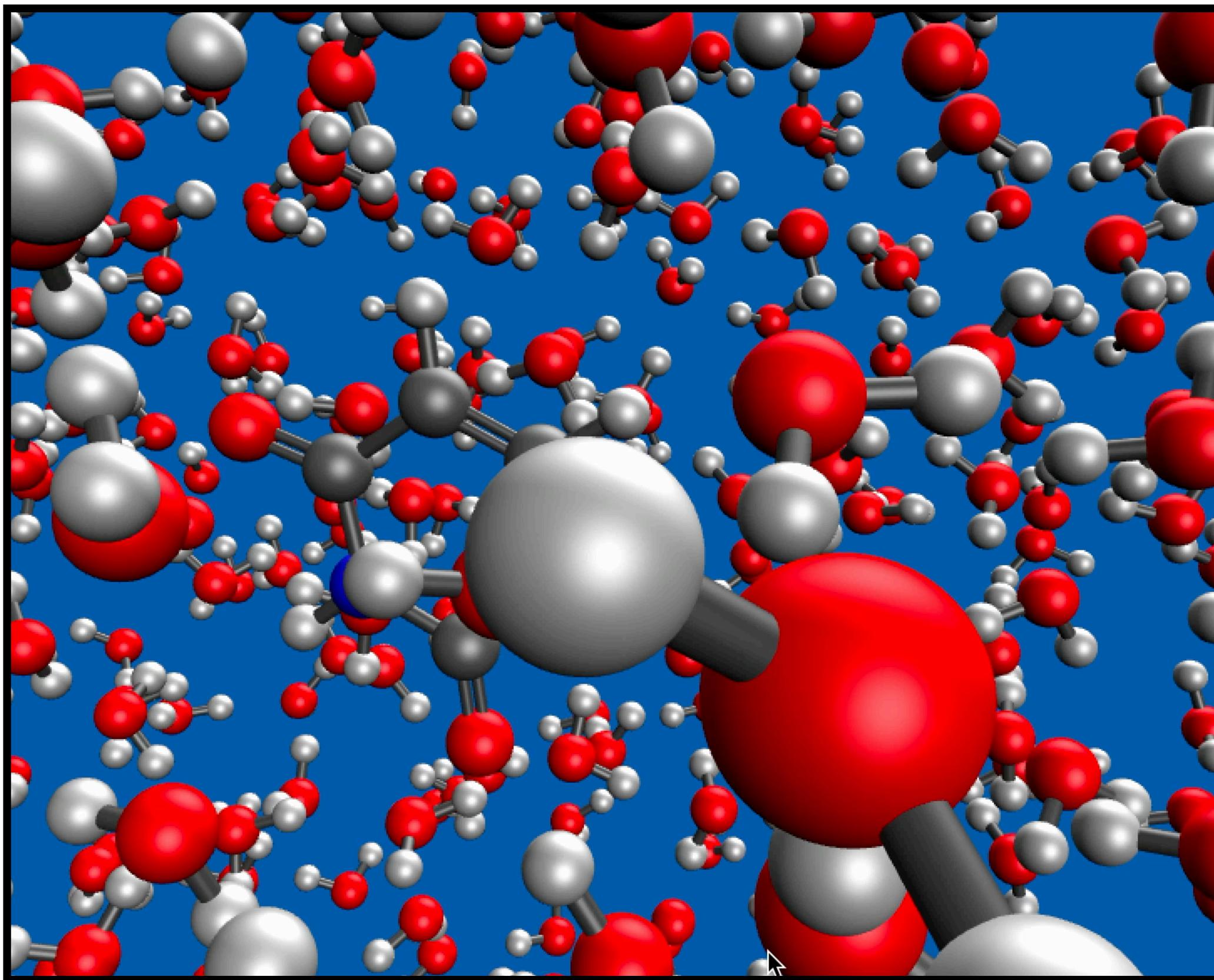


Excited State Dynamics of Nucleobases

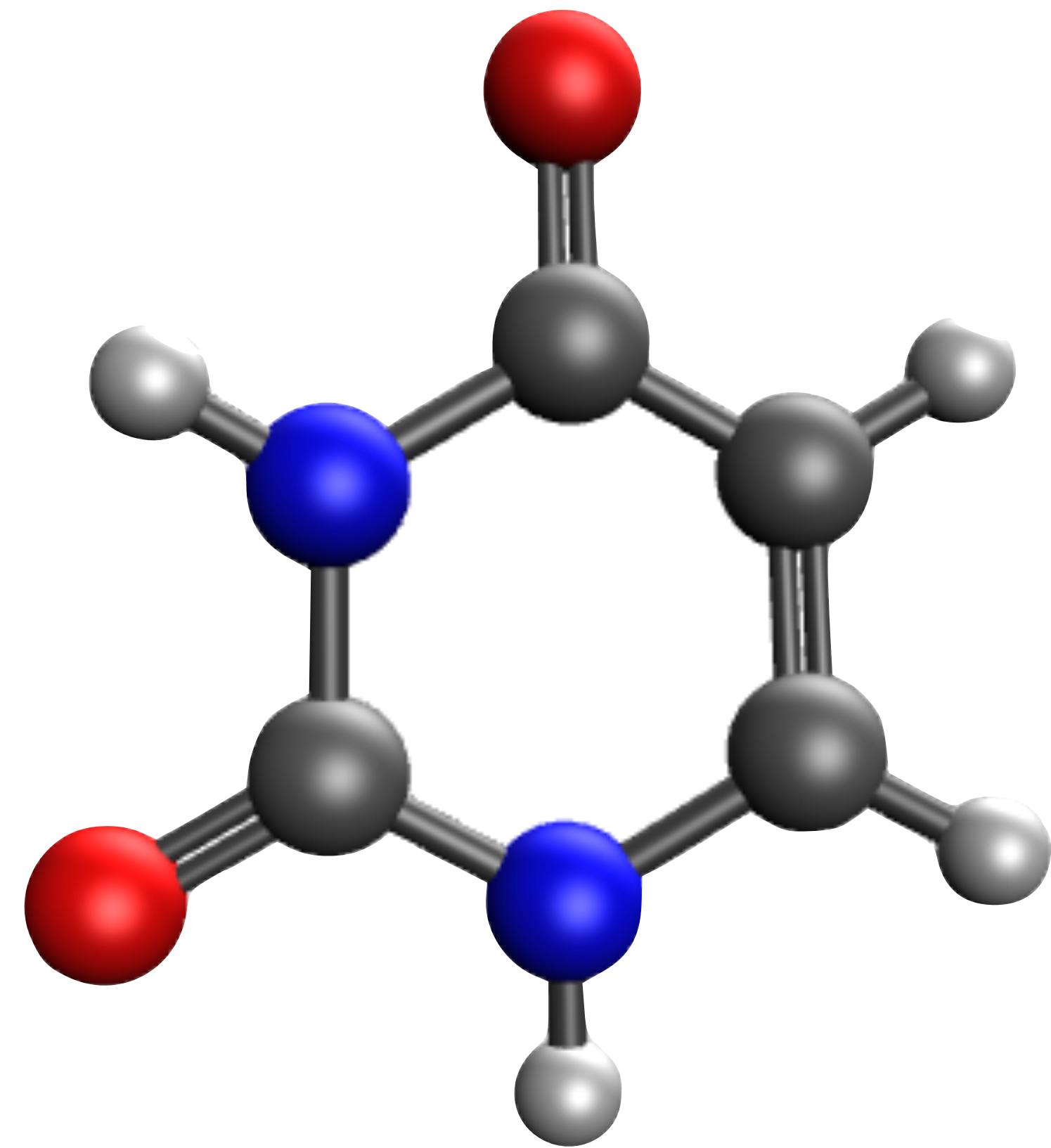
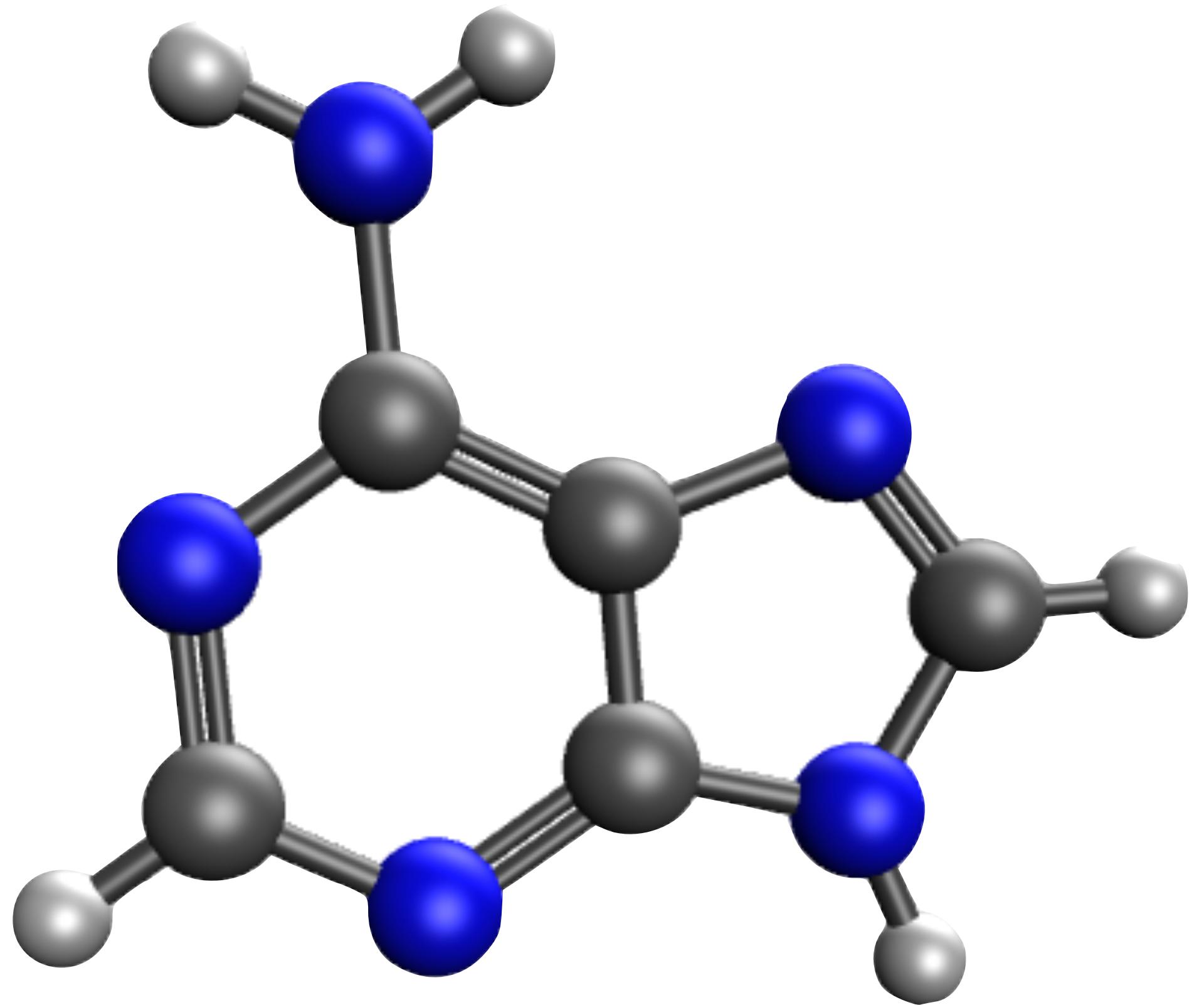
*An Exploratory Study in
SHARC and COBRAMM*



Presenter: Matthew Dutra
July 22, 2022

*Nonadiabatic Dynamics Workshop
Summer 2022*

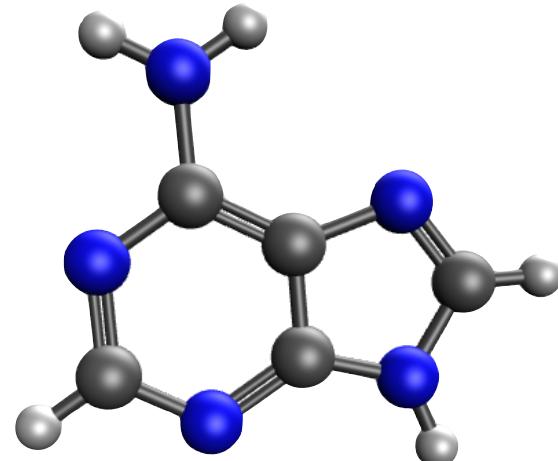
Adenine



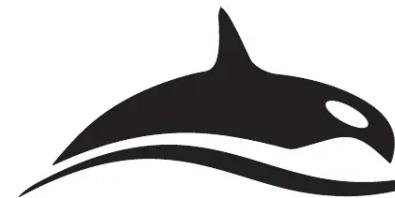
Uracil



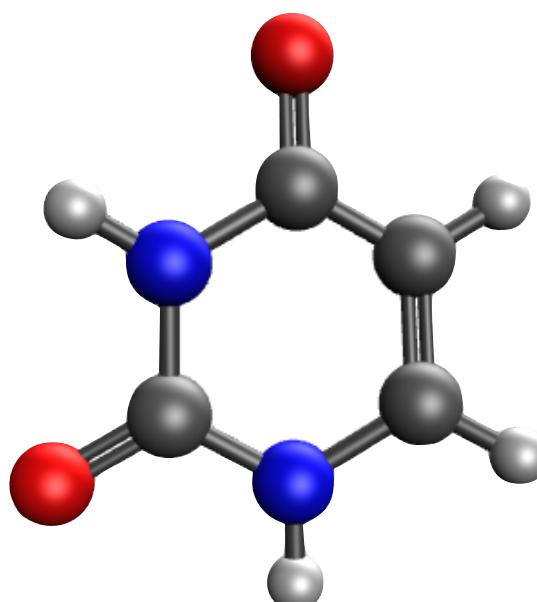
Methodology



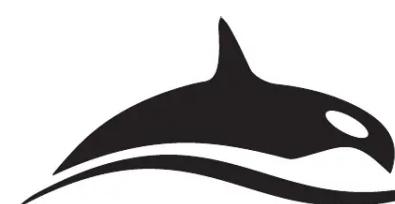
Adenine



Ground-state optimization and normal mode analysis
using [DFT//B3LYP+D3/def2-TZVP](#)



Uracil



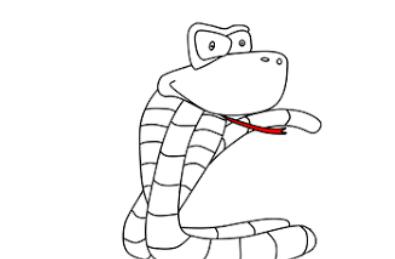
Vertical excitation energies using [DFT//B3LYP+D3/](#)
[def2-TZVP](#)



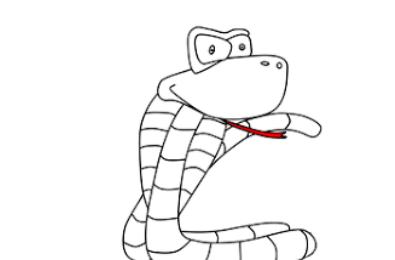
LVC-parameterized Hamiltonian for excited state
manifold



Surface hopping dynamics using ~400 trajectories
for 300 fs



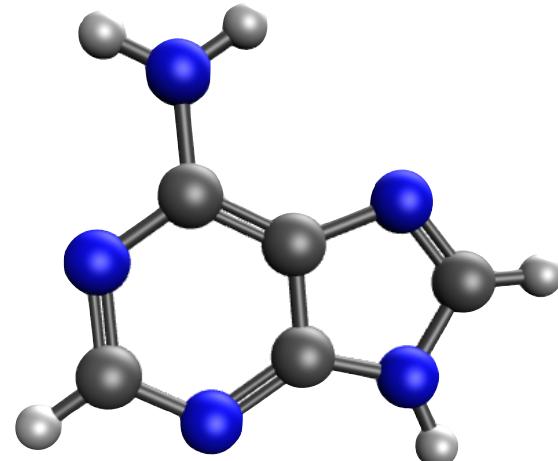
Solvation in water medium via classical MD



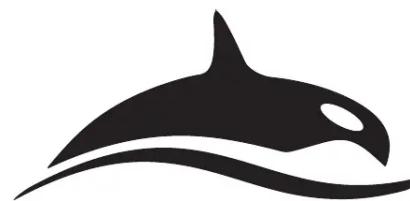
QM/MM dynamics of solvated molecules to elucidate
solvent effects



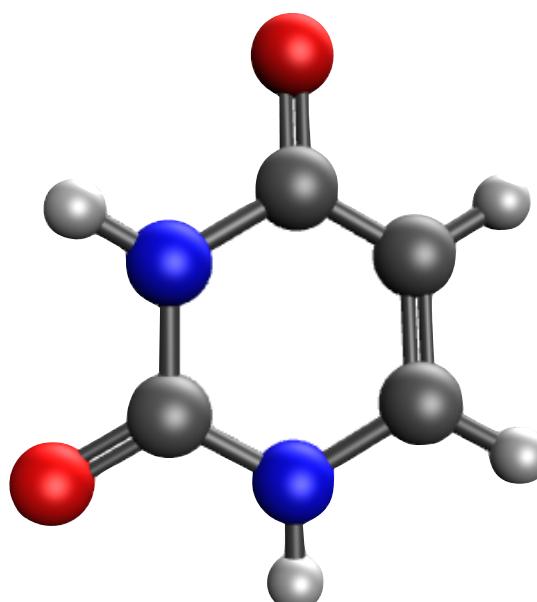
Methodology



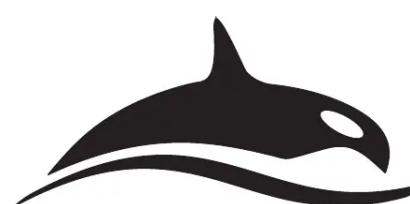
Adenine



Ground-state optimization and normal mode analysis
using [DFT//B3LYP+D3/def2-TZVP](#)



Uracil



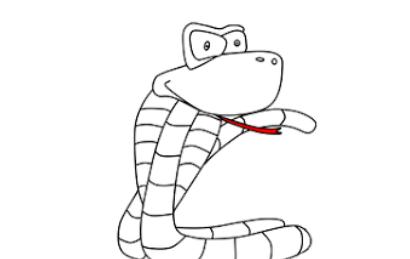
Vertical excitation energies using [DFT//B3LYP+D3/](#)
[def2-TZVP](#)



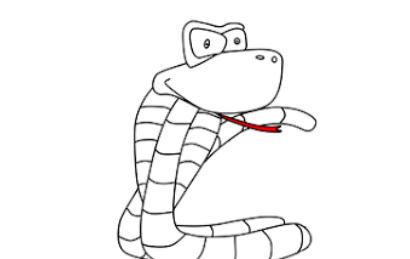
LVC-parameterized Hamiltonian for excited state
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Surface hopping dynamics using ~400 trajectories
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Solvation in water medium via classical MD



QM/MM dynamics of solvated molecules to elucidate
solvent effects



Article

Nonadiabatic Absorption Spectra and Ultrafast Dynamics of
DNA and RNA Photoexcited Nucleobases

James A. Green ^{1,†}, Martha Yaghoubi Jouybari ^{2,†}, Daniel Aranda ² and Roberto Impronta ^{1,*}
and Fabrizio Santoro ^{2,*}





LVC-parameterized Hamiltonian for excited state manifold

Linear Vibronic Coupling: model Hamiltonian consisting of harmonic oscillators linearly coupled to one another, used to describe molecular excited states in a diabatic picture, can shift to adiabatic states too

$$\hat{H} = \begin{pmatrix} \frac{\omega Q^2}{2} & \\ & \frac{\omega Q^2}{2} \end{pmatrix} + \begin{pmatrix} \epsilon_1 + \kappa_1 Q & \lambda_{12} Q \\ \lambda_{12} Q & \epsilon_2 + \kappa_2 Q \end{pmatrix}$$

GS oscillators w/ frequencies
Vertical excitation energies
Horizontal coordinate shifts
Coupling constants

