Supporting information

for

UV absorption spectra of DNA bases in the 350-190 nm range: Assignment and state specific analysis of solvation effects

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UV-vis spectra of DNA bases

UV-vis spectra of DNA bases were measured in mQ-water at 25C on a PG T80/T80+ spectrometer. Stock solutions of DNA bases were prepared by dissolving adenine (0.98 mg), cytosine (1.40 mg) or thymine (1.91 mg) in water (10 mL). These stock solutions were prior to the UV-vis measurements diluted ten times. A UV-vis cell was filled with the solution of a base (2.5 mL) and UV-vis spectrum was taken. This solution was then diluted with water and after each dilution a spectrum was measured. Dependence of the absorbance on the base concentration was fitted to linear equation and the molar absorption coefficient was determined from the slope.

Molar absorption coefficient for guanine is not available since guanine was not soluble in water. A suspension of guanine (1.2 mg) in water (10 mL) was diluted ten times and UV-vis spectrum was taken. The spectrum showed high offset at high wavelength region, indicating presence of crystalline sample that scattered light. Subtraction of the offset gave approximate qualitative spectrum of guanine in water.

Spectra of DNA bases in H_2O.

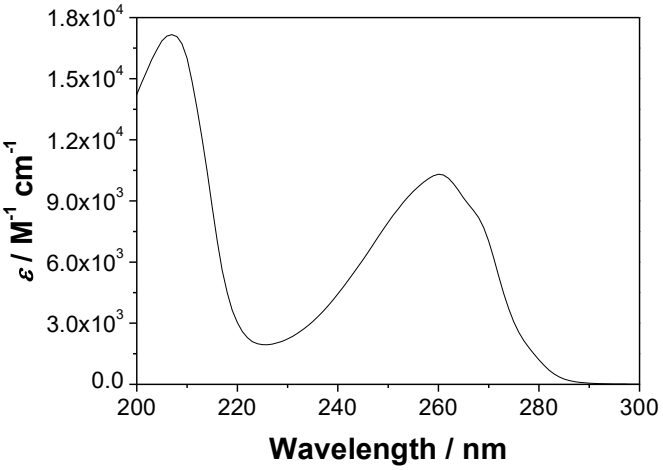

Figure S 1: Absorption spectrum of adenine in H_2O (ϵ_{260}= 10310 $\pm$ 30 M^{-1} cm^{-1}).

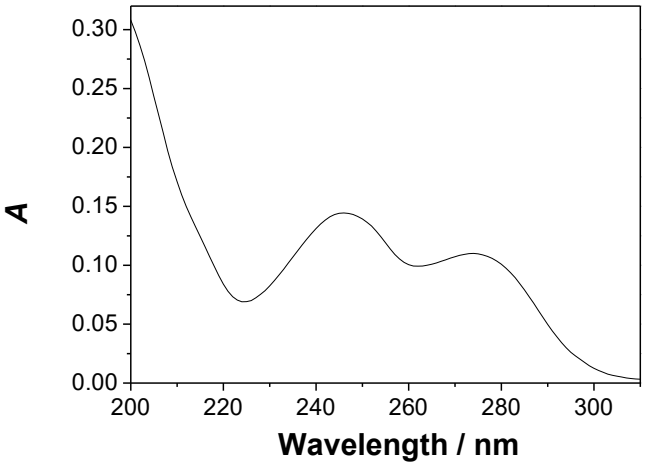

Figure S 2: Absorption spectrum of guanine in H_2O (c$\approx 5 \times 10^{-5}$ M).

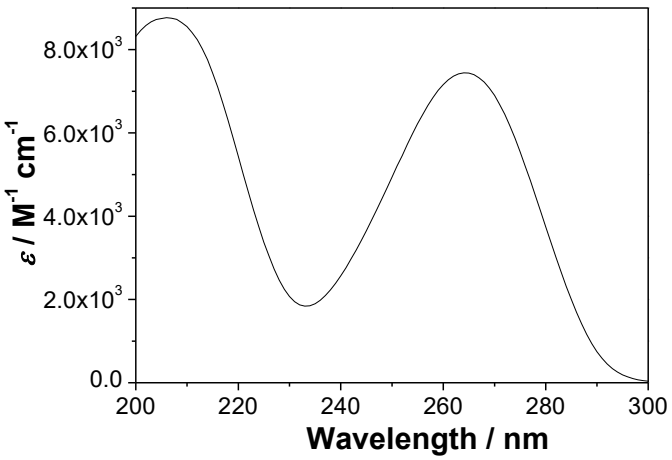

Figure S 3: Absorption spectrum of thymine in H_2O (ϵ_{264}= 7500 $\pm$ 100 M^{-1} cm^{-1}).

