

Electronic Supplementary Information: Unravelling the details of vitamin D photosynthesis by non-adiabatic molecular dynamics simulations

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1 Vertical excitation energies

The ground state equilibrium structures used for the computation of the vertical excitation energies of CHD and Pro were optimized by DFT using the PBE0 functional. Default convergence criteria and grid sizes were used as provided by TURBOMOLE¹. Single point vertical excitation energies are computed using LR-TDDFT² and the linear response second order approximate coupled cluster method (CC2)³. For both sets of calculations the SVP⁴ and the aug-cc-pVTZ^{5,6} basis sets were used. We used the frozen core approximation of the CC2 module⁷⁻¹⁰ of TURBOMOLE¹. In the case of CHD, the 6 lowest molecular orbitals are kept frozen, for Pro the lowest 21 molecular orbitals are frozen. In addition, the Coulomb repulsion is approximated by the resolution of identity (RI) method¹¹. Therefore optimized auxiliary basis sets for SVP¹² and aug-cc-pVTZ¹³ basis sets were used.

2 Ground state molecular dynamics and replica exchange MD

The 300 K Boltzmann ensembles of CHD, Pro and its isomers were generated by *ab initio* Born-Oppenheimer molecular dynamics (BOMD) using DFT with the PBE0 functional. A time step of 50 a.u. (1 a.u.=0.024 fs) was used to propagate the nuclear coordinates. We employed a Nosé-Hoover thermostat^{14,15} with a target temperature of 300 K and a response time of 500 au.

To obtain a 300K Boltzmann ensemble of the more flexible Pre, replica exchange¹⁶ molecular dynamics (REMD) was carried out on DFT/PBE level using the RI method¹¹ for the computation of the electrostatic repulsion integrals. A time

step of 50 a.u. was used. BOMD trajectories at temperatures 300, 600, 900, and 1200 K were run in parallel. Every 600 molecular dynamics (MD) steps a probability P_{REMD} to switch actual structures with the trajectory of the next higher temperature was computed according to¹⁶

$$P_{REMD} = \exp\left[\left(\frac{1}{k_B T_i} - \frac{1}{k_B T_j}\right)(E_i - E_j)\right], \quad (1)$$

where i and j denote two ensembles of different temperatures T , k_B is the Boltzmann constant, and E denotes the total energy of the system. P_{REMD} was compared to a random number from $[0; 1]$. If the random number was smaller than P_{REMD} , the actual structures were switched, velocities were rescaled to the current target temperature, and the MD simulation was continued. In order to obtain an equilibrated ensemble in the space of the dihedral angles ϕ_1 and ϕ_2 (defined in Figure 2 of the main article) the REMD simulation was carried out for 76 ps.

3 Low temperature excited states molecular dynamics

3.1 Computational details

To scan the reaction pathway of the excited state decay, we carry out MD simulations in S_1 at 10 K. Therefore we use a Nosé-Hoover thermostat with a target temperature of 10 K and a response time of 100 au. As starting structures we use the PBE0 ground state equilibrium structure of CHD and Pro. Nuclear forces were computed using TDPBE0/TDA. The position of the nuclei were propagated using a time step of 40 a.u.

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Table 1 Cartesian coordinates (Å) of the TDPBE0/TDA MinS₁ structure. The structure was optimized using TDPBE0/TDA excited state nuclear forces as implemented in TURBOMOLE. Default convergence criteria were used

C	0.6193994	-0.1903066	-1.3639348
C	1.4254149	0.6754720	-0.5986159
C	1.0720714	1.0357690	0.7215418
C	-0.1928301	0.7204380	1.2551486
C	-1.2608854	0.3055579	0.4166675
C	-0.4022428	-0.9686160	-0.7583631
H	-0.1356099	-1.6296812	0.0819597
H	2.3276692	1.1099064	-1.0444991
H	1.8142733	1.5396956	1.3515350
H	-1.5528881	0.9517049	-0.4268033
H	-1.1571421	-1.4129581	-1.4227881
H	-0.3077302	0.6448241	2.3452327
H	-2.1238308	-0.1738265	0.9007517
H	0.6787089	-0.1443501	-2.4600531