*no spin-orbit couplings or couplings to external electric field necessary here

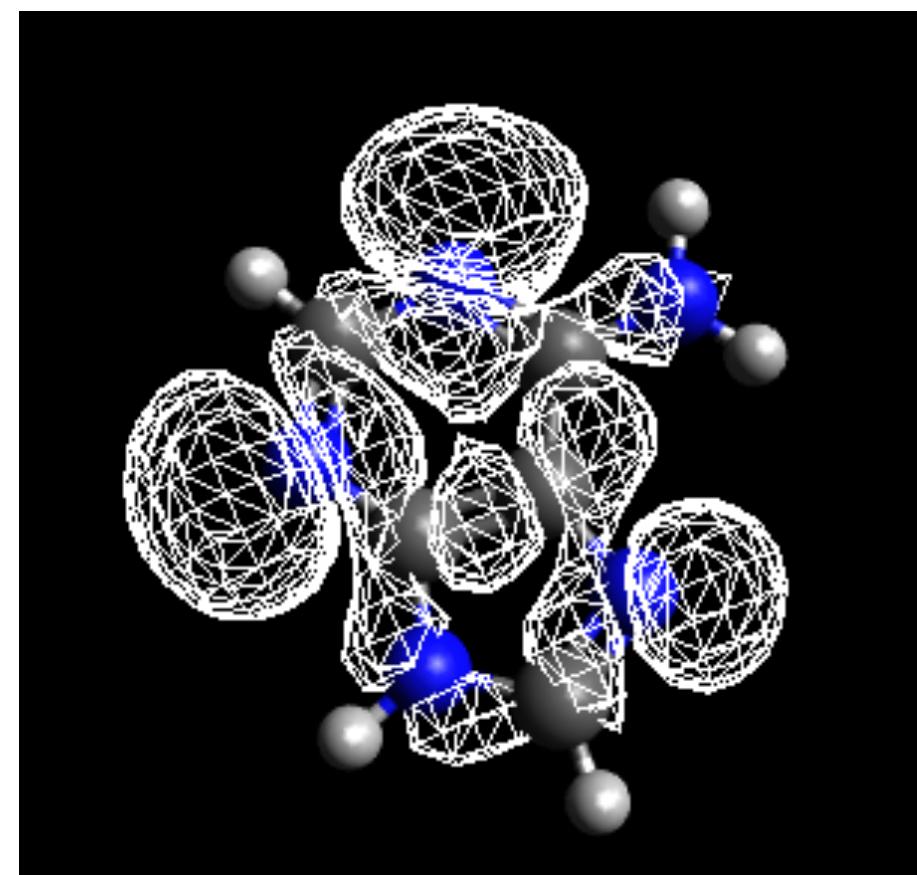
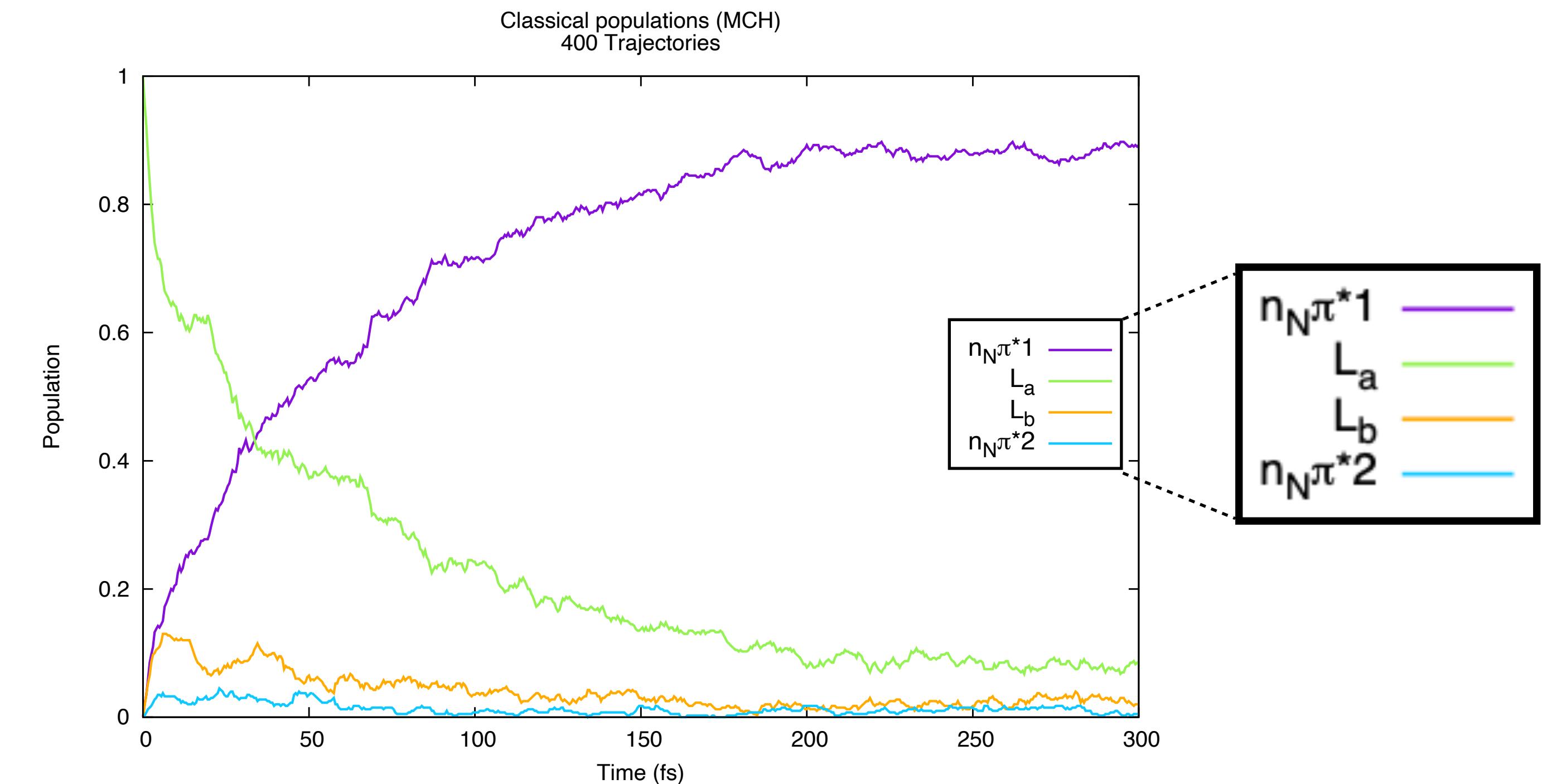




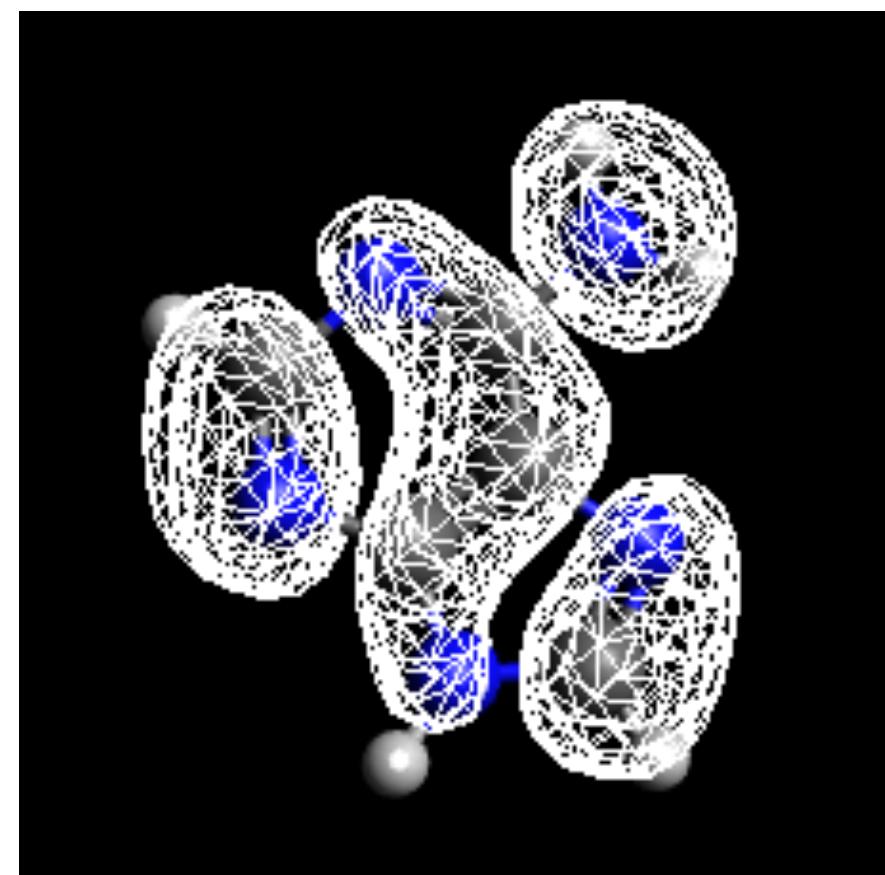
Adenine

State	ΔE (eV)	Orb. Trans.	Char.
S ₁	4.957	H-1 → L	$n_N\pi^*1$
S ₂	5.196	H → L	L _a
S ₃	5.425	H → L+1	L _b
S ₄	5.600	H → L+2	$\pi Ry_{\sigma}1$

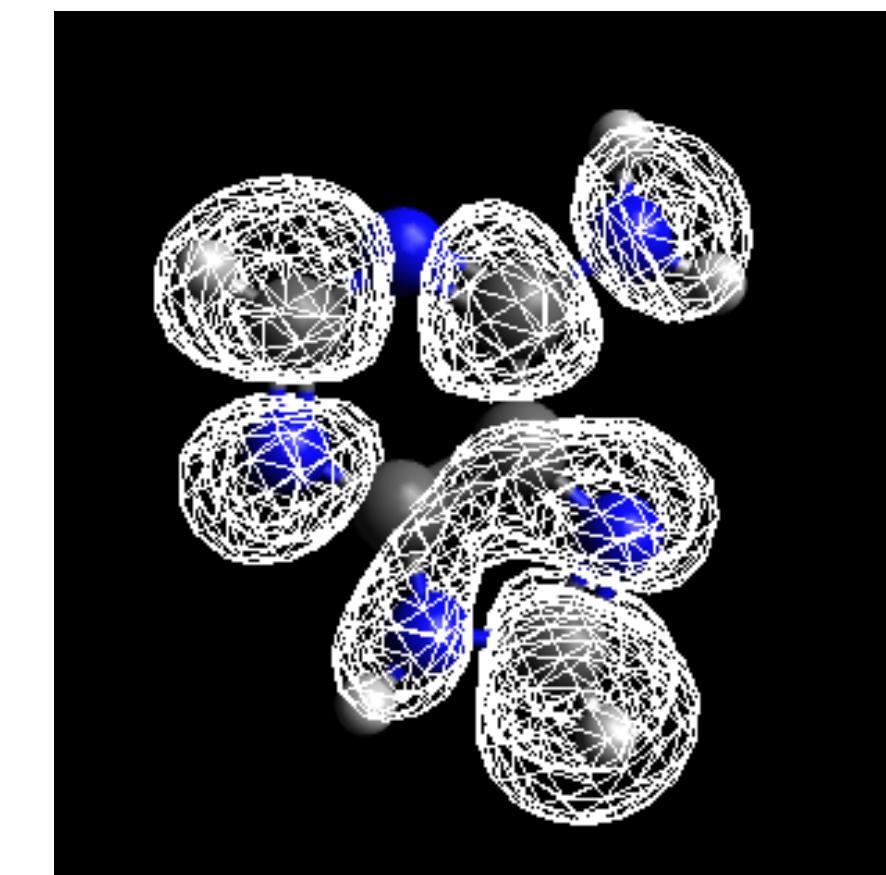
Excitation energies of adenine computed using
TDDFT//B3LYP-D3/def2-TZVP