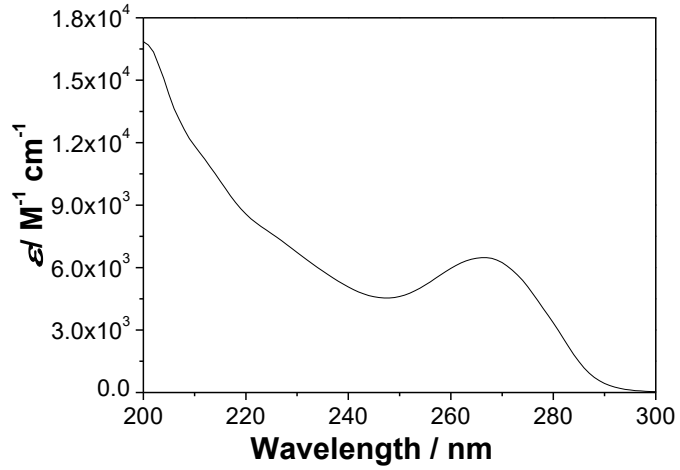

Figure S 4: Absorption spectrum of cytosine in H_2O (ϵ_{264}= 6490 $\pm$ 90 M^{-1} cm^{-1}).

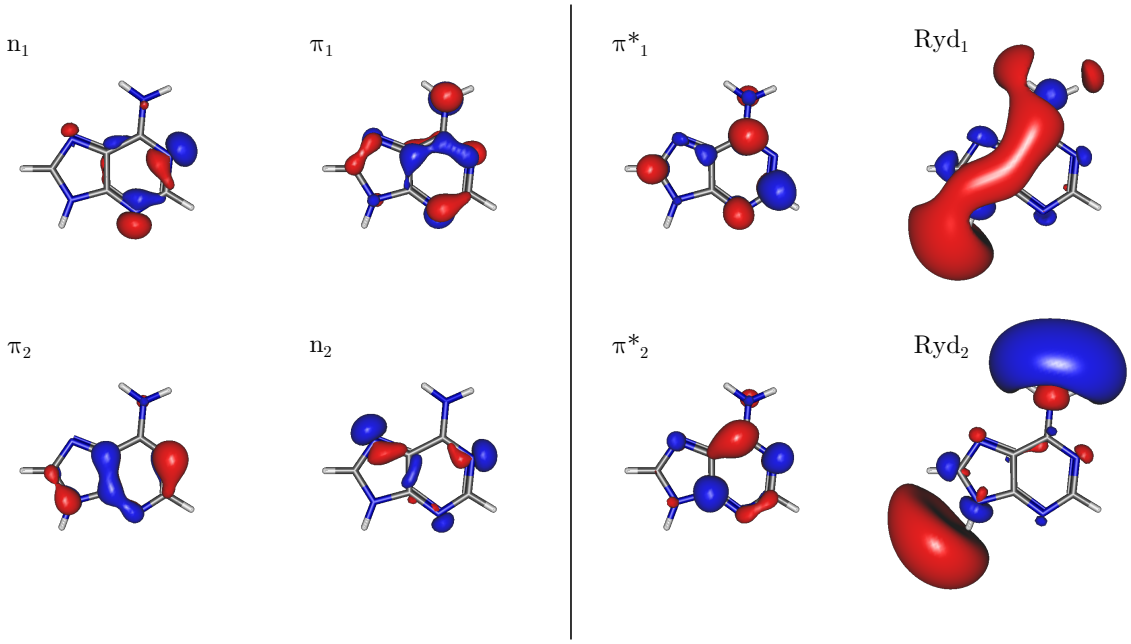

Figure S 5: Dominant hole (left) and particle (right) NTOs contributing to the most relevant transitions in adenine (see Table 1 for the spectral assignment).

