Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supplementary Information: Proton Transfer-Driven Intersystem Crossing in Apigenin

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Table SI1: Ground-state equilibrium geometry (S_0) of apigenin computed at B3LYP/6-311++G level of theory.

	Coordinates (Angstroms)		
Atom	X	Y	Z
C	-3.431053	1.912154	0.000000
C	-2.033885	1.912428	0.000000
C	-1.395619	0.682324	0.000000
C	-2.090600	-0.541130	0.000000
C	-3.510414	-0.495080	0.000000
C	-4.175885	0.728031	0.000000
H	-1.480693	2.837289	0.000000
C	-1.358730	-1.793553	0.000000
H	-5.256987	0.733075	0.000000
C	0.079537	-1.698088	0.000000
C	0.724289	-0.499057	0.000000
H	0.630256	-2.624387	0.000000
O	-4.039720	3.160257	0.000000
O	-4.242045	-1.648809	0.000000
O	-1.966866	-2.920536	0.000000
H	-5.010969	3.106986	0.000000
C	2.171734	-0.263285	0.000000
C	3.086992	-1.337236	0.000000
C	2.682723	1.047618	0.000000
C	4.456334	-1.111993	0.000000
H	2.732097	-2.357781	0.000000
C	4.055992	1.280266	0.000000
H	1.998955	1.881933	0.000000
C	4.941401	0.199480	0.000000
H	5.160638	-1.930746	0.000000
H	4.431230	2.296473	0.000000
H	-3.619121	-2.434447	0.000000
O	6.323045	0.353512	0.000000
H	6.602380	1.285291	0.000000
O	0.000000	0.689205	0.000000

Table SI2: Ground-state equilibrium geometry (S_0) of apigenin computed at M06/6-311++G level of theory.

	Coordinates (Angstroms)		
Atom	X	Y	Z
C	-3.405307	1.909847	0.000000
C	-2.013654	1.903939	0.000000
C	-1.382725	0.676255	0.000000
C	-2.079307	-0.540670	0.000000
C	-3.493209	-0.489524	0.000000
C	-4.150446	0.732211	0.000000
H	-1.455300	2.828462	0.000000
C	-1.353777	-1.791846	0.000000
H	-5.234110	0.739221	0.000000
C	0.080002	-1.692647	0.000000
C	0.717376	-0.495929	0.000000
H	0.633698	-2.620267	0.000000
O	-4.004732	3.145820	0.000000
O	-4.230258	-1.624683	0.000000
O	-1.954369	-2.910949	0.000000
H	-4.974144	3.101556	0.000000
C	2.157787	-0.262496	0.000000
C	3.066325	-1.333844	0.000000
C	2.665526	1.042742	0.000000
C	4.430349	-1.110901	0.000000
H	2.706230	-2.355437	0.000000
C	4.033391	1.273575	0.000000
H	1.978170	1.877531	0.000000
C	4.914205	0.195628	0.000000
H	5.139767	-1.928079	0.000000
H	4.413762	2.290187	0.000000
H	-3.631766	-2.422209	0.000000
O	6.281535	0.347882	0.000000
H	6.567071	1.275276	0.000000
O	0.000000	0.681397	0.000000

Table SI3: Vibrational harmonic frequencies (in cm^{-1}) along with the symmetries of apigenin computed at B3LYP/6-311++G method.

No.(Sym.)	Freq (in cm^{-1})	No.(Sym.)	Freq (in cm^{-1})	No.(Sym.)	Freq (in cm^{-1})
$\nu_1(a'')$	21.0551	$\nu_{31}(a')$	668.1652	$\nu_{61}(a')$	1364.3545
$\nu_2(a'')$	44.3235	$\nu_{32}(a')$	688.7340	$\nu_{62}(a')$	1383.4935
$\nu_3(a')$	87.4748	$\nu_{33}(a'')$	739.0246	$\nu_{63}(a')$	1409.0453
$\nu_4(a'')$	101.0717	$\nu_{34}(a')$	745.1154	$\nu_{64}(a')$	1425.7320
$\nu_5(a'')$	114.0339	$\nu_{35}(a'')$	816.8954	$\nu_{65}(a')$	1462.0017
$\nu_6(a'')$	176.1755	$\nu_{36}(a')$	830.8854	$\nu_{66}(a')$	1473.0006
$\nu_7(a'')$	223.4264	$\nu_{37}(a'')$	833.8180	$\nu_{67}(a')$	1525.7348
$\nu_8(a')$	234.2867	$\nu_{38}(a'')$	839.7686	$\nu_{68}(a')$	1545.9139
$\nu_9(a'')$	251.5519	$\nu_{39}(a'')$	856.5021	$\nu_{69}(a')$	1581.6788
$\nu_{10}(a')$	254.5063	$\nu_{40}(a'')$	861.4298	$\nu_{70}(a')$	1606.3080
$\nu_{11}(a'')$	275.3129	$\nu_{41}(a'')$	868.8143	$\nu_{71}(a')$	1619.9418
$\nu_{12}(a'')$	331.9436	$\nu_{42}(a')$	902.1819	$\nu_{72}(a')$	1640.1050
$\nu_{13}(a')$	343.9926	$\nu_{43}(a')$	976.6583	$\nu_{73}(a')$	1649.8043
$\nu_{14}(a'')$	345.1153	$\nu_{44}(a'')$	984.4103	$\nu_{74}(a')$	1688.6307
$\nu_{15}(a'')$	348.7601	$\nu_{45}(a'')$	1004.7884	$\nu_{75}(a')$	3131.3192
$\nu_{16}(a')$	355.6641	$\nu_{46}(a')$	1028.8569	$\nu_{76}(a')$	3160.5585
$\nu_{17}(a')$	407.3737	$\nu_{47}(a')$	1039.5380	$\nu_{77}(a')$	3188.7477
$\nu_{18}(a'')$	429.4497	$\nu_{48}(a')$	1089.1686	$\nu_{78}(a')$	3192.3589
$\nu_{19}(a')$	440.9686	$\nu_{49}(a')$	1127.4539	$\nu_{79}(a')$	3209.8996
$\nu_{20}(a')$	500.3044	$\nu_{50}(a')$	1138.9504	$\nu_{80}(a')$	3220.2177
$\nu_{21}(a'')$	510.9109	$\nu_{51}(a')$	1158.0356	$\nu_{81}(a')$	3232.4853
$\nu_{22}(a')$	517.1957	$\nu_{52}(a')$	1173.3613	$\nu_{82}(a')$	3233.9178
$\nu_{23}(a')$	567.8364	$\nu_{53}(a')$	1200.3330	$\nu_{83}(a')$	3690.9963
$\nu_{24}(a')$	581.2717	$\nu_{54}(a')$	1219.8845	$\nu_{84}(a')$	3693.2437
$\nu_{25}(a'')$	595.5369	$\nu_{55}(a')$	1241.6352		
$\nu_{26}(a'')$	603.6840	$\nu_{56}(a')$	1275.7804		
$\nu_{27}(a'')$	628.7692	$\nu_{57}(a')$	1287.3577		
$\nu_{28}(a')$	633.4901	$\nu_{58}(a')$	1294.0220		
$\nu_{29}(a'')$	645.1146	$\nu_{59}(a')$	1323.2457		
$\nu_{30}(a'')$	666.3321	$\nu_{60}(a')$	1345.8355		

Table SI4: Vibrational harmonic frequencies (in cm^{-1}) along with the symmetries of apigenin computed at M06/6-311++G method.

