Supporting Information:

Exploring Electronic Energy Level Structure and Excited Electronic States of β-carotene by DFT

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To obtain electron density difference diagram, we get the wave function information of the specified excited states, grid the wave function in real space, and subtract the electron densities of the corresponding states we cared. For the electron-hole analysis, first read the single excitation configuration function, and calculate the density of electrons and holes separately,

$$\rho^{hole}(\vec{r}) = \rho^{hole}_{(loc)}(\vec{r}) + \rho^{hole}_{(cross)}(\vec{r})$$

$$\rho^{hole}_{(loc)}(\vec{r}) = \sum_{i\to a}(\omega_i^a)^2 \varphi_i\varphi_i - \sum_{i\leftarrow a}\left(\omega_i^{'a}\right)^2 \varphi_i\varphi_i$$

$$\rho^{hole}_{(cross)}(\vec{r}) = \sum_{i\to a}\sum_{j\neq i\to a}\omega_i^a\omega_j^a\varphi_i\varphi_j - \sum_{i\leftarrow a}\sum_{j\neq i\leftarrow a}\omega_i^{'a}\omega_j^{'a}\varphi_i\varphi_j$$

Where r is the coordinate vector, φ is the orbital wave number, i and j are the occupied orbitals, a and b are the empty orbitals, ω is the coefficient of configuration function. This definition satisfies that the integral value of both holes and electrons in the whole space is 1. This analysis method was originally mentioned in the article Carbon, 165, 461-467 (2020). Next, the overlap degree of holes and electrons Sr, the distance of centroid between hole and electron D and the degree of dispersion σ were calculated to describe the electron-hole distribution and electron excitation types between different electron excited states.

$$S_r = \int S_r(\vec{r})d\vec{r} \equiv \int\sqrt{\rho^{hole}(\vec{r})\rho^{ele}(\vec{r})}d\vec{r}$$

$$D_x = \left|X_{ele} - X_{hole}\right| \qquad D_y = \left|Y_{ele} - Y_{hole}\right| \qquad D_z = \left|Z_{ele} - Z_{hole}\right|$$

$$\mathrm{D} = \sqrt{(D_x)^2 + (D_y)^2 + (D_z)^2}$$

$$\sigma_{hole,x} = \sqrt{\int \left(x - X_{hole}\right)^2 \rho^{hole}\left(\vec{r}\right) d\vec{r}}$$

where ρhole is the density of holes, ρele is the density of electrons, $\vec{r}$ is the coordinate vector, Xele, Yele and Zele are the electron's centroid X, Y, Z coordinate, respectively, Xhole, Yhole and Zhole are the hole's centroid X, Y, Z coordinate, respectively.

The parameters Sr, D and σ are all important for describing the electron-hole population, and they represent different properties. As the formula shows, Sr is related to the density distribution of electrons and holes in space, and it is a function that describes the degree of overlap between electron and hole distributions. The range of Sr is [0,1], Sr = 0 means that the electron and hole do not overlap, and Sr = 1 means that the electron and hole overlap completely. D is the distance between the hole and the electron's center of mass, a large value of D indicates the separation of the hole and the electron centroid. σ is the root-mean-square deviation of electron and hole distribution, reflects the width of electron - hole population. Both D and σ have the unit Å. For global excitation or local excitation, the main population ranges of holes and electrons are very close, and the overlap degree is large. The population ranges of holes and electrons are not obviously separated, and the distribution breadth is close. Therefore, Sr is large, D and σ are small. For single-direction charge transfer excitation, the distance between electron and hole must be large, and the overlap degree and distribution width cannot be determined. Therefore, D is large, Sr and σ not necessarily. For centrosymmetric charge transfer excitation, charge transfer can be carried out in many directions, and the breadth of population is large. Therefore, D is small, σ is large.

As for the transition density matrix (TDM) heatmap, the real space form T(r;r') of the TDM between the ground state and the excited state can be expressed as

$$T\left(\vec{r};\vec{r'}\right)\equiv T\left(\vec{r_1};\vec{r_1'}\right)$$
$$=\int\phi^0\left(X_1,X_2,\ldots,X_N\right)\psi^{exc}\left(X_1',X_2,\ldots,X_N\right)d\sigma_1 dX_2 dX_3\ldots dX_N$$

For single reference state method,

$$T\left(\vec{r};\vec{r'}\right)=\sum_i\sum_a\omega_i^a\varphi_i\left(\vec{r}\right)\varphi_a\left(\vec{r'}\right)$$

Where ϕ^0 is the ground state wave function, ψ^{exc} is an excited state wave function, σ is the spin coordinates, r is the space coordinates, a and i are the numbers of empty orbits and occupied orbits, respectively, and ω is the coefficient of the configuration function. We constructed the TDM in this way, and it was used to examine which regions of the system contribute to the transition probability between two states.

