Supporting Information for
Revealing ultrafast vibronic dynamics of tetracene molecules with sub-8-fs UV impulsive Raman spectroscopy

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Table S1. Calculated vibrational modes of tetracene in S_0 state

Vibrational Mode	Wave number(cm^{-1})	IR	Raman	Symmetry
1	51.23	1.1833	0	B_{3u}
2	89.2	0	0	A_u
3	152.36	0	3.9983	B_{1g}
4	163	2.6408	0	B_{1u}
5	193.06	0	0.6286	B_{2g}
6	278.3	1.4942	0	B_{3u}
7	307.5	0	9.0769	B_{3g}
8	317.23	0	53.8381	A_g
9	327.81	0	0	A_u
10	389.7	0	1.6347	B_{1g}
11	451.25	0.0905	0	B_{1u}
12	475.06	61.6483	0	B_{3u}
13	485.62	0	12.5719	B_{1g}
14	500.75	0	83.0758	B_{3g}
15	501.59	2.8437	0	B_{3u}
16	527.01	0	0.4744	B_{2g}
17	557.96	22.8057	0	B_{2u}
18	571.98	0	0	A_U
19	611.56	3.672	0	B_{1u}
20	625.42	0	18.5383	A_g
21	634.32	1.8407	0	B_{2u}
22	749.94	0	0.1819	B_{2g}
23	752.24	0	9.4406	B_{1g}
24	756.15	0.5233	0	B_{2u}
25	765.34	0	445.9083	A_g

26	766.08	154.7376	0	B_{3u}
27	775.85	0	1.6138	B_{3g}
28	785.15	0	0	A_u
29	787.86	0	0.5394	B_{2g}
30	854.96	0	0	A_u
31	866.57	0	0.3124	B_{2g}
32	872.57	0	5.9719	A_g
33	886.12	0	0.2471	B_{1g}
34	895.52	0	1.7837	B_{3g}
35	913.37	0	0	A_u
36	929.29	4.2219	0	B_{1u}
37	936.53	119.5096	0	B_{3u}
38	937.49	0	13.5505	B_{2g}
39	989.04	0	26.7823	B_{1g}
40	989.47	15.0724	0	B_{3u}
41	1011.01	0	11.2552	B_{2g}
42	1011.83	0	0	A_U
43	1013.08	23.4053	0	B_{2u}
44	1016.13	0	245.4923	A_g
45	1124.25	1.8438	0	B_{2u}
46	1142.53	13.3833	0	B_{1u}
47	1144.93	0	0.4102	B_{3g}
48	1170.91	0	109.2491	A_g
49	1178.02	0.8815	0	B_{2u}
50	1190.63	0	297.3627	B_{3g}
51	1213.79	2.1575	0	B_{1u}
52	1222.8	0	924.5528	A_g

53	1283.47	0	0.6285	B_{3g}
54	1295.73	1.3931	0	B_{1u}
55	1314.02	13.9203	0	B_{1u}
56	1320.76	1.4555	0	B_{2u}
57	1346.98	15.6415	0	B_{2u}
58	1348.12	0	5.3757	B_{3g}
59	1402.15	3.3937	0	B_{1u}
60	1425.16	0	6061.727	A_g
61	1441.81	0	956.092	A_g
62	1452.92	6.7918	0	B_{2u}
63	1469.55	0	13.2278	B_{3g}
64	1470.66	0	3653.623	A_g
65	1492.39	3.8456	0	B_{2u}
66	1561.06	0	45.8382	A_g
67	1590.57	13.2701	0	B_{2u}
68	1593.14	0	1111.578	A_g
69	1607.05	0.4127	0	B_{1u}
70	1656.81	0	232.5159	B_{3g}
71	1670.19	0	563.5572	B_{3g}
72	1681.82	6.6529	0	B_{1u}
73	3184.53	0	13.3233	B_{3g}
74	3185.57	9.2356	0	B_{1u}
75	3186.09	2.1054	0	B_{2u}
76	3187.22	0	540.1064	A_g
77	3187.46	0	4.5357	B_{3g}
78	3187.67	9.518	0	B_{1u}
79	3190.55	5.2398	0	B_{2u}

