Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information – The role of tachysterol in vitamin D photosynthesis – A non-adiabatic molecular dynamics study

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Table 1: Cartesian coordinates of the ground state equilibrium structures of the rotamers optimized by PBE/SVP with the resolution of identity.

	tEt	tEc	cEc	cEt
C	2.3340679 1.4027812 -3.9987101	2.4214169 0.6730639 -4.5658246	-8.1816339 -1.9612960 2.5500567	-9.9460430 -3.8778190 4.0931829
C	3.7227251 1.6499350 -3.4013562	3.4915531 -0.2991711 -4.0593459	-9.4216275 -2.1940631 3.4182460	-10.8080078 -2.6366456 3.8045313
C	4.0695780 0.5202828 -2.4228974	3.9067015 0.0721891 -2.6362118	-9.0529648 -3.0028527 4.6524622	-10.2047845 -1.3408897 4.4014373
C	3.0625076 0.5170317 -1.2663323	2.6922176 -0.0067945 -1.7025063	-8.0202454 -2.2306931 5.4783671	-8.7098033 -1.5149674 4.7392267
C	1.6071944 0.5553322 -1.7209405	1.4186219 0.6306874 -2.2421485	-6.8346282 -1.7040156 4.6706867	-7.9517691 -2.4590676 3.8126941
C	0.5850060 0.1917551 -0.7425759	0.3269539 0.8350312 -1.2955019	-5.6797753 -1.3550938 5.5024813	-6.6297344 -2.0167280 3.3641185
C	0.8113823 -0.1210543 0.5712485	0.3078430 0.4475667 0.0166663	-4.3478010 -1.3578515 5.1905084	-6.0283855 -2.3091675 2.1711540
C	-0.1445833 -0.4866788 1.6125127	-0.7914523 0.6511506 0.9667272	-3.2291454 -1.0087136 6.0764912	-4.7136356 -1.9161603 1.6686445
C	0.3597054 -0.8510448 2.8353907	-1.7077173 1.6586705 0.8616737	-3.3714308 -0.3939324 7.2884780	-4.3261701 -2.4194079 0.4526145
C	1.2828945 0.9538884 -3.0006246	1.3108033 0.9624912 -3.5743859	-6.9324654 -1.5490387 3.3086574	-8.5354183 -3.6767882 3.5714437
C	-0.4408377 -1.2763194 4.0351979	-2.8850954 1.8599205 1.7835931	-2.2452453 -0.0755301 8.2390213	-3.0093089 -2.1726648 -0.2312712
C	-1.9493048 -1.4387328 3.7576607	-2.9087234 0.9241394 3.0150457	-0.8295205 -0.3286331 7.6723599	-1.9895917 -1.4050787 0.6346941
C	-2.4351544 -0.3774477 2.7597003	-2.3513583 -0.4650741 2.6650129	-0.8138955 -1.5597028 6.7524519	-2.6962011 -0.3433262 1.4896082
C	-1.6565652 -0.5756624 1.4216099	-0.8893252 -0.2698644 2.1741034	-1.8132711 -1.2897383 5.5934993	-3.7013314 -1.0697127 2.4360498
C	-2.4425158 0.3058451 0.4201838	-0.3139298 -1.7004636 2.1385192	-1.5154346 -2.4126134 4.5794054	-4.1018696 0.0368141 3.4428158
C	-3.9173612 0.2300127 0.9181057	-1.0254999 -2.4144401 3.3277620	0.0218344 -2.6343714 4.7167866	-2.8188522 0.9124157 3.5781407
C	-3.8953621 -0.5600852 2.2586854	-2.1026720 -1.4215833 3.8675469	0.4921088 -1.7773743 5.9339407	-1.7964164 0.3682789 2.5386162
C	-2.2280998 1.0378703 3.3436263	-3.2389467 -1.1417400 1.5979263	-1.1809360 -2.8293392 7.5514830	-3.4023713 0.6885291 0.5815868
C	-0.1202863 1.0098298 -3.5542029	0.1133527 1.6291527 -4.2048208	-5.8365241 -0.9798572 2.4424534	-7.8941923 -4.8424304 2.8687887
C	-5.0179545 -0.1831341 3.2273622	-3.3260460 -2.1008644 4.4856262	1.6972419 -2.3538059 6.6787828	-0.8118218 1.4167266 2.0183014
O	4.1124369 -0.7474848 -3.0793264	4.9980790 -0.6997999 -2.1500461	-10.2416153 -3.2599734 5.3910064	-10.3132561 -0.2398051 3.4996594
H	-4.9487551 -0.7548413 4.1799099	-3.8309446 -2.7802378 3.7634462	1.9845386 -1.7209069 7.5486989	-0.1891720 1.8169465 2.8494587
H	-6.0132893 -0.4036365 2.7806242	-4.0760253 -1.3562808 4.8348955	2.5829911 -2.4142189 6.0073643	-1.3352066 2.2812190 1.5528023
H	3.1790681 -1.0218084 -3.2212526	4.6933995 -1.6334602 -2.1120769	-9.9788570 -3.7259730 6.2136751	-11.2563412 -0.1704382 3.2372729