No.(Sym.)	Freq (in cm^{-1})	No.(Sym.)	Freq (in cm^{-1})	No.(Sym.)	Freq (in cm^{-1})
$\nu_1(a'')$	17.6391	$\nu_{31}(a')$	663.9657	$\nu_{61}(a')$	1380.8165
$\nu_2(a'')$	43.0650	$\nu_{32}(a')$	695.3075	$\nu_{62}(a')$	1394.8557
$\nu_3(a')$	89.3830	$\nu_{33}(a'')$	728.6554	$\nu_{63}(a')$	1426.3621
$\nu_4(a'')$	97.6756	$\nu_{34}(a')$	750.1046	$\nu_{64}(a')$	1435.8394
$\nu_5(a'')$	112.5575	$\nu_{35}(a'')$	788.2692	$\nu_{65}(a')$	1471.6676
$\nu_6(a'')$	170.9637	$\nu_{36}(a'')$	817.1033	$\nu_{66}(a')$	1490.9452
$\nu_7(a'')$	221.6078	$\nu_{37}(a'')$	836.0188	$\nu_{67}(a')$	1538.4704
$\nu_8(a')$	238.1296	$\nu_{38}(a')$	841.2428	$\nu_{68}(a')$	1550.5388
$\nu_9(a'')$	247.1933	$\nu_{39}(a'')$	848.9124	$\nu_{69}(a')$	1612.0900
$\nu_{10}(a')$	257.9135	$\nu_{40}(a'')$	855.5546	$\nu_{70}(a')$	1627.2298
$\nu_{11}(a'')$	265.7575	$\nu_{41}(a'')$	862.3134	$\nu_{71}(a')$	1637.4573
$\nu_{12}(a'')$	330.9575	$\nu_{42}(a')$	913.3210	$\nu_{72}(a')$	1661.7726
$\nu_{13}(a')$	347.3812	$\nu_{43}(a'')$	981.2635	$\nu_{73}(a')$	1669.8882
$\nu_{14}(a'')$	350.9538	$\nu_{44}(a')$	993.1543	$\nu_{74}(a')$	1709.8330
$\nu_{15}(a'')$	358.7215	$\nu_{45}(a'')$	1008.2949	$\nu_{75}(a')$	3159.5226
$\nu_{16}(a')$	362.5625	$\nu_{46}(a')$	1034.9618	$\nu_{76}(a')$	3181.9074
$\nu_{17}(a')$	410.4287	$\nu_{47}(a')$	1042.0560	$\nu_{77}(a')$	3186.3579
$\nu_{18}(a'')$	424.6358	$\nu_{48}(a')$	1114.9726	$\nu_{78}(a')$	3203.4842
$\nu_{19}(a')$	444.0318	$\nu_{49}(a')$	1132.5106	$\nu_{79}(a')$	3210.0809
$\nu_{20}(a')$	499.5796	$\nu_{50}(a')$	1141.7090	$\nu_{80}(a')$	3227.4773
$\nu_{21}(a'')$	505.9754	$\nu_{51}(a')$	1158.6122	$\nu_{81}(a')$	3228.0195
$\nu_{22}(a')$	518.5229	$\nu_{52}(a')$	1168.8363	$\nu_{82}(a')$	3284.6471
$\nu_{23}(a')$	568.1736	$\nu_{53}(a')$	1199.8027	$\nu_{83}(a')$	3769.4841
$\nu_{24}(a'')$	572.1613	$\nu_{54}(a')$	1203.7417	$\nu_{84}(a')$	3770.5328
$\nu_{25}(a')$	585.6440	$\nu_{55}(a')$	1243.8353		
$\nu_{26}(a'')$	589.1712	$\nu_{56}(a')$	1285.5035		
$\nu_{27}(a'')$	617.1396	$\nu_{57}(a')$	1300.7118		
$\nu_{28}(a'')$	636.7859	$\nu_{58}(a')$	1313.9545		
$\nu_{29}(a')$	638.0286	$\nu_{59}(a')$	1336.1214		
$\nu_{30}(a'')$	660.3980	$\nu_{60}(a')$	1354.7492		

Vibronic Hamiltonian

Here, we briefly discuss the construction of a diabatic vibronic Hamiltonian for investigating the IC dynamics of coupled S_1-S_2 PESs of apigenin. The Hamiltonian can be expressed in terms of dimensionless normal coordinates (Q) of the ground electronic state (S_0) as:

$$\mathcal{H} = (\mathcal{T}_N + \mathcal{V}_0)\mathbf{1}_2 + W \tag{1}$$

where $\mathcal{T}_N$ and $\mathcal{V}_0$ are the kinetic energy and potential energy matrix elements of S_0, respectively. $\mathbf{1_2}$ is a 2×2 unit matrix. The matrix W contains the coupling between the involved electronic states, wherein the diagonal and off-diagonal elements can be written as:

$$W_{aa} = E_0^a + \sum_i \kappa_i^a \mathrm{Q_i} \tag{2}$$

$$W_{ab} = \sum_j \lambda_j^{ab} \mathrm{Q_j} \tag{3}$$

E_0^a and E_0^b are the vertical excitation energies of ath and bth states, respectively, at the reference geometry (FC geometry, i.e, Q = 0). κ^a and κ^b are the intrastate coupling parameters of ath and bth states associated with a′ vibrational mode. As this coupling parameter defines the gradient of the PES, it is responsible for tuning the energy gap between two states. Hence, the corresponding modes are known as tuning modes. The λ^{ab} denotes the interstate coupling parameter between a and b states. The symmetry selection rules can be employed to determine the vibrational modes that are causing λ^{ab}. For example; two electronic states of A′ symmetry will be coupled by a′ modes; whereas, the coupling between states having A′ and A″ symmetries is given by a″ modes. The numerical estimation of the involved vibronic coupling parameters is carried out as described in detail elsewhere [see Ref. H. K'oppel, W. Domcke and L. Cederbaum, Adv. Chem. Phys, 1984, 57, 140].

Table SI5: The LVC Hamiltonian employed to study the internal conversion dynamics of S_1-S_2 states of apigenin.

$$\mathcal{H} = (\mathcal{T}_N + \mathcal{V}_0)\mathbf{I}_2 + \begin{pmatrix} \mathrm{E}_0^{\mathrm{S}_1} + \sum\limits_{i\in a'} \kappa_i^{\mathrm{S}_1}\mathrm{Q}_i & \sum\limits_{j\in a''} \lambda_j^{\mathrm{S}_1-\mathrm{S}_2}\mathrm{Q}_j \\ h.c & \mathrm{E}_0^{\mathrm{S}_2} + \sum\limits_{i\in a'} \kappa_i^{\mathrm{S}_2}\mathrm{Q}_i \end{pmatrix}. \tag{4}$$

Table SI6: The LVC Hamiltonian employed to study the internal conversion dynamics of the triplet manifold of apigenin.

$$\mathcal{H} = (\mathcal{T}_N + \mathcal{V}_0)\mathbf{I}_4 + \begin{pmatrix} \mathrm{E}^0_{\mathrm{T}_1} + \sum\limits_{i\in a'} \kappa_i^{\mathrm{T}_1}\mathrm{Q}_i & \sum\limits_{i\in a'} \lambda_i^{\mathrm{T}_1-\mathrm{T}_2}\mathrm{Q}_i & \sum\limits_{i\in a'} \lambda_i^{\mathrm{T}_1-\mathrm{T}_3}\mathrm{Q}_i & \sum\limits_{j\in a''} \lambda_j^{\mathrm{T}_1-\mathrm{T}_4}\mathrm{Q}_j \\ & \mathrm{E}^0_{\mathrm{T}_2} + \sum\limits_{i\in a'} \kappa_i^{\mathrm{T}_2}\mathrm{Q}_i & \sum\limits_{i\in a'} \lambda_i^{\mathrm{T}_2-\mathrm{T}_3}\mathrm{Q}_i & \sum\limits_{j\in a''} \lambda_j^{\mathrm{T}_2-\mathrm{T}_4}\mathrm{Q}_j \\ & & \mathrm{E}^0_{\mathrm{T}_3} + \sum\limits_{i\in a'} \kappa_i^{\mathrm{T}_3}\mathrm{Q}_i & \sum\limits_{j\in a''} \lambda_j^{\mathrm{T}_3-\mathrm{T}_4}\mathrm{Q}_j \\ h.c. & & & \mathrm{E}^0_{\mathrm{T}_4} + \sum\limits_{i\in a'} \kappa_i^{\mathrm{T}_4}\mathrm{Q}_i \end{pmatrix}. \tag{5}$$

We note that the interstate coupling caused by a$'$ vibrational modes for T_1-T_2, T_1-T_2 and T_2-T_3 states is not taken into account during the triplet dynamics.