80	3190.67	0	714.1974	A_g
81	3205.59	36.8289	0	B_{1u}
82	3205.65	0	483.7045	B_{3g}
83	3217.1	37.8934	0	B_{2u}
84	3217.19	0	1531.766	A_g

Table S2. Calculated vibrational modes of tetracene in S_1 state

Vibrational Mode	Wave number(cm^{-1})	IR	Raman	Symmetry
1	47.05	1.4707	0.0057	B_{3u}
2	81.03	0.0000	1.2564	A_u
3	144.56	0.0000	9.4165	
4	157.02	2.8685	0.0373	
5	188.47	0.0000	2.1707	B_{2g}
6	281.95	2.1365	0.9397	B_{3g}
7	299.45	0.0000	96.5829	B_{3g}
8	308.94	0.0000	5.0492	B_{3g}
9	314.12	0.0000	886.9173	A_g
10	354.33	0.0000	11.6684	B_{1g}
11	432.53	44.2171	3.3058	B_{3u}
12	444.50	1.0524	0.1223	
13	469.92	8.6656	9.5597	
14	471.04	0.0000	21.2827	
15	487.33	0.0012	13.1906	
16	543.82	0.0002	0.2921	
17	549.34	53.4212	0.0136	
18	558.08	0.0001	0.4984	

19	606.86	25.2423	0.3444	
20	616.44	0.0094	5.5898	
21	616.72	0.0938	0.7375	
22	728.67	0.0000	0.4597	B_{2g}
23	742.31	0.0000	208.2723	B_{1g}
24	745.67	172.5310	0.7359	B_{3u}
25	754.62	0.0001	134.7290	
26	756.68	0.0000	3.0530	
27	764.33	172.0530	0.0631	B_{2u}
28	774.38	0.0000	7.0086	
29	779.15	0.0001	0.8461	
30	812.09	0.0000	1.1924	A_u
31	853.92	0.0000	1.8400	B_{2g}
32	854.90	0.0000	283.0582	B_{1g}
33	882.15	0.0000	3732.6041	
34	885.85	0.0003	19.8547	
35	898.22	0.0000	2.8756	A_u
36	902.36	108.8222	1.5273	B_{3u}
37	924.40	0.0000	31.5746	
38	925.52	0.0256	0.1107	
39	950.52	0.0000	77.6866	B_{1g}
40	950.73	31.7649	0.0617	B_{3u}
41	990.80	0.0000	1.2022	B_{2g}
42	991.21	0.0000	0.2091	A_u
43	1045.47	39.6691	0.1226	
44	1046.61	0.0020	2895.6678	
45	1120.23	11.0918	0.0847	

46	1123.85	0.0006	550.9574	
47	1158.01	12.6696	0.0242	B_{2u}
48	1168.91	0.0002	581.3734	
49	1171.83	0.0004	25.2331	
50	1187.34	39.6199	0.0947	
51	1225.27	0.2981	0.0366	
52	1238.19	0.0001	27144.0069	A_g
53	1281.20	0.0002	3.4485	
54	1298.32	20.0610	0.0352	
55	1298.48	1.3128	0.6302	
56	1302.31	16.0362	0.5426	
57	1316.10	0.0001	0.5656	
58	1353.91	5.1321	0.1819	
59	1403.25	0.0000	9872.3271	
60	1411.44	17.0556	0.0336	
61	1412.49	6.2387	0.2245	
62	1451.29	0.0018	166956.2251	
63	1457.58	0.0008	459.3484	
64	1469.90	0.0000	462.2450	A_g
65	1509.47	99.9146	117.3624	
66	1509.67	61.2058	197.6797	
67	1543.04	4.8955	0.2126	
68	1546.41	0.0002	22419.4896	
69	1578.90	19.0928	1.1560	
70	1593.12	0.0006	26397.2259	
71	1616.36	0.0000	3569.8545	
72	1631.59	2.2376	0.3695	