H	3.2447241 -0.4007693 -0.6644279	2.4973390 -1.0860631 -1.4770064	-8.5497648 -1.3820946 5.9767957	-8.2533224 -0.5032452 4.7494721
H	3.2655077 1.3758556 -0.5836899	2.9658182 0.4530813 -0.7274123	-7.6436841 -2.8830495 6.3022048	-8.6464768 -1.9078717 5.7819387
H	5.0945151 0.6666668 -2.0178225	4.2904290 1.1179458 -2.6427132	-8.5871047 -3.9659334 4.3125265	-10.7353469 -1.0947502 5.3568221
H	4.4862322 1.7066652 -4.2073153	3.0867669 -1.3401412 -4.0528285	-9.8508135 -1.2222841 3.7536407	-10.8419082 -2.4960988 2.7009970
H	3.7387671 2.6204796 -2.8547364	4.3822352 -0.2965323 -4.7248394	-10.2161186 -2.7214551 2.8466594	-11.8521620 -2.7895304 4.1596951
H	1.9676282 2.3184044 -4.5204393	2.9008177 1.6421007 -4.8561771	-7.9488469 -2.8884092 1.9666748	-9.9330859 -4.0780390 5.1951502
H	2.4074258 0.6344022 -4.8092818	1.9703705 0.2902462 -5.5117251	-8.4054193 -1.1919806 1.7754338	-10.4060901 -4.7772834 3.6278270
H	-0.4526008 0.1984044 -1.1007436	-0.5874791 1.3102405 -1.6889646	-5.9461608 -1.1234131 6.5535233	-6.1153550 -1.3326985 4.0598592
H	1.8573854 -0.1180875 0.9284159	1.1758282 -0.1062025 0.4167671	-4.0502888 -1.7027766 4.1874309	-6.6042520 -2.9231954 1.4547791
H	-0.1337904 0.6446818 -4.6070254	0.4436495 2.4580580 -4.8732699	-5.2025048 -0.2505421 2.9913149	-8.1560602 -5.7943672 3.3869695
H	-0.4905033 2.0626685 -3.5888179	-0.6097343 2.0525713 -3.4802412	-6.2664080 -0.4711683 1.5506471	-6.7879600 -4.7567649 2.8311536
H	-0.8628969 0.4152952 -2.9850008	-0.4419462 0.9122811 -4.8561800	-5.1561729 -1.7747951 2.0522916	-8.2572860 -4.9536814 1.8183212
H	1.4571407 -0.8191605 2.9736227	-1.6095135 2.3860359 0.0347279	-4.3841182 -0.1212402 7.6390078	-5.0428241 -3.0605458 -0.0955589
H	-0.0214067 -2.2253009 4.4457943	-2.9229717 2.9238735 2.1176226	-2.3318088 0.9828978 8.5818870	-2.5745977 -3.1449206 -0.5647136
H	-0.2765591 -0.5288268 4.8511808	-3.8212167 1.7269915 1.1854535	-2.3968567 -0.6763739 9.1707844	-3.2021251 -1.6174656 -1.1833881
H	-2.1438388 -2.4471992 3.3240433	-2.2809048 1.3611197 3.8256605	-0.5017188 0.5569240 7.0802592	-1.4653349 -2.1160924 1.3147489
H	-2.5188869 -1.3872441 4.7131830	-3.9454794 0.8566816 3.4171914	-0.1039007 -0.4374713 8.5110077	-1.2078070 -0.9483082 -0.0142167
H	-1.8604747 -1.6317365 1.1156159	-0.3622353 0.2496725 3.0126187	-1.4565450 -0.3455907 5.1108811	-3.0838778 -1.7954931 3.0205201
H	-1.1501748 1.2851410 3.4456819	-3.2017587 -0.5967050 0.6309758	-0.5205928 -2.9332210 8.4408865	-3.8125737 1.5463893 1.1566443
H	-2.6923584 1.1149090 4.3515627	-4.2993555 -1.1676122 1.9337207	-1.0672296 -3.7550197 6.9468303	-4.2498132 0.2319442 0.0277378
H	-2.6860172 1.8270157 2.7091333	-2.9312520 -2.1906667 1.3963992	-2.2320549 -2.7972119 7.9096880	-2.6906289 1.1032144 -0.1668415
H	-4.0047759 -1.6445814 2.0209156	-1.6261705 -0.7988351 4.6617308	0.7843063 -0.7712890 5.5506141	-1.2012212 -0.4376019 3.0307000
H	-4.3347579 1.2487846 1.0774933	-1.5052961 -3.3607607 2.9924888	0.2534508 -3.7090826 4.8868958	-3.0454394 1.9822326 3.3729746
H	-4.5816630 -0.2636222 0.1767155	-0.3126696 -2.6969072 4.1317844	0.5684209 -2.3425482 3.7942172	-2.3976412 0.8773280 4.6058247
H	-2.0653333 1.3505678 0.4247464	-0.5481237 -2.1953240 1.1704573	-2.0810941 -3.3354976 4.8350457	-4.9611271 0.6316731 3.0654946
H	-2.3546071 -0.0652644 -0.6221397	0.7918974 -1.7115287 2.2425943	-1.8073756 -2.1356948 3.5440937	-4.4053777 -0.3818007 4.4239546
H	-5.0008681 0.9008297 3.4771056	-3.0326956 -2.7155137 5.3660474	1.4982497 -3.3817242 7.0551282	-0.1173819 0.9896335 1.2600142

