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

Supporting information:

Direct observation of the doorway $^1n\pi^*$ state of methylcinnamate and hydrogen-bonding effects on the photochemistry of cinnamate-based sunscreens

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Contents

1. Structures of methylcinnamate (MC) and MC-MeOH 1:1 complex in S_0

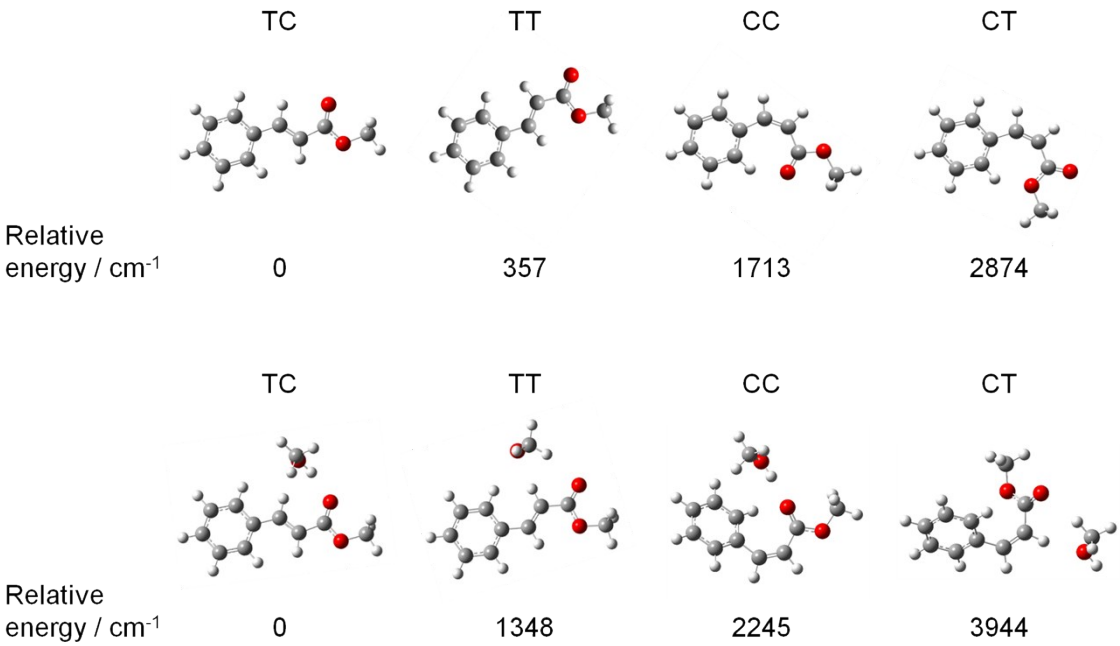

Fig. S1 (Upper) Structure and relative energy of TC, TT, CC and CT conformers of methylcinnamate (MC). (Lower) Structure and relative energy of MC-MeOH 1:1 complex. The level of the calculations is ωB97X-D/6-311G(d,p) level, and zero-point energy correction is carried out.

