

Supporting Information

for

Mechanism of Spectral Tuning Going from Retinal in Vacuo to Bovine Rhodopsin and its Mutants: Multireference *ab initio* Quantum Mechanics/Molecular Mechanics Studies

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VERTICAL EXCITATION ENERGIES AND OSCILLATOR STRENGTHS

Unless stated otherwise, all the calculations are with 6-31G* basis set, $T_{sel} = 10^{-6} E_h$ and QM region R1. The vertical excitation energies are given in nm.

1. PSB all-trans-6-s-trans retinal

1.1. At B3LYP geometry

CASSCF	DDCI2+Q	f	CASSCF	DDCI2+Q	f	
6-root CAS(12/12) with 6-31G*			3-root CAS(12/12) with 6-31G*			
553.3	545.2	2.28	548.1	543.6	2.14	
404.4	415.8	0.04	393.2	411.9	0.02	
299.7	307.5	0.01	3-root CAS(6/6) with 6-31G*			
273.7	295.5	0.01	381.8	558.6	2.08	
242.6	247.3	0.00	334.1	384.9	0.02	
6-root CAS(12/12) with SV(P)			3-root CAS(6/6) with 6-31G* and $T_{sel} = 10^{-7} E_h$			
565.6	554.9	2.24	381.8	544.6	2.09	
404.9	420.0	0.04	334.1	378.7	0.02	
300.9	311.5	0.01	6-root CAS(12/12) with TZVP			
271.4	297.9	0.01	572.2	570.4	2.22	
243.1	250.0	0.00	406.1	438.0	0.03	
6-root CAS(12/12) with BNANO-DZP			300.1	324.7	0.01	
559.0	554.7	2.20	274.9	306.4	0.02	
404.8	437.0	0.02	246.3	259.7	0.00	
299.8	6-root CAS(12/12) with BNANO-TZ2P			551.8	550.4	2.20
271.8	572.2	563.5	2.30	403.5	437.1	0.02
244.2	406.1	440.8	0.03	298.1		
6-root CAS(12/12) with VTZP			274.9	305.4	0.02	
572.2	563.5	2.30	246.4	261.8	0.00	
406.1	440.8	0.03				
300.1	325.2	0.01				
274.9	305.4	0.02				
246.4	261.8	0.00				

DDACPF/2a-2(12/12)	f	DDCI3+Q(6/6)	f	SORCI+Q(6/6)	f	MRCISD+Q(6/6)	f
527.1	2.36	640.2	1.91	625.7	1.88	604.1	1.98
394.1	0.04	473.9	0.01	490.5	0.04	457.5	0.02
292.8	0.01						
280.7	0.02						
238.3	0.00						

1.2. At CASSCF geometry

CASSCF(12/12)	DDCI2+Q(12/12)	f	CASSCF(6/6)	SORCI+Q(6/6)	f	MRCISD+Q(6/6)	f
526.0	539.4	1.70	421.1	565.1	1.56	603.5	1.38
344.6	359.9	0.30	294.9	395.0	0.27	412.5	0.37
293.5	313.2	0.07					
247.2	262.8	0.02					
237.1	257.4	0.02					

2. PSB all-trans-6-s-cis retinal

2.1. At B3LYP geometry

<u>CASSCF(12/12)</u>	<u>DDCI2+Q(12/12)</u>	<u>f</u>	<u>CASSCF(6/6)</u>	<u>SORCI+Q(6/6)</u>	<u>f</u>	<u>MRCISD+Q(6/6)</u>	<u>f</u>
545.0	550.9	1.94	466.8	610.1	1.66	603.8	1.72
390.4	412.0	0.12	349.7	474.9	0.15	493.1	0.13
308.7	328.3	0.06					
267.3	287.5	0.05					
246.6	257.8	0.00					

2.2. At CASSCF geometry

<u>CASSCF(12/12)</u>	<u>DDCI2+Q(12/12)</u>	<u>f</u>	<u>CASSCF(6/6)</u>	<u>SORCI+Q(6/6)</u>	<u>f</u>	<u>MRCISD+Q(6/6)</u>	<u>f</u>
456.7	469.7	1.52	415.1	505.0	1.19	545.5	0.95
311.5	361.2	0.22	328.4	395.6	0.22	421.3	0.34
299.0	315.2	0.10					
247.8	261.8	0.02					
218.9	246.4	0.03					