Intersystem Crossing Rate (K_{ISC})

Within the Fermi's golden rule, the intersystem crossing rate (K_{ISC}) involving S_n and T_m states can be obtained as:

$$k_{\mathrm{ISC}} = \frac{4\pi^2}{h}\rho_{\mathrm{FC}} \left|\langle \mathrm{S}_n|\hat{H}_{\mathrm{soc}}|\mathrm{T}_m\rangle\right|^2 \tag{6}$$

In the above equation, the ρ_{FC} is the Franck-Condon weighted density of states. h represents the Planck constant. The S_n-T_m spin-orbit coupling, ($\langle \mathrm{S}_n\,|\hat{H}_{\mathrm{soc}}|\mathrm{T}_m\,\rangle$), is computed using the PySOC code. [Ref. Gao, X., Chiodo, S. G., Barbatti, M. (2017). PySOC: Python-based spin-orbit coupling. Journal of Chemical Theory and Computation, 13(2), 515-524.] The Franck-Condon weighted density (ρ_{FC}) is approximated within the Marcus theory, as described in the Ref. [Beljonne, D.; Shuai, Z.; Pourtois, G.; Bredas, J. L. J. Phys. Chem. A2001, 105, 3899]:

$$\rho_{\mathrm{FC}} = \frac{1}{\sqrt{4\pi\lambda' k_B T}} \exp\left[-\frac{(\Delta E_{\mathrm{ST}} + \lambda')^2}{4\lambda' k_B T}\right] \tag{7}$$

In the above equation, the quantities $\lambda^{'}$, k_B, T and ΔE_{ST} represent the Marcus-reorganization energy, Boltzmann constant, temperature and the energy gap between singlet and triplet states at Franck-Condon point, respectively. The reorganization energy is approximated to be 0.2 eV while computing the rates.

Table SI7: Linear intrastate coupling parameters (κ) of S_1 and S_2 states of apigenin estimated at TD-B3LYP/6-311++G level of theory. All coupling parameters are in eV. The excitation strength ($\kappa^2/2\omega^2$) is given in the parentheses.

a′ mode [frequency]	κ^{S_1}	κ^{S_2}	a′ mode [frequency]	κ^{S_1}	κ^{S_2}
ν_3 (0.0108)	0.0051 (0.1112)	0.0040 (0.0672)	ν_{58} (0.1604)	0.0386 (0.0289)	0.0262 (0.0133)
ν_8 (0.0290)	-0.0011 (0.0008)	-0.0103 (0.0628)	ν_{59} (0.1641)	0.0797 (0.1179)	0.0013 (0.0000)
ν_{10} (0.0316)	0.0187 (0.1758)	-0.0029 (0.0041)	ν_{60} (0.1669)	0.0253 (0.0115)	-0.0316 (0.0179)
ν_{13} (0.0426)	-0.0031 (0.0027)	0.0032 (0.0027)	ν_{61} (0.1692)	-0.0107 (0.0020)	0.0142 (0.0035)
ν_{16} (0.0441)	0.0505 (0.6561)	-0.0125 (0.0399)	ν_{62} (0.1715)	-0.0065 (0.0007)	-0.0078 (0.0010)
ν_{17} (0.0505)	-0.0383 (0.2869)	0.0148 (0.0431)	ν_{63} (0.1747)	-0.0496 (0.0403)	-0.0338 (0.0187)
ν_{19} (0.0547)	-0.0492 (0.4041)	0.0128 (0.0275)	ν_{64} (0.1768)	-0.0911 (0.1328)	-0.0812 (0.1056)
ν_{20} (0.0620)	0.0069 (0.0061)	0.0038 (0.0019)	ν_{65} (0.1813)	-0.0082 (0.0010)	-0.0641 (0.0625)
ν_{22} (0.0641)	-0.0738 (0.6622)	-0.0218 (0.0579)	ν_{66} (0.1826)	-0.0482 (0.0348)	-0.0485 (0.0352)
ν_{23} (0.0704)	0.0028 (0.0008)	-0.0258 (0.0674)	ν_{67} (0.1892)	-0.1121 (0.1756)	-0.0442 (0.0272)
ν_{24} (0.0721)	0.0188 (0.0339)	-0.0066 (0.0042)	ν_{68} (0.1917)	0.0054 (0.0004)	0.0477 (0.0309)
ν_{28} (0.0785)	0.0336 (0.0914)	-0.0158 (0.0204)	ν_{69} (0.1961)	-0.0350 (0.0160)	-0.1682 (0.3680)
ν_{31} (0.0828)	-0.0020 (0.0003)	0.0008 (0.0000)	ν_{70} (0.1992)	0.1703 (0.3653)	0.0677 (0.0578)
ν_{32} (0.0854)	-0.0227 (0.0354)	-0.0065 (0.0029)	ν_{71} (0.2008)	0.0077 (0.0007)	0.0383 (0.0182)
ν_{34} (0.0924)	-0.0360 (0.0761)	0.0074 (0.0032)	ν_{72} (0.2033)	-0.0873 (0.0922)	-0.1089 (0.1435)
ν_{36} (0.1030)	-0.0208 (0.0204)	-0.0091 (0.0039)	ν_{73} (0.2046)	-0.0099 (0.0012)	-0.0443 (0.0234)
ν_{42} (0.1119)	-0.0212 (0.0180)	-0.0132 (0.0069)	ν_{74} (0.2094)	0.0492 (0.0277)	-0.1193 (0.1623)
ν_{43} (0.1211)	-0.0129 (0.0057)	-0.0048 (0.0008)	ν_{75} (0.3882)	0.1014 (0.0341)	-0.0606 (0.0122)
ν_{46} (0.1276)	-0.0091 (0.0025)	-0.0026 (0.0002)	ν_{76} (0.3919)	-0.0052 (0.0001)	-0.0025 (0.0000)
ν_{47} (0.1289)	0.0200 (0.0121)	0.0141 (0.0060)	ν_{77} (0.3954)	-0.0025 (0.0000)	0.0004 (0.0000)
ν_{48} (0.1350)	0.0269 (0.0198)	0.0334 (0.0305)	ν_{78} (0.3958)	-0.0037 (0.0000)	-0.0004 (0.0000)
ν_{49} (0.1398)	-0.0459 (0.0539)	-0.0238 (0.0145)	ν_{79} (0.3980)	0.0022 (0.0000)	0.0025 (0.0000)
ν_{50} (0.1412)	-0.0115 (0.0033)	-0.0040 (0.0004)	ν_{80} (0.3993)	0.0017 (0.0000)	0.0017 (0.0000)
ν_{51} (0.1436)	0.0365 (0.0322)	0.0036 (0.0003)	ν_{81} (0.4008)	0.0003 (0.0000)	-0.0027 (0.0000)
ν_{52} (0.1455)	-0.0078 (0.0014)	-0.0050 (0.0006)	ν_{82} (0.4010)	0.0035 (0.0000)	-0.0001 (0.0000)
ν_{53} (0.1488)	-0.0380 (0.0325)	-0.0092 (0.0019)	ν_{83} (0.4576)	0.0052 (0.0001)	0.0037 (0.0000)
ν_{54} (0.1512)	0.0414 (0.0375)	0.0210 (0.0097)	ν_{84} (0.4579)	0.0033 (0.0000)	-0.0009 (0.0000)
ν_{55} (0.1539)	0.0344 (0.0249)	-0.0170 (0.0061)			
ν_{56} (0.1582)	-0.0696 (0.0969)	-0.0619 (0.0767)			
ν_{57} (0.1596)	0.0640 (0.0803)	0.0567 (0.0630)			

Table SI8: Linear interstate coupling parameters (λ) associated with S_1-S_2 of apigenin estimated at TD-B3LYP/6-311++G level of theory. All λ parameters are given in eV. The excitation strength ($\lambda^2/2\omega^2$) is given in the parentheses.

