Supporting Information for: Analytical first and second derivatives for a fully polarizable QM/Classical Hamiltonian.

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Table 1: Harmonic vibrational frequencies (cm^{-1}) and intensities for pyrimidine in vacuo and in aqueous solution as described with three different models: C-PCM, MM with the AMBER force field and QEq charges, FQ.

	Vacuum		PCM		QEq		FQ	
	ν	Int	ν	Int	ν	Int	ν	Int
A1	3215	8.2	3229	4.8	3255	0.0	3230	5.2
A1	3186	15.7	3187	0.0	3194	4.5	3206	1.0
A1	3171	12.8	3182	34.9	3185	20.2	3203	7.9
A1	1614	48.0	1609	53.3	1616	28.6	1615	33.8
A1	1438	58.3	1434	81.4	1443	54.3	1441	56.4
A1	1160	1.0	1155	0.2	1168	0.4	1165	0.3
A1	1077	0.7	1076	0.5	1084	0.0	1082	0.2
A1	1011	3.6	1011	5.0	1018	0.9	1017	5.6
A1	694	3.3	690	3.5	696	1.7	694	2.9
A2	992	0.0	999	0.0	1000	0.2	1001	0.2
A2	409	0.0	408	0.0	429	0.0	422	0.0
B1	1013	0.0	1017	0.0	1021	5.6	1027	0.2
B1	973	0.0	976	0.0	971	0.3	982	0.1
B1	818	5.3	821	5.6	826	2.9	835	4.5
B1	733	41.8	731	46.6	736	35.5	739	35.3
B1	351	3.6	352	4.1	362	3.2	368	3.1
B2	3175	18.8	3188	18.2	3191	1.6	3210	7.7
B2	1613	81.2	1615	118.7	1632	76.1	1625	79.6
B2	1492	6.6	1494	8.3	1502	5.1	1505	6.5
B2	1391	0.2	1393	0.5	1402	0.3	1408	0.5
B2	1261	5.3	1260	4.0	1277	3.1	1274	5.2
B2	1227	8.3	1223	14.2	1236	6.5	1234	8.3
B2	1092	3.4	1093	6.8	1112	5.0	1106	4.6
B2	632	9.9	633	11.3	642	11.6	640	11.4

Table 2: Harmonic vibrational frequencies (cm^{-1}) and intensities for retinal in vacuo and shifts obtained using three different models for retinal embedded in a Rhodopsin mimic: IEF-PCM, MM with the AMBER force field, FQ.

	vacuo		PCM		MM		FQ	
Mode	ν	Int	$\Delta\nu$	ΔInt	$\Delta\nu$	ΔInt	$\Delta\nu$	ΔInt
1	16.99	0.8	0.31	0.4	56.16	0.7	52.51	1.8
2	28.85	0.6	1.60	0.6	47.81	1.5	46.79	0.9
3	33.56	1.0	-0.77	0.5	50.23	0.0	49.56	-0.4
4	46.83	0.9	1.16	0.6	45.80	0.4	46.15	-0.5
5	67.92	0.1	-1.01	1.2	29.72	0.0	37.49	0.1
6	84.51	2.0	-10.27	0.2	29.41	2.0	23.94	-0.7
7	103.72	0.2	-9.29	1.0	25.73	0.0	30.02	0.3
8	113.64	1.2	-0.13	0.1	29.62	1.6	34.63	-0.6
9	123.81	0.4	0.27	0.0	26.15	5.5	36.23	1.6
10	137.67	0.5	-0.28	-0.2	15.80	0.2	23.31	0.5