73	3182.02	0.0015	201.5648	
74	3182.56	8.6119	0.1826	
75	3184.09	14.6100	0.1788	
76	3184.99	0.0039	615.4750	
77	3190.07	0.0000	250.1573	B_{3g}
78	3190.12	11.2245	0.0620	B_{1u}
79	3192.82	0.0047	3003.4783	
80	3192.84	0.3594	40.4598	
81	3207.62	0.0176	1342.0560	
82	3207.63	22.7657	1.0990	
83	3221.53	84.8577	0.0024	B_{2u}
84	3221.77	0.0000	3110.6213	A_g

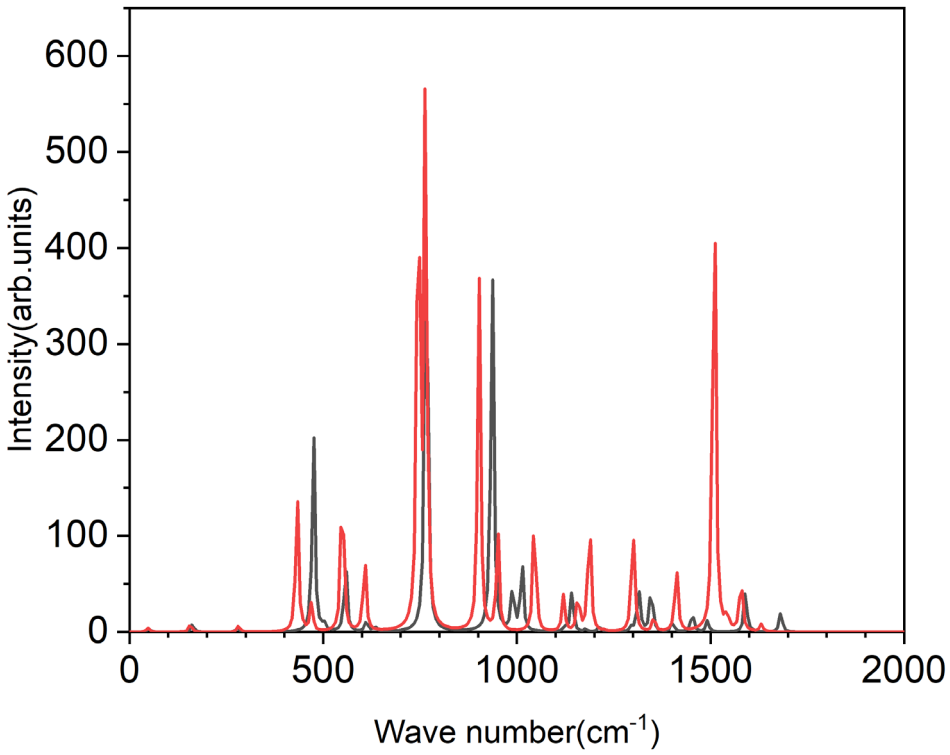

Fig. S1. Simulated IR absorption spectra of tetracene in the S_0 (black) and S_1 (red) state

Tables S3 Shift vector and Huang Rhys factors

Vibrational mode #	Shift Vector(atomic units)	Huang-Rhys Factor
1	-8.37599E-14	8.18743E-31
2	1.21136E-11	2.98197E-26
3	6.07627E-14	1.28151E-30
4	-8.04812E-10	2.40533E-22
5	-4.29316E-12	8.10641E-27
6	-7.91445E-13	3.97137E-28
7	-1.49528E-8	1.56628E-19
8	19.1527	0.26511
9	-1.69344E-10	2.14167E-23
10	3.46674E-13	1.06698E-28
11	5.98357E-10	3.68062E-22
12	5.3822E-14	3.13511E-30
13	-1.59743E-12	2.82309E-27
14	4.22089E-10	2.03245E-22
15	4.2301E-13	2.04472E-28
16	-1.50519E-12	2.7201E-27
17	-1.43402E-6	2.61396E-15
18	3.54531E-12	1.63786E-26
19	-2.01439E-9	5.65342E-21
20	-4.79052	0.0327
21	-1.60201E-5	3.7087E-13
22	-6.06203E-11	6.27834E-24
23	2.2803E-13	8.91096E-29
24	8.43228E-6	1.22486E-13
25	-4.73334	0.03906
26	-1.14476E-11	2.28711E-25
27	5.48662E-10	5.32072E-22
28	7.87954E-11	1.11056E-23
29	-2.83389E-11	1.44146E-24
30	-3.95721E-12	3.05006E-26
31	-2.70074E-12	1.43997E-26
32	1.30927	0.00341
33	8.54559E-13	1.47421E-27