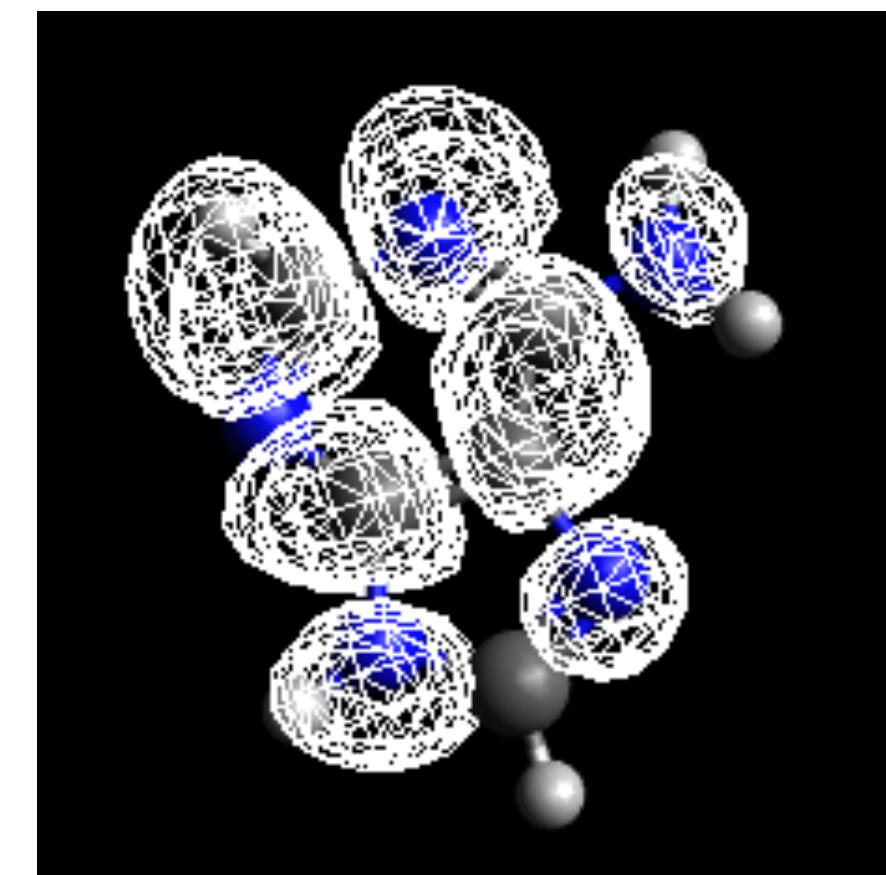
HOMO-1



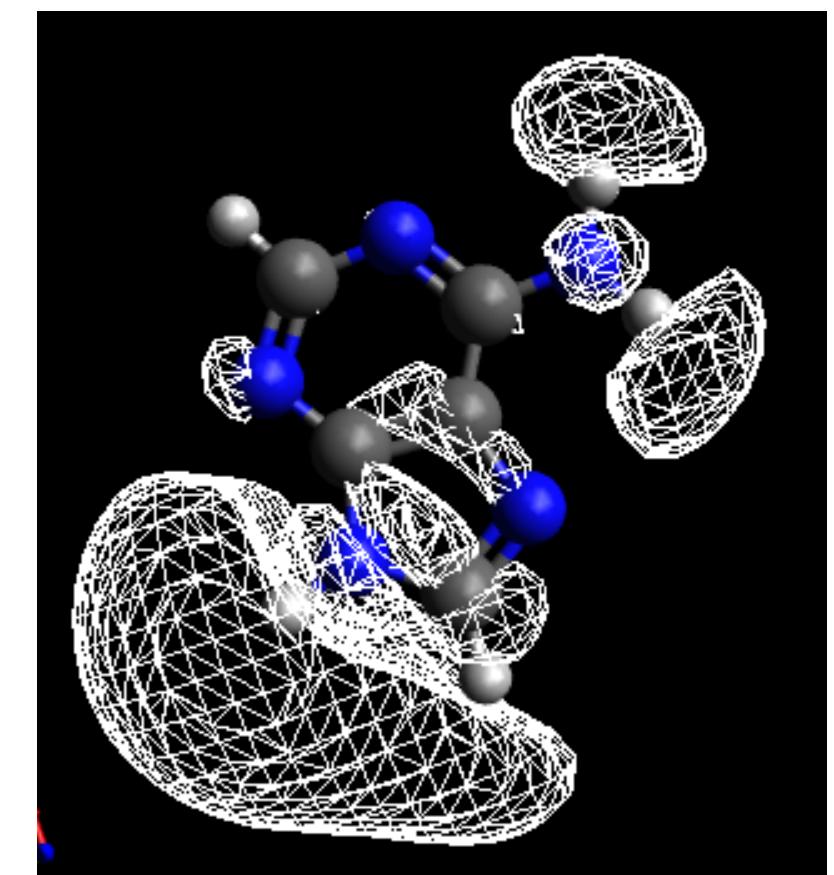
HOMO



LUMO



LUMO+1

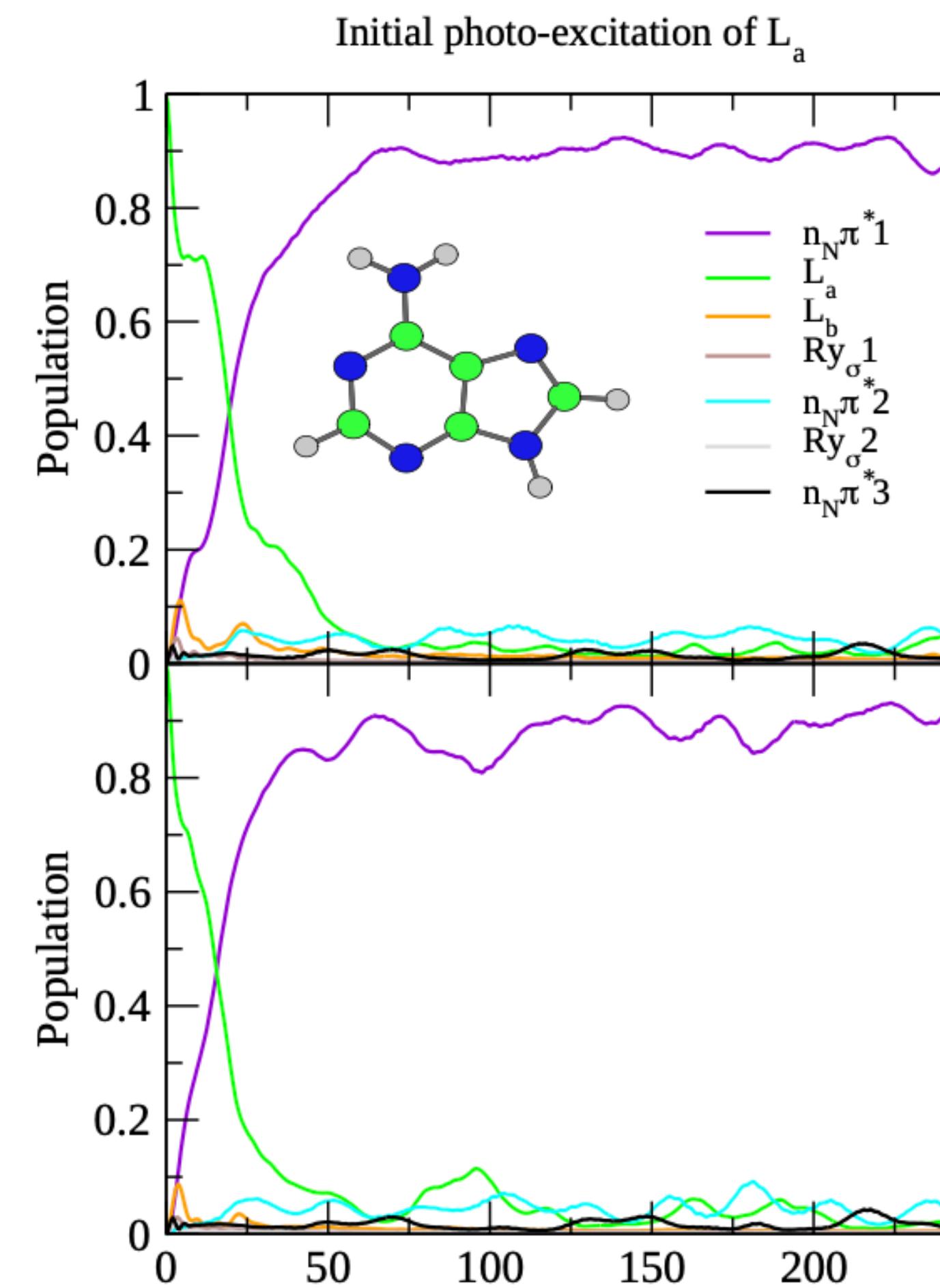


LUMO+2

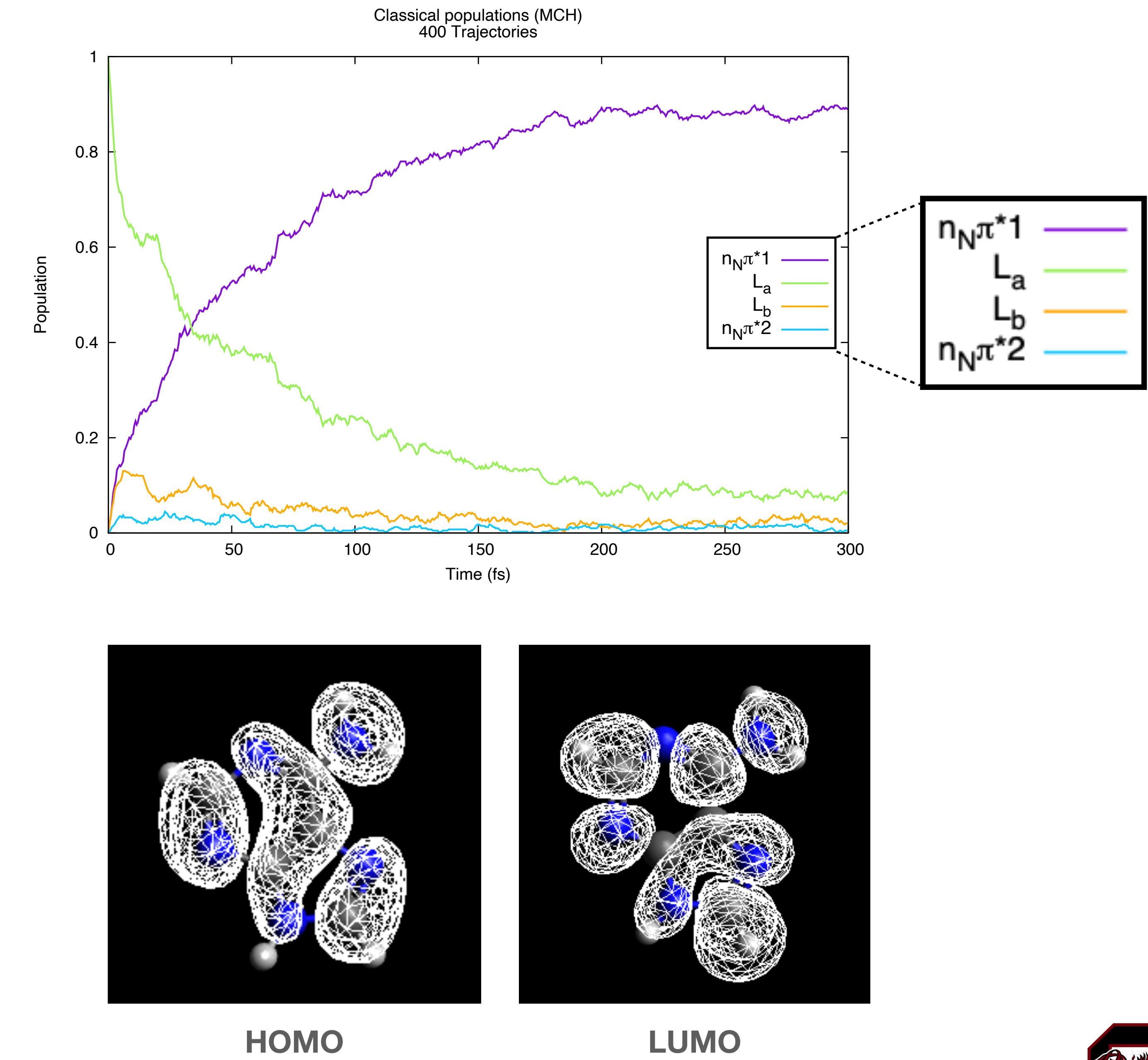




Adenine



Molecules 2021, 26, 1743.

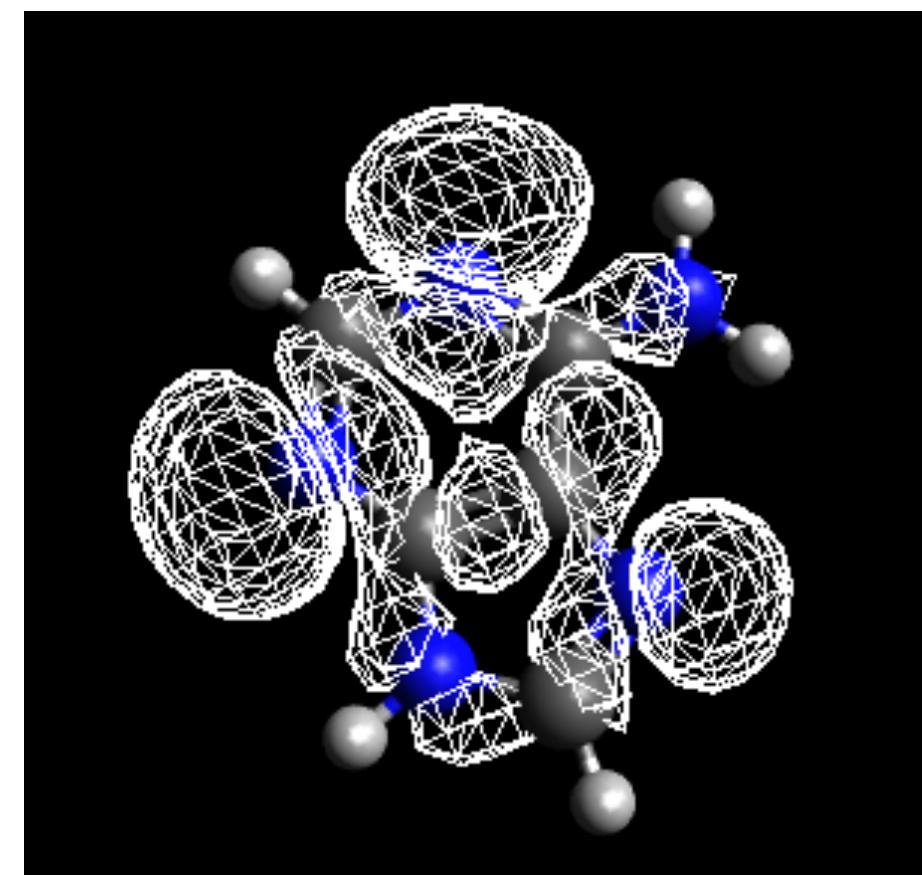
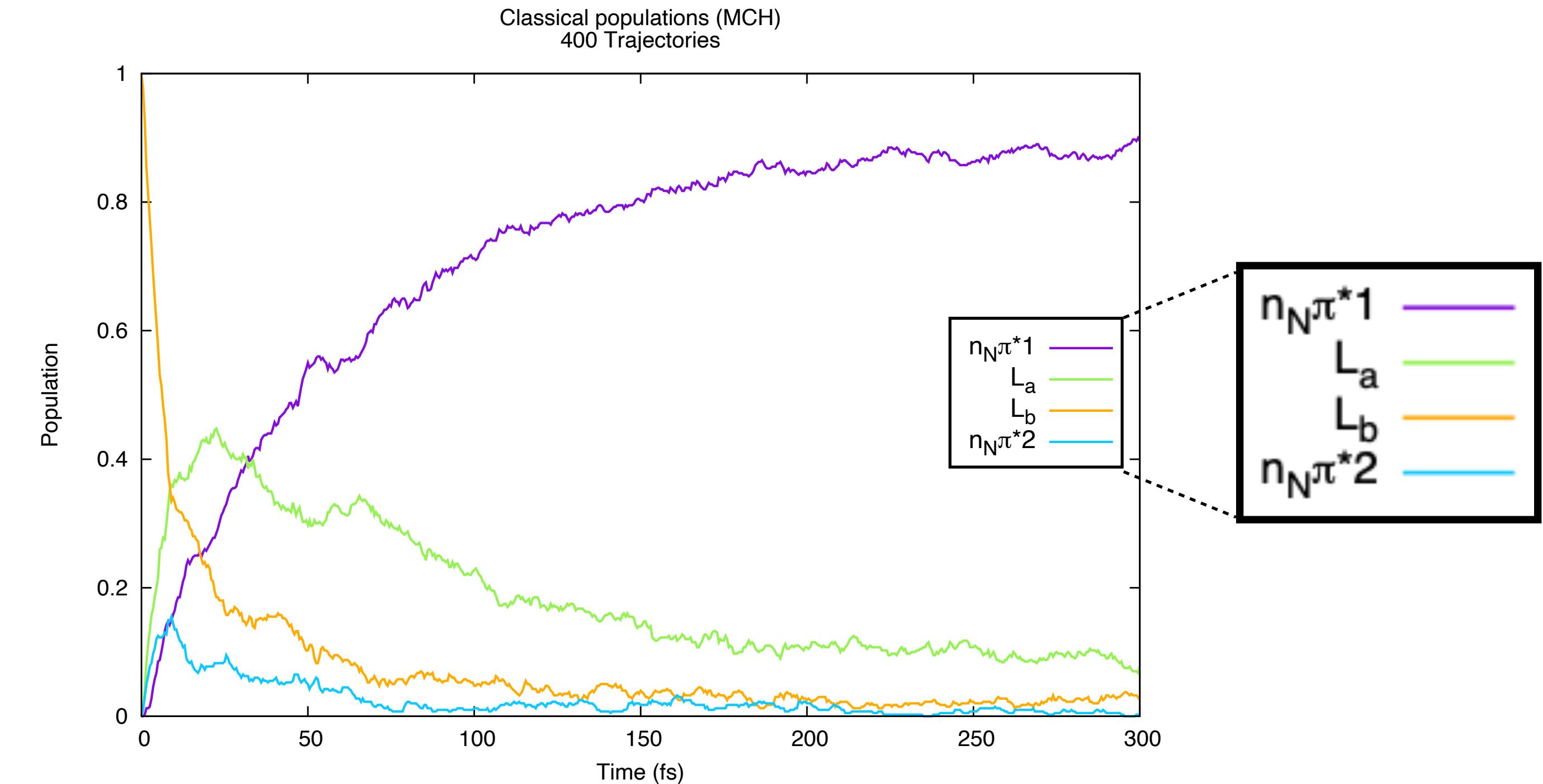




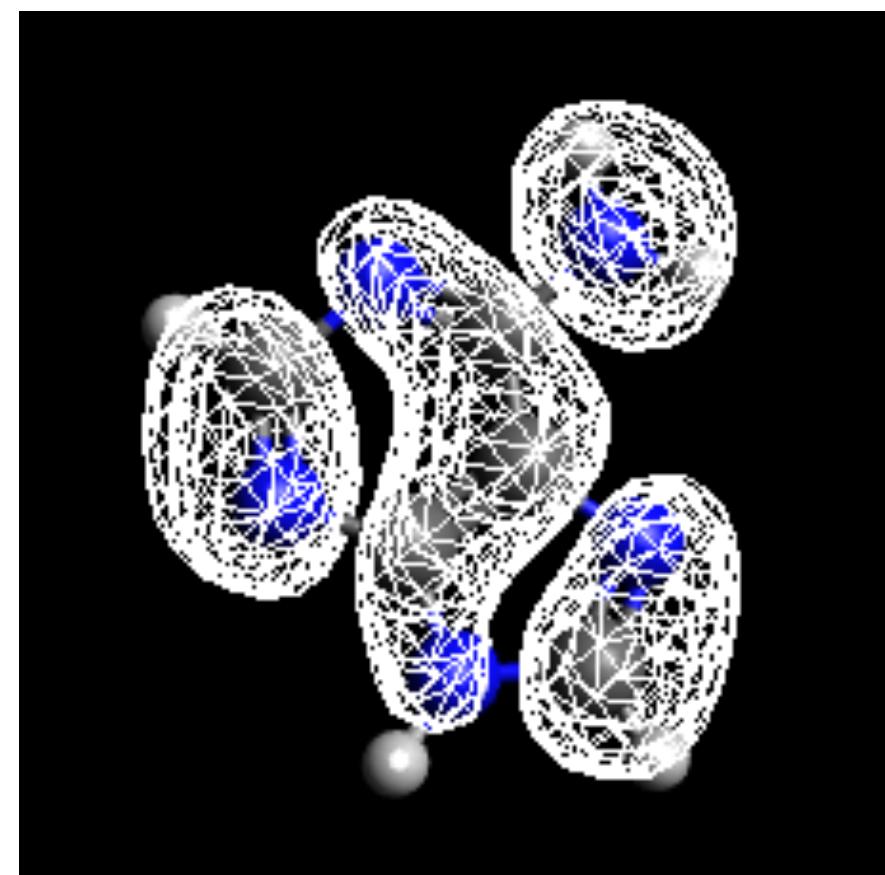
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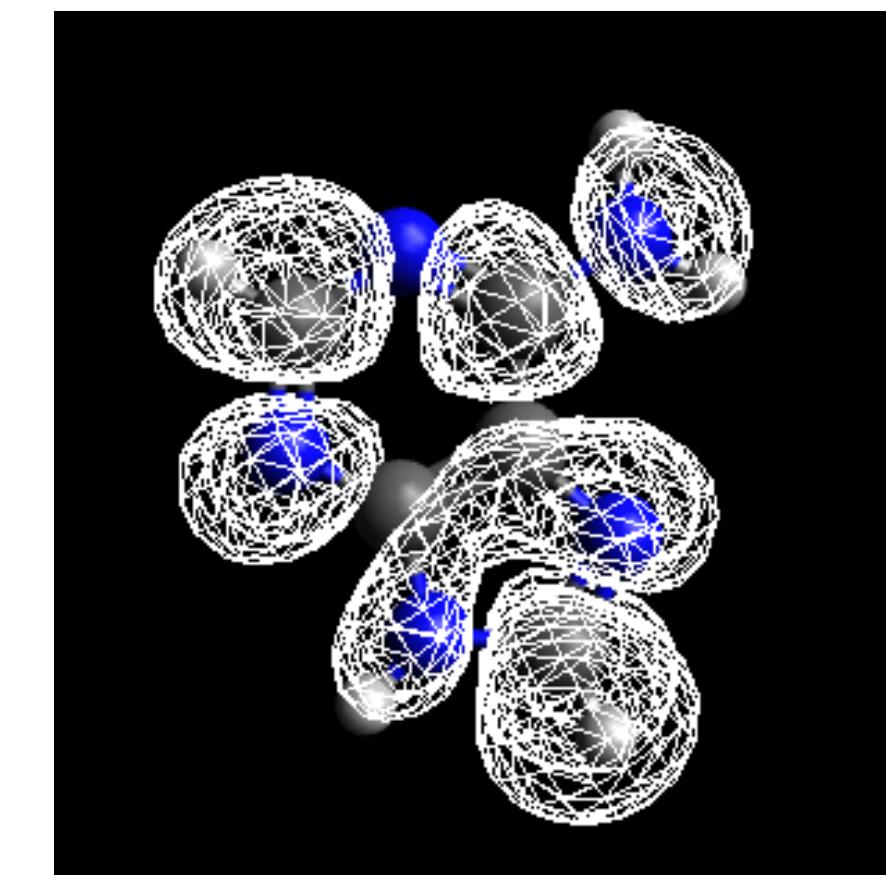
Excitation energies of adenine computed using
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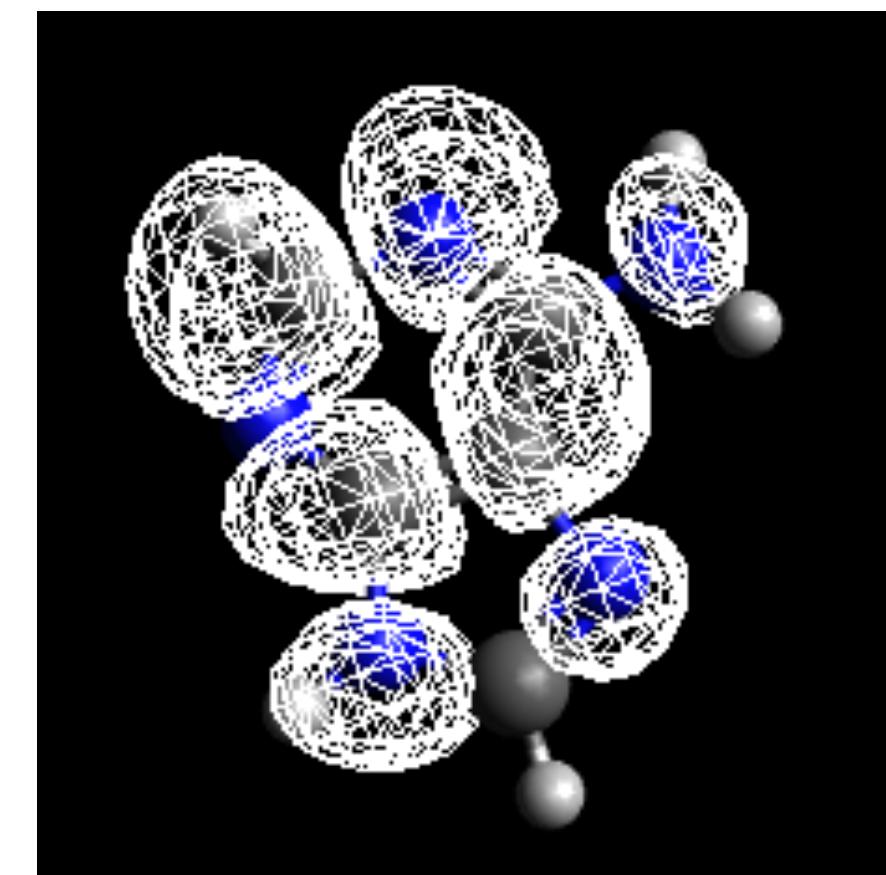
HOMO-1