a″ modes [frequency]	$\lambda_{S_1-S_2}$
ν_1 (0.0026)	0.0176 (22.85)
ν_2 (0.0055)	—
ν_4 (0.0125)	0.0047 (0.07)
ν_5 (0.0141)	0.0124 (0.39)
ν_6 (0.0218)	0.0020 (0.01)
ν_7 (0.0277)	—
ν_9 (0.0312)	—
ν_{11} (0.0341)	0.0152 (0.10)
ν_{12} (0.0412)	0.0146 (0.06)
ν_{14} (0.0428)	0.0046 (0.01)
ν_{15} (0.0432)	—
ν_{18} (0.0532)	—
ν_{21} (0.0633)	0.0201 (0.05)
ν_{25} (0.0738)	—
ν_{26} (0.0748)	0.0166 (0.02)
ν_{27} (0.0780)	0.0269 (0.06)
ν_{29} (0.0800)	0.0245 (0.05)
ν_{30} (0.0826)	0.0097 (0.01)
ν_{33} (0.0916)	0.0090 (0.01)
ν_{35} (0.1013)	—
ν_{37} (0.1034)	—
ν_{38} (0.1041)	0.0105 (0.01)
ν_{39} (0.1062)	—
ν_{40} (0.1068)	0.0053 (0.01)
ν_{41} (0.1077)	0.0042 (0.01)
ν_{44} (0.1221)	0.0140 (0.01)
ν_{45} (0.1246)	0.0100 (0.01)

Table SI9: Linear intrastate coupling parameters (κ) of T_1, T_2, T_3 and T_4 states of apigenin obtained at TD-B3LYP/6-311++G level of theory. All coupling parameters are in eV. The excitation strength ($\kappa^2/2\omega^2$) is given in the parentheses.

a′ mode [frequency]	κ^{T_1}	κ^{T_2}	κ^{T_3}	κ^{T_4}
ν_3 (0.0108)	0.0093 (0.3717)	0.0014 (0.0082)	-0.0042 (0.0743)	0.0020 (0.0171)
ν_8 (0.0290)	0.0033 (0.0066)	-0.0134 (0.1066)	-0.0048 (0.0138)	-0.0129 (0.0985)
ν_{10} (0.0316)	0.0018 (0.0017)	0.0011 (0.0006)	0.0026 (0.0033)	-0.0092 (0.0425)
ν_{13} (0.0426)	-0.0062 (0.0106)	-0.0144 (0.0570)	0.0159 (0.0700)	-0.0004 (0.0001)
ν_{16} (0.0441)	-0.0019 (0.0009)	0.0273 (0.1916)	0.0077 (0.0151)	-0.0276 (0.1952)
ν_{17} (0.0505)	-0.0052 (0.0053)	-0.0247 (0.1191)	-0.0088 (0.0153)	0.0126 (0.0313)
ν_{19} (0.0547)	-0.0068 (0.0077)	-0.0135 (0.0306)	-0.0210 (0.0734)	0.0182 (0.0551)
ν_{20} (0.0620)	-0.0058 (0.0044)	0.0248 (0.0800)	-0.0105 (0.0143)	0.0044 (0.0026)
ν_{22} (0.0641)	-0.0264 (0.0848)	-0.0510 (0.3166)	-0.0051 (0.0032)	-0.0208 (0.0527)
ν_{23} (0.0704)	-0.0005 (0.0000)	0.0049 (0.0024)	-0.0321 (0.1041)	-0.0234 (0.0552)
ν_{24} (0.0721)	0.0233 (0.0523)	0.0214 (0.0440)	0.0159 (0.0244)	-0.0085 (0.0069)
ν_{28} (0.0785)	-0.0064 (0.0033)	0.0049 (0.0020)	-0.0150 (0.0182)	-0.0186 (0.0281)
ν_{31} (0.0828)	0.0011 (0.0001)	0.0020 (0.0003)	-0.0011 (0.0001)	0.0002 (0.0000)
ν_{32} (0.0854)	0.0007 (0.0000)	-0.0399 (0.1091)	0.0194 (0.0257)	-0.0065 (0.0029)
ν_{34} (0.0924)	-0.0069 (0.0028)	-0.0274 (0.0438)	-0.0066 (0.0025)	0.0096 (0.0054)
ν_{36} (0.1030)	-0.0411 (0.0796)	-0.0096 (0.0043)	-0.0387 (0.0704)	-0.0058 (0.0016)
ν_{42} (0.1119)	-0.0395 (0.0623)	-0.0076 (0.0023)	-0.0216 (0.0187)	-0.0153 (0.0094)
ν_{43} (0.1211)	-0.0110 (0.0041)	0.0095 (0.0030)	-0.0137 (0.0064)	-0.0086 (0.0025)
ν_{46} (0.1276)	-0.0171 (0.0090)	-0.0031 (0.0003)	-0.0200 (0.0122)	-0.0047 (0.0007)
ν_{47} (0.1289)	0.0233 (0.0163)	0.0102 (0.0031)	0.0112 (0.0038)	0.0110 (0.0036)
ν_{48} (0.1350)	0.0152 (0.0063)	0.0251 (0.0172)	0.0299 (0.0245)	0.0348 (0.0332)
ν_{49} (0.1398)	-0.0062 (0.0010)	-0.0546 (0.0763)	-0.0190 (0.0092)	-0.0182 (0.0085)
ν_{50} (0.1412)	-0.0204 (0.0104)	-0.0081 (0.0016)	-0.0104 (0.0027)	-0.0004 (0.0000)
ν_{51} (0.1436)	0.0037 (0.0003)	0.0183 (0.0081)	0.0258 (0.0162)	-0.0030 (0.0002)
ν_{52} (0.1455)	-0.0223 (0.0118)	-0.0069 (0.0011)	-0.0201 (0.0095)	-0.0047 (0.0005)
ν_{53} (0.1488)	-0.0055 (0.0007)	-0.0503 (0.0571)	-0.0038 (0.0003)	-0.0071 (0.0011)
ν_{54} (0.1512)	0.0676 (0.0999)	0.0264 (0.0152)	0.0449 (0.0440)	0.0154 (0.0052)
ν_{55} (0.1539)	0.0041 (0.0004)	0.0351 (0.0261)	0.0284 (0.0170)	-0.0204 (0.0088)
ν_{56} (0.1582)	-0.0832 (0.1381)	-0.0522 (0.0544)	-0.0607 (0.0737)	-0.0543 (0.0589)
ν_{57} (0.1596)	0.0637 (0.0797)	0.0524 (0.0538)	0.0608 (0.0726)	0.0530 (0.0552)
ν_{58} (0.1604)	0.0289 (0.0162)	0.0168 (0.0055)	-0.0012 (0.0000)	0.0150 (0.0044)

Table SI10: Linear intrastate coupling parameters (κ) of T_1, T_2, T_3 and T_4 states of apigenin obtained at TD-B3LYP/6-311++G level of theory. All coupling parameters are in eV. The excitation strength ($\kappa^2/2\omega^2$) is given in the parentheses.