34	1.95315E-10	7.78274E-23
35	1.3357E-11	3.71236E-25
36	-2.55451E-11	1.3815E-24
37	-1.48182E-13	4.68487E-29
38	2.38449E-12	1.21435E-26
39	5.22064E-13	6.14108E-28
40	-6.28109E-14	8.89319E-30
41	-1.31561E-12	3.98655E-27
42	-8.84038E-11	1.80151E-23
43	-4.49712E-7	4.66763E-16
44	2.35152	0.0128
45	4.51763E-6	5.22723E-14
46	4.8733E-10	6.18161E-22
47	-1.21882E-9	3.87476E-21
48	-5.28587	0.07453
49	-7.05262E-7	1.33487E-15
50	3.47437E-9	3.27427E-20
51	-1.03858E-8	2.98271E-19
52	-7.03686	0.13794
53	-2.33045E-10	1.588E-22
54	1.3244E-9	5.17768E-21
55	3.08875E-10	2.85597E-22
56	-1.10706E-5	3.68768E-13
57	-3.19587E-6	3.13419E-14
58	6.43545E-10	1.27196E-21
59	2.73909E-10	2.39658E-22
60	-11.2344	0.40977
61	3.7612	0.04647
62	1.95986E-6	1.27138E-14
63	4.3036E-9	6.20061E-20
64	5.27251	0.09314
65	-1.26216E-5	5.41618E-13
66	0.28874	2.96504E-4
67	2.95815E-5	3.17087E-12
68	7.96306	0.23014

69	-2.44084E-9	2.18119E-20
70	-1.00559E-9	3.81678E-21
71	1.43262E-9	7.80935E-21
72	-1.44789E-9	8.03223E-21
73	-1.25588E-10	1.14426E-22
74	1.58124E-10	1.81454E-22
75	1.16075E-8	9.77956E-19
76	-0.02011	2.93757E-6
77	5.36044E-10	2.08656E-21
78	-4.63568E-10	1.56058E-21
79	4.40999E-9	1.4136E-19
80	-0.01902	2.62937E-6
81	4.09889E-11	1.22695E-23
82	-4.32221E-11	1.36431E-23
83	5.4607E-9	2.18548E-19
84	-0.16915	2.09701E-4

Table S4 Diagonal components in Duschninsky matrix

Vibrational mode in S_0 state	Vibrational mode in S_1 state	J_{ij}^2
3	3	0.98789
7	7	0.9613
10	10	0.98543
13	13	0.93789
16	16	0.97678
18	18	0.95171
20	20	0.9896
22	22	0.97777
23	23	0.97383
29	29	0.98032
30	30	0.71493
31	31	0.93434
35	35	0.80159

38	38	0.95919
39	39	0.98273
40	40	0.98379
41	41	0.93942
42	42	0.93987
43	43	0.92097
44	44	0.95999
48	48	0.97125
51	51	0.91947
52	52	0.94598
53	53	0.70676
55	55	0.87753
57	57	0.7261
63	63	0.87654
64	64	0.529
68	68	0.19835
71	71	0.23526
72	72	0.94698
73	73	0.86961

Table S5 Off-diagonal components in Duschninsky matrix

Vibrational mode in S_0 state	Vibrational mode in S_1 state	J_{ij}^2
9	8	0.93605
12	11	0.90055
15	14	0.83501
21	19	0.98723
24	27	0.97924
26	24	0.96667
28	26	0.86212
28	30	0.12791
30	26	0.10818
30	35	0.13111
33	32	0.98314
35	30	0.1256

