Journal Name

ARTICLE

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Supporting Information

A QM/MM study of the initial excited state dynamics of green-absorbing proteorhodopsin

Veniamin A. Borin, Christian Wiebeler and Igor Schapiro

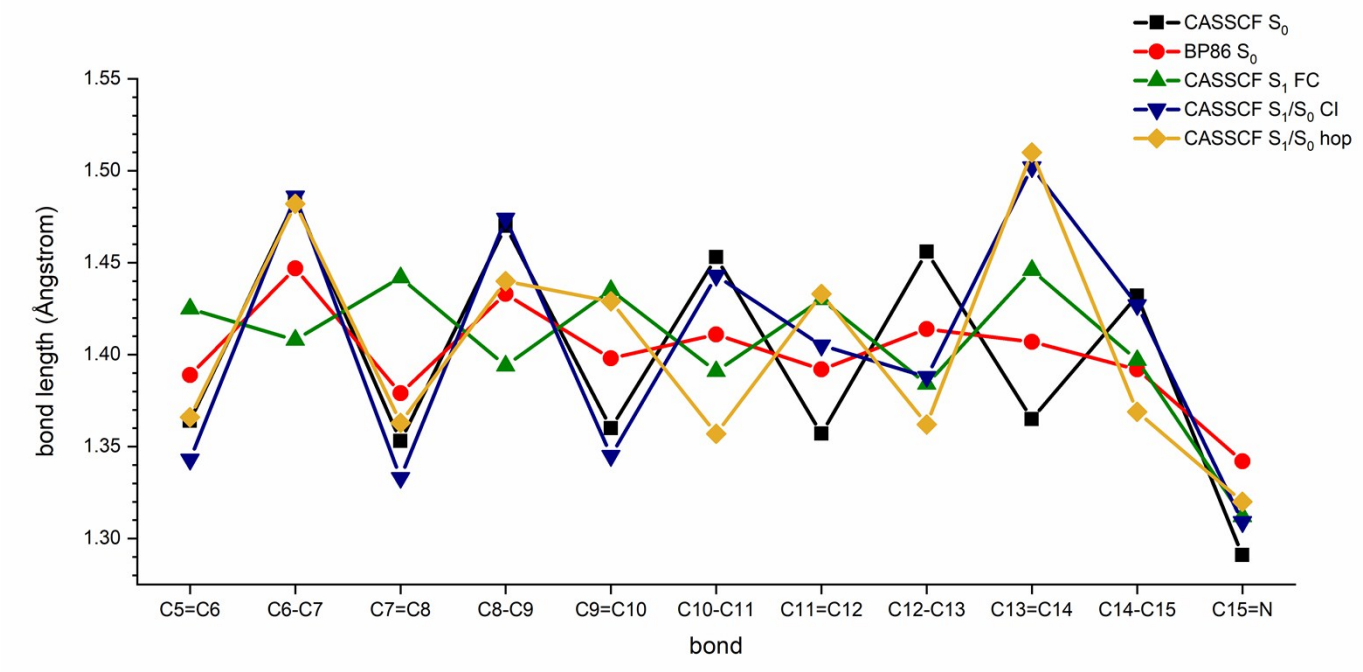

Figure S1. A comparison of bond lengths in different geometries. The method used for the QM part of the combined QM/MM calculation is varying: CASSCF/MM S_0 equilibrium geometry, BP86/MM S_0 equilibrium geometry, CASSCF/MM S_1 optimized geometry with C_{12}-C_{13}=C_{14}-C_{15} dihedral angle close to the one of the S_0 equilibrium (-170°), CASSCF/MM S_1/S_0 conical intersection geometry (-120°, from the relaxed scan), and CASSCF geometry at the S_1/S_0 surface hop (-115°, from the MD simulation).

