## Hydrogen Bond Dynamics Governs the Effective Photoprotection

## Mechanism of Plant Phenolic Sunscreens

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## **Electronic Supporting Information**

## **Technical Details of Theoretical Methods**

The minimum-energy geometries of the SA molecule and SA with one methanol molecule for the ground state (S<sub>0</sub>) were optimized at the DFT-D3/6-31G(d,p) level. The low-lying singlet excited state geometries and properties were also computed using the TDDFT/6-31G(d,p) method. Both *trans-* and *cis*-geometries were considered (Fig. S1). The optimized hydrogen bond length between SA and MeOH was in the range of 2.7 ~ 3.3 Å.

The TDDFT method is used to perform the excited state dynamics calculations. For validation, our results at the TDDFT level were compared with available experimental data. The B3LYP, BHandHLYP, LC-BLYP, CAM-B3LYP, wB97XD, M06-2X and M06-HF functionals were used in estimating the absorption spectrum. Additionally, we further perform the ADC(2)/6-31G(d,p) calculations to benchmark the functionals, beyond the available experimental spectrum data (Table S2). The calculations of the absorption spectrum were performed by similar procedure in our previous work (JPCB, 2016, 120, 6721). And 100 configurations were randomly selected from the MD trajectories in order to calculate the absorption spectrum. For each conformation, the first twenty excited states were used in the calculation of the absorption spectrum, which is sufficient for a complete characterization of our interested first absorption band. The Gaussian function with a half width at half-maximum (HWHM) of 0.30 eV was used to produce a smooth profile of optical spectrum. In our experience, such kind of treatment usually provides a very good consistence with the experimental spectrum data for molecule systems with strong intermolecular interactions. The B3LYP functional predicts quite reasonable spectroscopic properties as the ADC(2) calculations and experimental observations. Furthermore, we also calculate the PES along with the proton / hydrogen transfer process along a specific trajectory. Although the value of excited state energy for some functionals may cause larger derivation from ADC(2) or experimental values as shown in Table S2, the general shape of the excited state potential energy curve was very similar (Figure S5). Therefore, the B3LYP was selected as one of the most promising functional in this work.

The larger SA-(MeOH)<sub>n</sub> clusters beyond the isolated SA molecule would introduce more complicated inter-molecular interactions (i.e. hydrogen bonds or electrostatic interaction), which may play an important role in the photoinduced energy dispersion mechanism. Thus, the hydrogen bond is used as an indicator to identify the most possible interaction patterns, along with the classical MD trajectories. Based on geometric optimization and MD simulation, the criteria of the hydrogen bond were set to 3.8 Å and 45°. This is in the range of medium strength hydrogen bonds, which usually has a lifetime of a few picoseconds, very close to the excited state decay dynamics of the SA in experimental facts. And the size of n = 4 or 5 has reached the first coordinate shell in the radial distribution function (RDF) analysis (Fig. S2). At least for distances less than approximately 8.0 Å, the value of RDF is greater than unity, indicating that "mobile" solvents do not randomly distribute over the simulation cell but form well-defined clusters.

Another important question is that the microsolvented choromphore may introduce significant alteration of excited state dynamics. It is difficult to comment on the exact nature of larger clusters responsible for the excited state dynamics behavior. Thus, it is very interesting to exam the evolution of the excited state decay with increasing number of the methanol molecule in SA-(MeOH)<sub>n</sub> clusters, whereas, *n* is the number of solvents. In this work, the excited state dynamics were performed at pure QM level, and gradually grow the sizes of SA-(MeOH)<sub>n</sub> clusters, in order to rationalize the trends of excited state behavior of various SA-MeOH clusters. The pure QM calculation provides a consistent description of the excited state of solute and solvent on the same footing. The solvent effects could also be steadily incorporated in this protocol. Considering the simulation timescale (~1.0 ps) of the excited state dynamics, the larger solvent rearrangement is not possible (Fig. S11), and the most possible inter-molecular motion should be the hydrogen bonds dynamics. It should also be noted that, even longer time scale dynamics may require even larger cluster model or the QM/MM approaches is more suitable, although the boundary treatment in the strong hydrogen bonded system may introduce more uncertainties or artificial effects.

trans-SA and cis-SA



Possible *trans*-SA-MeOH complex



Possible *cis*-SA-MeOH complex



**Fig. S1** The optimized geometries of SA and SA with one methanol molecule are summarized; both the *trans-* and *cis-*geometries are considered.