The calculated peak of the absorption spectrum should correspond to the 0-0 peak in the experiment since coupling was not considered in the quantitative calculations. The UV-Vis absorption spectrum of β-carotene dissolved in the chloroform solution obtained by experimental and theoretical calculations are shown in Fig.2. The calculation results of functionals CAM-B3LYP and wB97XD were the same as the experimental results. CAM-B3LYP was a long-range correction version of the functional B3LYP, and it was more commonly used in organic large-scale conjugate systems[34]. The subsequent calculations of the β-carotene excited state were performed using the CAM-B3LYP functional.

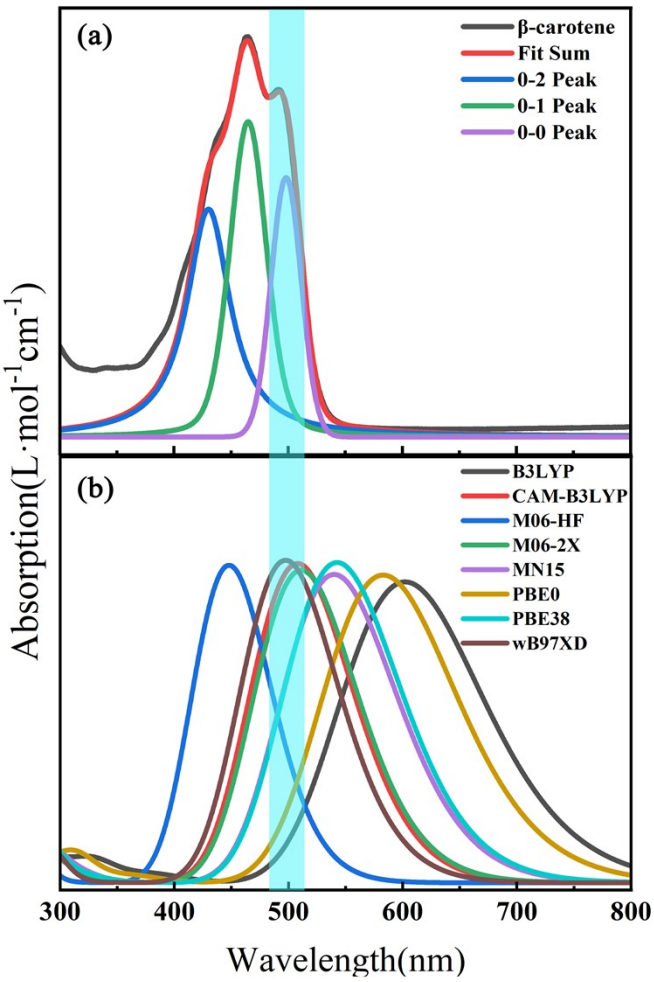

Figure S1. UV-Vis absorption spectrum of β-carotene dissolved in chloroform solution obtained by experimental (a) and theoretical calculations (b). The basis set selected for calculation is def-TZVP.

Table S1. The position of the maximum absorption peak of functionals.

Functional	Peak(nm)	Functional	Peak(nm)
M06-HF	447	MN15	539
ωB97XD	497	PBE38	542

CAM-B3LYP	509	PBE0	583
M06-2X	514	B3LYP	603

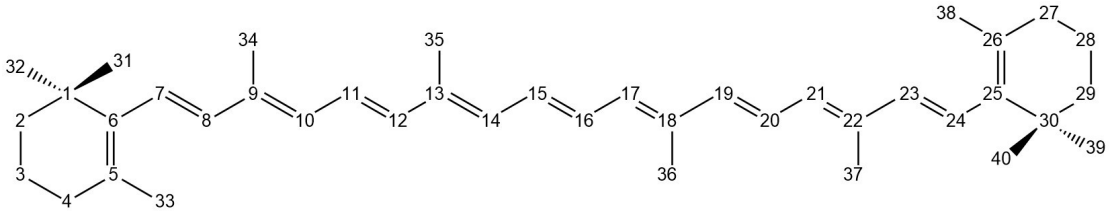

Figure S2. Chemical structure diagram of β-carotene.