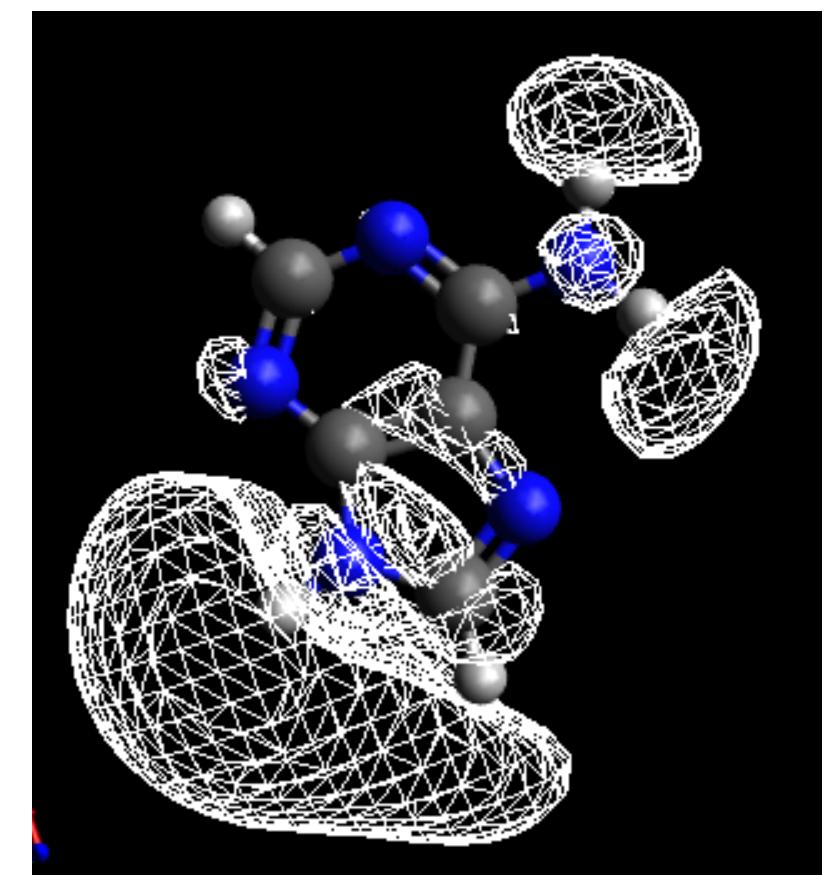
HOMO



LUMO



LUMO+1

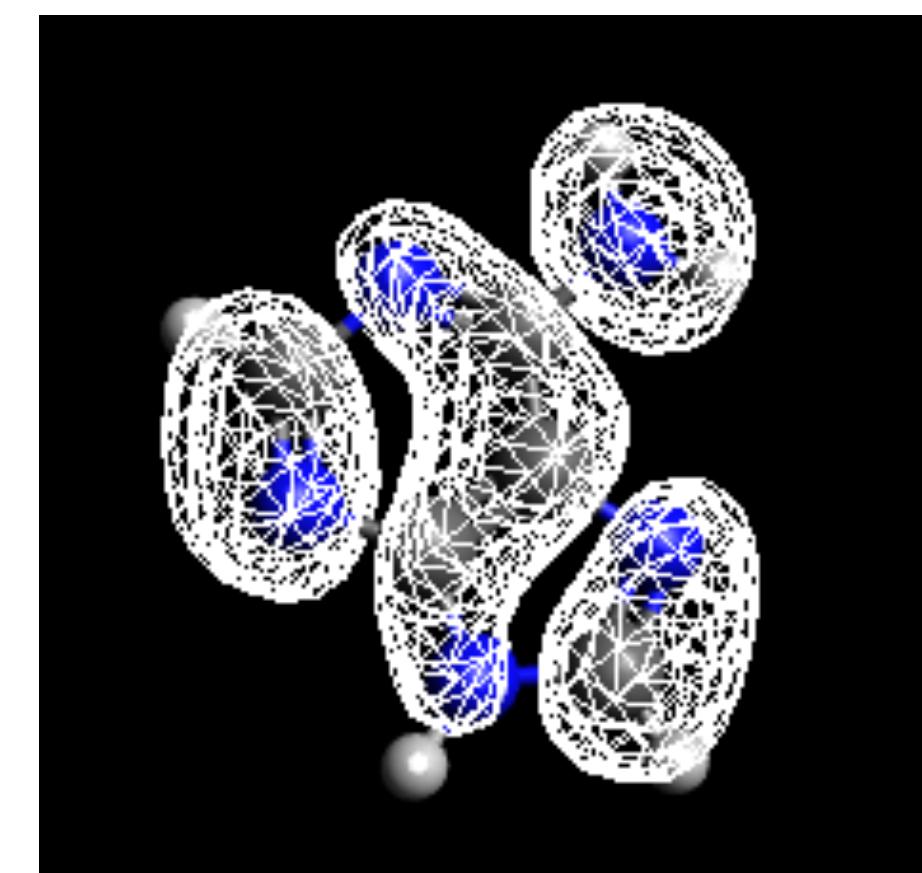
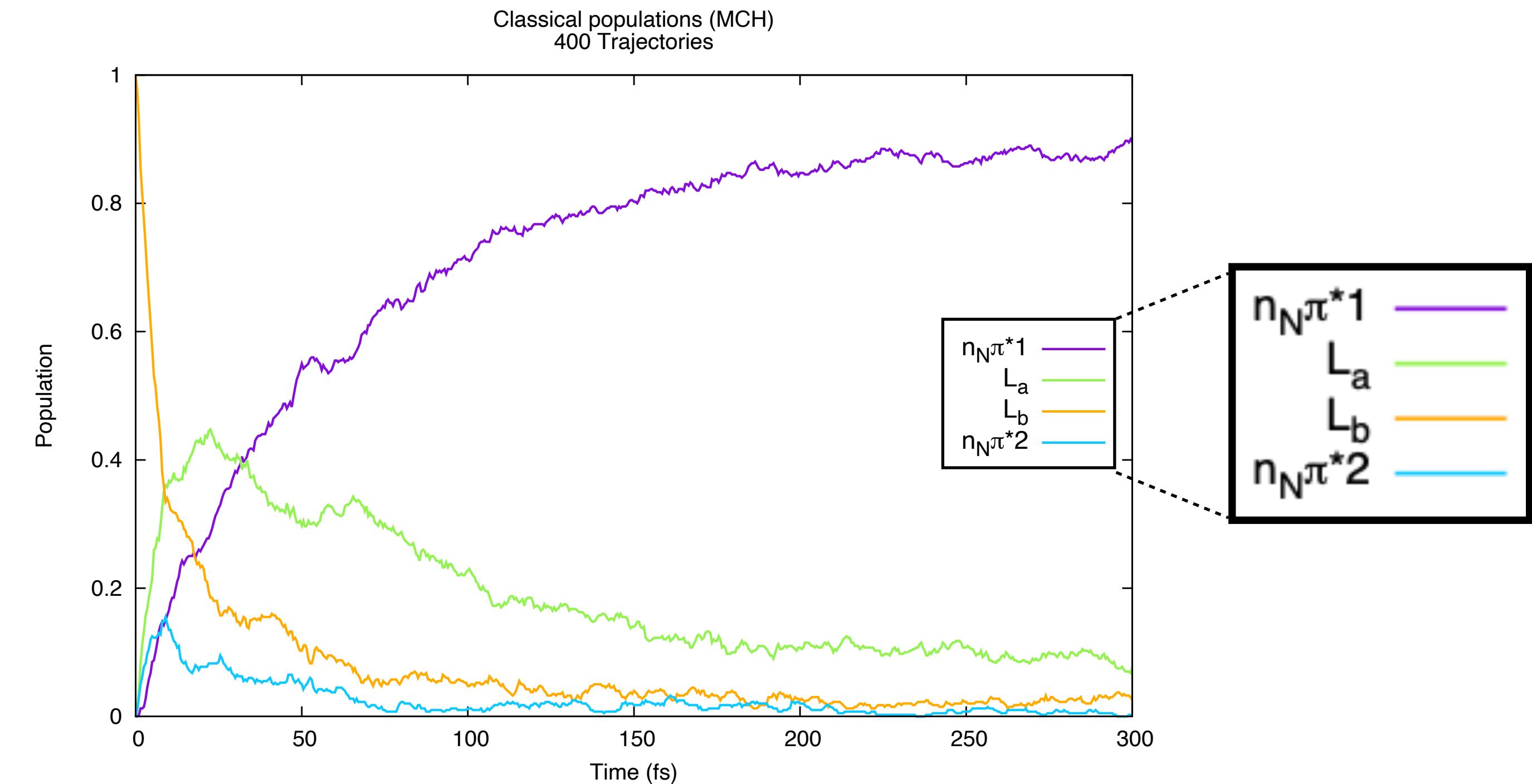
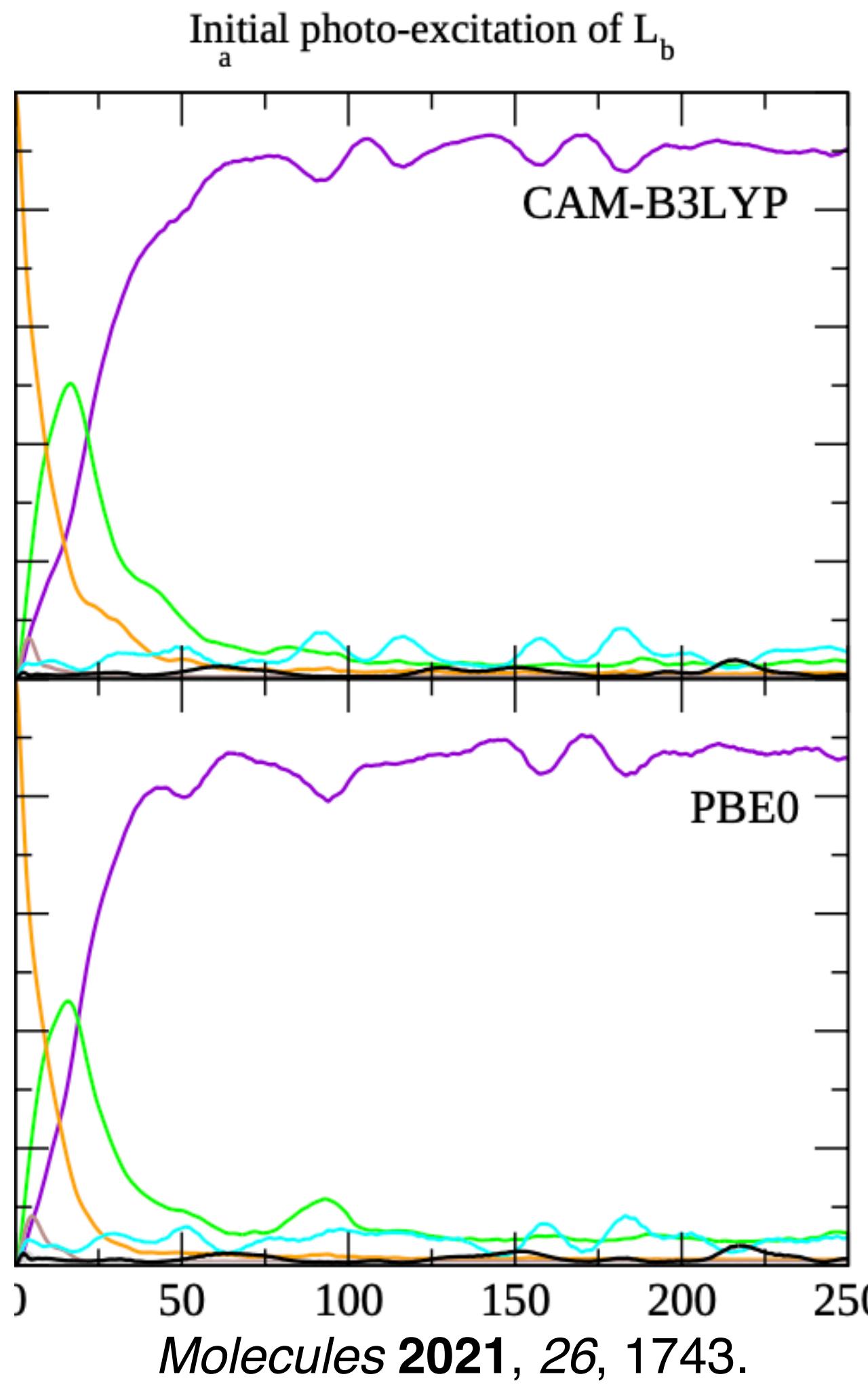


LUMO+2

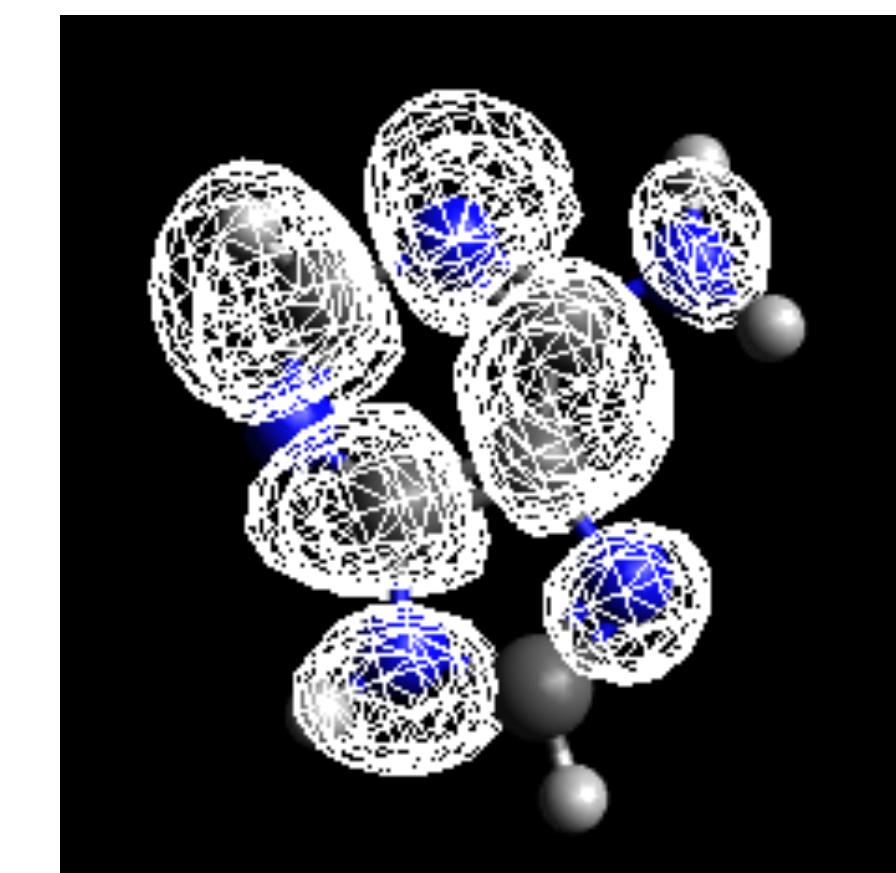




Adenine



HOMO



LUMO+1

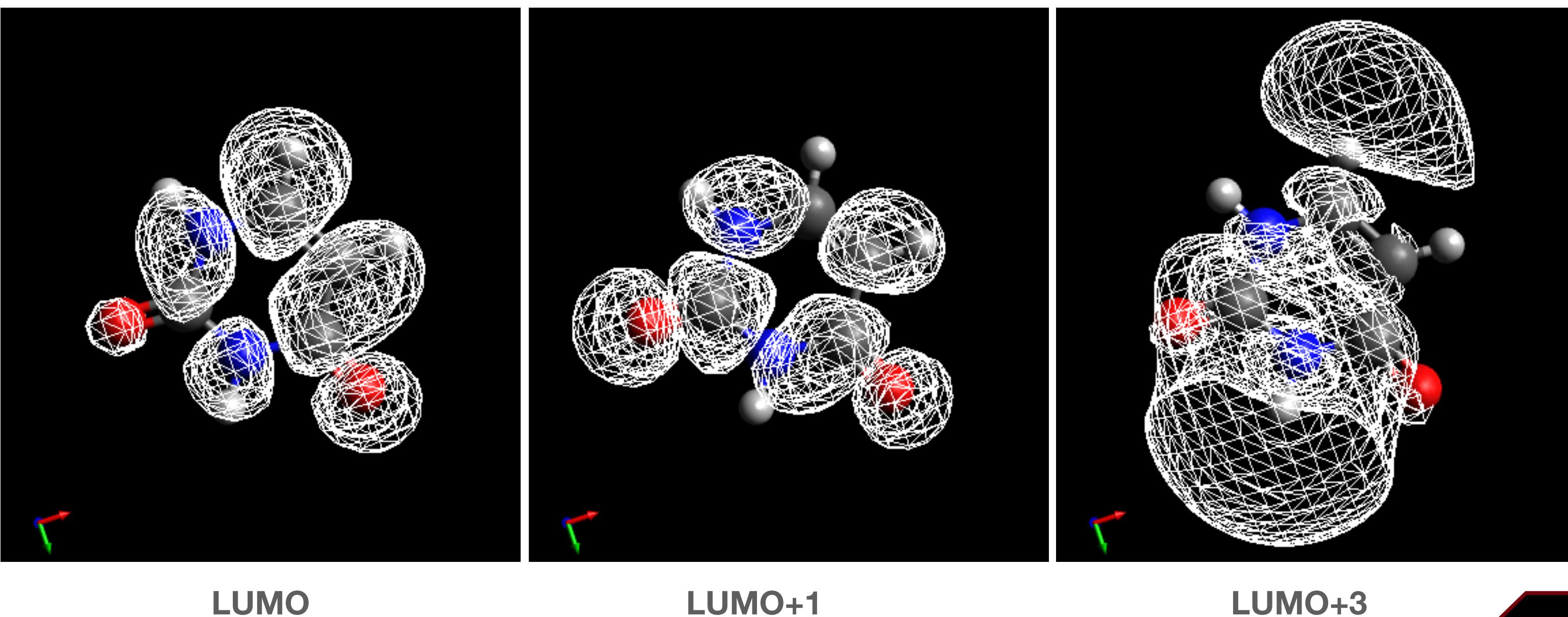
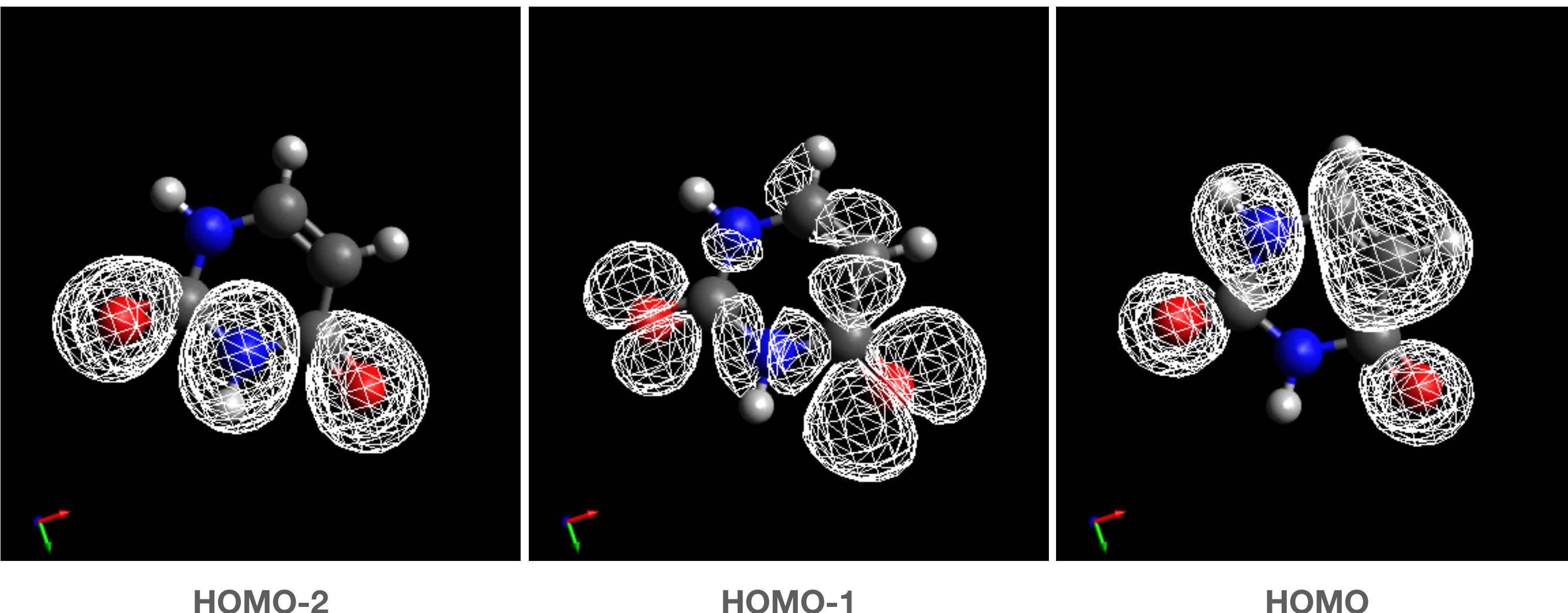




Uracil

State	ΔE (eV)	Orb. Trans.	Char.
S ₁	4.708	H-1 → L	n _O π*1
S ₂	5.431	H → L	ππ*1
S ₃	5.818	H → L+1	πRy _σ 1
S ₄	6.071	H-1 → L+3	n _O π*2
S ₅	6.238	H-2 → L	ππ*2
S ₆	6.399	H → L+3	ππ*3