2. Optimized structures of $S_1(n\pi^*)$, $S_2(\pi\pi^*)$ and $T_1(\pi\pi^*)$ of MC

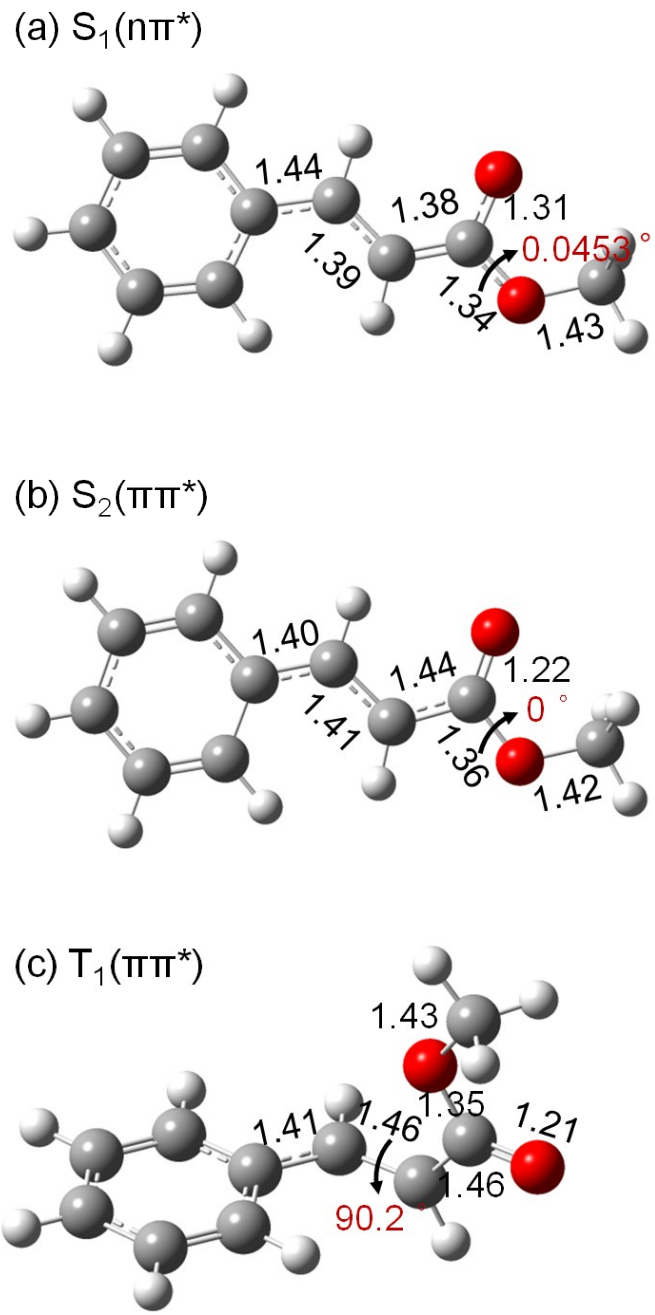

Fig. S2 Optimized structure of (a) $S_1(n\pi^*)$, (b) $S_2(\pi\pi^*)$ and (c) $T_1(\pi\pi^*)$. All of the structures were optimized at ωB97X-D/6-311G(d, p) level. Bond length (black) and dihedral angle (red) are also shown. The unit of bond length is Å.