11	151.88	0.0	-2.80	0.0	8.64	0.3	14.02	1.2
12	163.79	0.1	-1.07	0.4	9.33	0.9	17.61	0.7
13	170.90	0.1	-4.63	0.5	15.85	0.3	30.17	6.9
14	178.07	5.2	5.45	0.5	17.88	-2.9	31.65	-4.1
15	187.66	3.9	1.07	4.7	31.30	2.2	30.74	2.2
16	195.12	1.4	3.59	1.7	45.37	-1.0	32.74	-1.0
17	216.16	0.1	2.30	0.2	33.18	4.1	28.76	0.8
18	241.47	1.3	0.12	1.5	18.94	-0.8	17.17	4.2
19	243.58	0.3	0.74	0.3	32.35	0.8	24.18	1.4
20	266.53	0.0	1.58	0.0	23.88	2.2	3.57	0.2
21	274.76	0.1	-0.32	0.1	17.81	1.8	15.77	0.8
22	279.37	0.0	0.62	0.0	23.91	1.8	29.27	3.5
23	303.91	0.5	-0.28	0.6	19.36	-0.4	15.46	-0.4
24	308.65	1.8	-0.16	0.4	41.66	1.5	31.61	5.1
25	353.29	0.1	-2.34	0.1	8.47	3.3	-0.50	0.4
26	356.84	0.3	1.14	0.0	29.31	0.7	23.19	0.0
27	381.74	0.9	-0.23	1.6	16.65	1.8	20.90	3.9
28	388.68	2.9	1.08	3.3	10.97	1.8	21.63	4.1
29	411.17	1.6	1.11	1.3	15.58	-0.5	19.63	-0.6
30	414.98	9.3	1.64	10.4	30.70	-4.6	23.95	11.3
31	456.24	8.2	1.05	16.2	12.45	-0.7	14.79	-0.9
32	463.37	5.6	-0.14	7.8	13.29	5.6	14.62	26.1
33	484.24	12.5	-0.38	13.8	8.33	5.7	10.58	9.6
34	501.69	0.5	0.76	3.0	5.27	2.1	10.18	5.0
35	514.94	1.5	4.94	0.9	14.69	4.0	12.38	-0.1
36	535.59	1.0	0.40	0.8	5.13	-0.2	8.20	1.0
37	552.83	1.1	6.79	0.3	7.03	0.7	12.69	2.2
38	582.74	5.3	0.16	3.8	12.69	6.8	12.76	6.3
39	614.57	3.4	-1.04	2.0	4.20	0.0	3.56	0.2
40	655.24	2.2	1.27	4.9	9.79	7.2	11.67	7.6
41	672.59	1.4	-1.36	2.0	2.88	5.4	2.65	3.1
42	708.87	7.8	-0.80	14.3	4.36	5.8	3.82	11.5
43	823.93	9.0	-1.06	15.6	2.96	4.3	4.08	3.7
44	848.70	2.9	-1.05	30.7	2.10	1.2	4.53	-0.4
45	853.54	4.6	2.52	2.4	3.59	-2.1	3.70	3.6
46	858.82	2.1	-0.73	2.0	1.39	2.5	3.74	-1.5
47	873.76	3.2	1.21	17.8	2.23	30.5	12.26	56.7

	vacuo		PCM		MM		FQ	
Mode	ν	Int	$\Delta\nu$	ΔInt	$\Delta\nu$	ΔInt	$\Delta\nu$	ΔInt
48	880.11	16.7	0.00	11.7	3.76	-15.2	8.42	-16.4
49	891.36	1.1	-1.45	1.6	7.30	1.3	10.01	1.1
50	904.87	4.5	-0.87	6.7	6.82	-0.3	13.45	3.3
51	920.70	8.1	-2.28	6.0	-1.68	79.5	-1.22	28.7
52	928.54	0.8	2.10	2.5	0.69	4.1	11.68	1.3
53	947.35	0.4	-0.38	0.3	5.41	0.0	9.78	0.3
54	960.01	0.8	-0.98	0.8	8.80	3.7	12.79	1.8
55	999.17	5.0	-1.70	21.1	1.77	125.1	5.82	34.5
56	1004.87	13.0	-0.14	14.3	-2.49	13.1	6.69	2.1