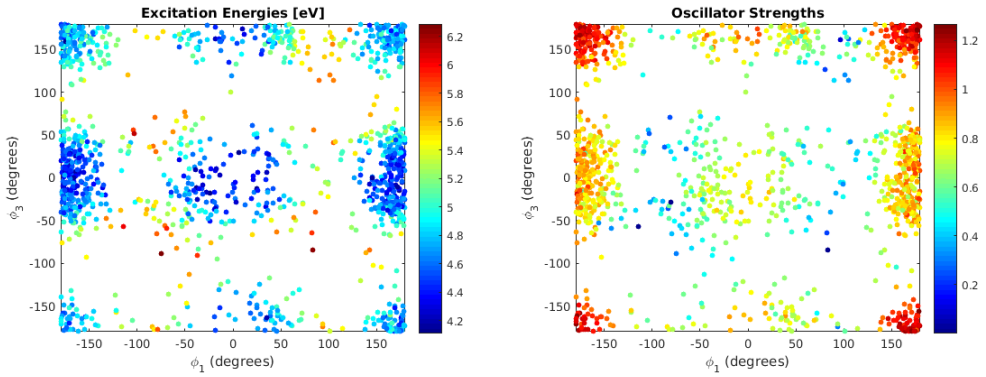

Figure 1: CC2 $S_1 \leftarrow S_0$ excitation energy (left) and oscillator strength (right) as a function the dihedral angles ϕ_1 and ϕ_2.