3. Fluorescence decay curves of MC in a supersonic free jet

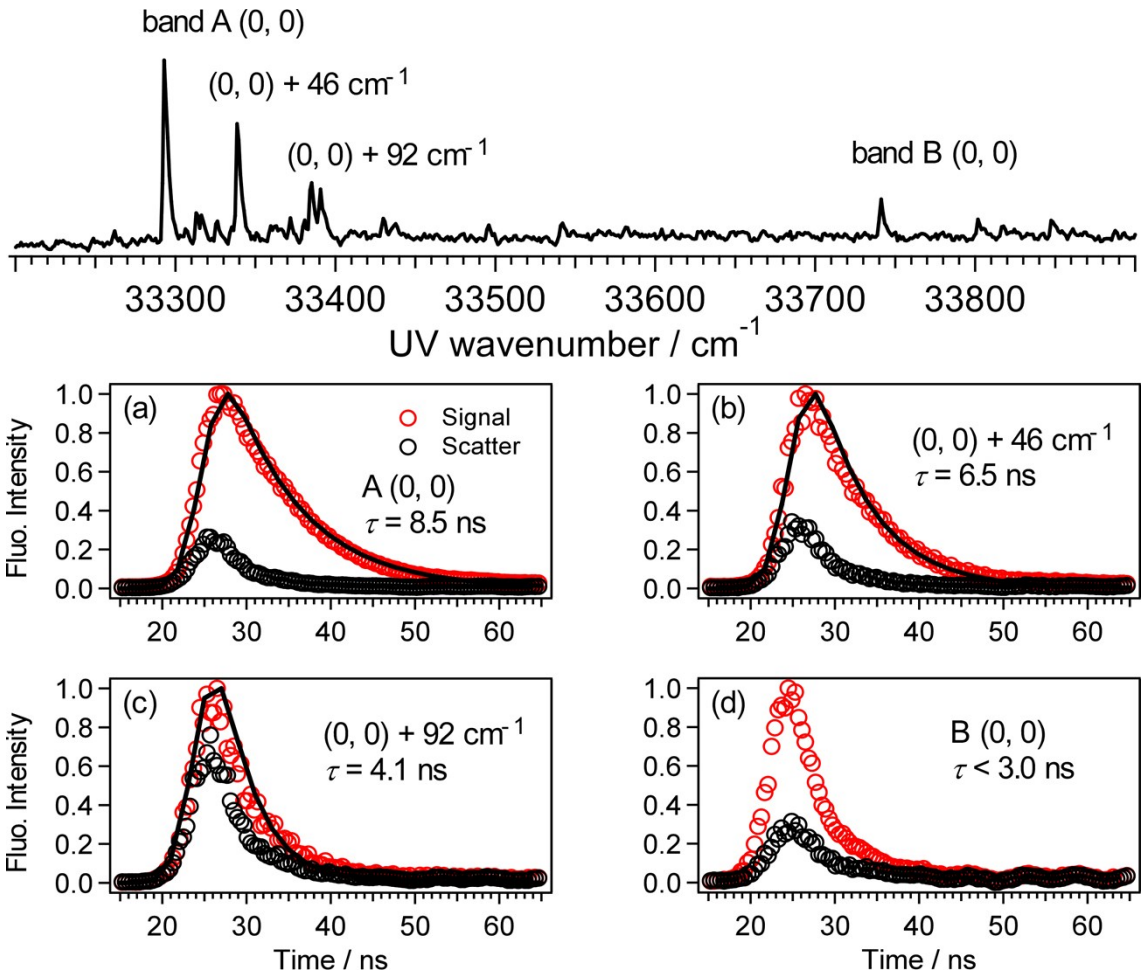

Fig. S3 Fluorescence decay curves (red plots) of "band A (0,0) (TC)" , "(0,0) + 46 cm^{-1} (TC)", "(0,0) + 92 cm^{-1} (TC)" and "band B(0,0) (TT)". The profiles of scatters of light (black plots) are also shown.

4. **Fluorescence decay curves of MC-MeOH 1:1 complex in a supersonic free jet**

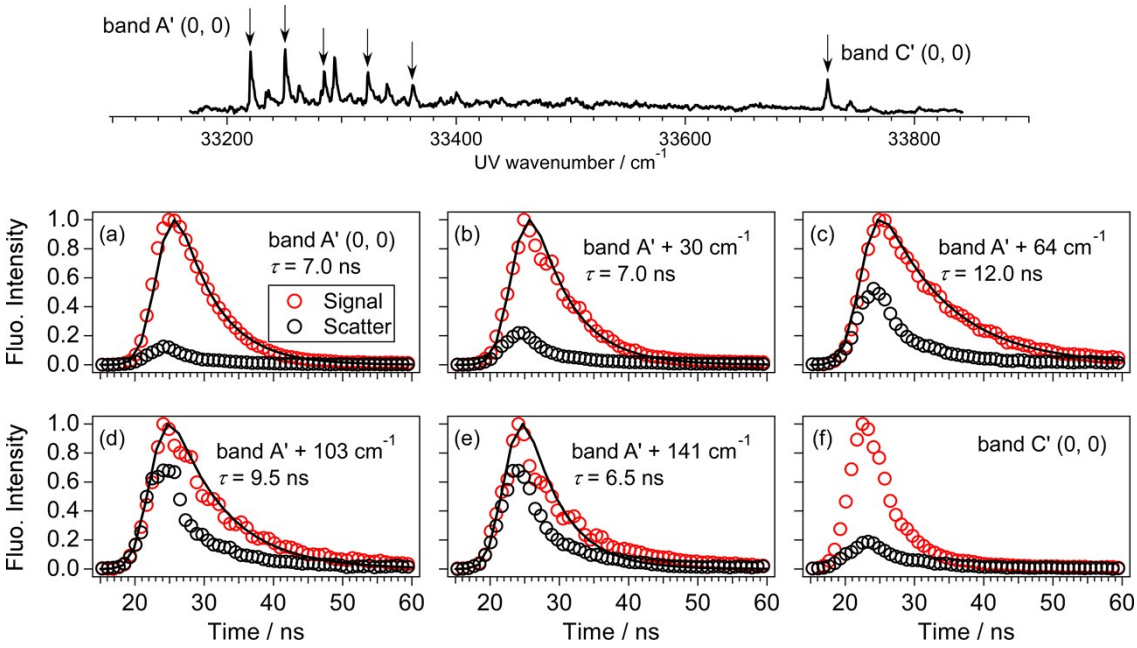

Fig. S4 Fluorescence decay curves (red plots) of "band A'(0,0)" , "(0,0) + 30 cm^{-1}", "(0,0) + 64 cm^{-1}", "(0,0) + 103 cm^{-1}", "(0,0) + 141 cm^{-1}" and "band C'(0,0)". The profiles of scatters of light (black plots) are also shown.