Excitation energies of uracil computed using
TDDFT//B3LYP-D3/def2-TZVP

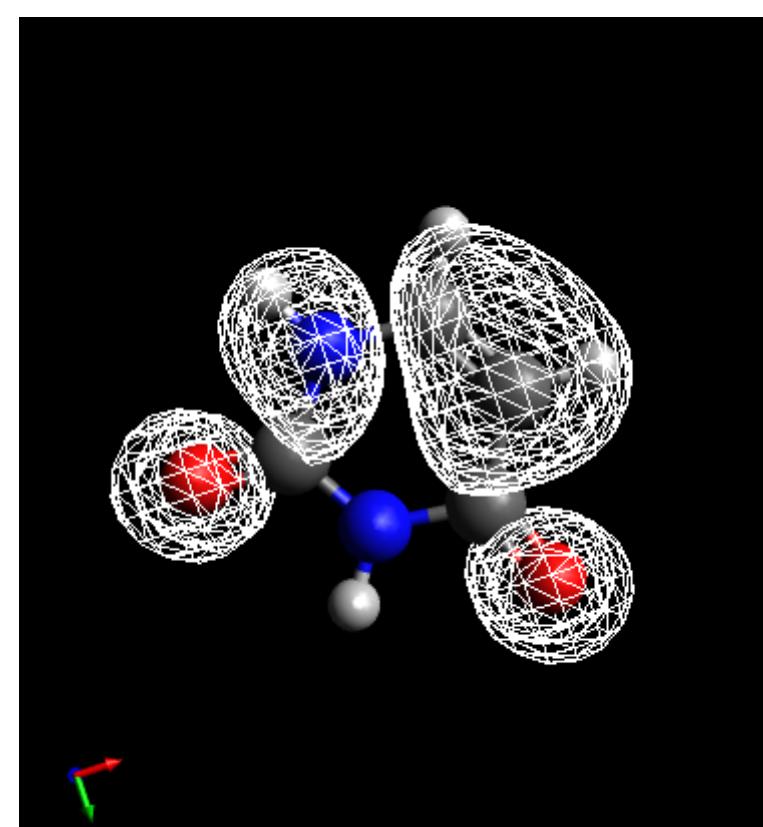




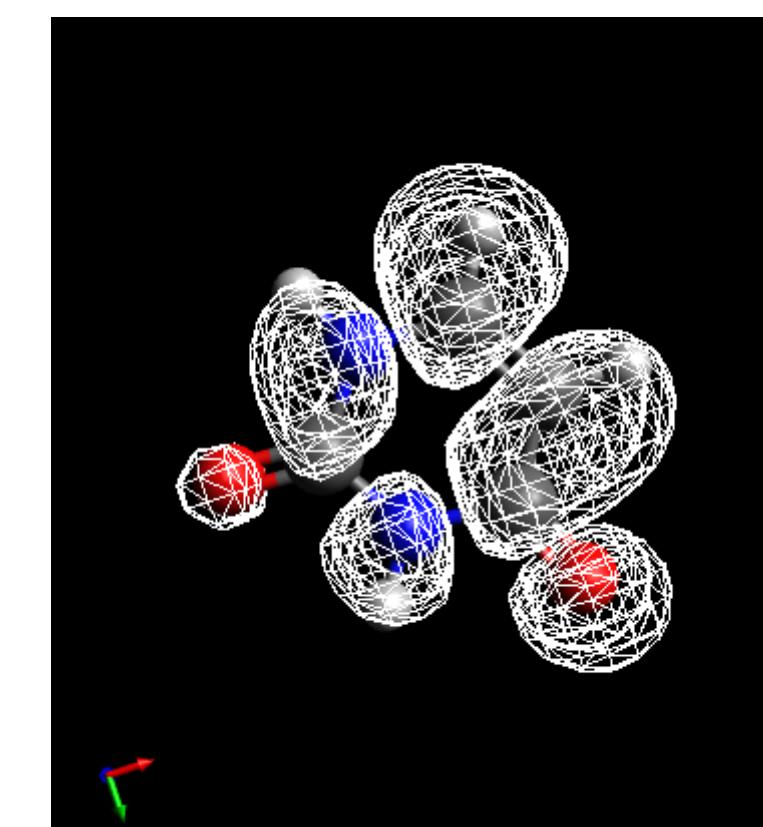
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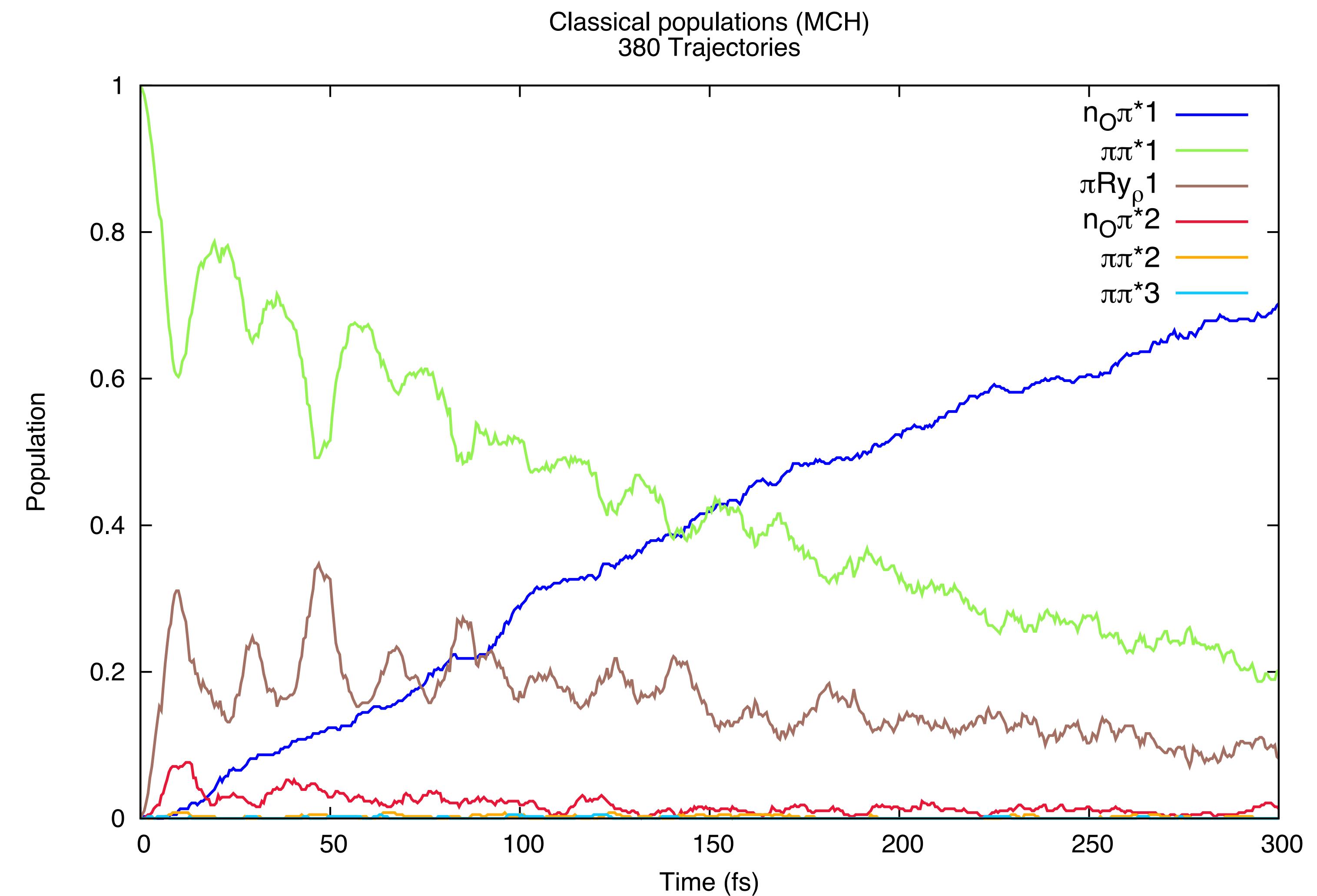
Excitation energies of uracil computed using
TDDFT//B3LYP-D3/def2-TZVP



HOMO

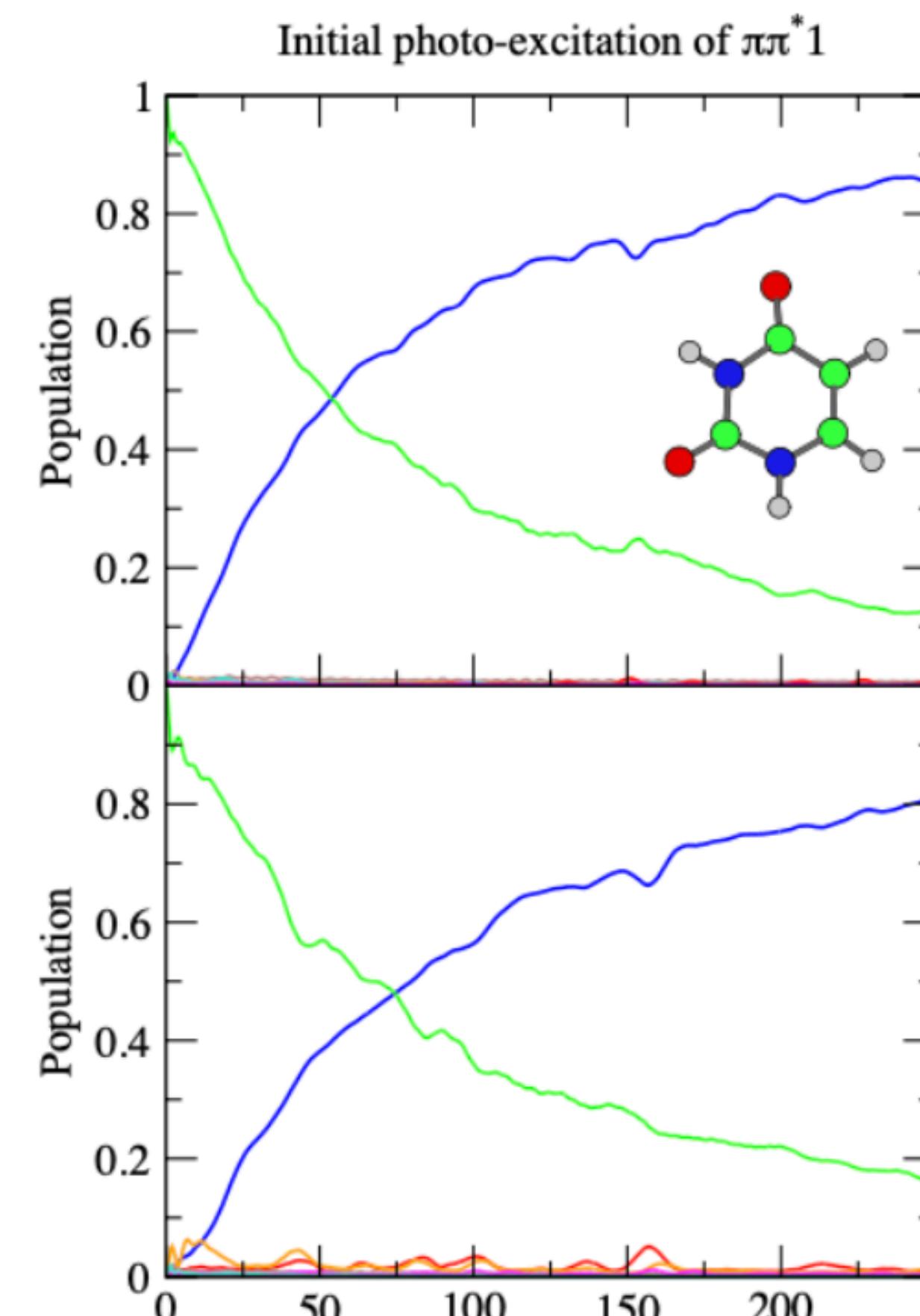


LUMO

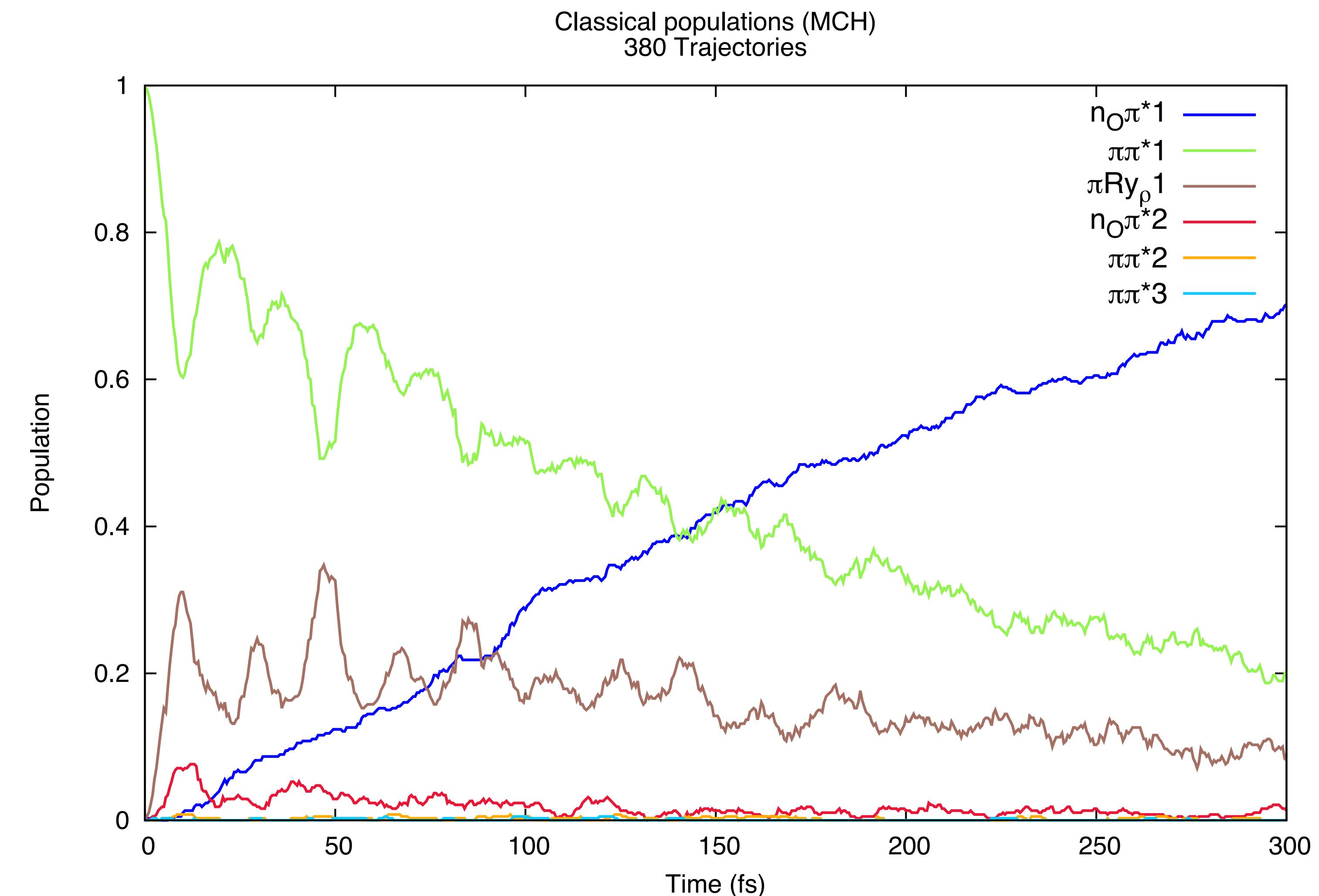




Uracil



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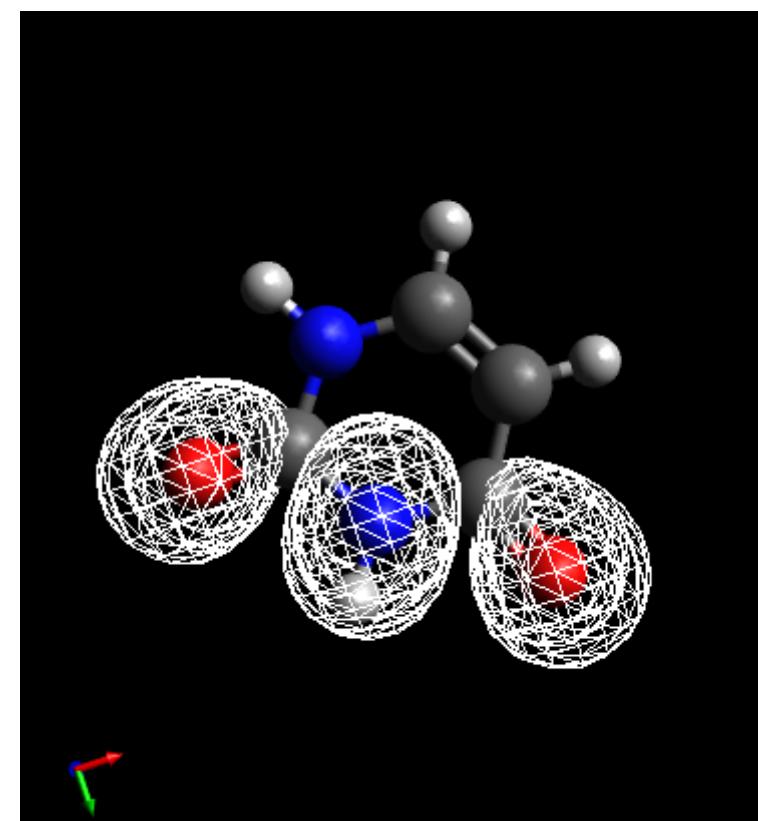




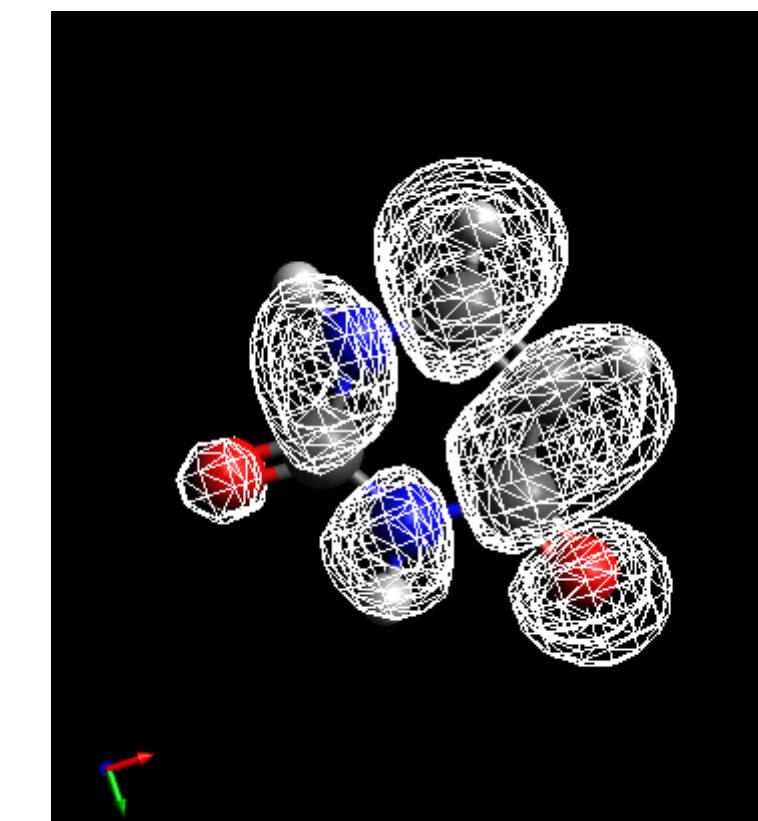
Uracil

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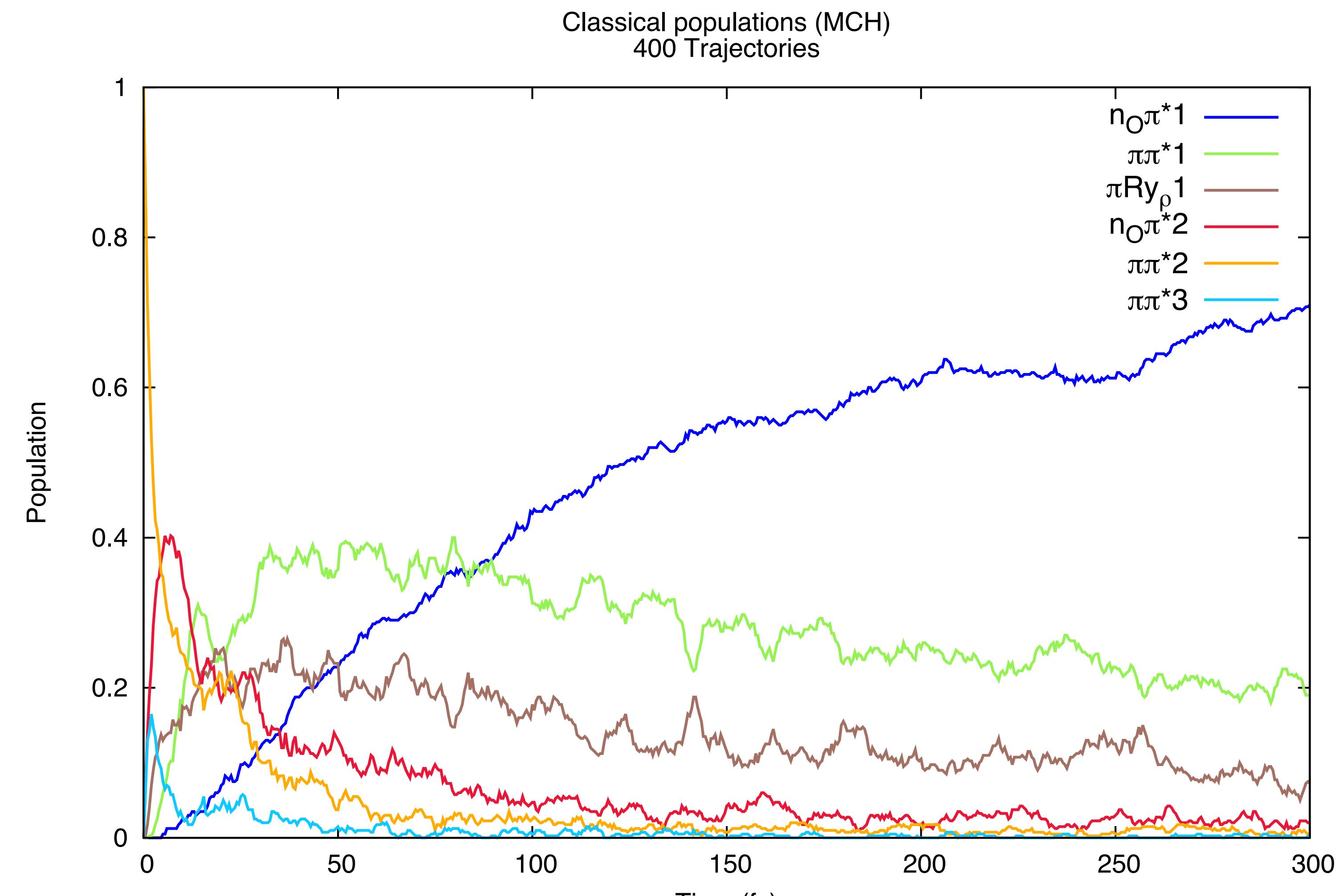
Excitation energies of uracil computed using
TDDFT//B3LYP-D3/def2-TZVP