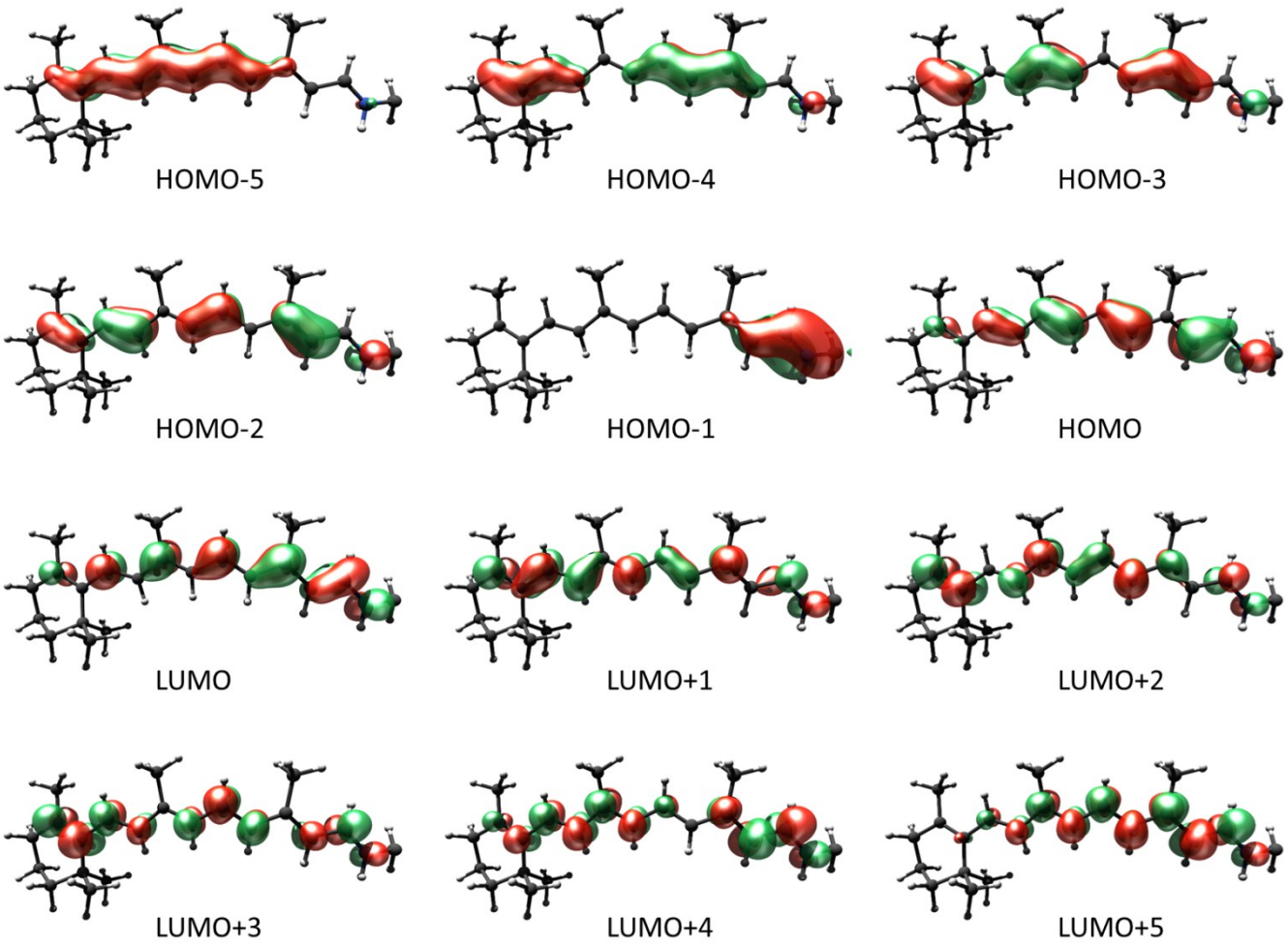

Figure S2. The orbitals included into the active space for CASSCF and CASPT2 calculation

Table S1. Excitation energies in eV (nm) and oscillator strengths obtained from RI-CC2/cc-pVDZ for models optimized via DFT and CASSCF as the quantum chemical part in the QM/MM approach. Experimentally, the first absorption maximum for GPR is found at ca. 2.40 eV (516 nm) at pH 9.2.

Optimization via	BP86/MM			CASSCF/MM			CASSCF/MM		
Environment	Point charges			Point charges			Vacuum		
RI-CC2	E_{Vert} [eV]	E_{Vert} [nm]	f	E_{Vert} [eV]	E_{Vert} [nm]	f	E_{Vert} [eV]	E_{Vert} [nm]	f
S_1	2.45	507	2.20	2.46	505	1.72	2.07	598	1.69
S_2	3.84	323	0.31	3.89	319	0.21	3.49	355	0.29
S_3	4.39	283	0.27	4.62	268	0.58	4.34	286	0.38
S_4	4.85	255	0.05	4.99	249	0.05	4.59	270	0.01
S_5	5.43	228	0.00	5.31	234	0.00	4.74	262	0.05

Table S2. Excitation energies in eV (nm) and oscillator strengths obtained from RI-ADC(2)/cc-pVDZ for models optimized via DFT and CASSCF as the quantum chemical part in the QM/MM approach. Experimentally, the first absorption maximum for GPR is found at ca. 2.40 eV (516 nm) at pH 9.2.