3. PSB 11-cis-6-s-cis retinal at B3LYP geometry

<u>CASSCF(12/12)</u>	<u>DDCI2+Q(12/12)</u>	<u>f</u>	<u>CASSCF(6/6)</u>	<u>SORCI+Q(6/6)</u>	<u>f</u>	<u>MRCISD+Q(6/6)</u>	<u>f</u>
534.6	541.4	1.67	362.0	625.2	1.35	600.8	1.06
383.1	402.8	0.11	313.0	473.3	0.06	454.2	0.02
302.5	328.1	0.10					
261.4	283.9	0.07					
244.7	259.5	0.03					

DDCI2+Q(12/12) f

555.5	1.50
370.2	0.06

4. SB 11-cis-6-s-cis retinal at B3LYP geometry

<u>6-31G*</u>			<u>6-31G*</u>		
<u>CASSCF(12/12)</u>	<u>DDCI2+Q(12/12)</u>	<u>f</u>	<u>CASSCF(10,10)</u>	<u>DDCI2+Q(10,10)</u>	<u>f</u>
285.2	309.5	1.84	285.2	299.4	1.82
230.8	308.5	0.06	230.4	291.8	0.01
211.1	255.9	0.01	205.2	243.9	0.01
203.6	225.5	0.03	199.3	216.1	0.03
190.8	204.3	0.03	190.9	194.2	0.00

<u>BNANO-TZ2P</u>			<u>DDCI2+Q(6/6)/6-31G*</u>				
<u>CASSCF(10,10)</u>	<u>DDCI2+Q(10,10)</u>	<u>f</u>	<u>CASSCF(6/6)</u>	<u>T_{sel}=10⁻⁶</u>	<u>f</u>	<u>T_{sel}=10⁻⁷</u>	<u>f</u>
284.6	319.7	1.72	246.2	283.4	1.69	281.7	1.36
229.9	293.3	0.01	231.7	273.5	0.35	269.3	0.71
205.2	246.7	0.01					
201.7	219.8	0.01					
190.5	195.9	0.00					

<u>BNANO-TZ2P</u>		
<u>CASSCF(6/6)</u>	<u>DDCI2+Q(6/6)</u>	<u>f</u>
246.5	297.6	1.79
234.7	277.8	0.19

5. Bovine rhodopsin at B3LYP/AMBER geometry

5.1. PSBR

<u>CASSCF(12/12)</u>	<u>DDCI2+Q(12/12)</u>	<u>f</u>	<u>CASSCF(12/12)</u>	<u>DDCI2+Q(12/12)</u>	<u>f</u>
<u>QM-none with R1</u>			<u>QM-none with R2</u>		
504.2	526.5	1.49	341.4	548.8	0.01

359.2	391.3	0.11	332.4	488.7	0.02
295.8	341.3	0.08	325.8	394.5	1.58
254.8	274.6	0.10	307.9	353.8	0.01
237.5	261.6	0.09	242.4	296.8	0.03
<u>QM/MM with R1</u>			<u>QM/MM with R2</u>		
356.8	435.1	0.74	357.8	431.7	1.52
306.7	385.7	1.15	319.3	366.4	0.02
267.6	316.6	0.04	265.6	291.4	0.02
232.4	284.6	0.10	231.9	265.1	0.15
210.8	255.6	0.08	211.1	254.4	0.02

<u>CASSCF(6/6) SORCI+Q(6/6)/f MRCISD+Q(6/6)/f</u>	<u>CASSCF(6/6) SORCI+Q(6/6)/f MRCISD+Q(6/6)/f</u>
<u>QM-none with R1</u>	<u>QM/MM with R1</u>
424.0 615.7/1.21 625.5/1.25	332.6 495.3/1.41 498.9/1.59
318.8 458.6/0.15 449.9/0.16	300.6 438.6/0.03 435.5/0.01