37	36	0.93079
45	47	0.43617
45	50	0.4677
46	45	0.95802
47	46	0.91201
49	47	0.48825
49	50	0.45396
50	49	0.88229
53	57	0.25139
54	56	0.94862
56	54	0.66086
56	58	0.2664
57	53	0.20966
58	61	0.83563
59	60	0.97438
60	62	0.96523
61	59	0.52852
61	64	0.37705
62	54	0.21466
62	58	0.55721
62	69	0.15712
64	59	0.19194
64	68	0.17736
65	66	0.82975
65	69	0.14702
66	59	0.18724
66	68	0.59328
66	70	0.11251
67	58	0.12615
67	66	0.13568
67	69	0.68817
68	70	0.79033
69	67	0.9559
70	65	0.2244
70	71	0.69609

71	65	0.72051
73	77	0.12872
74	75	0.55496
74	78	0.43978
76	73	0.13025
76	77	0.86315
77	75	0.44482
77	78	0.55104
78	76	0.98683
79	80	0.98846
80	79	0.97756
81	82	0.96176
82	81	0.96283

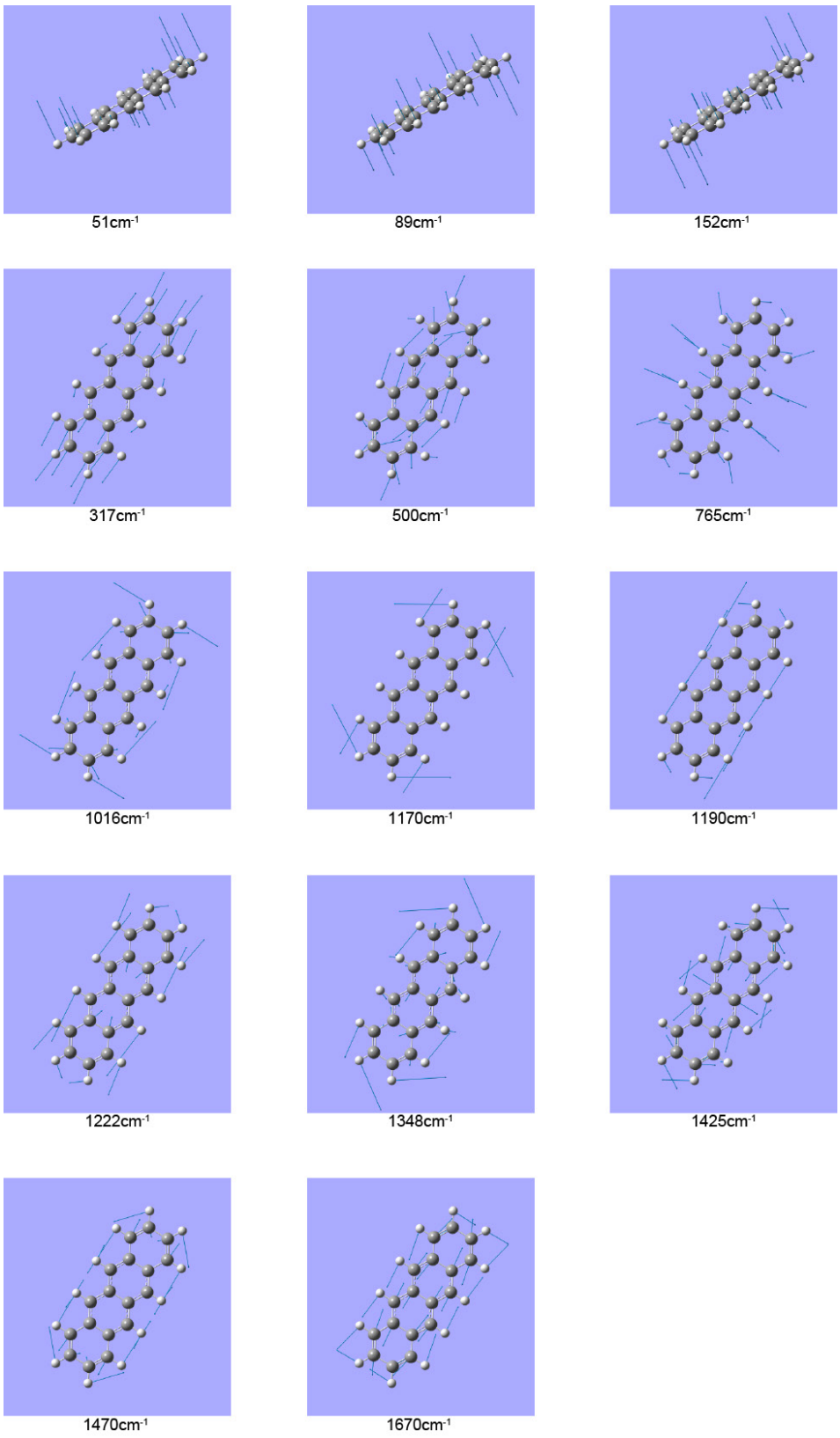

Fig. S2. Vibrational modes of tetracene in S_0 state

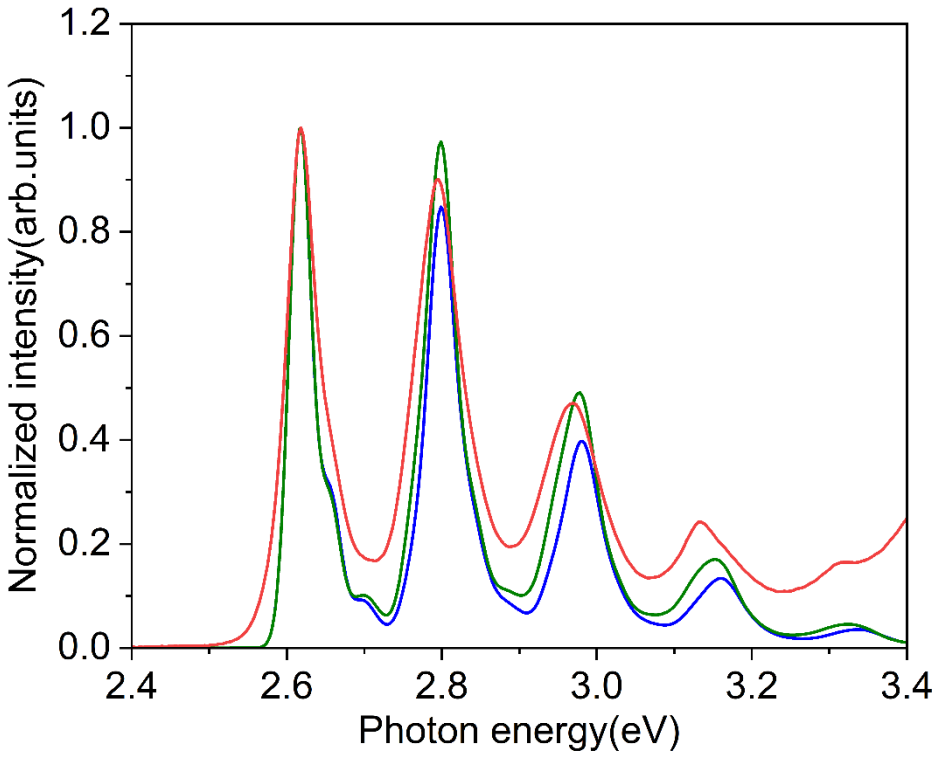

Fig. S3. Simulated vibronic spectra of tetracene in THF solution with FCHT approximation. Experimental result of stationary absorption spectra(Red). The simulation with Duschinsky matrix (Blue) and simulation with identity matrix instead of Duschinsky matrix(Green).