Optimization via	BP86/MM			CASSCF/MM			CASSCF/MM		
Environment	Point charges			Point charges			Vacuum		
RI-ADC(2)	E_{Vert} [eV]	E_{Vert} [nm]	f	E_{Vert} [eV]	E_{Vert} [nm]	f	E_{Vert} [eV]	E_{Vert} [nm]	f
S_1	2.30	539	1.81	2.37	523	1.26	1.96	633	1.03
S_2	3.76	330	0.20	3.83	324	0.22	3.40	365	0.32
S_3	4.37	284	0.25	4.62	269	0.69	4.33	286	0.60
S_4	4.75	261	0.06	4.91	253	0.08	4.59	270	0.04
S_5	5.49	226	0.01	5.39	230	0.00	4.70	264	0.01

Table S3. Excitation energies in eV (nm) and oscillator strengths obtained from TD-BP86/cc-pVDZ for models optimized via DFT and CASSCF as the quantum chemical part in the QM/MM approach. Experimentally, the first absorption maximum for GPR is found at ca. 2.40 eV (516 nm) at pH 9.2..

Optimization via	BP86/MM			CASSCF/MM			CASSCF/MM		
Environment	Point charges			Point charges			Vacuum		
TD-BP86	E_{Vert} [eV]	E_{Vert} [nm]	f	E_{Vert} [eV]	E_{Vert} [nm]	f	E_{Vert} [eV]	E_{Vert} [nm]	f
S_1	2.27	547	1.41	2.04	607	0.81	1.91	649	0.79
S_2	2.84	437	0.81	2.91	426	0.94	2.72	456	0.05
S_3	3.45	360	0.00	3.21	387	0.03	2.80	442	0.85
S_4	3.56	349	0.00	3.42	363	0.17	3.08	403	0.03
S_5	3.91	317	0.00	3.58	346	0.02	3.21	386	0.05

Table S4. Excitation energies in eV (nm) and oscillator strengths obtained from TD-B3LYP/cc-pVDZ for models optimized via DFT and CASSCF as the quantum chemical part in the QM/MM approach. Experimentally, the first absorption maximum for GPR is found at ca. 2.40 eV (516 nm) at pH 9.2..

Optimization via	BP86/MM			CASSCF/MM			CASSCF/MM		
Environment	Point charges			Point charges			Vacuum		
TD-B3LYP	E_{Vert} [eV]	E_{Vert} [nm]	f	E_{Vert} [eV]	E_{Vert} [nm]	f	E_{Vert} [eV]	E_{Vert} [nm]	f
S_1	2.43	511	1.90	2.32	534	1.22	2.14	579	1.14
S_2	3.30	376	0.41	3.33	372	0.68	3.18	390	0.71
S_3	3.99	311	0.03	3.98	311	0.21	3.67	338	0.00
S_4	4.42	281	0.04	4.22	294	0.01	3.83	324	0.12
S_5	4.50	276	0.00	4.49	276	0.04	4.07	305	0.00

Table S5. Excitation energies in eV (nm) and oscillator strengths obtained from TD-CAM-B3LYP/cc-pVDZ for models optimized via DFT and CASSCF as the quantum chemical part in the QM/MM approach. Experimentally, the first absorption maximum for GPR is found at ca. 2.40 eV (516 nm) at pH 9.2.

Optimization via	BP86/MM			CASSCF/MM			CASSCF/MM		
Environment	Point charges			Point charges			Vacuum		
TD-CAM-B3LYP	E_{Vert} [eV]	E_{Vert} [nm]	f	E_{Vert} [eV]	E_{Vert} [nm]	f	E_{Vert} [eV]	E_{Vert} [nm]	f
S_1	2.56	484	2.16	2.70	460	1.72	2.49	499	1.60
S_2	4.02	308	0.14	4.08	304	0.21	3.84	323	0.29
S_3	4.48	277	0.12	4.64	267	0.33	4.48	277	0.24
S_4	4.98	249	0.05	5.09	244	0.07	4.94	251	0.01
S_5	5.49	226	0.00	5.47	227	0.00	5.02	247	0.09