5.2. SBR with protonated Glu113

<u>CASSCF(12/12) DDCI2+Q(12/12) f</u>	<u>CASSCF(12/12) DDCI2+Q(12/12) f</u>				
<u>QM-none with R1</u>	<u>QM-none with R2</u>				
296.8	276.9	321.0	308.6	0.06	1.64
235.7	243.6	317.9	289.2	1.70	0.00
215.7	214.4	284.1	258.7	1.11	0.00
208.9	208.2	232.2	240.2	0.03	0.01
195.6	203.1	213.8	222.9	0.05	0.01
<u>QM/MM with R1</u>	<u>QM/MM with R2</u>				
299.2	290.3	335.7	336.5	1.70	1.38
237.8	276.6	316.0	321.1	0.01	0.00
227.1	228.0	260.9	318.0	0.07	0.02
210.4	216.0	236.9		0.03	
196.6	215.0	224.6		0.08	

5.3. SBR with deprotonated Glu113

<u>CASSCF(12/12) DDCI2+Q(12/12) f</u>	<u>CASSCF(12/12) DDCI2+Q(12/12) f</u>				
<u>QM-none with R1</u>	<u>QM-none with R2</u>				
281.3	281.9	312.6	331.7	1.73	0.00
264.0	270.1	302.9	327.7	0.01	0.00
226.9	257.6	299.1	297.5	0.00	1.85
208.4	217.6	259.3	286.4	0.02	0.00
202.0	207.1	238.7	230.5	0.04	0.01
<u>QM/MM with R1</u>	<u>QM/MM with R2</u>				
279.7	270.0	312.5	306.3	0.00	0.00
271.1	255.4	308.8	297.8	1.74	0.01
226.4	253.6	302.1	293.7	0.01	1.87
206.9	218.8	253.9	285.4	0.02	0.02
201.2	211.3	232.6	236.3	0.01	0.01

6. E122Q mutant of bovine rhodopsin with PSBR at B3LYP/AMBER geometry

<u>CASSCF(12/12) DDCI2+Q(12/12) f</u>	<u>CASSCF(12/12) DDCI2+Q(12/12) f</u>				
<u>QM-none with R1</u>	<u>QM/MM with R1</u>				
496.7	348.3	521.9	426.9	1.47	1.76
352.1	298.5	385.6	376.2	0.15	0.00
294.4	263.0	338.6	304.9	0.06	0.03
252.0	228.1	272.3	277.9	0.08	0.10
235.9	208.2	261.1	254.2	0.04	0.09

<u>CASSCF(6/6) SORCI+Q(6/6)/f MRCISD+Q(6/6)/f</u>	<u>CASSCF(6/6) SORCI+Q(6/6)/f MRCISD+Q(6/6)/f</u>
<u>QM-none with R1</u>	<u>QM/MM with R1</u>
474.9 586.4/1.19 584.0/1.20	290.7 461.7/1.42 489.8/1.50
328.9 423.8/0.29 410.4/0.32	278.8 399.7/0.03 409.4/0.01

7. E113Q mutant of bovine rhodopsin with SBR at B3LYP/AMBER geometry

<u>CASSCF(12/12) DDCI2+Q(12/12) f</u>			<u>CASSCF(12/12) DDCI2+Q(12/12) f</u>		
<u>QM-none with R1</u>			<u>QM/MM with R1</u>		
285.6	310.2	1.70	283.9	319.7	1.71
229.9	307.7	0.07	228.9	300.8	0.01
211.4	254.9	0.01	214.7	259.8	0.02
204.3	229.9	0.04	204.1	231.8	0.04
192.2	204.8	0.02	192.2	205.6	0.02

<u>CASSCF(6/6) SORCI+Q(6/6)/f MRCISD+Q(6/6)/f</u>			<u>CASSCF(6/6) SORCI+Q(6/6)/f MRCISD+Q(6/6)/f</u>		
<u>QM-none with R1</u>			<u>QM/MM with R1</u>		
247.1	349.5/0.05	340.7/0.00	244.6	332.9/0.06	331.2/0.00
232.1	326.5/1.70	322.5/2.06	226.7	329.6/1.60	322.2/1.95