4 Non-adiabatic excited states molecular dynamics

All excited state MD simulations employed the PBE0 functional. This was necessary to increase charge transfer excitation energies and to eliminate interactions of artificially low charge transfer states with localized states¹⁷⁻¹⁹. In order to minimize instability problems of TDDFT²⁰⁻²² the TDA²³ to TDDFT was used. In case a trajectory reached an instability, which corresponds to a negative excitation energy in the TDA, the trajectory was set to the ground state. A total of 2 excited states were computed at every time step, but only the non-adiabatic couplings between the first excited state and the ground state was computed and only the first excited state and the ground state were considered in the surface hopping. The large energy gap (> 0.3 eV) between first and second excited state justifies the neglect of the second excited state.

A time step of 40 a.u. was used for the propagation of the nuclear positions. For the surface hopping, the molecules were prepared in the first excited state and the nuclear positions were propagated starting from the velocities generated by the ground state BOMD. The total energy of the system was kept constant (NVE ensemble). We carry out non-adiabatic MD simulations with CHD, Pro, and Pre, using 118, 116, and 188 different starting structures and velocities, respectively. Excited state simulations were performed for 1-2 ps. In the case of Pro, after all trajectories have relaxed to the ground state, trajectories were extended by ground state BOMD to sample the process of rotational isomerization around the single bonds. For CHD and Pro starting structures were chosen from the 300 K BOMD trajectories. For the isomers Lumi,

Table 2 Cartesian coordinates (Å) of the TDPBE0/TDA CXMin structure. The structure was found by excited state molecular dynamics at 200 K starting from the S₁ minimum energy structure

C	0.4598957	-0.4504458	-1.3962702
C	1.1789225	0.4336020	-0.5575969
C	0.8449421	0.6836214	0.7647545
C	-0.3992211	0.4652030	1.3733362
C	-1.5299648	0.2475875	0.5513604
C	-0.4070654	-1.3138544	-0.7247163
H	-0.1768543	-1.7678860	0.2522852
H	2.0397201	1.0037430	-0.9515748
H	1.6775044	1.0759607	1.3731771
H	-1.5900137	0.6931710	-0.4359169
H	-1.2046085	-1.7319934	-1.3568457
H	-0.4996210	0.3175497	2.4396003
H	-2.4535087	-0.0749052	1.0499747
H	0.4496384	-0.2986956	-2.5002009

Iso, and Pyro 50 trajectories each were propagated for about 1 ps. For the more flexible Pre, the starting structures for the TDDFT-SH were chosen from the REMD trajectory. Therefore the statistical weights of the different conformations in the $\phi_1 - \phi_2$ space as obtained from the REMD simulations is reflected approximately by the set of starting structures.