a′ mode [frequency]	κ^{T_1}	κ^{T_2}	κ^{T_3}	κ^{T_4}
ν_{59} (0.1641)	-0.0041 (0.0003)	0.0550 (0.0561)	0.0555 (0.0572)	-0.0043 (0.0003)
ν_{60} (0.1669)	-0.0423 (0.0321)	0.0350 (0.0220)	0.0304 (0.0165)	-0.0370 (0.0246)
ν_{61} (0.1692)	-0.0057 (0.0006)	0.0074 (0.0010)	0.0015 (0.0000)	0.0126 (0.0028)
ν_{62} (0.1715)	-0.0261 (0.0116)	-0.0034 (0.0002)	-0.0044 (0.0003)	-0.0060 (0.0006)
ν_{63} (0.1747)	-0.0105 (0.0018)	-0.0794 (0.1034)	-0.0490 (0.0394)	-0.0284 (0.0132)
ν_{64} (0.1768)	-0.0311 (0.0155)	-0.0229 (0.0084)	-0.0490 (0.0384)	-0.0763 (0.0930)
ν_{65} (0.1813)	-0.0038 (0.0002)	-0.0528 (0.0425)	-0.0447 (0.0304)	-0.0715 (0.0779)
ν_{66} (0.1826)	-0.0360 (0.0194)	-0.0424 (0.0270)	-0.0464 (0.0324)	-0.0466 (0.0325)
ν_{67} (0.1892)	-0.0572 (0.0458)	-0.0568 (0.0450)	-0.0540 (0.0407)	-0.0404 (0.0228)
ν_{68} (0.1917)	-0.0182 (0.0045)	0.0193 (0.0050)	0.0349 (0.0166)	0.0552 (0.0414)
ν_{69} (0.1961)	0.0219 (0.0062)	-0.0753 (0.0738)	-0.0746 (0.0723)	-0.1840 (0.4403)
ν_{70} (0.1992)	0.1751 (0.3865)	0.1156 (0.1684)	0.0081 (0.0008)	0.0518 (0.0338)
ν_{71} (0.2008)	0.0477 (0.0282)	-0.0180 (0.0040)	0.0525 (0.0341)	0.0353 (0.0155)
ν_{72} (0.2033)	-0.1792 (0.3885)	-0.0074 (0.0007)	-0.1078 (0.1406)	-0.0936 (0.1060)
ν_{73} (0.2046)	0.0358 (0.0153)	0.0077 (0.0007)	0.0001 (0.0000)	-0.0453 (0.0245)
ν_{74} (0.2094)	-0.0863 (0.0850)	-0.0074 (0.0006)	-0.0381 (0.0165)	-0.1144 (0.1491)
ν_{75} (0.3882)	-0.0060 (0.0001)	0.0463 (0.0071)	0.0066 (0.0001)	-0.0815 (0.0220)
ν_{76} (0.3919)	-0.0016 (0.0000)	-0.0030 (0.0000)	-0.0015 (0.0000)	-0.0021 (0.0000)
ν_{77} (0.3954)	-0.0035 (0.0000)	-0.0022 (0.0000)	-0.0041 (0.0001)	0.0006 (0.0000)
ν_{78} (0.3958)	-0.0003 (0.0000)	-0.0019 (0.0000)	-0.0008 (0.0000)	-0.0000 (0.0000)
ν_{79} (0.3980)	-0.0005 (0.0000)	0.0007 (0.0000)	-0.0014 (0.0000)	0.0023 (0.0000)
ν_{80} (0.3993)	0.0071 (0.0002)	0.0014 (0.0000)	0.0043 (0.0001)	0.0015 (0.0000)
ν_{81} (0.4008)	-0.0084 (0.0002)	0.0033 (0.0000)	0.0022 (0.0000)	-0.0008 (0.0000)
ν_{82} (0.4010)	0.0005 (0.0000)	0.0046 (0.0001)	0.0015 (0.0000)	-0.0003 (0.0000)
ν_{83} (0.4576)	-0.0013 (0.0000)	0.0032 (0.0000)	0.0011 (0.0000)	0.0034 (0.0000)
ν_{84} (0.4579)	-0.0004 (0.0000)	0.0006 (0.0000)	0.0042 (0.0000)	-0.0017 (0.0000)

Table SI11: Linear interstate coupling parameters (λ) associated with T_1-T_4, T_2-T_4 and T_3-T_4 of apigenin estimated at TD-B3LYP/6-311++G level of theory. All λ parameters are given in eV. The excitation strength ($\lambda^2/2\omega^2$) is given in the parentheses.

a″ modes [frequency]	$\lambda_{T_1-T_4}$	$\lambda_{T_2-T_4}$	$\lambda_{T_3-T_4}$
ν_1 (0.0026)	0.0921 (627.3710)	0.0208 (31.9639)	0.0308 (70.3200)
ν_2 (0.0055)	—	0.0078 (1.0014)	—
ν_4 (0.0125)	0.0038 (0.0457)	0.0053 (0.0908)	0.0000 (0.0000)
ν_5 (0.0141)	0.0060 (0.0898)	0.0129 (0.4207)	0.0040 (0.0407)
ν_6 (0.0218)	—	0.0087 (0.0805)	0.0088 (0.0821)
ν_7 (0.0277)	—	0.0078 (0.0397)	—
ν_9 (0.0312)	0.0269 (0.3729)	0.0224 (0.2587)	0.0106 (0.0574)
ν_{11} (0.0341)	0.0015 (0.0009)	0.0186 (0.1487)	0.0085 (0.0313)
ν_{12} (0.0412)	0.0294 (0.2548)	—	0.0096 (0.0272)
ν_{14} (0.0428)	—	—	0.0039 (0.0041)
ν_{15} (0.0432)	—	—	0.0052 (0.0073)
ν_{18} (0.0532)	0.0209 (0.0772)	0.0036 (0.0023)	0.0091 (0.0148)
ν_{21} (0.0633)	0.0593 (0.4382)	0.0117 (0.0172)	0.0181 (0.0408)
ν_{25} (0.0738)	—	0.0318 (0.0928)	0.0153 (0.0216)
ν_{26} (0.0748)	—	0.0431 (0.1660)	0.0201 (0.0360)
ν_{27} (0.0780)	—	0.0355 (0.1033)	0.0122 (0.0122)
ν_{29} (0.0800)	—	0.0057 (0.0026)	—
ν_{30} (0.0826)	0.0460 (0.1549)	—	—
ν_{33} (0.0916)	0.0447 (0.1190)	—	0.0137 (0.0111)
ν_{35} (0.1013)	—	—	—
ν_{37} (0.1034)	—	—	—
ν_{38} (0.1041)	0.0397 (0.0727)	0.0088 (0.0036)	0.0136 (0.0085)
ν_{39} (0.1062)	—	0.0123 (0.0067)	—
ν_{40} (0.1068)	0.0447 (0.0876)	—	0.0101 (0.0045)
ν_{41} (0.1077)	0.0489 (0.1031)	—	0.0097 (0.0041)
ν_{44} (0.1221)	0.0342 (0.0391)	0.0043 (0.0006)	0.0114 (0.0044)
ν_{45} (0.1246)	0.0306 (0.0301)	0.0042 (0.0006)	0.0111 (0.0040)

Table SI12: Linear intrastate coupling parameters (κ) of S_1 and S_2 states of apigenin estimated at TD-M06/6-311++G level of theory. All coupling parameters are in eV. The excitation strength ($\kappa^2/2\omega^2$) is given in the parentheses.