57	1007.80	2.3	2.14	56.5	-2.96	6.8	5.97	-0.7
58	1011.46	43.5	1.36	-31.2	10.09	-14.2	14.07	9.9
59	1013.98	7.9	-0.80	-1.9	17.31	15.9	16.73	4.9
60	1035.54	7.2	-1.17	85.4	5.80	57.9	7.78	33.9
61	1040.25	9.4	-1.89	24.2	10.72	-0.9	12.21	3.2
62	1054.79	5.4	-1.45	31.5	7.56	13.8	15.41	64.5
63	1070.90	0.9	-3.17	1.2	-1.81	37.4	4.42	20.9
64	1074.09	6.3	-1.94	-1.1	4.39	-2.5	6.20	5.7
65	1076.28	0.3	-3.22	13.8	10.10	6.1	8.42	14.9
66	1077.68	1.9	-1.35	1.9	17.70	14.2	12.85	22.3
67	1088.41	4.9	-2.61	3.1	12.66	1.0	12.00	3.3
68	1142.70	170.2	4.33	3.9	14.93	-49.6	17.62	-28.0
69	1153.77	66.5	3.41	142.8	11.65	-4.0	16.47	34.0
70	1163.83	41.1	0.09	294.7	10.02	27.9	15.15	137.8
71	1203.90	38.1	-1.58	46.0	5.87	-34.8	6.77	-30.1
72	1207.91	253.7	-2.60	906.2	7.97	481.6	9.62	989.0
73	1221.24	62.7	-2.10	123.2	3.55	-20.0	4.47	-6.9
74	1239.94	96.2	-3.10	110.0	0.91	-70.7	1.74	-64.3
75	1246.12	39.3	-0.70	52.8	5.43	-29.7	5.79	-22.1
76	1248.08	2.5	-1.27	46.5	8.24	1.4	9.89	0.2
77	1260.44	30.7	2.30	4.2	3.80	-26.1	10.75	-21.3
78	1314.07	41.9	-2.58	39.7	5.09	120.0	8.89	270.1
79	1316.34	40.4	-0.62	163.6	3.84	-32.8	10.30	-40.0
80	1338.29	1.6	-1.25	3.7	6.66	5.2	5.92	1.4
81	1345.95	19.3	-0.15	42.7	6.27	-11.6	9.05	5.9
82	1358.63	28.5	-0.55	37.7	2.14	491.0	-0.59	207.4
83	1379.43	130.7	0.57	318.5	0.06	-123.7	-1.03	67.9
84	1388.88	2.4	-1.38	-0.4	-5.97	22.9	0.57	184.0
85	1392.52	2.0	-0.85	7.5	0.31	-0.6	2.14	-1.9
86	1402.12	9.1	-2.23	8.4	4.43	-6.5	7.18	-7.7
87	1409.67	29.9	-1.52	26.0	4.13	-28.4	7.84	-10.8
88	1417.13	16.5	-1.05	17.9	-0.39	12.8	5.45	4.0
89	1429.36	5.4	-4.12	-0.1	-0.39	-1.3	5.23	-0.7
90	1438.49	27.3	-6.91	52.7	2.19	-19.0	12.57	5.1
91	1442.37	17.9	-3.52	6.0	7.58	-17.3	14.34	21.5
92	1449.20	3.7	-4.99	45.1	1.87	35.1	8.27	0.0
93	1455.09	4.8	-4.47	-0.1	1.44	4.2	8.84	11.6
94	1457.88	10.6	-2.96	56.3	9.95	44.3	12.78	37.9

	vacuo		PCM		MM		FQ	
Mode	ν	Int	$\Delta\nu$	ΔInt	$\Delta\nu$	ΔInt	$\Delta\nu$	ΔInt
95	1495.89	8.7	-8.50	12.4	-7.04	22.1	-2.86	15.4
96	1510.70	1.9	-7.99	12.7	-1.04	27.4	5.80	47.8
97	1511.34	7.4	-7.96	20.8	6.58	-3.8	6.74	-7.2
98	1514.63	7.8	-9.81	2.0	7.08	-6.7	4.07	-3.8
99	1515.85	17.4	-9.26	-14.9	10.95	23.1	5.60	68.2