HOMO-2



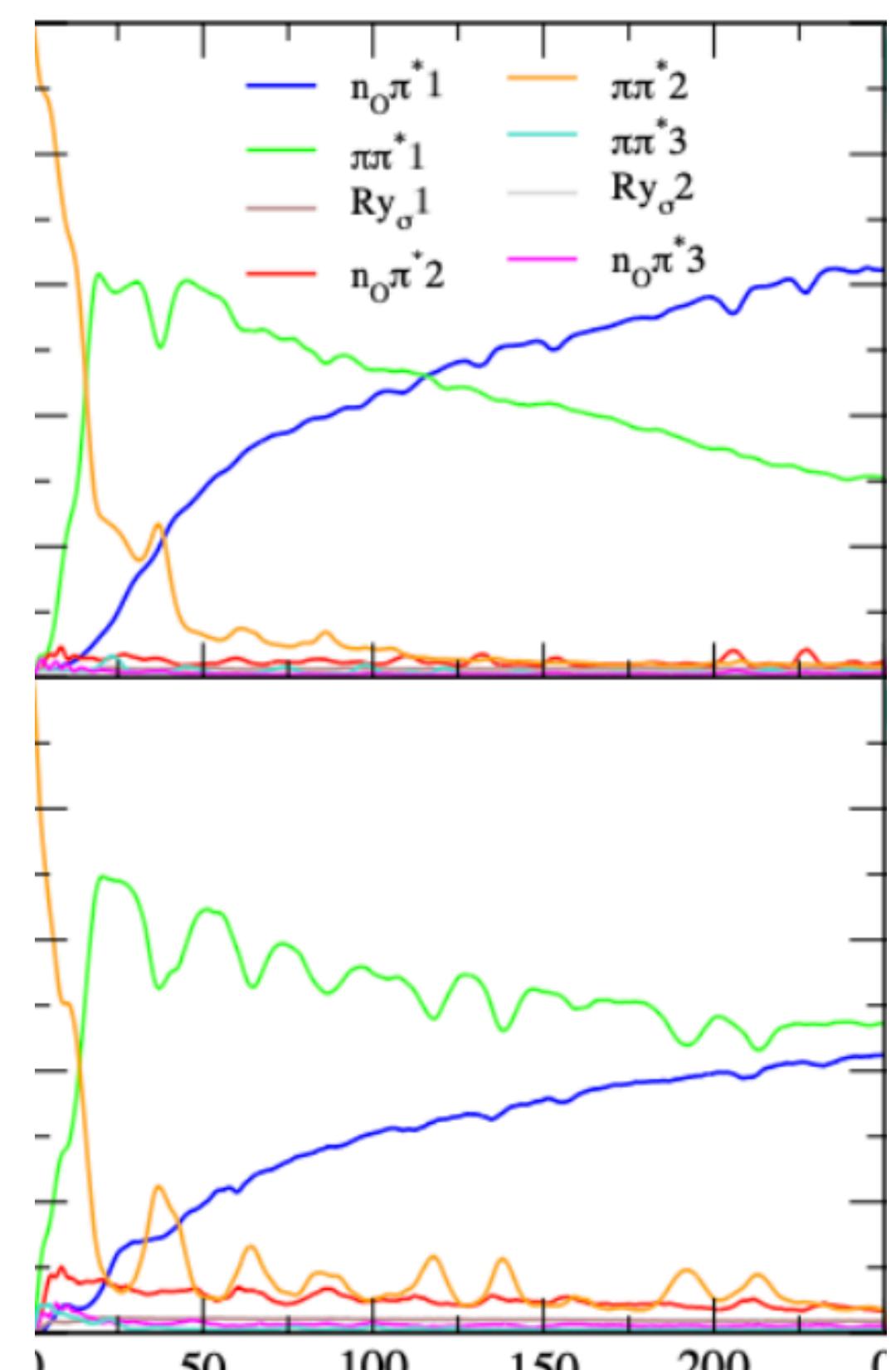
LUMO





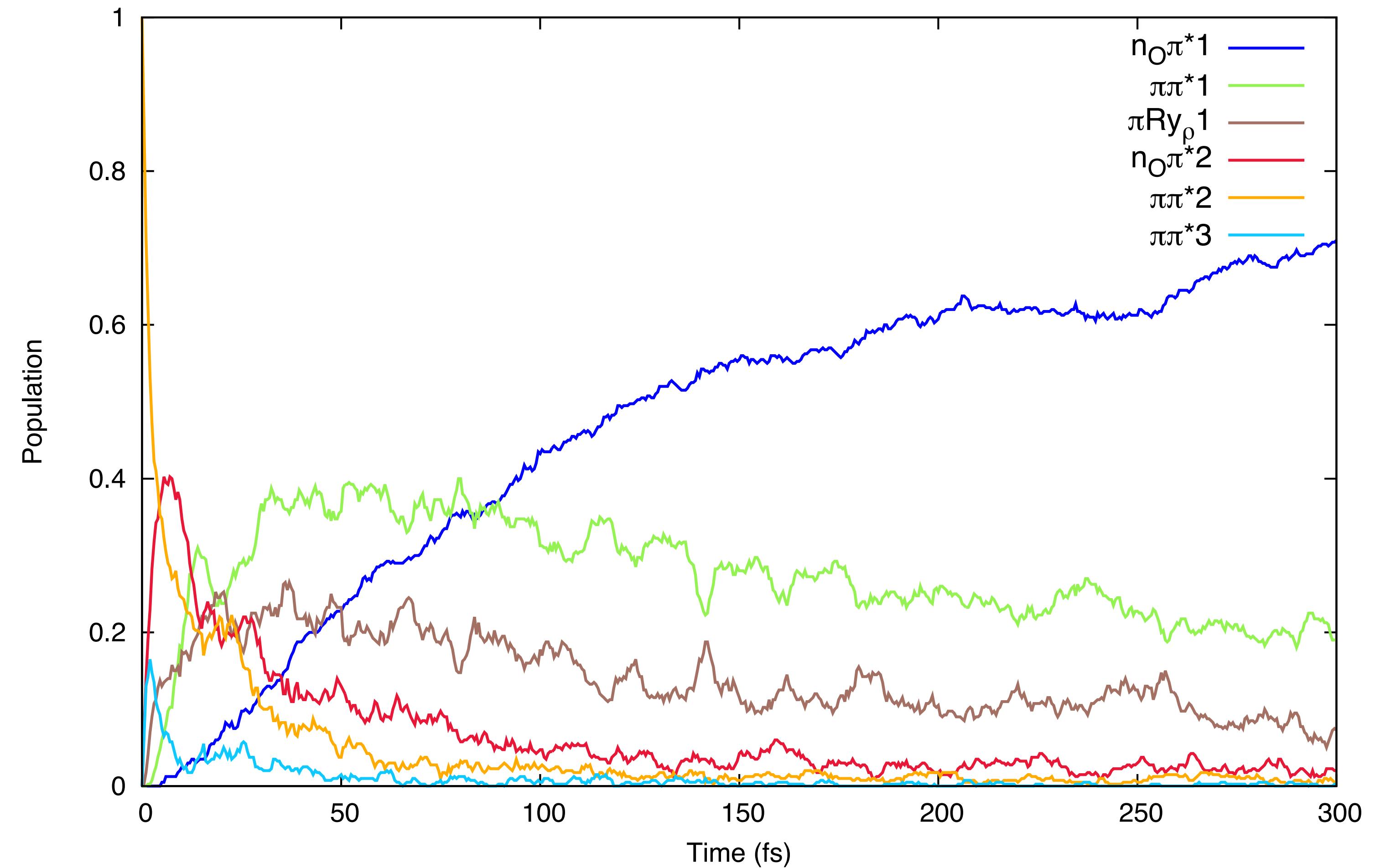
Uracil

Initial photo-excitation of $\pi\pi^*2$



Molecules 2021, 26, 1743.

Classical populations (MCH)
400 Trajectories

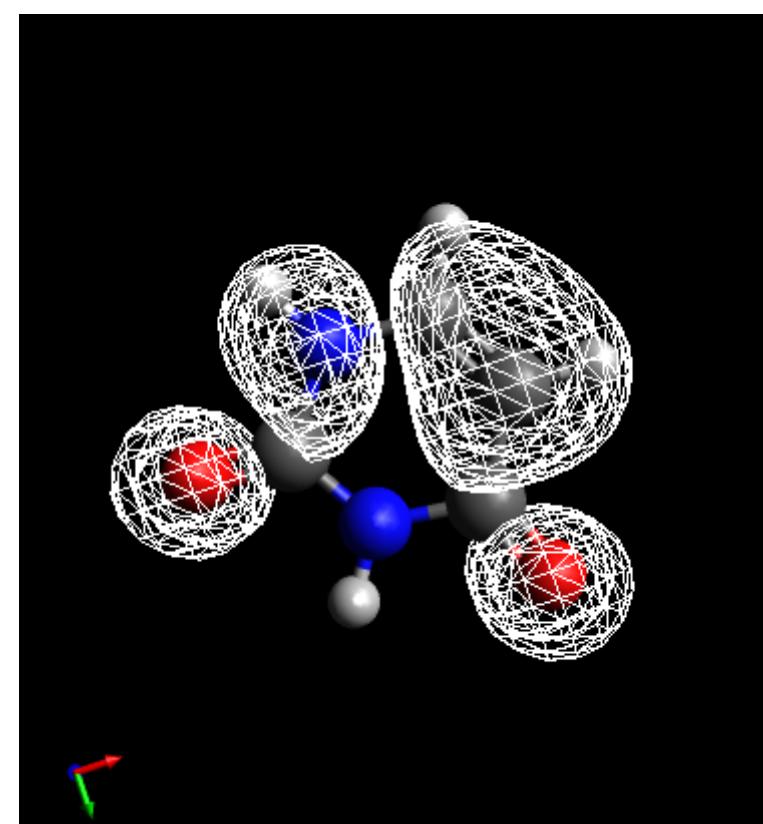




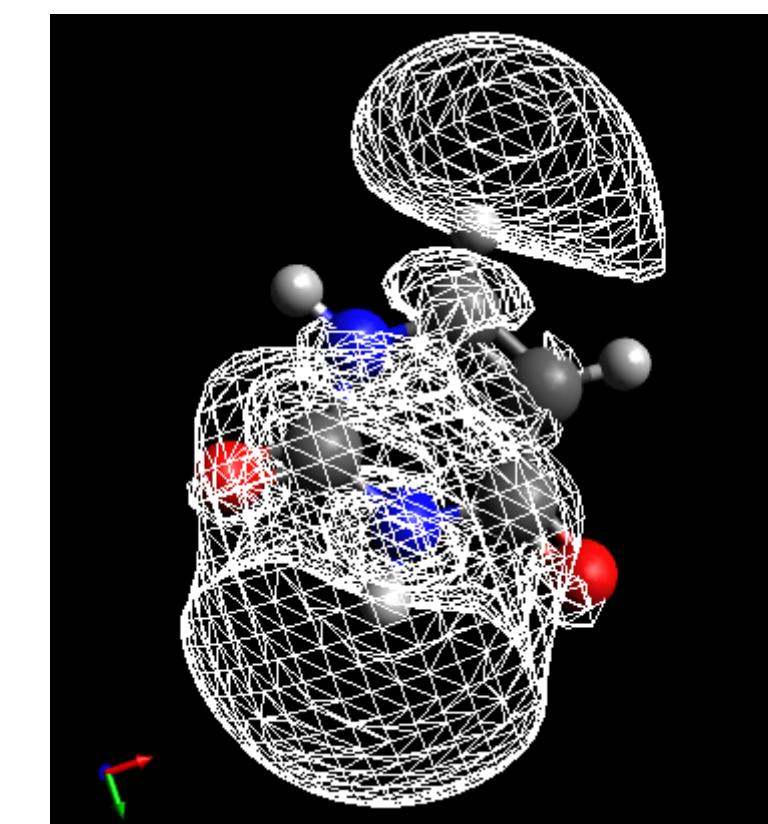
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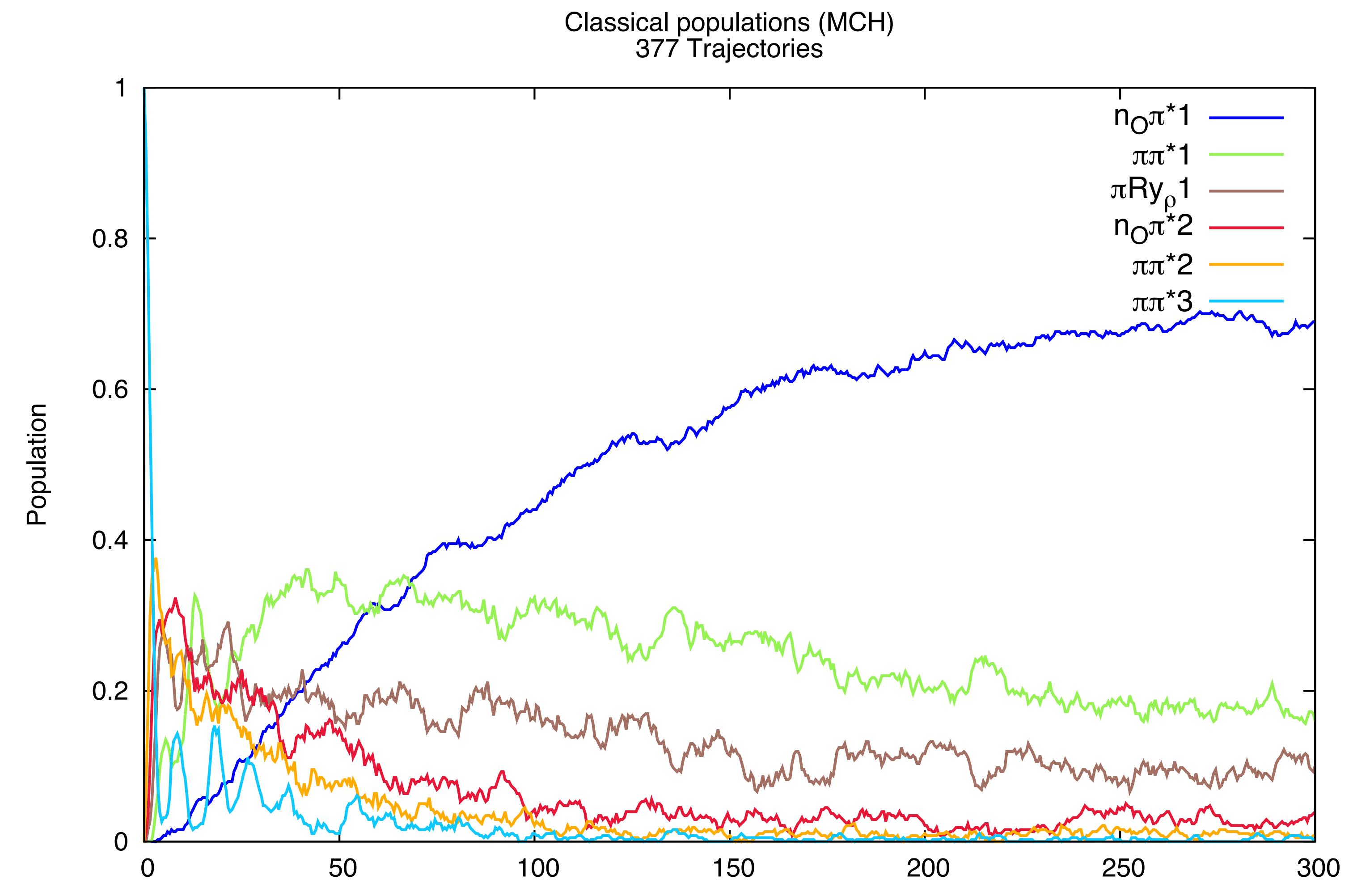
Excitation energies of uracil computed using
TDDFT//B3LYP-D3/def2-TZVP