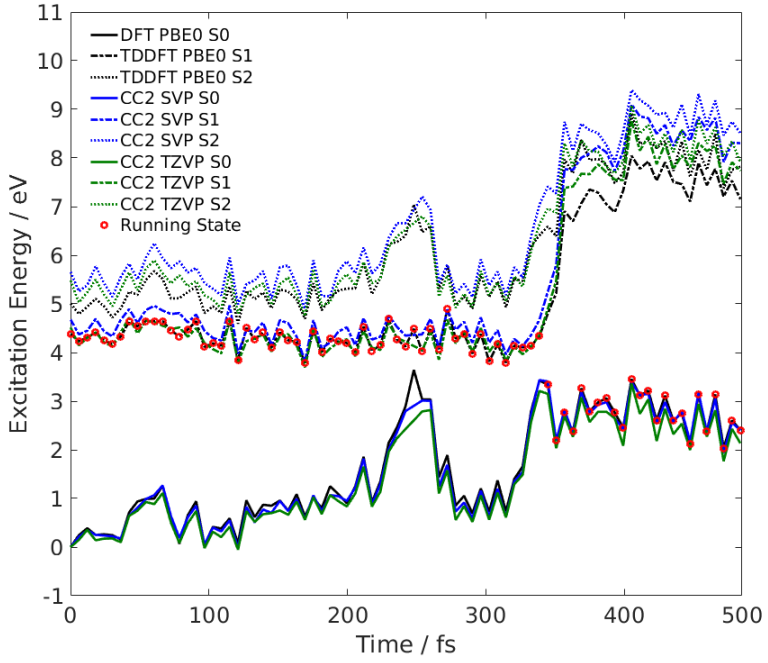

Figure 2: Comparison between CC2 and TDPBE0 potential energy surface along [1,5]-sigmatropic hydrogen shift reaction. The trajectory was generated using TDDFT-SH in the Tamm-Dancoff approximation employing the PBE0 exchange-correlation functional. CC2 ground and excited state energies were computed every 5 time steps of the simulation.

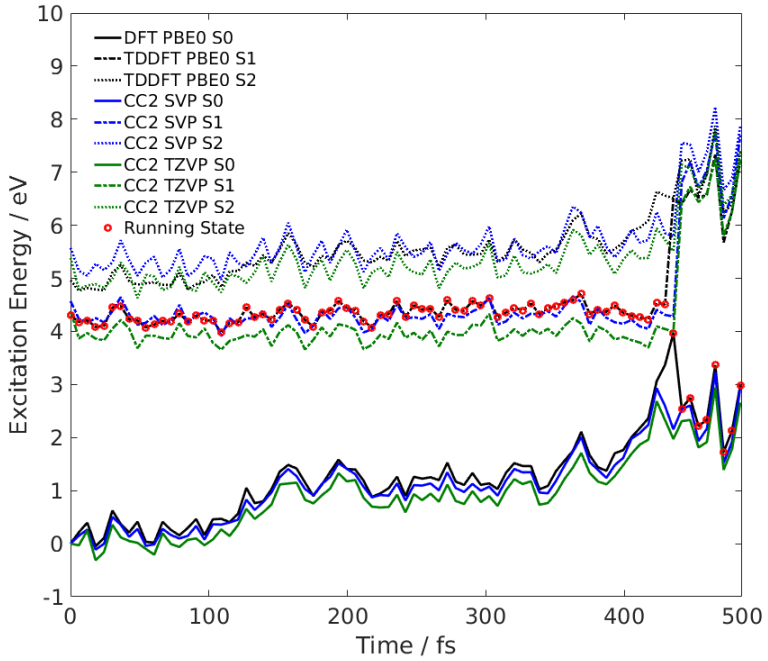

Figure 3: Comparison between CC2 and TDPBE0 potential energy surface along double-bond isomerization. The trajectory was generated using TDDFT-SH in the Tamm-Dancoff approximation employing the PBE0 exchange-correlation functional. CC2 ground and excited state energies were computed every 5 time steps of the simulation.

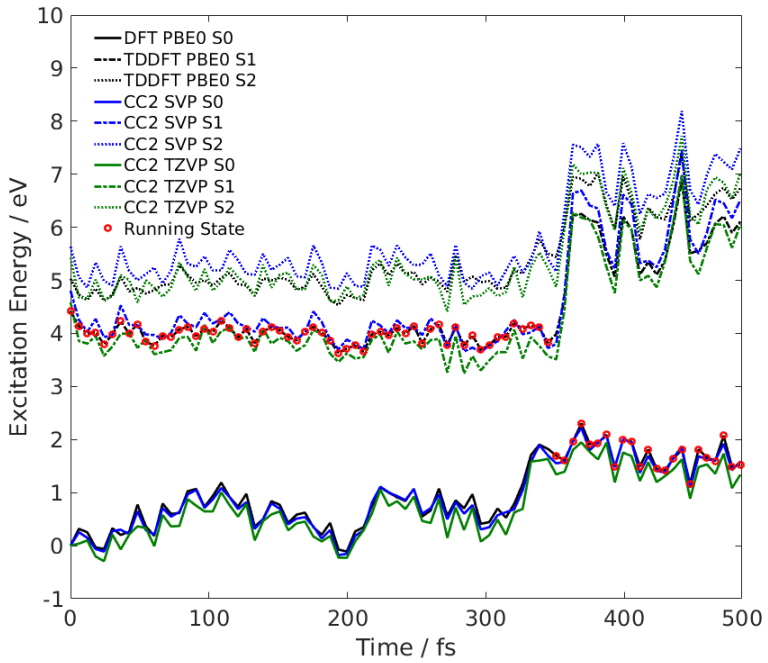

Figure 4: Comparison between CC2 and TDPBE0 potential energy surface along un unreactive trajectory. The trajectory was generated using TDDFT-SH in the Tamm-Dancoff approximation employing the PBE0 exchange-correlation functional. CC2 ground and excited state energies were computed every 5 time steps of the simulation.