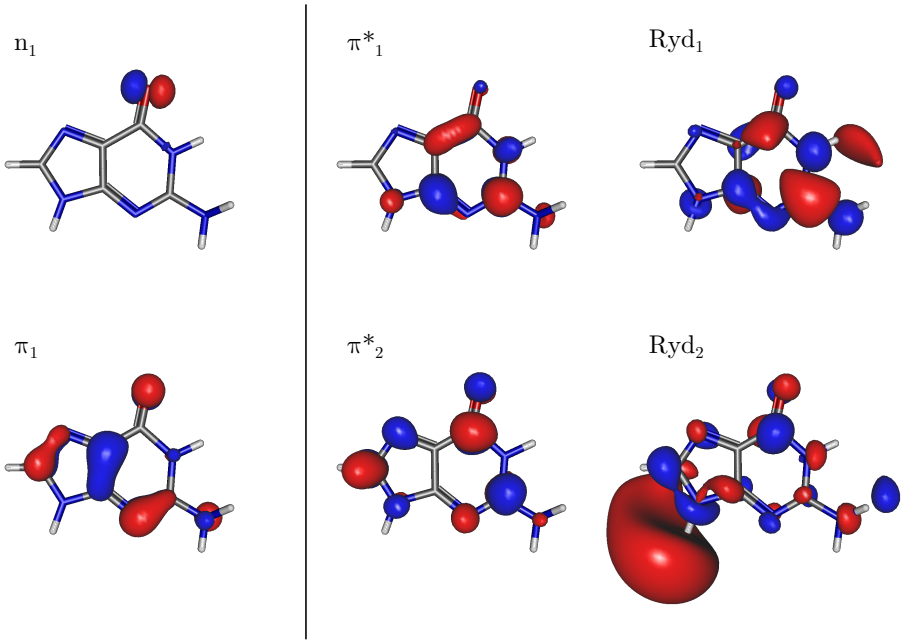

Figure S 6: Dominant hole (left) and particle (right) NTOs contributing to the most relevant transitions in guanine (see Table 2 for the spectral assignment).

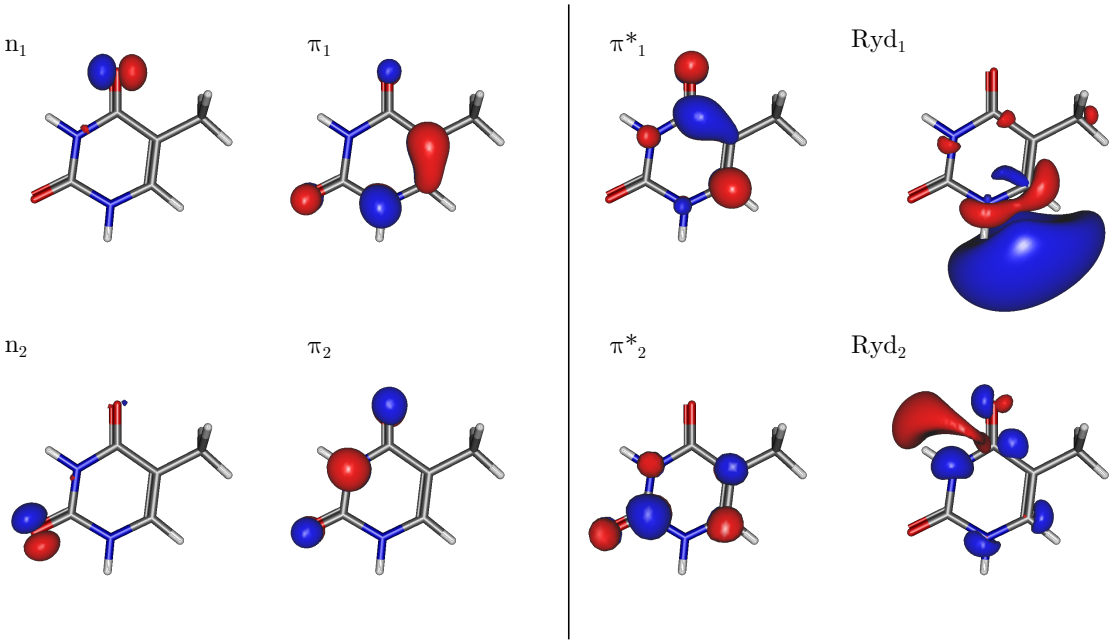

Figure S 7: Dominant hole (left) and particle (right) NTOs contributing to the most relevant transitions in thymine (see Table 3 for the spectral assignment).

