603694   1.615605   1.216972
H    2.000255   0.504587   3.097652
```