Fig. S2 The radial distribution function (RDF) between the oxygen atom of SA and methanol solvent.



**Fig. S3** Typical structures of *trans-* and *cis*-SA-(MeOH)<sub>n</sub> clusters sampled along the classical MD trajectories.



Fig. S4 The predicted absorption spectroscopic properties of the *trans-* and *cis-*SA in gas phase.



**Fig. S5** The calculated PES with various functionals along with the proton / hydrogen transfer process for a specific trajectory.

The *trans*-SA model



The cis-SA model



**Fig. S6** The convergence of the occupation of surface hopping trajectories for the isolated SA model, with N=20, 40, 60, 80 and 100 trajectories.



**Fig. S7** The average fractional occupation of trajectories reveals that the population of each state  $SA-(MeOH)_n$ , whereas, n=0-5, starting from (a) *trans-* and (b) *cis-*SA.



**Fig. S8** For the *cis*-SA molecule, the possible intra-molecular hydrogen bond altering is observed during the excited state dynamics simulation. (a) The isolated; (b) microsolvated *cis*-SA model. The top panel is the definition of intra-molecular hydrogen bonds, whereas  $r_1$  is shown in blue and  $r_2$  is shown in red line. The intra-molecular hydrogen bond was observed during the excited state dynamics in *cis*-SA model.



**Fig. S9** The orientation correlation between the phenyl ring and carboxyl moiety along the trajectories is shown. (a) The isolated *trans*-SA (b) *cis*-SA model; (c) the microsolvated *trans*-SA and (d) *cis*-SA model. The square in the top panel is used to define the molecular plane and highlights the orientation between the phenyl ring and carboxyl moiety.



Fig. S10 Hydrogen bonds motion for a few specific trajectories. The typical geometries at hopping point were given, and the definition of the length  $r_1$  and  $r_2$  is also shown.



**Fig. S11** The relative energy differences between the  $S_1$  ( ${}^{1}\pi\pi^*$ ) and  $S_2$  ( ${}^{1}\pi\sigma^*$ ) states were computed for two specific trajectories. The shape of the molecular orbitals computed at the B3LYP/6-31G(d,p) level involved in the electronic excitations is also shown.



**Fig. S12** The SDF analysis of the distribution evolution of the solvents is given, along the trajectories. The SDFs at 0 fs, 1000 fs and near the internal conversion (IC) points were averaged over the available excited state dynamics trajectories.



**Fig. S13** The auto-correlation function (ACF) for dynamic formation and breaking of various hydrogen bonded clusters.

Number of methanol	trans-		cis-	
molecules ( <i>n</i> )	count	%	count	%
0	61	0.61	105	1.05
1	696	6.96	920	9.20
2	3414	34.14	3443	34.43
3	3803	38.03	3756	37.56
4	1654	16.54	1471	14.71
5	342	3.42	275	2.75
6	31	0.31	27	0.27
7	2	0.02	4	0.04

**Table S1.** Statistical analysis of the SA-(MeOH)<sub>n</sub> clusters, with 10,000 snapshots along the classical MD trajectories.

**Table S2.** Statistical analysis for TD-DFT/6-31G(d,p) with respect to the excitation energies (eV) of ADC(2) calculations and the experimental values. The first absorption peak position, which is related to the first singlet excited state, is given.

Methods	Excited state energy (eV)		
B3LYP	3.79		
BHandHLYP	4.30		
LC-BLYP	4.53		
CAM-B3LYP	4.11		
wB97XD	4.40		
M06-2X	4.24		
M06HF	4.47		
ADC(2)	3.90		
exp. <sup>a</sup>	3.81~3.83		

<sup>a.</sup> Values are taken from ref. J. Am. Chem. Soc., 2014, 136, 14780.