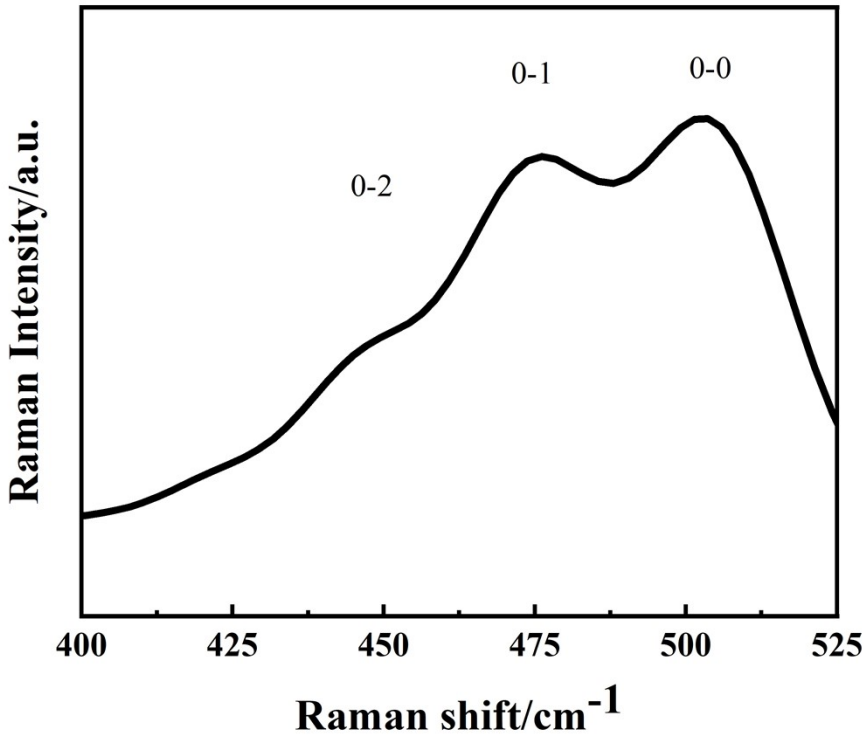

Figure S3. The vibration-resolved UV-Vis absorption spectrum

Table S2. Numerical data for the excited states

Exc.state	Exc.energy(eV)	Multi.	MO pairs	Normalization
2	2.49850	1	20242	0.500004
3	3.54040	1	21390	0.499998
4	3.88800	1	13162	0.499995
5	4.29560	1	20405	0.500000
6	4.66040	1	18303	0.499998
7	4.85060	1	19122	0.500006
8	5.19610	1	16869	0.499997
9	5.23170	1	17485	0.499998
10	5.40450	1	20377	0.500006

The β-carotene atomic coordinates of the ground state

1	6	-0.000002898	0.000000695	-0.000001050
2	6	0.000000779	0.000003579	-0.000000707
3	6	0.000000836	0.000001729	-0.000003530
4	6	-0.000004074	0.000006558	-0.000001615
5	6	0.000006519	-0.000006146	0.000006249
6	6	0.000002635	-0.000000926	-0.000001899

7	6	0.000004812	-0.000003660	0.000001838
8	6	-0.000003444	-0.000000053	-0.000004298
9	6	-0.000000500	0.000001590	0.000004816
10	6	0.000006366	0.000001961	-0.000000293
11	6	0.000003307	-0.000004394	-0.000002811
12	6	-0.000006997	-0.000000088	0.000000645
13	6	0.000001203	0.000000890	0.000001716
14	6	0.000003841	0.000000706	0.000000203
15	6	0.000003718	-0.000003442	-0.000000428
16	6	-0.000000889	0.000004619	-0.000001164
17	6	-0.000004660	-0.000002104	0.000002259
18	6	-0.000003577	-0.000000497	-0.000003044
19	6	0.000007524	0.000001552	-0.000000755
20	6	-0.000001816	0.000005747	-0.000001446
21	6	-0.000006721	-0.000004003	0.000001924
22	6	0.000000977	-0.000001111	0.000001185
23	6	0.000002229	-0.000000339	-0.000000196
24	6	-0.000008436	0.000008247	0.000005425
25	6	0.000001962	-0.000005048	-0.000007951
26	6	0.000002827	0.000003628	-0.000000921
27	6	0.000001369	-0.000003590	0.000001832
28	6	-0.000001922	-0.000002324	-0.000002405
29	6	-0.000000660	-0.000002780	-0.000000154
30	6	0.000000400	0.000001002	0.000003000
31	6	-0.000000525	-0.000000942	-0.000001761
32	6	0.000000287	-0.000002291	-0.000000131
33	6	-0.000003892	-0.000003574	0.000001503
34	6	-0.000003559	-0.000000394	-0.000002549
35	6	-0.000002734	0.000000295	-0.000001112
36	6	0.000001625	-0.000001231	0.000000117
37	6	0.000001747	-0.000000485	-0.000003714
38	6	-0.000000868	0.000000362	0.000003440
39	6	0.000001199	0.000001092	-0.000001941
40	6	0.000000055	0.000002118	-0.000000138
41	1	-0.000001410	-0.000000469	0.000000653
42	1	0.000002291	-0.000000457	-0.000001072
43	1	-0.000000500	-0.000000584	0.000000881
44	1	0.000000258	0.000001046	0.000000959
45	1	0.000000259	0.000000420	-0.000000281
46	1	0.000000396	0.000000620	-0.000001115
47	1	0.000000699	0.000000555	-0.000001685
48	1	0.000000696	-0.000000297	-0.000001359
49	1	-0.000000136	0.000000237	0.000000248
50	1	0.000000088	0.000000762	0.000000087
51	1	0.000000740	0.000001006	0.000000034
52	1	-0.000000170	0.000000553	-0.000000021
53	1	-0.000001711	0.000000260	0.000000189
54	1	-0.000001727	0.000001251	0.000000350
55	1	-0.000001291	-0.000000851	0.000000179
56	1	-0.000003768	0.000003719	0.000002919