a′ mode [frequency]	κ^{S_1}	κ^{S_2}	a′ mode [frequency]	κ^{S_1}	κ^{S_2}
ν_3 (0.0111)	0.0063 (0.1604)	0.0031 (0.0385)	ν_{58} (0.1629)	0.0112 (0.0023)	-0.0100 (0.0019)
ν_8 (0.0295)	-0.0018 (0.0019)	-0.0120 (0.0830)	ν_{59} (0.1657)	0.0667 (0.0809)	-0.0004 (0.0000)
ν_{10} (0.0320)	0.0116 (0.0659)	-0.0046 (0.0104)	ν_{60} (0.1680)	-0.0461 (0.0377)	0.0206 (0.0075)
ν_{13} (0.0431)	-0.0029 (0.0022)	0.0007 (0.0001)	ν_{61} (0.1712)	0.0041 (0.0003)	0.0333 (0.0189)
ν_{16} (0.0450)	0.0393 (0.3817)	-0.0150 (0.0555)	ν_{62} (0.1729)	-0.0037 (0.0002)	0.0111 (0.0021)
ν_{17} (0.0509)	-0.0358 (0.2475)	0.0156 (0.0467)	ν_{63} (0.1768)	-0.0080 (0.0010)	0.0109 (0.0019)
ν_{19} (0.0551)	-0.0409 (0.2749)	0.0142 (0.0334)	ν_{64} (0.1780)	-0.0894 (0.1260)	-0.0848 (0.1135)
ν_{20} (0.0619)	-0.0006 (0.0000)	0.0030 (0.0012)	ν_{65} (0.1825)	-0.0411 (0.0253)	-0.0188 (0.0053)
ν_{22} (0.0643)	-0.0690 (0.5761)	-0.0214 (0.0552)	ν_{66} (0.1849)	-0.0445 (0.0290)	-0.0613 (0.0550)
ν_{23} (0.0704)	0.0071 (0.0051)	-0.0247 (0.0614)	ν_{67} (0.1907)	-0.0950 (0.1240)	-0.0227 (0.0071)
ν_{25} (0.0726)	0.0220 (0.0460)	-0.0031 (0.0009)	ν_{68} (0.1922)	0.0253 (0.0087)	0.0380 (0.0196)
ν_{29} (0.0791)	0.0261 (0.0544)	-0.0163 (0.0213)	ν_{69} (0.1999)	-0.0775 (0.0752)	-0.1799 (0.4051)
ν_{31} (0.0823)	-0.0026 (0.0005)	0.0008 (0.0000)	ν_{70} (0.2018)	-0.1530 (0.2874)	-0.0187 (0.0043)
ν_{32} (0.0862)	-0.0198 (0.0263)	-0.0086 (0.0050)	ν_{71} (0.2030)	-0.0127 (0.0020)	0.0467 (0.0265)
ν_{34} (0.0930)	-0.0318 (0.0586)	0.0073 (0.0031)	ν_{72} (0.2060)	-0.0924 (0.1006)	-0.0958 (0.1082)
ν_{38} (0.1043)	-0.0225 (0.0234)	-0.0073 (0.0025)	ν_{73} (0.2070)	-0.0315 (0.0116)	-0.0846 (0.0836)
ν_{42} (0.1132)	-0.0136 (0.0072)	-0.0120 (0.0056)	ν_{74} (0.2120)	0.0233 (0.0060)	-0.1172 (0.1529)
ν_{44} (0.1231)	-0.0119 (0.0047)	-0.0069 (0.0016)	ν_{75} (0.3917)	-0.0039 (0.0001)	-0.0029 (0.0000)
ν_{46} (0.1283)	0.0190 (0.0109)	0.0120 (0.0044)	ν_{76} (0.3945)	-0.0022 (0.0000)	0.0000 (0.0000)
ν_{47} (0.1292)	-0.0044 (0.0006)	-0.0019 (0.0001)	ν_{77} (0.3951)	-0.0040 (0.0001)	0.0005 (0.0000)
ν_{48} (0.1382)	0.0141 (0.0052)	0.0320 (0.0268)	ν_{78} (0.3972)	0.0020 (0.0000)	0.0024 (0.0000)
ν_{49} (0.1404)	0.0159 (0.0064)	0.0007 (0.0000)	ν_{79} (0.3980)	0.0026 (0.0000)	0.0014 (0.0000)
ν_{50} (0.1416)	-0.0480 (0.0575)	-0.0234 (0.0136)	ν_{80} (0.4002)	0.0010 (0.0000)	-0.0015 (0.0000)
ν_{51} (0.1437)	0.0167 (0.0067)	-0.0015 (0.0001)	ν_{81} (0.4002)	0.0052 (0.0001)	-0.0013 (0.0000)
ν_{52} (0.1449)	-0.0063 (0.0010)	-0.0026 (0.0002)	ν_{82} (0.4072)	0.0861 (0.0224)	-0.0683 (0.0141)
ν_{53} (0.1488)	-0.0111 (0.0028)	-0.0025 (0.0001)	ν_{83} (0.4674)	0.0050 (0.0001)	-0.0007 (0.0000)
ν_{54} (0.1492)	0.0414 (0.0385)	0.0186 (0.0078)	ν_{84} (0.4675)	0.0039 (0.0000)	0.0045 (0.0000)
ν_{55} (0.1542)	-0.0383 (0.0309)	0.0078 (0.0013)			
ν_{56} (0.1594)	0.0763 (0.1145)	0.0635 (0.0792)			
ν_{57} (0.1613)	0.0171 (0.0056)	0.0236 (0.0107)			

Table SI13: Linear interstate coupling parameters (λ) associated with S_1-S_2 of apigenin estimated at TD-M06/6-311++G level of theory. All λ parameters are given in eV. The excitation strength ($\lambda^2/2\omega^2$) is given in the parentheses.

a″ modes [frequency]	$\lambda_{S_1-S_2}$
ν_1 (0.0022)	0.0203 (42.6881)
ν_2 (0.0053)	—
ν_4 (0.0121)	0.0070 (0.1669)
ν_5 (0.0140)	0.0108 (0.2972)
ν_6 (0.0212)	0.0028 (0.0086)
ν_7 (0.0275)	—
ν_9 (0.0306)	0.0084 (0.0377)
ν_{11} (0.0329)	0.0112 (0.0581)
ν_{12} (0.0410)	0.0116 (0.0403)
ν_{14} (0.0435)	—
ν_{15} (0.0445)	0.0130 (0.0427)
ν_{18} (0.0526)	—
ν_{21} (0.0627)	0.0178 (0.0404)
ν_{24} (0.0709)	0.0172 (0.0295)
ν_{26} (0.0730)	—
ν_{27} (0.0765)	0.0200 (0.0343)
ν_{28} (0.0790)	0.0364 (0.1060)
ν_{30} (0.0819)	0.0173 (0.0224)
ν_{33} (0.0903)	0.0119 (0.0086)
ν_{35} (0.0977)	—
ν_{36} (0.1013)	—
ν_{37} (0.1037)	0.0074 (0.0025)
ν_{39} (0.1053)	—
ν_{40} (0.1061)	0.0093 (0.0038)
ν_{41} (0.1069)	0.0107 (0.0050)
ν_{43} (0.1217)	0.0113 (0.0043)
ν_{45} (0.1250)	0.0103 (0.0034)

Table SI14: Linear intrastate coupling parameters (κ) of T_1, T_2, T_3 and T_4 states of apigenin obtained at TD-M06/6-311++G level of theory. All coupling parameters are in eV. The excitation strength ($\kappa^2/2\omega^2$) is given in the parentheses.

a′ mode [frequency]	κ^{T_1}	κ^{T_2}	κ^{T_3}	κ^{T_4}
ν_3 (0.0111)	0.0096 (0.3735)	-0.0006 (0.0013)	-0.0031 (0.0380)	0.0018 (0.0132)
ν_8 (0.0295)	0.0019 (0.0020)	-0.0119 (0.0809)	-0.0126 (0.0911)	-0.0135 (0.1049)
ν_{10} (0.0320)	0.0006 (0.0001)	-0.0080 (0.0311)	-0.0046 (0.0103)	-0.0081 (0.0316)
ν_{13} (0.0431)	-0.0056 (0.0085)	-0.0150 (0.0603)	0.0117 (0.0365)	-0.0025 (0.0016)
ν_{16} (0.0450)	-0.0017 (0.0007)	0.0170 (0.0714)	-0.0014 (0.0005)	-0.0237 (0.1391)
ν_{17} (0.0509)	-0.0018 (0.0006)	-0.0287 (0.1588)	-0.0070 (0.0094)	0.0147 (0.0416)
ν_{19} (0.0551)	-0.0035 (0.0020)	-0.0129 (0.0274)	-0.0116 (0.0223)	0.0178 (0.0520)
ν_{20} (0.0619)	-0.0077 (0.0078)	0.0252 (0.0829)	-0.0053 (0.0036)	0.0039 (0.0020)
ν_{22} (0.0643)	-0.0244 (0.0718)	-0.0458 (0.2534)	0.0024 (0.0007)	-0.0202 (0.0493)
ν_{23} (0.0704)	0.0043 (0.0018)	-0.0016 (0.0003)	-0.0232 (0.0542)	-0.0231 (0.0538)
ν_{25} (0.0726)	0.0204 (0.0394)	0.0245 (0.0569)	0.0175 (0.0292)	-0.0050 (0.0024)
ν_{29} (0.0791)	-0.0070 (0.0039)	0.0013 (0.0001)	-0.0237 (0.0450)	-0.0178 (0.0252)
ν_{31} (0.0823)	0.0017 (0.0002)	0.0032 (0.0008)	0.0018 (0.0002)	0.0004 (0.0000)
ν_{32} (0.0862)	-0.0002 (0.0000)	-0.0419 (0.1181)	0.0128 (0.0111)	-0.0088 (0.0052)
ν_{34} (0.0930)	-0.0082 (0.0039)	-0.0165 (0.0158)	-0.0025 (0.0004)	0.0091 (0.0048)
ν_{38} (0.1043)	-0.0510 (0.1194)	-0.0137 (0.0086)	-0.0373 (0.0640)	-0.0050 (0.0011)
ν_{42} (0.1132)	-0.0482 (0.0908)	-0.0035 (0.0005)	-0.0164 (0.0105)	-0.0140 (0.0076)
ν_{44} (0.1231)	-0.0103 (0.0035)	0.0238 (0.0187)	-0.0109 (0.0039)	-0.0092 (0.0028)
ν_{46} (0.1283)	0.0305 (0.0283)	0.0077 (0.0018)	0.0142 (0.0061)	0.0108 (0.0036)
ν_{47} (0.1292)	-0.0102 (0.0031)	0.0070 (0.0015)	-0.0181 (0.0098)	-0.0041 (0.0005)
ν_{48} (0.1382)	0.0171 (0.0077)	0.0131 (0.0045)	0.0154 (0.0062)	0.0329 (0.0283)
ν_{49} (0.1404)	0.0130 (0.0043)	0.0143 (0.0052)	0.0074 (0.0014)	-0.0023 (0.0001)
ν_{50} (0.1416)	0.0012 (0.0000)	-0.0633 (0.1000)	-0.0170 (0.0072)	-0.0192 (0.0091)
ν_{51} (0.1437)	0.0017 (0.0001)	0.0083 (0.0017)	0.0146 (0.0052)	-0.0043 (0.0005)
ν_{52} (0.1449)	-0.0188 (0.0084)	-0.0065 (0.0010)	-0.0105 (0.0026)	-0.0022 (0.0001)
ν_{53} (0.1488)	0.0151 (0.0051)	-0.0219 (0.0108)	0.0113 (0.0029)	-0.0031 (0.0002)
ν_{54} (0.1492)	0.0639 (0.0917)	0.0323 (0.0235)	0.0259 (0.0151)	0.0156 (0.0055)
ν_{55} (0.1542)	-0.0208 (0.0091)	-0.0444 (0.0415)	-0.0193 (0.0078)	0.0105 (0.0023)
ν_{56} (0.1594)	0.0962 (0.1820)	0.0325 (0.0208)	0.0518 (0.0527)	0.0557 (0.0611)
ν_{57} (0.1613)	0.0280 (0.0150)	0.0221 (0.0094)	0.0193 (0.0071)	0.0260 (0.0130)