100	1519.69	51.8	-9.56	148.0	7.98	-38.0	3.76	-48.4
101	1520.31	0.5	-7.19	0.2	12.25	1.6	9.96	107.6
102	1523.06	14.5	-6.99	18.9	12.57	30.1	14.98	-13.4
103	1527.21	2.7	-6.40	0.2	9.70	9.8	13.24	184.7
104	1528.60	5.2	-6.13	0.6	9.29	5.3	12.28	22.8
105	1532.80	3.2	-7.76	-1.7	8.41	1.6	9.37	0.7
106	1538.02	6.0	-6.81	14.4	14.62	2.1	12.95	8.8
107	1545.37	3.0	-7.20	3.7	17.87	38.2	7.42	-2.0
108	1615.50	265.3	-16.72	2193.4	-19.90	313.2	-15.13	1099.3
109	1627.33	583.9	-13.70	323.4	-9.55	888.8	-9.52	907.2
110	1641.24	9.6	-8.76	-0.4	-4.97	4.6	-8.01	61.2
111	1663.31	46.4	-10.71	-9.1	-8.22	-13.1	-5.83	-2.1
112	1675.83	17.7	-8.16	82.5	-0.41	44.0	-0.18	185.0
113	1757.07	637.8	-38.77	433.3	5.81	151.2	-33.66	366.0
114	2933.23	221.5	28.29	108.4	-9.24	21.0	22.34	-14.0
115	2987.56	47.0	4.22	35.8	6.31	-22.9	-5.51	-1.1
116	3024.51	26.7	-1.28	24.5	4.84	0.9	-4.56	3.7
117	3030.58	10.4	3.45	2.9	18.61	44.1	5.41	83.0
118	3037.34	48.5	1.14	39.2	18.49	-30.4	7.15	-29.5
119	3047.70	29.4	-0.74	-6.6	12.96	-9.0	11.18	-11.1
120	3048.30	13.6	1.87	94.0	19.46	2.7	11.85	-1.9
121	3051.21	57.8	-0.08	5.2	16.61	-39.2	14.28	-50.6
122	3053.92	26.5	-1.51	7.7	25.36	-21.1	15.53	-19.6
123	3054.82	12.6	5.47	5.2	32.53	23.9	33.89	55.2
124	3070.50	74.1	-0.99	39.8	31.11	-73.4	20.97	-48.1
125	3086.38	51.6	-1.46	39.5	21.48	38.4	21.69	10.3
126	3094.29	14.8	3.82	6.1	21.26	3.3	14.40	42.0
127	3097.05	23.0	2.53	15.1	25.09	-19.2	15.19	-15.6
128	3103.15	14.0	3.82	39.7	19.11	10.7	18.30	89.9
129	3110.39	30.1	-0.67	-14.6	15.41	13.8	17.22	8.8
130	3114.16	38.2	-2.82	24.0	19.94	-16.0	25.30	-23.8
131	3119.02	28.1	4.80	9.2	30.20	-13.5	30.51	-19.4
132	3145.18	3.8	-2.21	51.8	18.80	19.1	5.73	13.5
133	3146.48	37.2	0.94	-21.5	22.70	1.2	12.64	-19.2
134	3157.17	33.0	-3.75	29.2	13.16	9.8	13.58	-13.7
135	3157.33	20.5	0.77	-6.8	13.96	4.7	20.81	0.4
136	3158.45	1.4	4.42	15.1	15.71	3.6	20.74	4.6
137	3172.13	25.1	-1.37	7.5	10.65	-21.4	16.27	-13.6
138	3176.67	10.5	-2.03	32.4	11.87	-4.0	18.60	-7.8
139	3200.01	26.4	5.94	56.4	1.03	-18.5	-0.66	4.0
140	3208.37	0.4	1.96	4.8	10.23	10.3	-0.15	19.4
141	3218.04	31.4	2.40	6.0	6.10	-10.4	12.76	-12.7