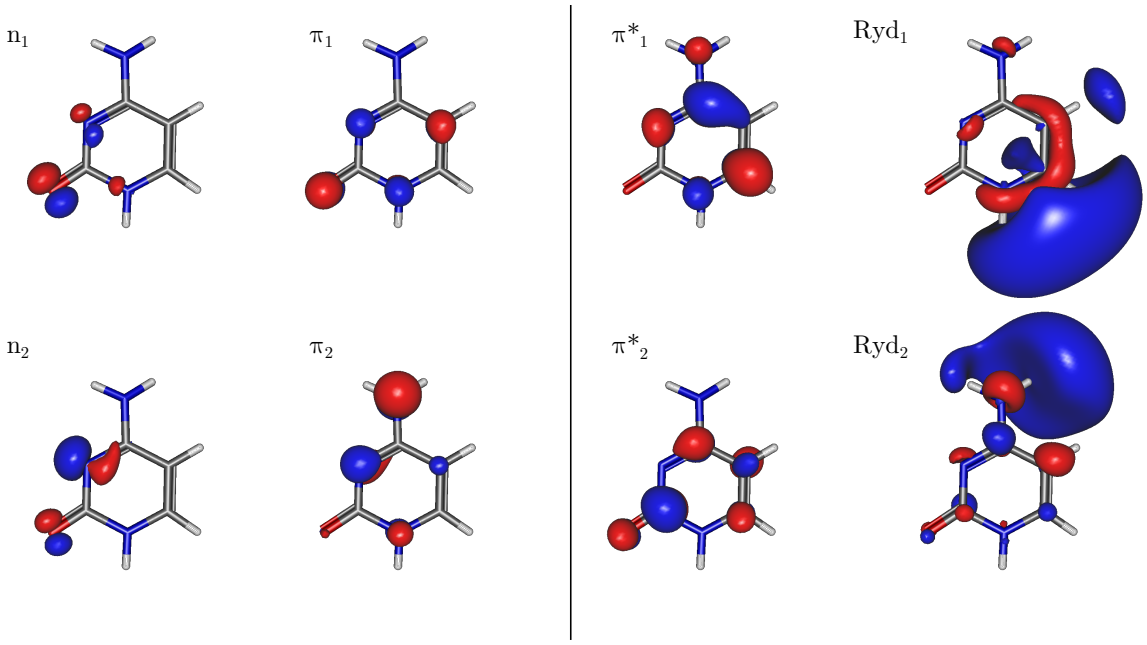

Figure S 8: Dominant hole (left) and particle (right) NTOs contributing to the most relevant transitions in cytosine (see Table 4 for the spectral assignment).

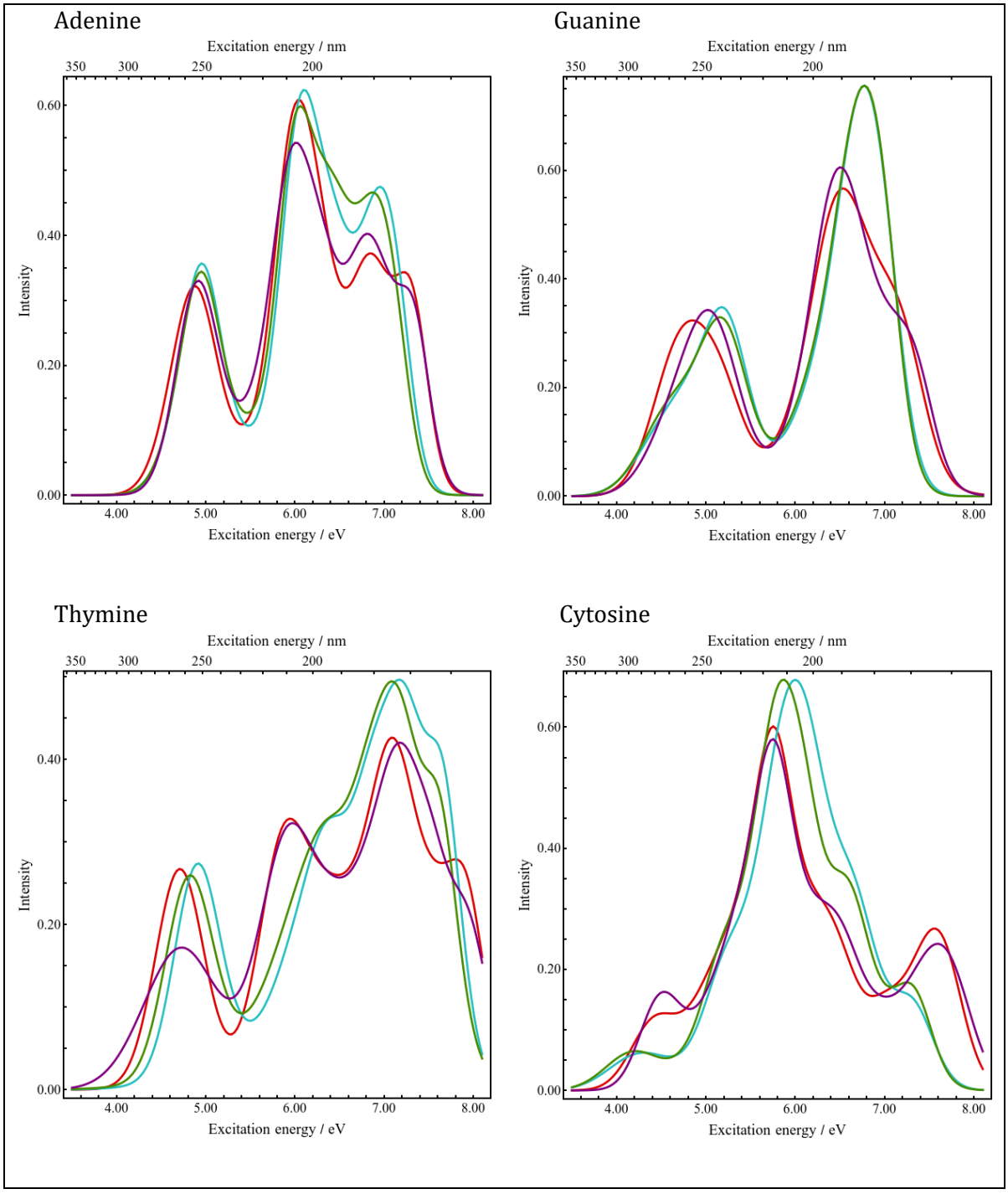

Figure S 9: Cumulative effect of solvation on the computed UV absorption spectra of DNA nucleobases. Gas phase spectra at 0K (light blue) and 298 K (green), spectra upon inclusion of the COSMO environment (purple) and solvent-induced structural changes (red).