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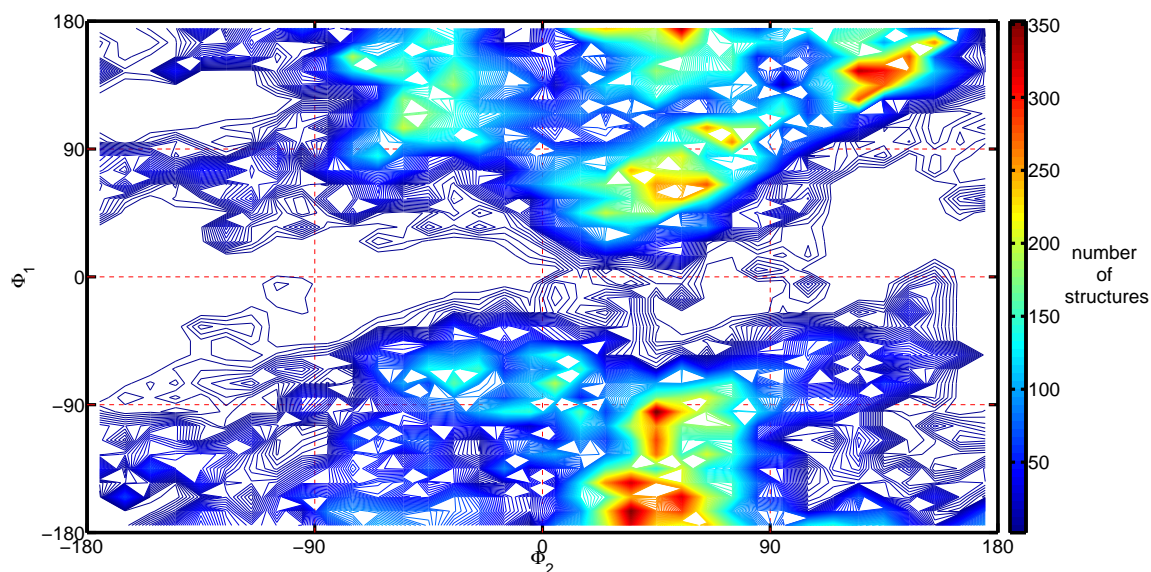


Fig. 1 Distribution of angles from the REMD simulations of Pre at 600 K. Dihedral angles ϕ_1 and ϕ_2 are defined in Figure 2 of the main article. A total of 63074 structures was evaluated. The contour plot shows the number of structures in an area of $10^\circ \times 10^\circ$.

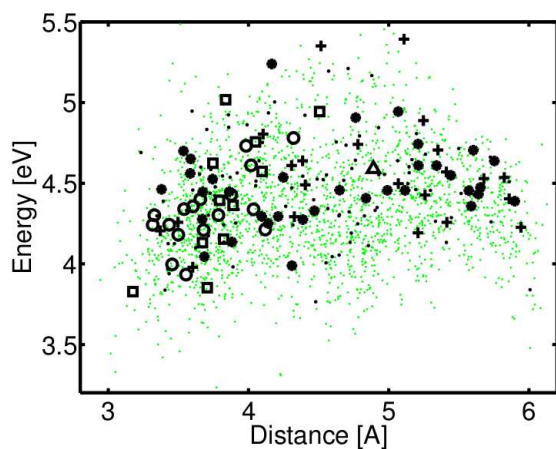


Fig. 2 Dependence of the C9-C10 distance, excitation energy and photo product. Symbols are defined in the caption of Figure 9 of the main article.

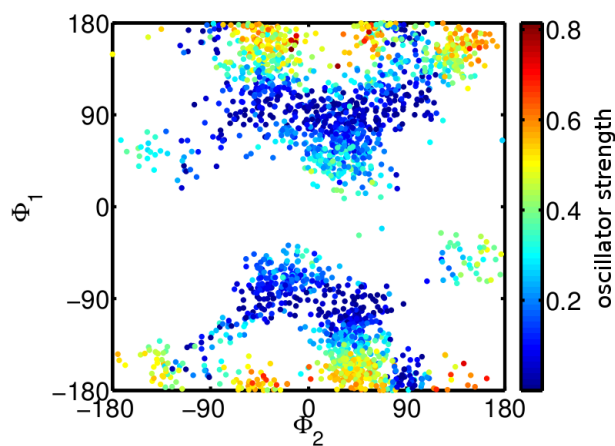


Fig. 3 Oscillator strengths as a function of the dihedral angles ϕ_1 and ϕ_2 (defined in Figure 2 of the main article).

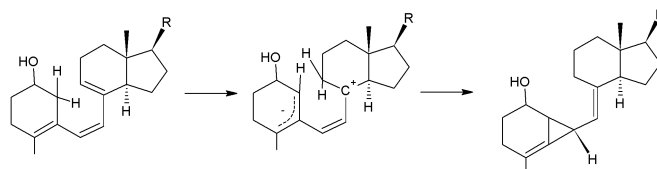


Fig. 4 Reaction mechanism of the observed toxisterol formation.

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