Table SI15: Linear intrastate coupling parameters (κ) of T_1, T_2, T_3 and T_4 states of apigenin obtained at TD-M06/6-311++G level of theory. All coupling parameters are in eV. The excitation strength ($\kappa^2/2\omega^2$) is given in the parentheses.

a′ mode [frequency]	κ^{T_1}	κ^{T_2}	κ^{T_3}	κ^{T_4}
ν_{58} (0.1629)	-0.0301 (0.0170)	-0.0088 (0.0015)	-0.0114 (0.0025)	-0.0148 (0.0041)
ν_{59} (0.1657)	0.0107 (0.0021)	0.0395 (0.0284)	0.0469 (0.0400)	-0.0030 (0.0002)
ν_{60} (0.1680)	-0.0062 (0.0007)	-0.0307 (0.0167)	-0.0320 (0.0182)	0.0237 (0.0100)
ν_{61} (0.1712)	0.0412 (0.0290)	-0.0119 (0.0024)	-0.0066 (0.0007)	0.0341 (0.0198)
ν_{62} (0.1729)	0.0182 (0.0055)	-0.0199 (0.0067)	-0.0138 (0.0032)	0.0142 (0.0034)
ν_{63} (0.1768)	-0.0001 (0.0000)	-0.0497 (0.0395)	-0.0169 (0.0045)	0.0121 (0.0023)
ν_{64} (0.1780)	-0.0175 (0.0048)	-0.0449 (0.0318)	-0.0631 (0.0627)	-0.0797 (0.1003)
ν_{65} (0.1825)	-0.0331 (0.0164)	-0.0139 (0.0029)	-0.0190 (0.0054)	-0.0153 (0.0035)
ν_{66} (0.1849)	-0.0183 (0.0049)	-0.0416 (0.0253)	-0.0679 (0.0674)	-0.0631 (0.0582)
ν_{67} (0.1907)	-0.0491 (0.0332)	-0.0435 (0.0260)	-0.0310 (0.0132)	-0.0193 (0.0051)
ν_{68} (0.1922)	0.0101 (0.0014)	0.0188 (0.0048)	0.0295 (0.0118)	0.0407 (0.0224)
ν_{69} (0.1999)	0.0095 (0.0011)	-0.1091 (0.1489)	-0.0837 (0.0877)	-0.1899 (0.4513)
ν_{70} (0.2018)	-0.1837 (0.4141)	-0.1018 (0.1272)	0.0169 (0.0035)	-0.0060 (0.0004)
ν_{71} (0.2030)	0.0103 (0.0013)	-0.0299 (0.0108)	0.0452 (0.0248)	0.0490 (0.0291)
ν_{72} (0.2060)	-0.2023 (0.4820)	-0.0165 (0.0032)	-0.0859 (0.0870)	-0.0870 (0.0891)
ν_{73} (0.2070)	0.0003 (0.0000)	0.0058 (0.0004)	-0.0496 (0.0287)	-0.0840 (0.0824)
ν_{74} (0.2120)	-0.0974 (0.1054)	0.0166 (0.0031)	-0.0690 (0.0529)	-0.1147 (0.1463)
ν_{75} (0.3917)	-0.0016 (0.0000)	-0.0017 (0.0000)	-0.0011 (0.0000)	-0.0027 (0.0000)
ν_{76} (0.3945)	-0.0044 (0.0001)	-0.0022 (0.0000)	-0.0028 (0.0000)	0.0001 (0.0000)
ν_{77} (0.3951)	-0.0006 (0.0000)	-0.0033 (0.0000)	-0.0002 (0.0000)	0.0009 (0.0000)
ν_{78} (0.3972)	-0.0005 (0.0000)	0.0001 (0.0000)	-0.0009 (0.0000)	0.0023 (0.0000)
ν_{79} (0.3980)	0.0088 (0.0002)	0.0021 (0.0000)	0.0043 (0.0001)	0.0012 (0.0000)
ν_{80} (0.4002)	-0.0115 (0.0004)	0.0034 (0.0000)	0.0027 (0.0000)	-0.0003 (0.0000)
ν_{81} (0.4002)	0.0018 (0.0000)	0.0081 (0.0002)	0.0005 (0.0000)	-0.0019 (0.0000)
ν_{82} (0.4072)	-0.0064 (0.0001)	0.0374 (0.0042)	-0.0118 (0.0004)	-0.0810 (0.0198)
ν_{83} (0.4674)	0.0002 (0.0000)	-0.0014 (0.0000)	0.0042 (0.0000)	-0.0013 (0.0000)
ν_{84} (0.4675)	-0.0002 (0.0000)	0.0032 (0.0000)	0.0023 (0.0000)	0.0044 (0.0000)

Table SI16: Linear interstate coupling parameters (λ) associated with T_1-T_4, T_2-T_4 and T_3-T_4 of apigenin estimated at TD-M06/6-311++G level of theory. All λ parameters are given in eV. The excitation strength ($\lambda^2/2\omega^2$) is given in the parentheses.