Table S 1: Mean values and standard deviations of electronic excitation energies (eV) and oscillator strengths (in parenthesis) of 9H-adenine. Computations are performed at the ADC(2)/aug-cc-pVDZ level. All transition below 6.53 eV (190 nm) and selected transitions with large oscillator strengths at higher energies are included. The effects of vibrational averaging (E_0^{gas}), temperature (E_{298}^{gas}), electrostatics (E_{298}^{COSMO}) and solvent-induced structural changes (E_{298}^{sol}) on the mean excitation energies are analyzed. For the assignment of the states see Table 1.

S	E_{ref}	E_0^{gas}	E_{298}^{gas}	E_{298}^{COSMO}	E_{298}^{sol}
S_1	4.99	4.81 ± 0.28	4.77 ± 0.28	5.04 ± 0.29	5.01 ± 0.26
	(0.0127)	(0.033 ± 0.042)	(0.028 ±0.038)	(0.062 ± 0.086)	(0.038 ± 0.042)
S_2	5.10	4.92 ± 0.25	4.92 ± 0.26	4.87 ± 0.24	4.82 ± 0.27
	(0.2509)	(0.175 ± 0.075)	(0.165 ±0.076)	(0.150 ± 0.108)	(0.216 ± 0.096)
S_3	5.12	4.99 ± 0.18	4.96 ± 0.18	4.93 ± 0.22	4.92 ± 0.22
	(0.0359)	(0.055 ± 0.054)	(0.060 ±0.062)	(0.105 ± 0.095)	(0.077 ± 0.077)
S_4	5.38	5.29 ± 0.24	5.31 ± 0.22	5.54 ± 0.22	5.48 ± 0.20
	(0.0103)	(0.024 ± 0.018)	(0.028 ±0.027)	(0.049 ± 0.070)	(0.030 ± 0.033)
S_5	5.63	5.54 ± 0.25	5.47 ± 0.29	5.69 ± 0.28	5.67 ± 0.28
	(0.0024)	(0.017 ± 0.020)	(0.019 ±0.026)	(0.066 ± 0.104)	(0.031 ± 0.041)
S_6	5.69	5.63 ± 0.24	5.64 ± 0.21	6.11 ± 0.22	6.06 ± 0.22
	(0.0043)	(0.015 ± 0.027)	(0.017 ±0.028)	(0.051 ± 0.070)	(0.036 ± 0.049)
S_7	5.96	5.90 ± 0.26	5.88 ± 0.21	6.33 ± 0.22	6.28 ± 0.17
	(0.0216)	(0.032 ± 0.028)	(0.029 ±0.021)	(0.063 ± 0.073)	(0.051 ± 0.040)
S_8	6.03	5.89 ± 0.21	5.85 ± 0.25	6.09 ± 0.25	6.06 ± 0.27
	(0.0011)	(0.040 ± 0.044)	(0.052 ±0.051)	(0.076 ± 0.099)	(0.062 ± 0.058)
S_9	6.17	6.12 ± 0.24	6.15 ± 0.20	6.28 ± 0.21	6.21 ± 0.22
	(0.0084)	(0.022 ± 0.023)	(0.027 ±0.032)	(0.040 ± 0.056)	(0.021 ± 0.027)
S_{10}	6.20	6.05 ± 0.19	6.00 ± 0.18	5.92 ± 0.20	5.96 ± 0.21
	(0.4251)	(0.234 ± 0.100)	(0.207 ±0.093)	(0.241 ± 0.149)	(0.320 ± 0.116)
S_{11}	6.40	6.33 ± 0.25	6.31 ± 0.20	6.96 ± 0.21	6.92 ± 0.20
	(0.0975)	(0.055 ± 0.059)	(0.070 ±0.063)	(0.032 ± 0.038)	(0.032 ± 0.033)
S_{12}	6.42	6.36 ± 0.25	6.37 ± 0.23	6.75 ± 0.23	6.68 ± 0.25
	(0.0319)	(0.036 ± 0.045)	(0.032 ±0.040)	(0.022 ± 0.025)	(0.018 ± 0.025)
S_{13}	6.46	6.34 ± 0.22	6.36 ± 0.26	6.40 ± 0.23	6.36 ± 0.25
	(0.0056)	(0.032 ± 0.041)	(0.039 ±0.037)	(0.035 ± 0.038)	(0.034 ± 0.033)
S_{14}	6.50	6.41 ± 0.23	6.38 ± 0.20	6.72 ± 0.21	6.76 ± 0.24
	(0.0019)	(0.020 ± 0.018)	(0.023 ±0.025)	(0.037 ± 0.043)	(0.033 ± 0.034)
S_{15}	6.56	6.51 ± 0.24	6.54 ± 0.20	6.82 ± 0.19	6.76 ± 0.22
	(0.0022)	(0.021 ± 0.028)	(0.015 ±0.014)	(0.029 ± 0.048)	(0.015 ± 0.017)
S_{16}	6.59	6.40 ± 0.19	6.41 ± 0.21	6.28 ± 0.22	6.28 ± 0.23
	(0.0391)	(0.065 ± 0.057)	(0.060 ±0.047)	(0.078 ± 0.069)	(0.103 ± 0.077)