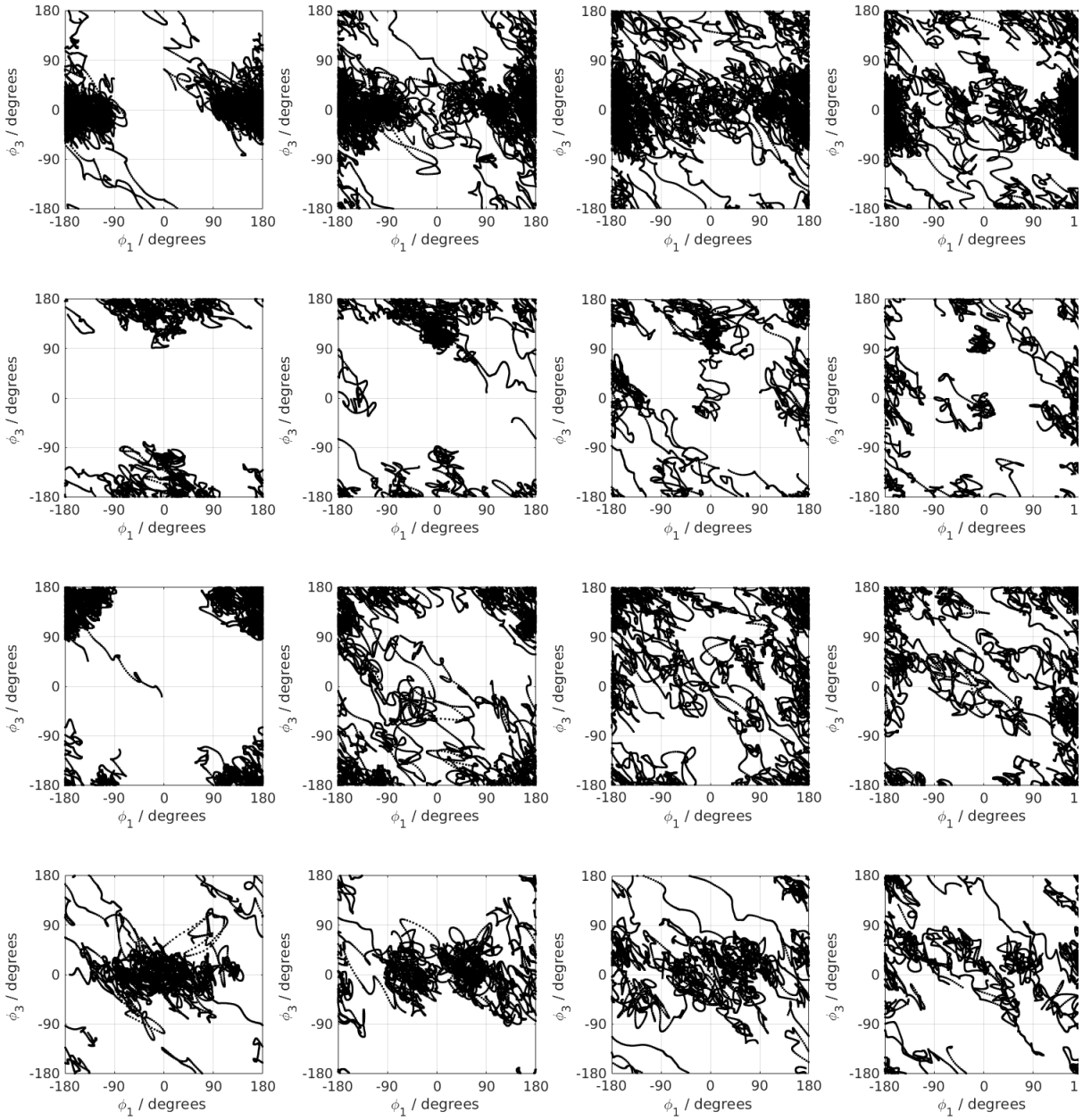

Figure 5: Evolution of the dihedral angles ϕ_1 and ϕ_2 during excited state dynamics for the different rotamers tEc, cEt, tEt, cEc (order from top to bottom). Each plot shows the evolution for a time intervall of 500 fs and each line shows the evolution of the first 2 ps for the given rotamer.