5. Cold matrix-isolated FTIR spectra of MC

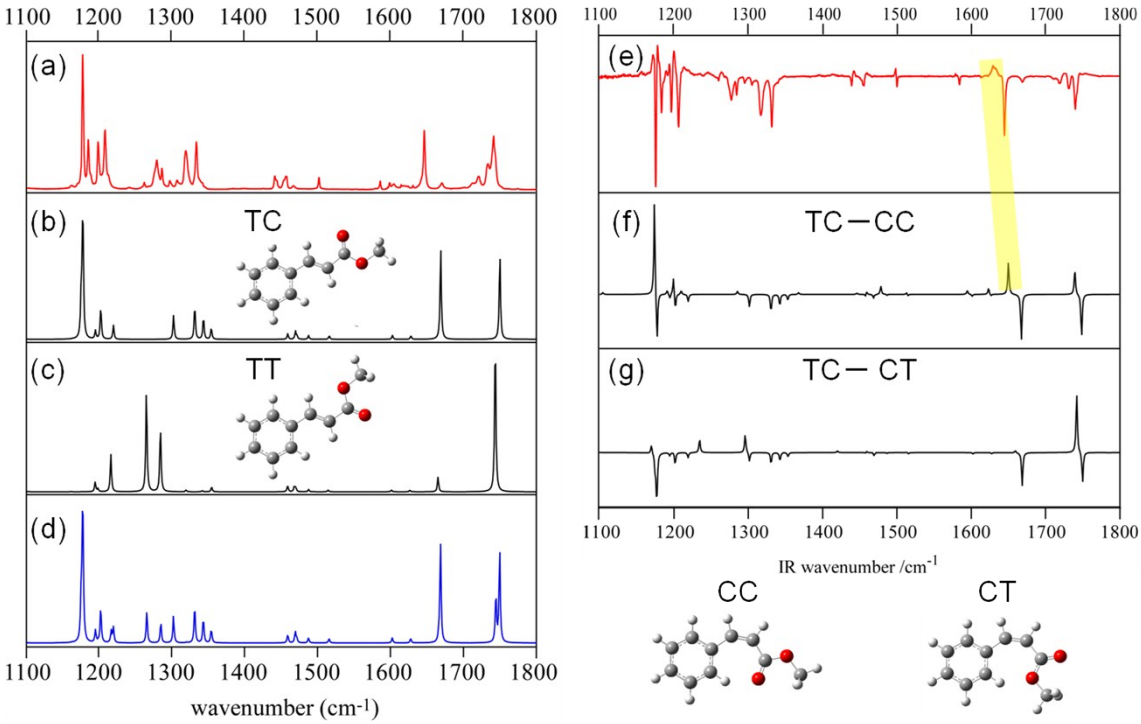

Fig. S5 (a) IR spectrum of MC deposited on the low temperature Ne matrix before UV irradiation. (b and c) Calculated IR spectrum of TC and TT conformer at B3LYP/6-311++G(d,p) level. (d) Calculated IR spectrum obtained by combining the two conformers assuming a Boltzmann distribution at the vaporized temperature (302 K). Here, we used a scaling factor of 0.994. (e) Different IR spectrum of the matrix-isolated MC before and after UV irradiation at $\lambda_{UV} \geq 300$ nm. Positive peaks are due to the product and negative ones are depletion of the reactant. (f and g) Comparison of the IR spectra of the *cis*-products. The typical vibrations, such as propenyl C=C stretching at 1640 cm^{-1} of the *cis*-products are highlighted.