HOMO



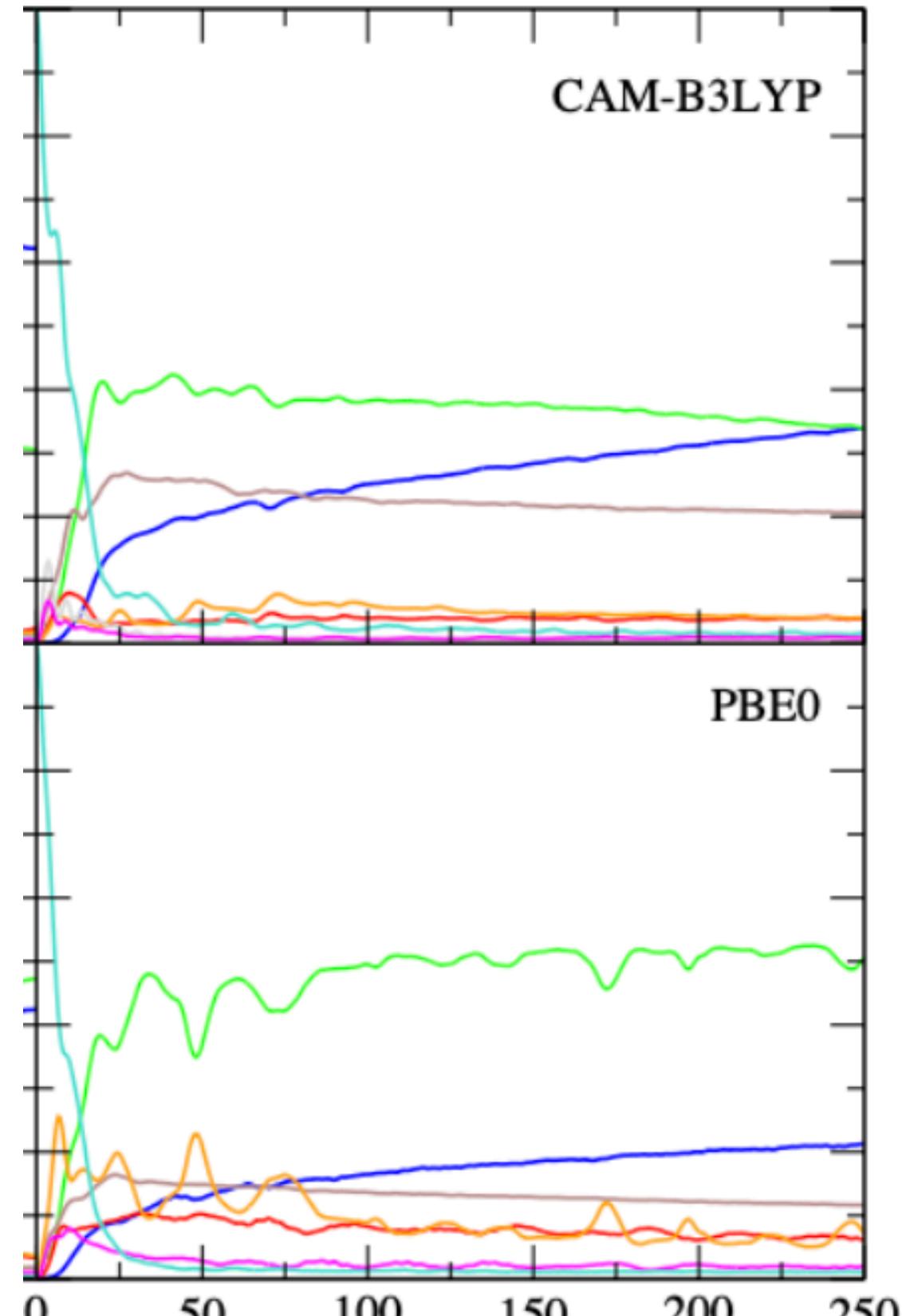
LUMO+3





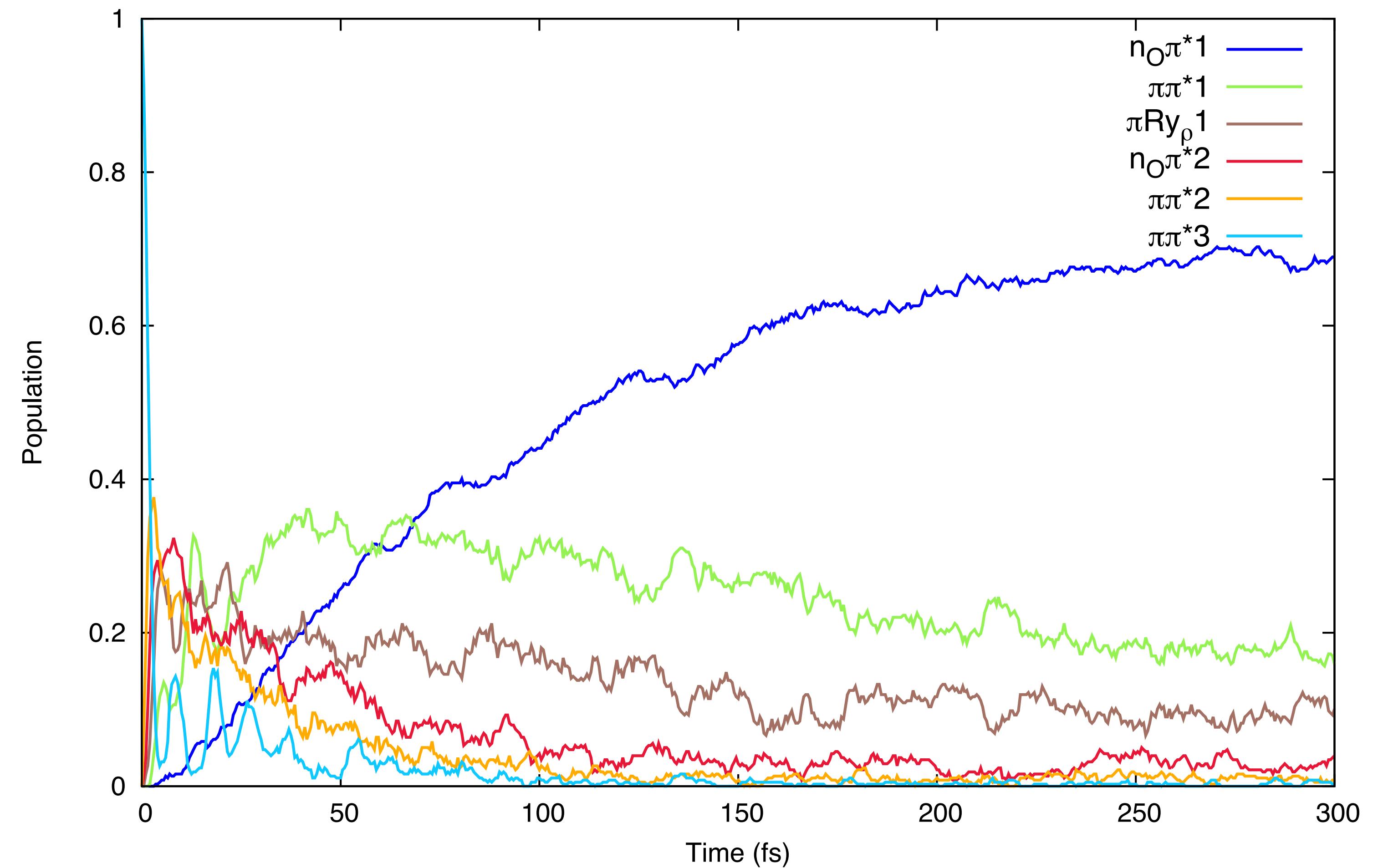
Uracil

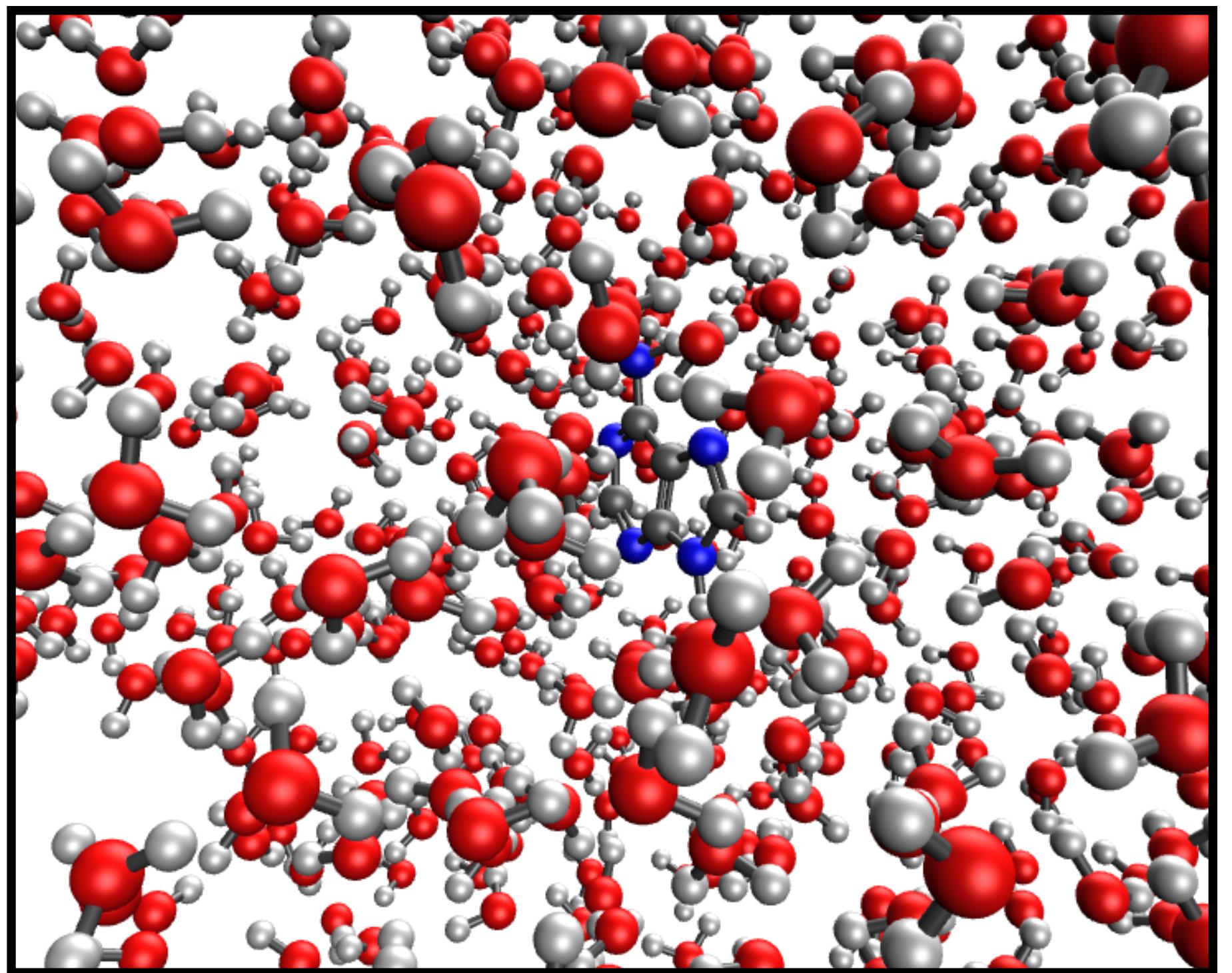
Initial photo-excitation of $\pi\pi^*3$



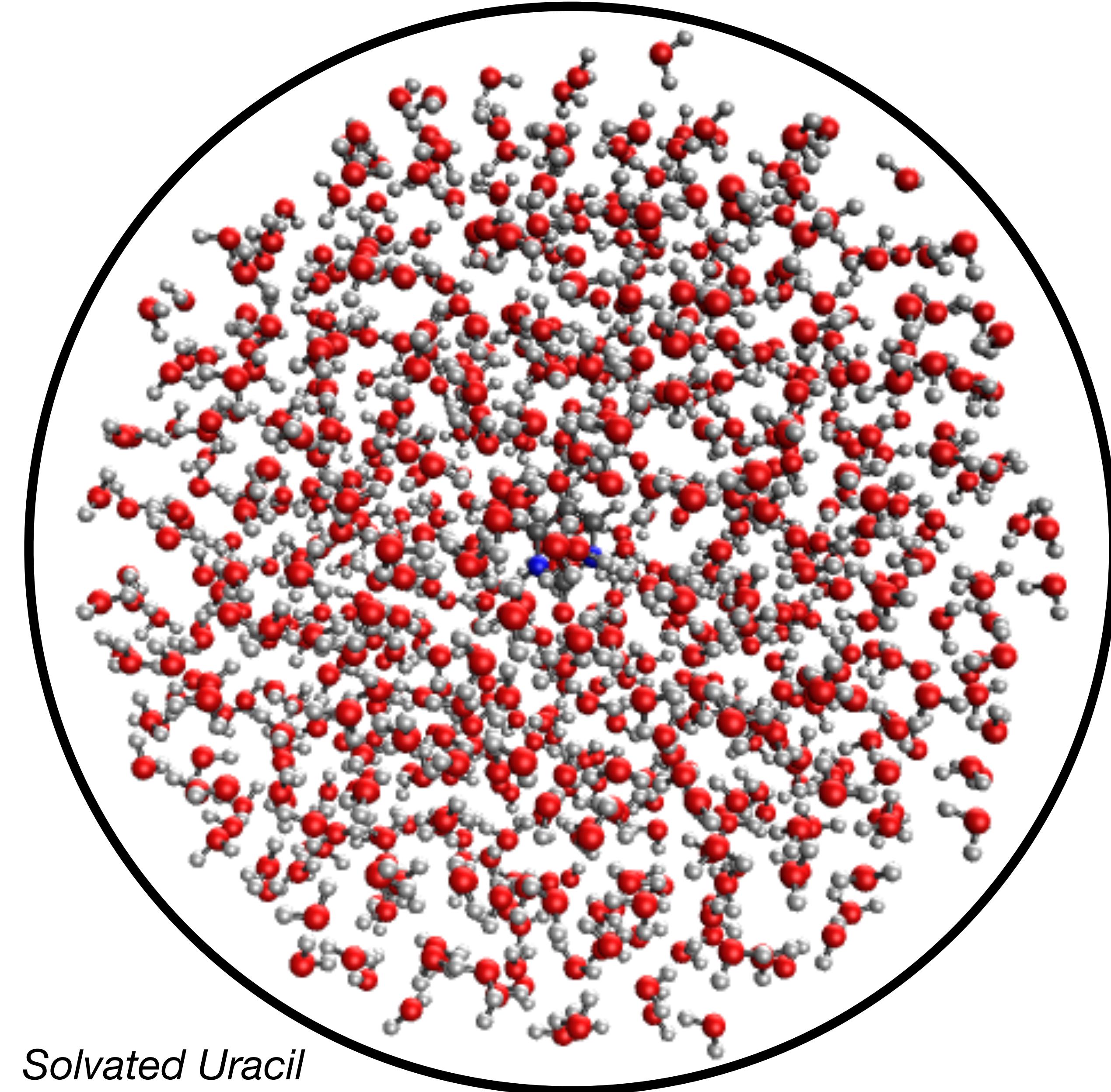
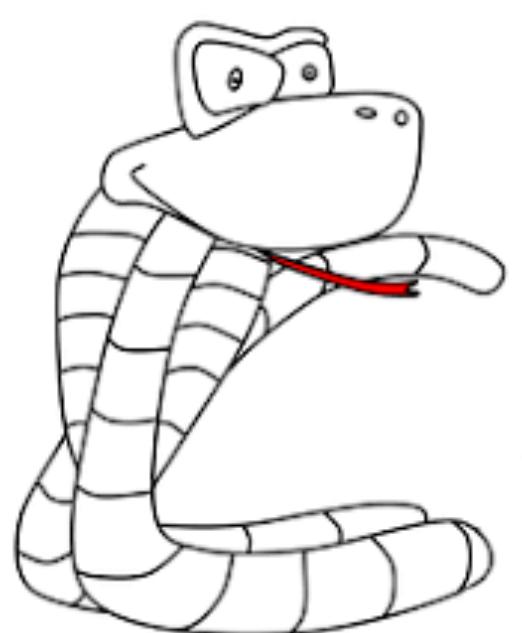
Molecules 2021, 26, 1743.

Classical populations (MCH)
377 Trajectories





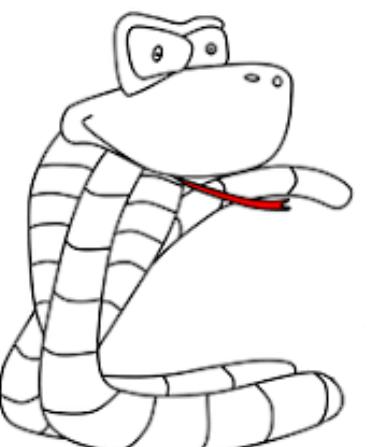
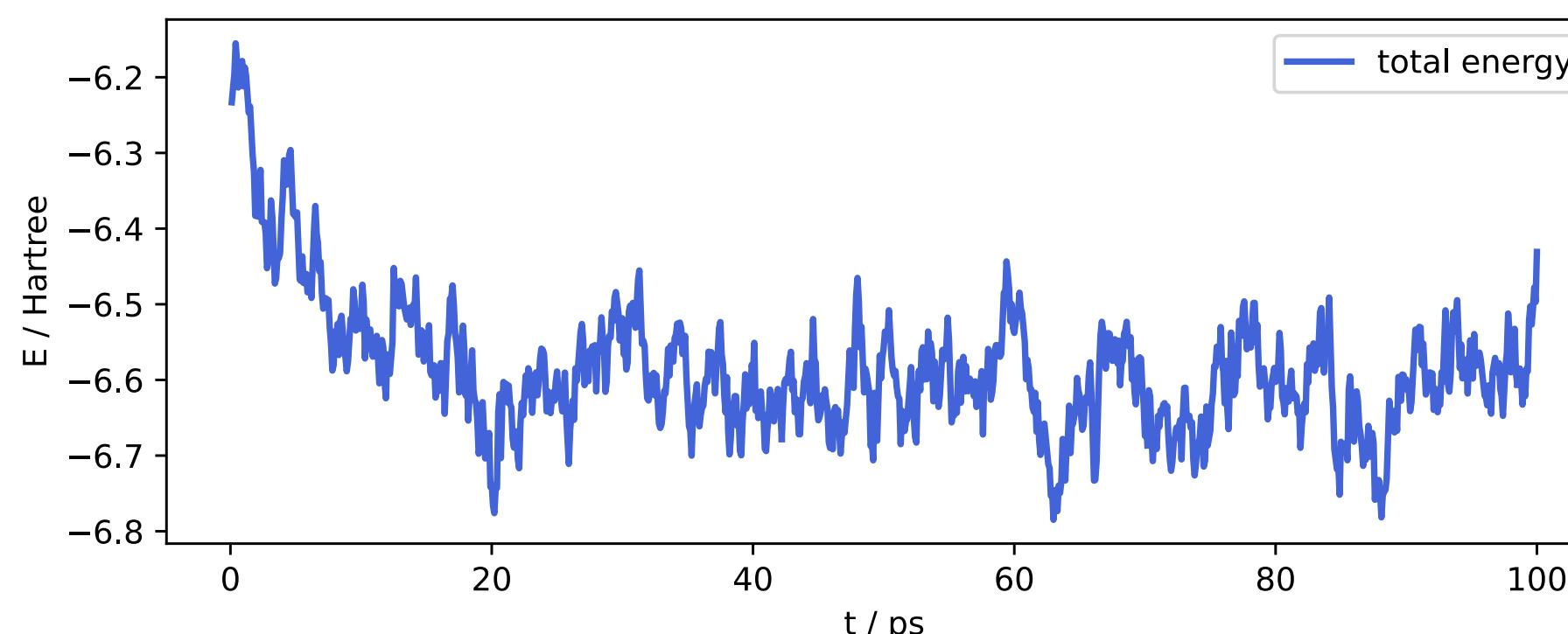
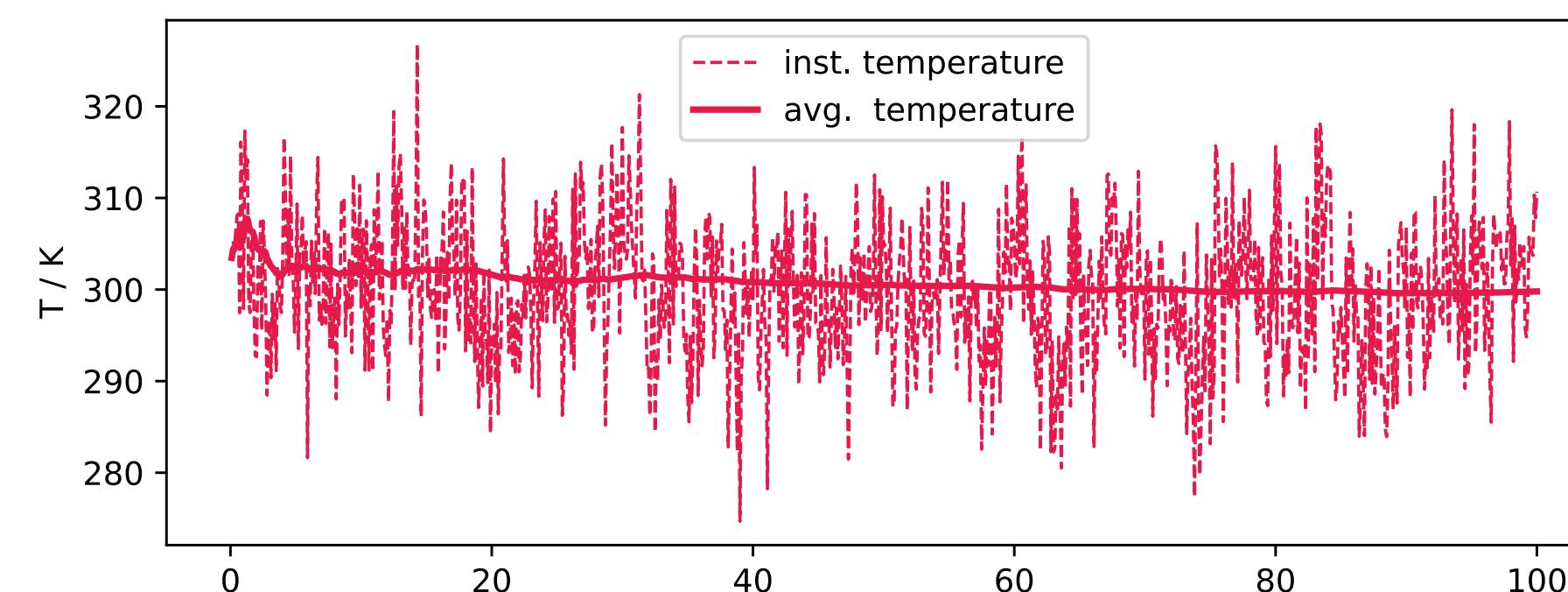
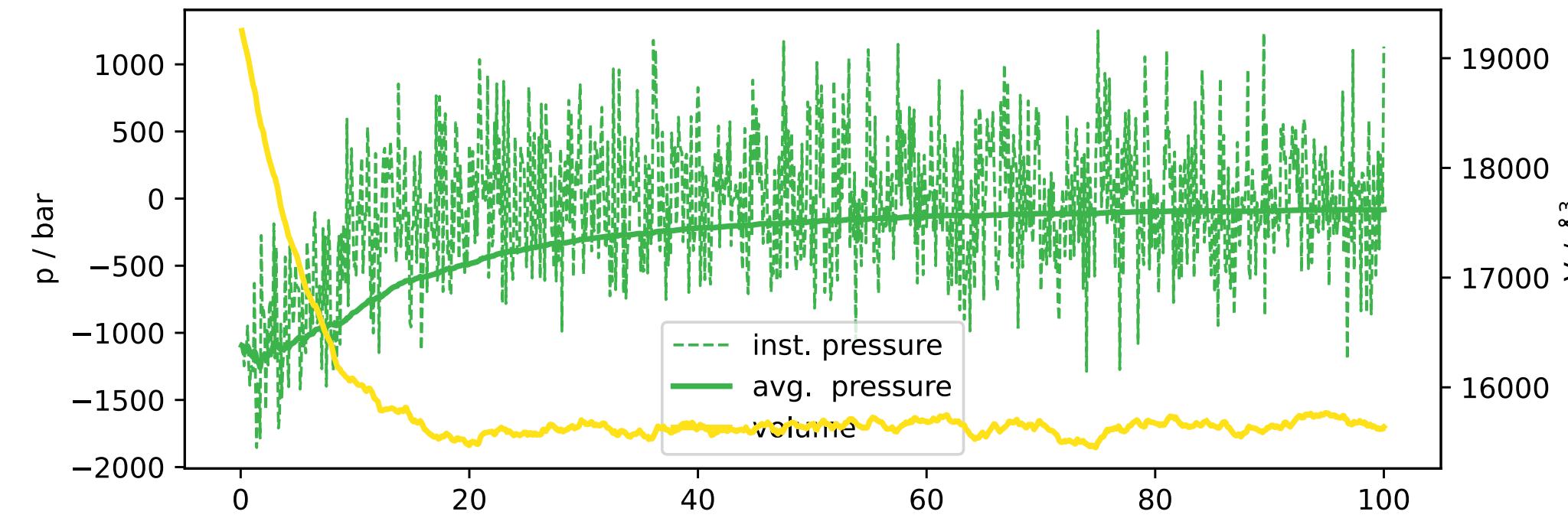
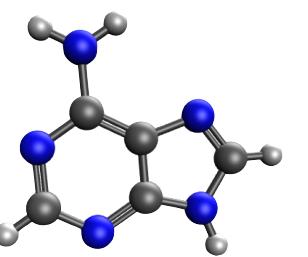
Solvated Adenine



