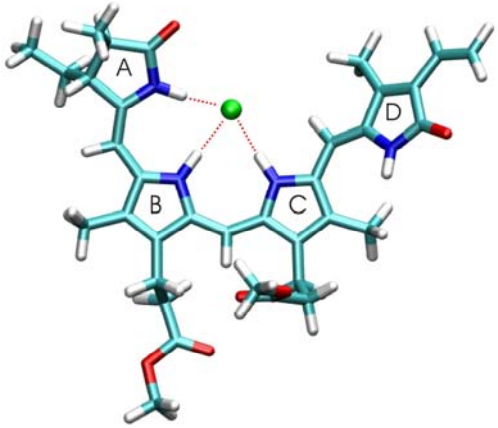
Supplementary Materials

Fourier transform infrared study of the photoreactions of plant phytochrome phyA using isopically labbeled chromophores and density functional theory calculations

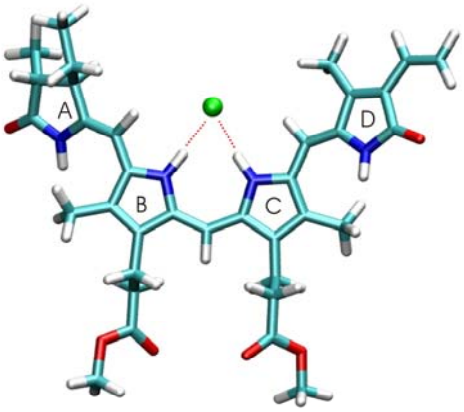
Content:

1. Structural models for the protein bound Phytochromobilin chromophore

ZZZssa



ZZZasa



2. ***Phytochromobilin molecule***

Table 2.1 : Calculated normal modes for the ***ZZZasa*** configuration of PΦB chromophores

Mode	freq. (n.a.) (cm^{-1})	IR int. (km/mol)	PED		freq. (N-D) (cm^{-1})	freq. (^{13}C10) (cm^{-1})
44	1778	621	C=O (A)		1774	1778
45	1764	131	C=O pps		1764	1764
46	1762	257	C=O pps		1762	1762
47	1743	800	C=O (D)		1738	1743
48	1643	373	C=C (vinyl)		1641	1643
49	1642	815	C=C (AB)		1633	1641
50	1625	256	C=C (CD)		1619	1624
51	1599	2321	C-C (BC), CH rock (BC)		1591	1578
52	1575	16	C=C (D)		1574	1575
53	1565	146	N-H ip (B,C)		1057	1565
54	1526	86	C-C		1525	1526
55	1518	11	C-C		1516	1518
56	1510	532	C-C, N-H ip (B,C)		1028	1506

Table 2.2 : Calculated normal modes for the ***ZZZssa*** configuration of PΦB chromophores

Mode	freq. (n.a.) (cm^{-1})	IR int. (km/mol)	PED		freq. (N-D) (cm^{-1})	freq. (^{13}C10) (cm^{-1})
44	1784	287	C=O (A)		1779	1784
45	1752	112	C=O pps		1752	1752
46	1745	406	C=O pps		1744	1745
47	1741	593	C=O (D)		1735	1741
48	1644	41	C=C (vinyl),C=C (CD)		1642	1644

49	1627	53	C=C (CD), C=C (vinyl)		1622	1627
50	1623	564	C=C (AB), C-C (BC)		1613	1615
51	1597	1466	C-C (AB), C-C (B)		1589	1585
52	1574	8	C=C (D)		1573	1574
53	1559	343	N-H ip (B,C)		1063	1558
54	1547	962	C-C (B)		1545	1545
55	1525	99	N-H ip (C)		1037	1523
56	1502	120	C-C (B)		1505	1502

Table 2.3: Calculated normal modes for the ***ZZEasa*** configuration of PΦB chromophores

Mode	freq. (n.a.) (cm^{-1})	IR int (km/mol)	PED		freq. (N-D) (cm^{-1})	freq. (^{13}C10) (cm^{-1})
44	1779	683	C=O (A)		1775	1779
45	1768	245	C=O pps		1768	1768
46	1752	219	C=O pps		1752	1752
47	1743	880	C=O (D)		1737	1743
48	1639	1212	C=C (AB)		1634	1639
49	1635	5	C=C (vinyl)		1631	1635
50	1608	132	C=C (CD)		1604	1608
51	1598	2361	C-C (BC), CH rock (BC)		1591	1577
52	1566	157	N-H ip (B,C)		1058	1565
53	1558	42	C=C (D)		1558	1557
54	1533	122	C-C (B)		1532	1532
55	1514	239	N-H ip (B,C)		1028	1512
56	1507	234	C-C (C), N-C (C)		1507	1506

Table 2.4 : Calculated normal modes for the ***ZZEssa*** configuration of PΦB chromophores