6. Cartesian Coordinates of the optimized structures of the $S_1(n\pi^*)$, $S_2(\pi\pi^*)$ and $T_1(\pi\pi^*)$ states of MC at the ωB97X-D/6-311G(d, p) level

(a) $S_1(n\pi^*)$ -537.320228232678 (ZPE: -537.145201389151) hartree

C	3.748901047951	0.694109909007	-0.000042594103
C	2.416749107383	1.072451851260	-0.000059999075
C	1.382520706346	0.117956220794	0.000027283347
C	1.756454208973	-1.239190706308	0.000161154986
C	3.089537830611	-1.612957975113	0.000172757463
C	4.097158093443	-0.652471826107	0.000067354927
H	4.522140786598	1.454578641147	-0.000121036916
H	2.157738881783	2.126510632964	-0.000157081118
H	0.996042229560	-2.011745587348	0.000268128410
H	3.347796004588	-2.666416416273	0.000271044657
H	5.138986078212	-0.950737235741	0.000076162158
C	0.010942014823	0.564209521170	-0.000051803834
C	-1.109674058815	-0.257637735837	-0.000195882185
H	-0.133095528423	1.638960889298	-0.000051377628
H	-1.046955609774	-1.339124576350	-0.000305008645
C	-2.394758351754	0.230511031490	-0.000281888992
O	-2.689486848065	1.505779120432	-0.000033300601
O	-3.454126677448	-0.583748510534	-0.000715421916
C	-4.771318080130	-0.020988848100	0.000120335883
H	-4.938213429311	0.582454861506	-0.894306667006
H	-4.937578358422	0.581234814099	0.895489010214
H	-5.441342880188	-0.876396296736	-0.000231981326

(b) $S_2(\pi\pi^*)$ -537.317084959649 (ZPE: -537.142907421254) hartree

C	3.744252223376	0.680779144166	-0.000000367064
C	2.448630567502	1.111416302198	-0.000004104760
C	1.355645384125	0.175790785849	-0.000003154361
C	1.689032810548	-1.238797205233	0.000001810081
C	3.005386295479	-1.642525610734	0.000005534091
C	4.038972865478	-0.705196704538	0.000004496317
H	4.556062001090	1.398676599861	-0.000001157182
H	2.215980182916	2.170814810633	-0.000008024016
H	0.894696381571	-1.974104845867	0.000003710911
H	3.242643506105	-2.700375170190	0.000009442791
H	5.071381164133	-1.035343902644	0.000007208902
C	0.031988507645	0.622462873348	-0.000006133055
C	-1.091035931471	-0.235831085139	-0.000008602182
H	-0.174227290048	1.688067797298	-0.000005353572
H	-1.002106713175	-1.314658668668	-0.000019039221
C	-2.415844279330	0.331493363185	-0.000000217486
O	-2.668479023912	1.526085956672	0.000012424895
O	-3.377840546213	-0.623984901779	-0.000007692847
C	-4.712695114731	-0.136238077885	0.000002177523
H	-4.904625305375	0.472830024867	-0.886778697143
H	-4.904621198726	0.472804787235	0.886801328310
H	-5.351034002537	-1.017984426199	-0.000008737380

(c) $T_1(\pi\pi^*)$ −537.3952265 (ZPE: −537.2207123) hartree

C	-3.37157600	0.17325600	0.79263800
C	-2.20863700	0.91374900	0.85986400
C	-1.10877300	0.62206800	0.01499200
C	-1.24454400	-0.45660600	-0.89416300
C	-2.41414100	-1.18887100	-0.95329200
C	-3.48519400	-0.88186000	-0.11395300
H	-4.20051200	0.41396700	1.44879700
H	-2.12470800	1.73170000	1.56781800
H	-0.41635300	-0.70385900	-1.55008200
H	-2.49826200	-2.00838100	-1.65827900
H	-4.40071700	-1.45949700	-0.16492200
C	0.07696500	1.38635900	0.09203500
C	1.25279600	1.16141700	-0.73821100
H	0.12612700	2.18845600	0.82626600
H	1.38262700	1.67608800	-1.68633900
C	2.34717600	0.27024500	-0.37921700
O	3.32635800	0.08722800	-1.06795700
O	2.14685400	-0.33597900	0.80554000
C	3.17069800	-1.24020100	1.21093600
H	4.12096600	-0.71749400	1.33770500
H	3.30071200	-2.03166400	0.47024800
H	2.83580300	-1.65663700	2.15833600