57	1	-0.000000370	0.000002047	0.000002535
58	1	0.000000285	0.000001783	-0.000000715
59	1	-0.000001060	0.000000324	0.000000861
60	1	0.000000311	-0.000000466	0.000000588
61	1	0.000000918	0.000000772	-0.000000456
62	1	-0.000000387	-0.000000328	0.000000010
63	1	0.000002161	0.000001456	0.000001862
64	1	0.000000413	-0.000000294	0.000000092
65	1	-0.000000254	0.000001082	-0.000001145
66	1	0.000000888	0.000000995	0.000001069
67	1	0.000001004	0.000000021	-0.000000872
68	1	0.000000155	0.000000468	0.000000386
69	1	-0.000000089	-0.000000627	0.000000980
70	1	-0.000000721	-0.000001902	-0.000000030
71	1	-0.000000448	0.000000553	0.000001813
72	1	-0.000000150	-0.000000963	-0.000000399
73	1	-0.000000451	-0.000000302	0.000000552
74	1	-0.000001155	-0.000001562	0.000002642
75	1	0.000000819	0.000000307	-0.000000521
76	1	-0.000001506	-0.000001001	-0.000000860
77	1	0.000000277	-0.000000471	0.000000993
78	1	0.000000477	0.000000957	0.000001449
79	1	0.000001551	0.000000621	-0.000000019
80	1	0.000000857	0.000001067	-0.000000689
81	1	0.000001058	-0.000000661	-0.000000984
82	1	0.000001634	0.000000803	-0.000000635
83	1	0.000000191	-0.000000735	-0.000000240
84	1	0.000001212	-0.000000165	0.000000616
85	1	-0.000000002	-0.000000643	-0.000000317
86	1	-0.000001576	0.000002165	-0.000000029
87	1	0.000000744	0.000000107	0.000000691
88	1	0.000000111	-0.000001257	0.000000772
89	1	-0.000000150	-0.000000533	-0.000000168
90	1	-0.000001293	-0.000001757	0.000000532
91	1	-0.000000909	-0.000000050	-0.000001622
92	1	-0.000000764	0.000000028	0.000000261
93	1	-0.000000193	-0.000000653	0.000000035
94	1	0.000001375	-0.000000072	0.000000053
95	1	0.000002921	-0.000003673	0.000000355
96	1	-0.000000644	-0.000002158	-0.000000549

The β-carotene atomic coordinates of the first excited state

1	6	-0.000003822	0.000004930	-0.000007809
2	6	-0.000002571	-0.000003241	0.000010444
3	6	-0.000001860	-0.000002616	-0.000002635
4	6	0.000006018	-0.000009357	0.000001134
5	6	0.000004941	0.000001549	-0.000000467
6	6	-0.000007561	0.000019617	-0.000001086