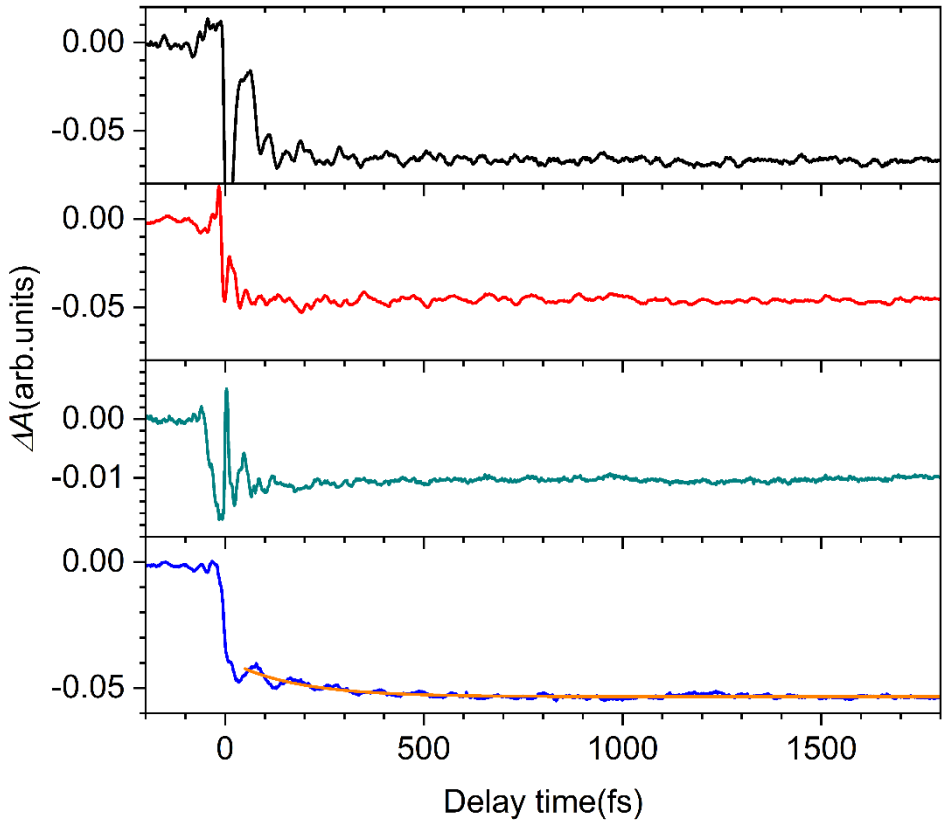

Fig. S4. Real time trace of ΔA of tetracene in THF solution. The traces are the same as in Fig.5(b). The result of exponential fitting is also described in the figure(orange line)