Table S 2: Mean values and standard deviations of electronic excitation energies (eV) and oscillator strengths (in parenthesis) of 9H-guanine. Computations are performed at the ADC(2)/aug-cc-pVDZ level. All transition below 6.53 eV (190 nm) and selected transitions with large oscillator strengths at higher energies are included. The effects of vibrational averaging (E_0^{gas}), temperature (E_{298}^{gas}), electrostatics (E_{298}^{COSMO}) and solvent-induced structural changes (E_{298}^{sol}) on the mean excitation energies are analyzed. For the assignment of the states see Table 2.

S	E_{ref}	E_0^{gas}	E_{298}^{gas}	E_{298}^{COSMO}	E_{298}^{sol}
S_1	4.85	4.57 ± 0.33	4.57 ± 0.32	4.68 ± 0.32	(4.64 ± 0.30)
	(0.151)	(0.130 ± 0.050)	(0.135 ± 0.055)	(0.183 ± 0.046)	(0.197 ± 0.055)
S_2	4.95	4.84 ± 0.25	4.82 ± 0.29	5.29 ± 0.26	(5.24 ± 0.23)
	(0.023)	(0.047 ± 0.048)	(0.043 ± 0.045)	(0.051 ± 0.057)	(0.058 ± 0.055)
S_3	5.12	4.93 ± 0.40	4.99 ± 0.41	5.40 ± 0.33	(5.23 ± 0.33)
	(0.001)	(0.012 ± 0.019)	(0.014 ± 0.019)	(0.014 ± 0.028)	(0.011 ± 0.023)
S_4	5.29	5.22 ± 0.24	5.21 ± 0.24	5.85 ± 0.22	(5.78 ± 0.22)
	(0.038)	(0.040 ± 0.049)	(0.041 ± 0.045)	(0.022 ± 0.030)	(0.016 ± 0.014)
S_5	5.34	5.22 ± 0.25	5.20 ± 0.26	5.06 ± 0.28	(4.97 ± 0.32)
	(0.290)	(0.199 ± 0.070)	(0.187 ± 0.071)	(0.273 ± 0.075)	(0.269 ± 0.077)
S_6	5.85	5.66 ± 0.44	5.73 ± 0.45	6.63 ± 0.36	(6.42 ± 0.37)
	(0.004)	(0.013 ± 0.022)	(0.014 ± 0.017)	(0.042 ± 0.050)	(0.038 ± 0.041)
S_7	5.90	5.80 ± 0.25	5.79 ± 0.28	6.10 ± 0.24	(6.03 ± 0.22)
	(0.004)	(0.009 ± 0.012)	(0.010 ± 0.012)	(0.013 ± 0.018)	(0.011 ± 0.019)
S_8	5.91	5.81 ± 0.45	5.85 ± 0.43	6.59 ± 0.34	(6.42 ± 0.32)
	(0.005)	(0.012 ± 0.014)	(0.016 ± 0.020)	(0.038 ± 0.033)	(0.041 ± 0.042)
S_9	6.06	5.99 ± 0.23	5.99 ± 0.25	6.49 ± 0.24	(6.40 ± 0.24)
	(0.001)	(0.010 ± 0.013)	(0.011 ± 0.013)	(0.034 ± 0.042)	(0.023 ± 0.030)
S_{10}	6.12	5.86 ± 0.35	5.85 ± 0.32	6.28 ± 0.34	(6.27 ± 0.32)
	(0.000)	(0.010 ± 0.014)	(0.014 ± 0.019)	(0.032 ± 0.032)	(0.032 ± 0.036)
S_{11}	6.20	6.14 ± 0.20	6.17 ± 0.24	6.42 ± 0.27	(6.35 ± 0.24)
	(0.001)	(0.009 ± 0.012)	(0.011 ± 0.024)	(0.030 ± 0.029)	(0.033 ± 0.041)
S_{12}	6.28	6.25 ± 0.23	6.24 ± 0.24	6.47 ± 0.24	(6.40 ± 0.26)
	(0.004)	(0.020 ± 0.032)	(0.015 ± 0.019)	(0.031 ± 0.037)	(0.032 ± 0.040)
S_{13}	6.31	6.20 ± 0.31	6.19 ± 0.27	6.25 ± 0.29	(6.12 ± 0.34)
	(0.002)	(0.017 ± 0.022)	(0.015 ± 0.023)	(0.046 ± 0.049)	(0.041 ± 0.047)
S_{14}	6.33	6.20 ± 0.28	6.16 ± 0.23	6.54 ± 0.45	(6.36 ± 0.42)
	(0.013)	(0.021 ± 0.023)	(0.017 ± 0.021)	(0.041 ± 0.053)	(0.036 ± 0.047)
S_{15}	6.37	6.27 ± 0.28	6.28 ± 0.25	6.63 ± 0.47	(6.72 ± 0.38)
	(0.009)	(0.022 ± 0.035)	(0.020 ± 0.022)	(0.026 ± 0.026)	(0.033 ± 0.041)
S_{22}	6.91	6.67 ± 0.25	6.68 ± 0.25	6.41 ± 0.28	(6.44 ± 0.31)
	(0.245)	(0.132 ± 0.083)	(0.137 ± 0.088)	(0.198 ± 0.095)	(0.194 ± 0.103)
S_{24}	6.97	6.80 ± 0.24	6.76 ± 0.25	6.53 ± 0.28	(6.62 ± 0.29)
	(0.400)	(0.151 ± 0.084)	(0.152 ± 0.072)	(0.191 ± 0.093)	(0.189 ± 0.103)