7	6	-0.000004870	-0.000004903	0.000007516
8	6	0.000017920	0.000006554	-0.000006810
9	6	0.000000410	-0.000011562	-0.000006392
10	6	-0.000006124	0.000008475	0.000003883
11	6	0.000003485	0.000000475	0.000000126
12	6	0.000008043	-0.000017917	0.000005530
13	6	0.000002976	0.000007117	0.000003872
14	6	-0.000000483	0.000010909	-0.000004119
15	6	-0.000002490	0.000003000	0.000007589
16	6	0.000004547	-0.000002361	0.000006754
17	6	-0.000000208	-0.000011262	-0.000003023
18	6	-0.000002123	-0.000006924	0.000005493
19	6	-0.000005423	0.000018712	0.000005875
20	6	-0.000004274	-0.000000867	0.000001521
21	6	0.000008547	-0.000007536	0.000002500
22	6	-0.000004051	0.000009821	-0.000006236
23	6	-0.000014105	-0.000002620	-0.000004017
24	6	0.000003131	0.000004244	0.000003850
25	6	0.000003324	-0.000012040	-0.000005459
26	6	0.000001026	-0.000009241	0.000001596
27	6	-0.000004266	0.000010994	0.000002061
28	6	0.000000845	0.000003098	-0.000003215
29	6	0.000005925	0.000003819	0.000008967
30	6	0.000001704	-0.000005494	-0.000004927
31	6	0.000000380	-0.000001573	-0.000005473
32	6	0.000000752	0.000002970	0.000001536
33	6	-0.000002736	0.000001892	-0.000002078
34	6	0.000002991	0.000003504	0.000008034
35	6	0.000008954	-0.000002947	0.000004768
36	6	-0.000007245	0.000003536	0.000006794
37	6	-0.000000651	-0.000002628	0.000008398
38	6	-0.000001764	-0.000002880	0.000003810
39	6	-0.000000533	0.000000980	-0.000004136
40	6	-0.000000320	-0.000002838	0.000001368
41	1	0.000003875	-0.000000732	0.000000643
42	1	-0.000000745	0.000000457	-0.000000632
43	1	-0.000000395	0.000000247	-0.000000375
44	1	0.000001012	0.000002706	-0.000002570
45	1	-0.000000066	0.000000012	-0.000000801
46	1	0.000000940	0.000003471	-0.000003487
47	1	0.000000429	0.000000112	0.000000390
48	1	-0.000001586	0.000000331	0.000000096
49	1	0.000000783	-0.000001307	-0.000001451
50	1	-0.000000628	-0.000000432	0.000001392
51	1	0.000001343	0.000001469	-0.000000154
52	1	0.000001849	0.000002034	0.000001588
53	1	-0.000003208	-0.000004942	-0.000004978
54	1	0.000000159	-0.000004929	0.000002686
55	1	-0.000003383	-0.000003499	-0.000001676
56	1	0.000001201	-0.000003148	0.000005880

57	1	-0.000002922	0.000002992	0.000008435
58	1	-0.000000475	-0.000000557	0.000001191
59	1	0.000006165	0.000003362	-0.000001628
60	1	-0.000004736	0.000000307	-0.000002035
61	1	-0.000005010	0.000000759	-0.000005092
62	1	0.000008180	0.000000377	-0.000005444
63	1	-0.000002408	-0.000000944	-0.000000997
64	1	-0.000004319	0.000002514	0.000000412
65	1	0.000001135	-0.000003354	-0.000003611
66	1	-0.000004987	0.000002517	-0.000002808
67	1	-0.000008222	0.000003453	-0.000003333
68	1	0.000004045	-0.000009662	-0.000001592
69	1	-0.000004465	0.000009514	-0.000001300
70	1	0.000006917	-0.000003871	-0.000005229
71	1	0.000004012	-0.000002842	-0.000003871
72	1	-0.000002206	0.000003025	-0.000003311
73	1	0.000004433	-0.000002673	-0.000000507
74	1	0.000002131	0.000000917	-0.000001696
75	1	-0.000009433	-0.000000774	-0.000002730
76	1	0.000003301	-0.000001323	-0.000006314
77	1	0.000004268	0.000002652	0.000002161
78	1	0.000003938	-0.000000585	-0.000003407
79	1	-0.000003633	0.000001088	0.000001799
80	1	0.000002403	0.000001455	-0.000002356
81	1	0.000000262	0.000004538	0.000001211
82	1	-0.000000557	-0.000001051	-0.000001460
83	1	-0.000001231	-0.000001962	0.000002260
84	1	-0.000001133	-0.000001446	0.000000338
85	1	0.000000875	0.000000609	0.000001142
86	1	0.000000725	-0.000000503	-0.000000616
87	1	0.000000322	-0.000000361	-0.000000313
88	1	-0.000001649	-0.000003103	-0.000001843
89	1	-0.000000126	0.000000011	-0.000000885
90	1	-0.000001406	-0.000003645	-0.000002117
91	1	-0.000000144	0.000000499	0.000000973
92	1	0.000001688	-0.000000242	-0.000000102
93	1	-0.000000999	0.000001012	-0.000001347
94	1	-0.000006377	-0.000003433	0.000000455
95	1	0.000000819	0.000002865	0.000002861
96	1	0.000000797	0.000000627	0.000000618