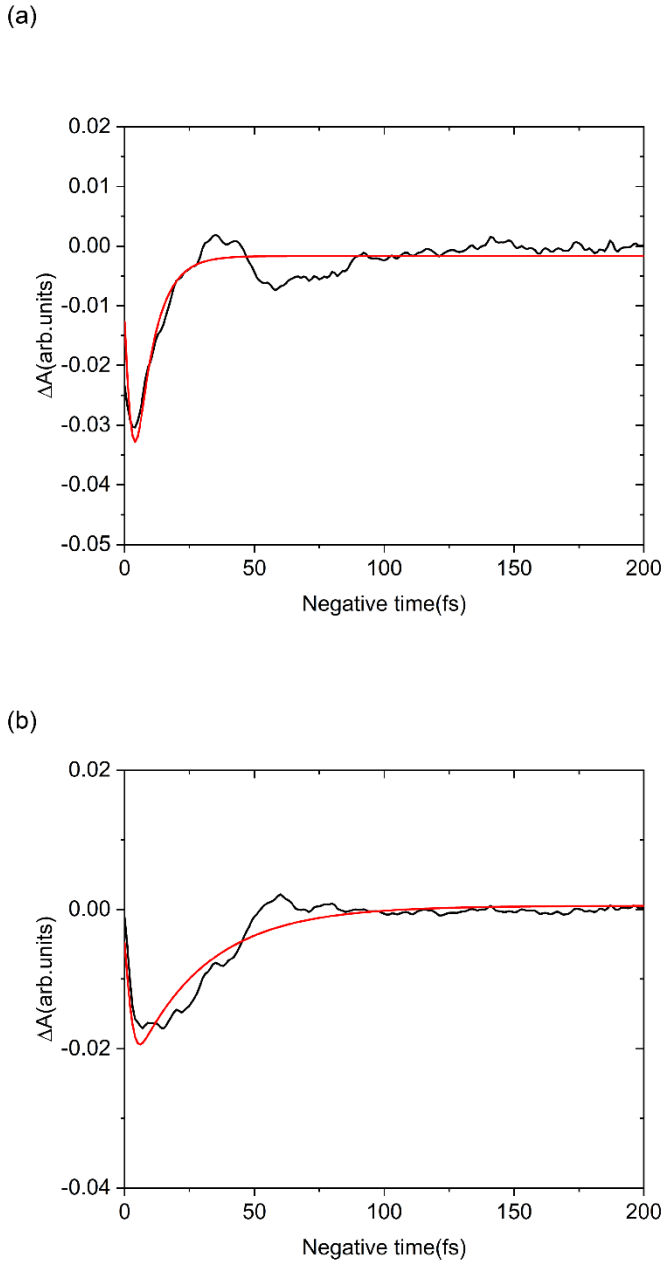

Fig. S5. Perturbed free induction decay signal in the negative time region. Fitting with the convolution of Gaussian function(FWHM 7.5fs) and exponential decay was applied to the time traces of ΔA at the photon energy of (a) 3.279eV and (b) 3.320eV,respectively.

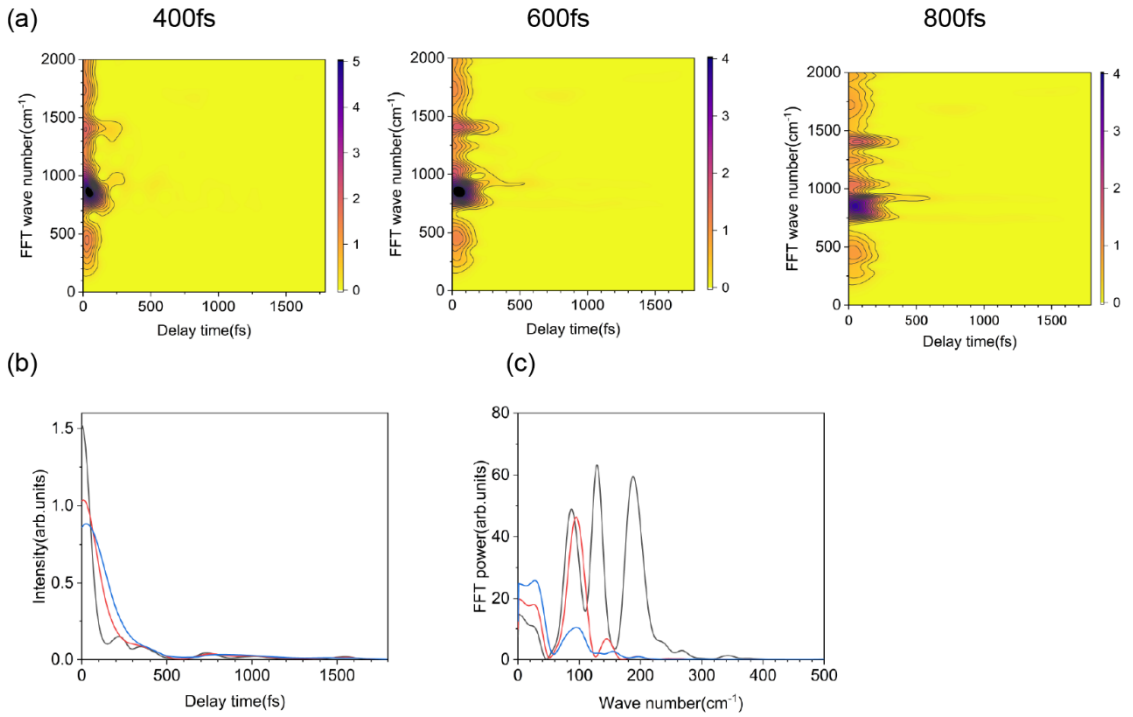

Fig. S6. Spectrogram of tetracene at photon energy of 3.11eV. (a)The spectrograms with window width of 400, 600 and 800 fs are shown(from left to right). (b) Time trace of peak tracking at 1240cm^{-1} signal with 400(black) 600(red) and 800(blue) fs time window. (c) FFT spectra of (b).