Table S 3: Mean values and standard deviations of electronic excitation energies (eV) and oscillator strengths (in parenthesis) of thymine. Computations are performed at the ADC(2)/aug-cc-pVDZ level. All transition below 6.53 eV (190 nm) and selected transitions with large oscillator strengths at higher energies are included. The effects of vibrational averaging (E_0^{gas}), temperature (E_{298}^{gas}), electrostatics (E_{298}^{COSMO}) and solvent-induced structural changes (E_{298}^{sol}) on the mean excitation energies are analyzed. For the assignment of the states see Table 3.

S	E_{ref}	E_0^{gas}	E_{298}^{gas}	E_{298}^{COSMO}	E_{298}^{sol}
S_1	4.55	4.38 ± 0.37	4.33 ± 0.44	4.79 ± 0.39	4.84 ± 0.32
	(0.000) (0.004 ± 0.015)	(0.005 ± 0.014)	(0.018 ± 0.026)	(0.015 ± 0.023)	
S_2	5.07	4.91 ± 0.26	4.82 ± 0.27	4.72 ± 0.42	4.80 ± 0.28
	(0.203) (0.188 ± 0.030)	(0.181 ± 0.039)	(0.214 ± 0.040)	(0.221 ± 0.030)	
S_3	5.58	5.44 ± 0.22	5.42 ± 0.26	5.79 ± 0.30	5.78 ± 0.20
	(0.001) (0.008 ± 0.011)	(0.012 ± 0.020)	(0.041 ± 0.037)	(0.038 ± 0.036)	
S_4	5.91	5.71 ± 0.40	5.65 ± 0.39	6.04 ± 0.30	6.10 ± 0.35
	(0.000) (0.007 ± 0.011)	(0.008 ± 0.011)	(0.022 ± 0.026)	(0.019 ± 0.027)	
S_5	6.05	5.86 ± 0.35	5.79 ± 0.36	6.03 ± 0.36	6.10 ± 0.33
	(0.038) (0.041 ± 0.033)	(0.044 ± 0.038)	(0.085 ± 0.056)	(0.089 ± 0.062)	
S_6	6.16	5.98 ± 0.28	5.96 ± 0.28	6.48 ± 0.21	6.51 ± 0.20
	(0.038) (0.026 ± 0.025)	(0.024 ± 0.022)	(0.029 ± 0.025)	(0.035 ± 0.032)	
S_7	6.37	6.27 ± 0.22	6.26 ± 0.27	6.38 ± 0.21	6.40 ± 0.19
	(0.001) (0.023 ± 0.025)	(0.025 ± 0.022)	(0.017 ± 0.022)	(0.016 ± 0.020)	
S_8	6.38	6.31 ± 0.36	6.22 ± 0.46	6.58 ± 0.36	6.68 ± 0.30
	(0.001) (0.017 ± 0.023)	(0.022 ± 0.022)	(0.027 ± 0.033)	(0.019 ± 0.028)	
S_9	6.42	6.27 ± 0.34	6.19 ± 0.35	5.93 ± 0.31	6.02 ± 0.33
	(0.187) (0.101 ± 0.041)	(0.101 ± 0.050)	(0.178 ± 0.066)	(0.182 ± 0.066)	
S_{10}	6.49	6.40 ± 0.19	6.39 ± 0.22	6.55 ± 0.24	6.56 ± 0.18
	(0.000) (0.028 ± 0.029)	(0.024 ± 0.022)	(0.011 ± 0.015)	(0.014 ± 0.019)	
S_{19}	7.26	7.15 ± 0.25	7.10 ± 0.26	7.02 ± 0.33	7.10 ± 0.29
	(0.329) (0.161 ± 0.075)	(0.151 ± 0.071)	(0.156 ± 0.068)	(0.174 ± 0.074)	