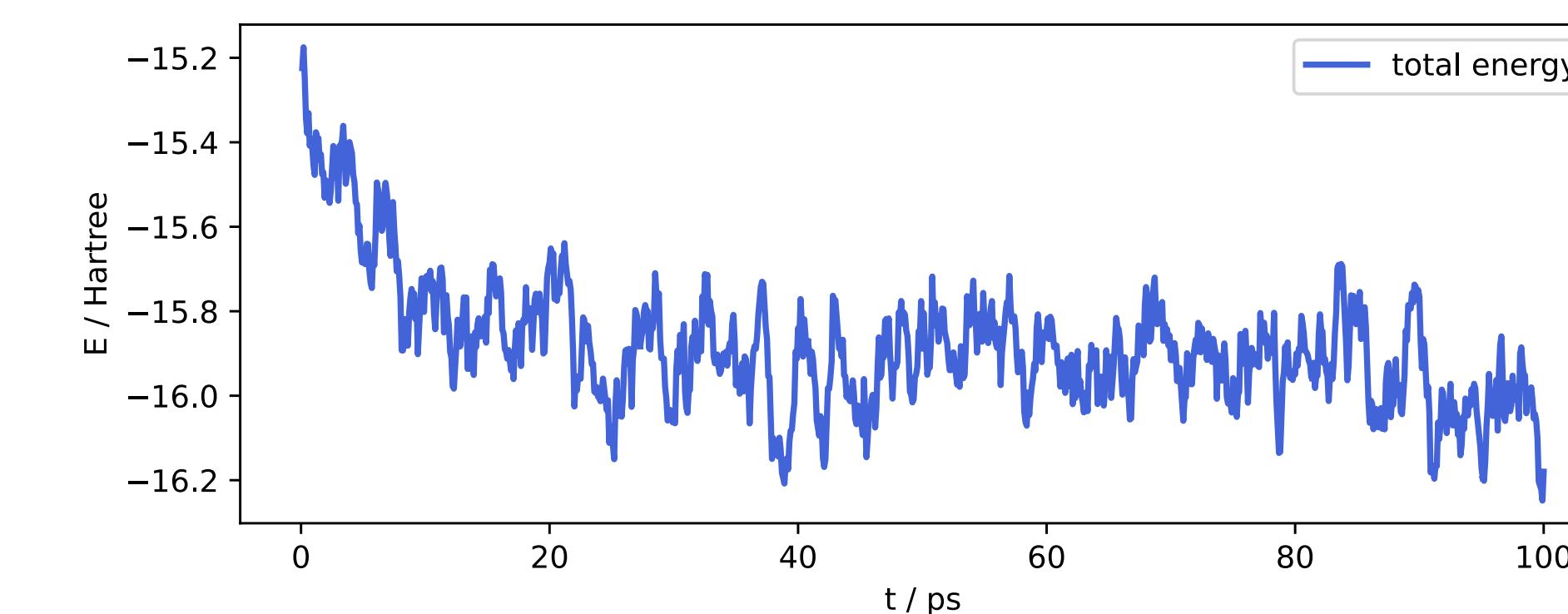
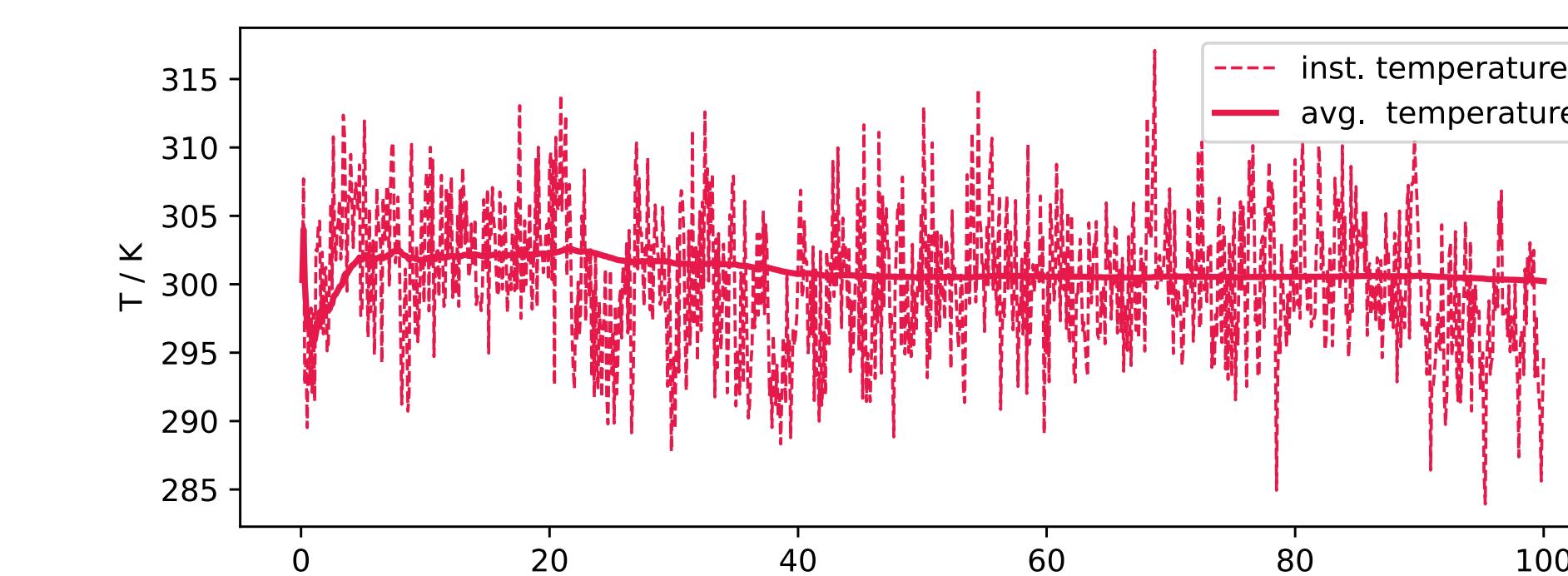
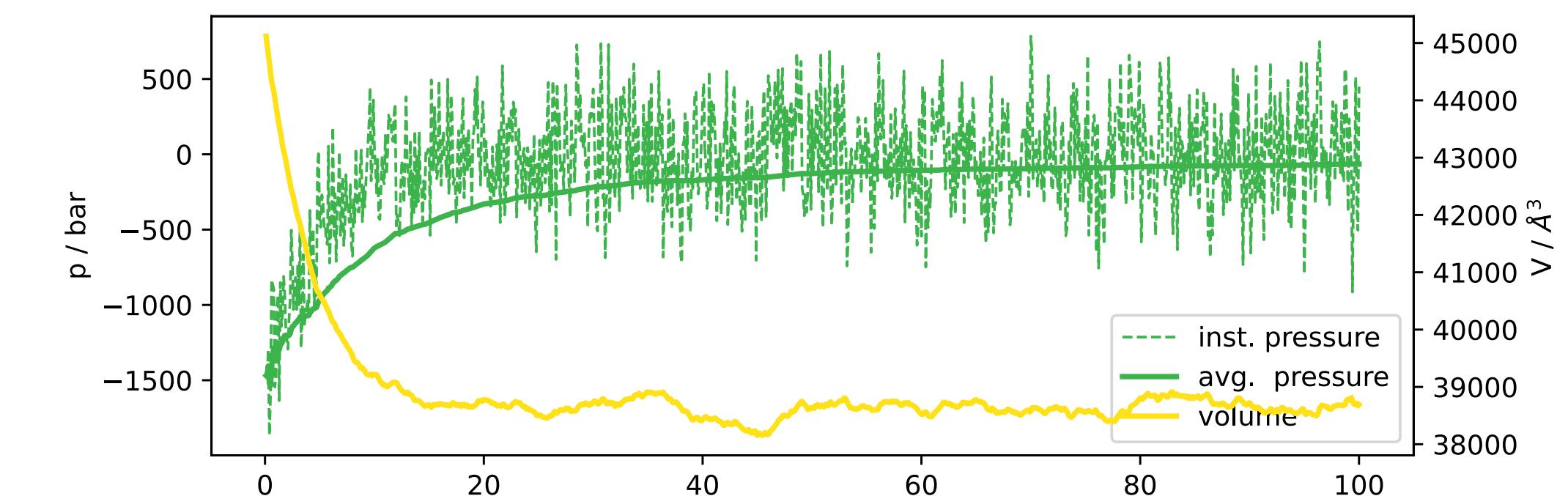
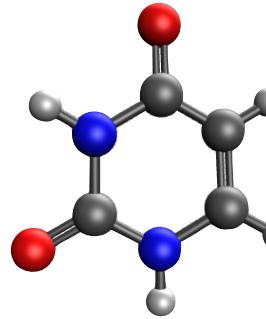
Solvated Uracil



Adenine

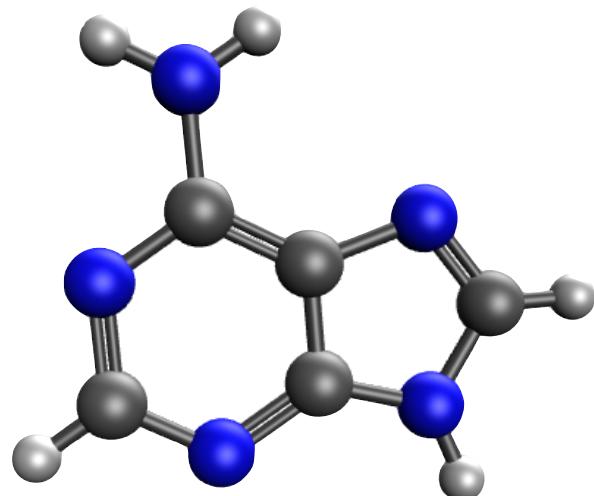


Uracil

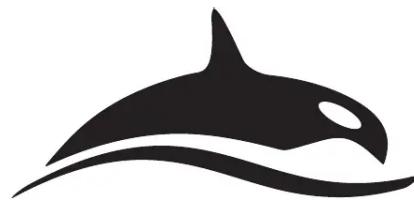
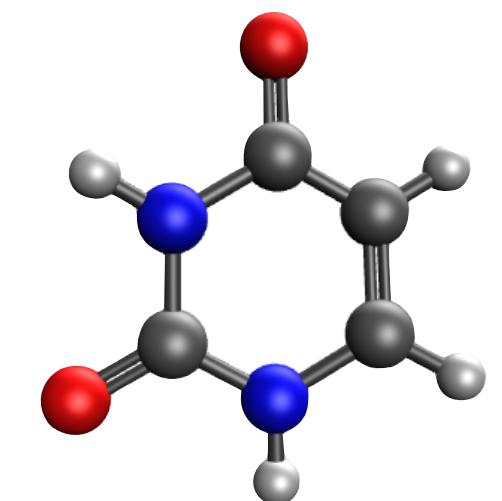




Thank You!



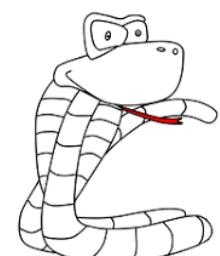
Green, J.A.; Yaghoubi Jouybari, M.; Aranda, D.; Improta, R.; Santoro, F. Nonadiabatic Absorption Spectra and Ultrafast Dynamics of DNA and RNA Photoexcited Nucleobases. *Molecules* **2021**, *26*, 1743. <https://doi.org/10.3390/molecules26061743>



Reese, F. (2012). The ORCA program system. Wiley Interdisciplinary



S. Mai, M. Richter, M. Heindl, M. F. S. J. Menger, A. Atkins, M. Ruckenbauer, F. Plasser, L.M. Ibele, S. Kropf, M. Oppel, P. Marquetand, L. González **SHARC2.1: Surface Hopping Including Arbitrary Couplings – Program Package for Non-Adiabatic Dynamics**, sharc-md.org (2019).

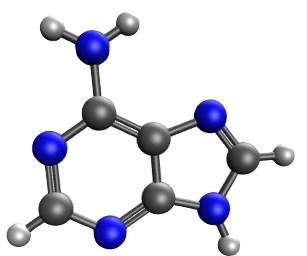


Weingart, O., Nenov, A., Altoè, P. et al. COBRAMM 2.0 — A software interface for tailoring molecular electronic structure calculations and running nanoscale (QM/MM) simulations. *J Mol Model* **24**, 271 (2018). <https://doi.org/10.1007/s00894-018-3769-6>

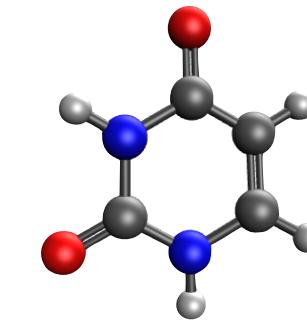




Adenine



Uracil



State	CAM-B3LYP				PBE0			
	E_i^0	f_i	Trans.	Char.	E_i^0	f_i	Trans.	Char.
6-311+G(d,p)								
S_1	5.37	0.0000	H-1 \rightarrow L	$n_N\pi^*1$	5.11	0.0005	H-1 \rightarrow L	$n_N\pi^*1$
S_2	5.39	0.2856	H \rightarrow L	L_a	5.16	0.2313	H \rightarrow L	L_a
S_3	5.52	0.015	H \rightarrow L+3	L_b	5.41	0.0369	H \rightarrow L+1	L_b
			H-2 \rightarrow L				H-2 \rightarrow L	
S_4	5.87	0.0085	H \rightarrow L+1	$\pi Ry_\sigma1$	5.65	0.0069	H \rightarrow L+2	$\pi Ry_\sigma1$
			H \rightarrow L+2				H \rightarrow L+2	
S_5	5.95	0.0033	H-1 \rightarrow L+3	$n_N\pi^*2$	5.73	0.0019	H-1 \rightarrow L+1	$n_N\pi^*2$
S_6	6.21	0.0014	H \rightarrow L+2	$\pi Ry_\sigma2$	5.93	0.0028	H \rightarrow L+3	$\pi Ry_\sigma2$
			H \rightarrow L+1				H \rightarrow L+1	
S_7	6.31	0.001	H-3 \rightarrow L	$n_N\pi^*3$	6.06	0.0005	H-3 \rightarrow L	$n_N\pi^*3$
6-31G(d)								
S_1	5.44	0.0003	H-1 \rightarrow L	$n_N\pi^*1$	5.18	0.0002	H-1 \rightarrow L	$n_N\pi^*1$
S_2	5.57	0.2013	H \rightarrow L	L_a	5.32	0.1883	H \rightarrow L	L_a
S_3	5.64	0.0822	H \rightarrow L+1	L_b	5.52	0.0642	H \rightarrow L+1	L_b
			H-2 \rightarrow L				H-2 \rightarrow L	
S_4	6.03	0.0012	H-1 \rightarrow L+1	$n_N\pi^*2$	5.80	0.0009	H-1 \rightarrow L+1	$n_N\pi^*2$
S_5	6.42	0.0007	H-3 \rightarrow L	$n_N\pi^*3$	6.17	0.0003	H-3 \rightarrow L	$n_N\pi^*3$

State	CAM-B3LYP				PBE0			
	E_i^0	f_i	Trans.	Char.	E_i^0	f_i	Trans.	Char.
6-311+G(d,p)								
S_1	5.10	0.0000	H-1 \rightarrow L	$n_O\pi^*1$	4.82	0.0000	H-1 \rightarrow L	$n_O\pi^*1$
S_2	5.50	0.1902	H \rightarrow L	$\pi\pi^*1$	5.33	0.1496	H \rightarrow L	$\pi\pi^*1$
S_3	6.18	0.0032	H \rightarrow L+1	$\pi Ry_\sigma1$	6.02	0.0001	H-3 \rightarrow L	$n_O\pi^*2$
S_4	6.38	0.0000	H-1 \rightarrow L+3	$n_O\pi^*2$	6.05	0.0024	H \rightarrow L+1	$\pi Ry_\sigma1$
			H-3 \rightarrow L+3				H-3 \rightarrow L+3	
S_5	6.62	0.0452	H-2 \rightarrow L	$\pi\pi^*2$	6.14	0.0392	H-2 \rightarrow L	$\pi\pi^*2$
S_6	6.88	0.1680	H \rightarrow L+3	$\pi\pi^*3$	6.44	0.0004	H-1 \rightarrow L+2	$n_O\pi^*3$
S_7	7.17	0.0007	H \rightarrow L+2	$\pi Ry_\sigma2$	6.63	0.1263	H \rightarrow L+2	$\pi\pi^*3$
S_8	7.17	0.0002	H-3 \rightarrow L	$n_O\pi^*3$				
6-31G(d)								
S_1	5.09	0.0001	H-1 \rightarrow L	$n_O\pi^*1$	4.82	0.0001	H-1 \rightarrow L	$n_O\pi^*1$
S_2	5.65	0.1724	H \rightarrow L	$\pi\pi^*1$	5.46	0.1336	H \rightarrow L	$\pi\pi^*1$
S_3	6.40	0.0000	H-1 \rightarrow L+1	$n_O\pi^*2$	6.05	0.0000	H-3 \rightarrow L	$n_O\pi^*2$
			H-3 \rightarrow L+1				H-3 \rightarrow L+1	
S_4	6.73	0.0444	H-2 \rightarrow L	$\pi\pi^*2$	6.22	0.0397	H-2 \rightarrow L	$\pi\pi^*2$
S_5	7.18	0.1395	H \rightarrow L+1	$\pi\pi^*3$	6.49	0.0000	H-1 \rightarrow L+1	$n_O\pi^*3$
S_6	7.23	0.0000	H-3 \rightarrow L	$n_O\pi^*3$	6.89	0.1170	H \rightarrow L+1	$\pi\pi^*3$