Mode	freq. (n.a.) (cm^{-1})	IR int (km/mol)	PED		freq. (N-D) (cm^{-1})	freq. (^{13}C10) (cm^{-1})
44	1786	272	C=O (A)		1781	1786
45	1768	309	C=O pps		1768	1768
46	1748	220	C=O pps		1748	1748
47	1743	846	C=O (D)		1737	1743
48	1635	3	C=C (vinyl)		1635	1635
49	1618	480	C=C (AB), C-C (BC)		1609	1611
50	1611	189	C=C (CD)		1606	1610
51	1594	1285	C=C (AB), C-C (B)		1587	1582
52	1561	208	C=C (D), N-H ip (B,C)		1558	1561
53	1556	169	C=C (D), N-H ip (B,C)		1062	1556
54	1546	1215	C-C (B)		1543	1542
55	1526	143	N-H ip (C), C-C (AB)		1038	1523
56	1500	179	C-C (C), N-C (C)		1502	1500

2. ***Phycocyanobilin molecule***

Table 2.1 : Calculated normal modes for the ***ZZZasa*** configuration of PCB chromophores

Mode	freq.(n.a.) (cm^{-1})	IR int. (km/mol)	PED		freq. (N-D) (cm^{-1})	freq. ($^{13}C5$) (cm^{-1})	freq. (^{15}N) (cm^{-1})
46	1775	603	C=O (A)		1772	1775	1776
47	1766	145	C=O pps		1766	1766	1766
48	1741	843	C=O (D)		1738	1741	1742
49	1737	290	C=O pps		1736	1737	1737
50	1644	816	C=C (AB)		1638	1622	1645
51	1634	471	C=C (CD)		1630	1634	1634
52	1629	3	C=C (D)		1628	1629	1628
53	1602	2157	C-C (BC), CH rock (BC)		1595	1600	1601
54	1567	117	N-H ip (B,C)			1566	1558
55	1525	21	C-C (C)		1524	1525	1523
56	1516	127	C-C (B)		1515	1516	1515
57	1514	336	N-H ip (B,C)			1513	1505

Table 2.2 : Calculated normal modes for the ***ZZZssa*** configuration of PCB chromophores

Mode	freq.(n.a.) (cm^{-1})	IR int. (km/mol)	PED		freq. (N-D) (cm^{-1})	freq. ($^{13}C5$) (cm^{-1})	freq. (^{15}N) (cm^{-1})
46	1782	289	C=O (A)		1778	1782	1782
47	1754	130	C=O pps		1754	1754	1754
48	1742	502	C=O pps		1742	1742	1472
49	1739	643	C=O (D)		1735	1739	1740
50	1634	145	C=C (CD)		1632	1636	1636
51	1627	2	C=C (D)		1627	1627	1627
52	1622	584	C=C (AB), C-C (BC), CH rock (BC)		1614	1617	1620
53	1596	1403	C-C (B), C=C (AB)		1589	1586	1594
54	1558	410	N-H ip (B,C)		1063	1556	1551
55	1545	1046	C-C (B)		1545	1540	1541
56	1523	51	N-H ip (B,C)		1055	1521	1515
57	1501	111	C-C (C)		1504	1501	1500

Table 2.3 : Calculated normal modes for the ***ZZEasa*** configuration of PCB chromophores

Mode	freq.(n.a.) (cm^{-1})	IR int. (km/mol)	PED		freq. (N-D) (cm^{-1})	freq. ($^{13}C5$) (cm^{-1})	freq. (^{15}N) (cm^{-1})
46	1778	587	C=O (A)		1772	1775	1776
47	1758	142	C=O pps		1758	1758	1758
48	1743	816	C=O (D)		1740	1743	1744
49	1740	295	C=O pps		1739	1740	1740
50	1642	931	C=C (AB)		1636	1621	1643
51	1620	292	C=C (CD)		1617	1620	1621
52	1613	16	C=C (D)		1612	1613	1613
53	1603	2214	C-C (BC), CH rock (BC)		1596	1601	1062
54	1564	140	N-H ip (B,C)			1563	1555
55	1530	83	C-C (B)		1529	1529	1528
56	1515	317	N-H ip (B,C)			1514	1507
57	1511	94	C-C (B)		1511	1511	1511

Table 2.4 : Calculated normal modes for the ***ZZEssa*** configuration of PCB chromophores

Mode	freq.(n.a.) (cm^{-1})	IR int. (km/mol)	PED		freq. (N-D) (cm^{-1})	freq. ($^{13}C5$) (cm^{-1})	freq. (^{15}N) (cm^{-1})
46	1784	291	C=O (A)		1780	1784	1784
47	1774	191	C=O pps		1774	1774	1774
48	1761	254	C=O pps		1761	1761	1761
49	1741	908	C=O (D)		1737	1741	1442
50	1620	84	C=C (CD)		1617	1620	1621
51	1619	613	C=C (AB), C-C (BC)		1613	1614	1617
52	1614	28	C=C (D)		1610	1611	1614
53	1593	1258	C-C (B), C=C (AB)		1587	1584	1591
54	1557	350	N-H ip (B,C)			1556	1549
55	1542	1122	C-C (B)		1542	1538	1540
56	1521	66	N-H ip (B,C)			1519	1513
57	1506	206	C-C (C)		1507	1506	1504