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S	E_{ref}	E_0^{gas}	E_{298}^{gas}	E_{298}^{COSMO}	E_{298}^{sol}
S_1	4.44	(4.25 ± 0.34)	4.17 ± 0.30	4.49 ± 0.23	4.42 ± 0.26
	(0.050)	(0.045 ± 0.017)	(0.042 ± 0.018)	(0.112 ± 0.030)	(0.095 ± 0.029)
S_2	4.65	(4.39 ± 0.37)	4.34 ± 0.38	5.29 ± 0.36	5.15 ± 0.34
	(0.002)	(0.009 ± 0.012)	(0.010 ± 0.010)	(0.044 ± 0.050)	(0.033 ± 0.035)
S_3	5.10	(5.04 ± 0.40)	5.01 ± 0.37	5.77 ± 0.41	5.48 ± 0.40
	(0.002)	(0.015 ± 0.020)	(0.019 ± 0.017)	(0.043 ± 0.047)	(0.038 ± 0.042)
S_4	5.31	(5.20 ± 0.21)	5.15 ± 0.17	5.77 ± 0.17	5.77 ± 0.17
	(0.006)	(0.017 ± 0.020)	(0.014 ± 0.015)	(0.067 ± 0.057)	(0.078 ± 0.062)
S_5	5.43	(5.27 ± 0.28)	5.26 ± 0.29	5.27 ± 0.34	5.17 ± 0.32
	(0.141)	(0.105 ± 0.058)	(0.111 ± 0.078)	(0.169 ± 0.093)	(0.159 ± 0.077)
S_6	5.50	(5.36 ± 0.38)	5.26 ± 0.42	5.92 ± 0.40	5.78 ± 0.32
	(0.000)	(0.007 ± 0.009)	(0.017 ± 0.031)	(0.048 ± 0.045)	(0.054 ± 0.053)
S_7	5.66	(5.57 ± 0.37)	5.50 ± 0.34	6.56 ± 0.25	6.37 ± 0.26
	(0.025)	(0.027 ± 0.035)	(0.031 ± 0.036)	(0.038 ± 0.028)	(0.037 ± 0.033)
S_8	5.86	(5.71 ± 0.26)	5.71 ± 0.27	6.50 ± 0.23	6.41 ± 0.25
	(0.039)	(0.050 ± 0.060)	(0.067 ± 0.093)	(0.024 ± 0.030)	(0.025 ± 0.039)
S_9	5.95	(5.87 ± 0.24)	5.86 ± 0.20	6.27 ± 0.22	6.25 ± 0.27
	(0.011)	(0.032 ± 0.041)	(0.036 ± 0.044)	(0.029 ± 0.034)	(0.037 ± 0.038)
S_{10}	6.08	(5.92 ± 0.27)	5.83 ± 0.25	5.74 ± 0.27	5.73 ± 0.27
	(0.459)	(0.273 ± 0.132)	(0.245 ± 0.118)	(0.262 ± 0.096)	(0.292 ± 0.098)
S_{11}	6.23	(6.13 ± 0.28)	6.04 ± 0.29	7.09 ± 0.27	7.02 ± 0.26
	(0.036)	(0.052 ± 0.070)	(0.053 ± 0.072)	(0.012 ± 0.012)	(0.014 ± 0.015)
S_{12}	6.26	(6.16 ± 0.19)	6.12 ± 0.16	6.57 ± 0.19	6.60 ± 0.18
	(0.037)	(0.045 ± 0.058)	(0.042 ± 0.046)	(0.018 ± 0.019)	(0.015 ± 0.014)
S_{13}	6.38	(6.36 ± 0.36)	6.39 ± 0.34	7.38 ± 0.20	7.18 ± 0.27
	(0.007)	(0.021 ± 0.021)	(0.022 ± 0.025)	(0.023 ± 0.016)	(0.020 ± 0.016)
S_{14}	6.47	(6.39 ± 0.28)	6.41 ± 0.29	6.65 ± 0.35	6.59 ± 0.28
	(0.005)	(0.041 ± 0.049)	(0.034 ± 0.039)	(0.031 ± 0.040)	(0.033 ± 0.038)
S_{15}	6.51	(6.42 ± 0.29)	6.43 ± 0.32	6.99 ± 0.27	6.97 ± 0.25
	(0.001)	(0.025 ± 0.027)	(0.022 ± 0.022)	(0.013 ± 0.015)	(0.014 ± 0.016)
S_{17}	6.60	(6.53 ± 0.27)	6.48 ± 0.24	6.29 ± 0.32	6.27 ± 0.28
	(0.104)	(0.073 ± 0.052)	(0.069 ± 0.052)	(0.133 ± 0.076)	(0.117 ± 0.070)