a″ modes [frequency]	$\lambda_{T_1-T_4}$	$\lambda_{T_2-T_4}$	$\lambda_{T_3-T_4}$
ν_1 (0.0022)	0.1231 (1565.45)	0.0358 (132.6152)	0.0317 (103.5102)
ν_2 (0.0053)	—	0.0109 (2.1255)	0.0057 (0.5814)
ν_4 (0.0121)	—	0.0017 (0.0101)	0.0064 (0.1419)
ν_5 (0.0140)	0.0153 (0.5951)	0.0149 (0.5679)	0.0072 (0.1323)
ν_6 (0.0212)	—	0.0041 (0.0189)	0.0096 (0.1026)
ν_7 (0.0275)	—	0.0167 (0.1839)	—
ν_9 (0.0306)	0.0266 (0.3774)	0.0250 (0.3345)	0.0112 (0.0670)
ν_{11} (0.0329)	—	0.0275 (0.3483)	0.0100 (0.0466)
ν_{12} (0.0410)	0.0391 (0.4541)	0.0063 (0.0118)	0.0112 (0.0374)
ν_{14} (0.0435)	—	0.0081 (0.0172)	0.0112 (0.0333)
ν_{15} (0.0445)	0.0263 (0.1744)	0.0086 (0.0187)	0.0106 (0.0281)
ν_{18} (0.0526)	0.0313 (0.1765)	0.0139 (0.0351)	0.0130 (0.0304)
ν_{21} (0.0627)	0.0699 (0.6216)	0.0149 (0.0282)	0.0174 (0.0384)
ν_{24} (0.0709)	—	0.0543 (0.2929)	0.0217 (0.0469)
ν_{26} (0.0730)	—	0.0348 (0.1133)	0.0131 (0.0161)
ν_{27} (0.0765)	—	0.0316 (0.0853)	0.0073 (0.0045)
ν_{28} (0.0790)	—	0.0175 (0.0246)	—
ν_{30} (0.0819)	0.0718 (0.3839)	—	0.0100 (0.0075)
ν_{33} (0.0903)	0.0589 (0.2126)	0.0099 (0.0060)	0.0161 (0.0159)
ν_{35} (0.0977)	—	—	—
ν_{36} (0.1013)	—	0.0214 (0.0224)	—
ν_{37} (0.1037)	0.0525 (0.1282)	0.0151 (0.0105)	0.0143 (0.0096)
ν_{39} (0.1053)	0.0125 (0.0070)	0.0326 (0.0478)	0.0058 (0.0015)
ν_{40} (0.1061)	0.0605 (0.1627)	0.0082 (0.0030)	0.0105 (0.0049)
ν_{41} (0.1069)	0.0574 (0.1442)	0.0141 (0.0088)	0.0155 (0.0106)
ν_{43} (0.1217)	0.0503 (0.0854)	0.0118 (0.0047)	0.0147 (0.0073)
ν_{45} (0.1250)	0.0449 (0.0646)	0.0119 (0.0045)	0.0139 (0.0062)

Table SI17: Second-order coupling parameters (γ) of S_1 and S_2 states of apigenin estimated at different level of theory. All coupling parameters are in eV.

TD-B3LYP/6-311++G			TD-M06/6-311++G		
a′ mode [frequency]	γ^{S_1}	γ^{S_2}	a′ mode [frequency]	γ^{S_1}	γ^{S_2}
ν_3	-0.002161	-0.002148	ν_3	-0.002638	-0.001817
ν_8	-0.000796	-0.000962	ν_8	-0.001337	-0.000612
ν_{10}	-0.002270	-0.003396	ν_{10}	-0.002218	-0.002299
ν_{13}	-0.000909	-0.003110	ν_{13}	-0.001498	-0.004304
ν_{16}	-0.006776	-0.010526	ν_{16}	-0.005947	-0.007262
ν_{17}	-0.003080	-0.002065	ν_{17}	-0.004327	-0.001422
ν_{19}	-0.003218	-0.001806	ν_{19}	-0.004327	-0.001422
ν_{20}	-0.001899	-0.004345	ν_{20}	-0.003385	-0.001319
ν_{22}	-0.003939	-0.004424	ν_{22}	-0.004704	-0.005081
ν_{23}	-0.003029	-0.004534	ν_{23}	-0.002938	-0.004973
ν_{24}	-0.001801	-0.001550	ν_{25}	-0.002347	-0.002129
ν_{28}	-0.006460	-0.004285	ν_{29}	-0.006949	-0.004063
ν_{31}	-0.000089	0.000018	ν_{31}	-0.000775	0.000018
ν_{32}	-0.001634	-0.002398	ν_{32}	-0.001954	-0.002404
ν_{34}	-0.004307	-0.004895	ν_{34}	-0.005074	-0.005116
ν_{36}	-0.002603	-0.001606	ν_{38}	-0.002806	-0.001409
ν_{42}	-0.001294	-0.002535	ν_{42}	-0.002711	-0.003110
ν_{43}	-0.001732	0.000275	ν_{44}	-0.001649	0.000376
ν_{46}	-0.001371	0.000189	ν_{46}	-0.001349	-0.000694
ν_{47}	-0.001423	-0.001259	ν_{47}	-0.001842	0.000353
ν_{48}	-0.003571	-0.001408	ν_{48}	-0.002788	-0.002478
ν_{49}	-0.003026	-0.004170	ν_{49}	-0.001003	-0.000341
ν_{50}	-0.000323	-0.000000	ν_{50}	-0.005089	-0.005351
ν_{51}	-0.005407	-0.004845	ν_{51}	-0.004485	-0.003200
ν_{52}	-0.000514	-0.000381	ν_{52}	-0.000872	-0.000202
ν_{53}	-0.000871	0.000754	ν_{53}	-0.002041	0.000821
ν_{54}	-0.002742	-0.002117	ν_{54}	-0.002222	-0.001284
ν_{55}	-0.002264	-0.000010	ν_{55}	-0.003598	0.000906
ν_{56}	-0.000992	0.001375	ν_{56}	-0.004672	0.002254
ν_{57}	-0.002926	-0.001187	ν_{57}	-0.003911	-0.000640
ν_{58}	-0.007353	0.001644	ν_{58}	-0.005120	-0.000736
ν_{59}	-0.003076	-0.003110	ν_{59}	-0.002404	-0.000615

Table SI18: Second-order coupling parameters (γ) of S_1 and S_2 states of apigenin estimated at different level of theory. All coupling parameters are in eV.

TD-B3LYP/6-311++G			TD-M06/6-311++G		
a′ mode [frequency]	γ^{S_1}	γ^{S_2}	a′ mode [frequency]	γ^{S_1}	γ^{S_2}
ν_{60}	0.000274	0.003507	ν_{60}	-0.001153	-0.000311
ν_{61}	0.000575	0.001063	ν_{61}	0.002609	0.001247
ν_{62}	-0.000548	-0.000781	ν_{62}	0.000315	0.002790
ν_{63}	-0.002478	-0.008555	ν_{63}	-0.001217	-0.004256
ν_{64}	-0.024840	-0.030681	ν_{64}	-0.030550	-0.033460
ν_{65}	-0.004000	-0.010039	ν_{65}	-0.007336	-0.006979
ν_{66}	-0.000841	-0.001396	ν_{66}	0.000601	-0.001715
ν_{67}	-0.012569	-0.011641	ν_{67}	-0.017116	-0.014203
ν_{68}	-0.001689	-0.001926	ν_{68}	-0.002273	-0.000813
ν_{69}	-0.006795	-0.017771	ν_{69}	-0.011512	-0.017039
ν_{70}	-0.022548	-0.012188	ν_{70}	-0.021919	-0.014077
ν_{71}	-0.009021	-0.004244	ν_{71}	-0.008357	-0.003714
ν_{72}	-0.018046	-0.019489	ν_{72}	-0.015369	-0.017251
ν_{73}	-0.007737	-0.004244	ν_{73}	-0.014114	-0.008590
ν_{74}	-0.033648	-0.016573	ν_{74}	-0.038836	-0.017453
ν_{75}	-0.026121	-0.001662	ν_{75}	-0.000824	-0.000316
ν_{76}	-0.000871	-0.000816	ν_{76}	-0.000864	-0.000646
ν_{77}	-0.000975	-0.001634	ν_{77}	0.000394	-0.000035
ν_{78}	0.001266	-0.000064	ν_{78}	-0.000383	-0.000281
ν_{79}	-0.000841	-0.000846	ν_{79}	-0.000839	-0.000417
ν_{80}	-0.001149	-0.000920	ν_{80}	-0.000028	-0.000448
ν_{81}	0.000673	-0.001020	ν_{81}	0.000772	0.000281
ν_{82}	0.002734	0.000424	ν_{82}	-0.023457	0.004716
ν_{83}	-0.000753	-0.000746	ν_{83}	-0.000083	-0.000109
ν_{84}	0.001055	-0.000445	ν_{84}	-0.001003	-0.000281

Table SI19: The global minimum of S_1 and S_2 states and the S_1-S_2 MECI of apigenin estimated within the LVC formaliSI by using the different TDDFT vibronic coupling parameters. All parameters are in eV.

	TD-B3LYP	TD-M06
MECI	3.50	3.61
$S_{1,min.}$	3.10	3.36
$S_{2,min.}$	3.50	3.60

Table SI20: The minimum energy conical intersections (MECI) and state minimum of triplet manifolds of apigenin obtained at different TDDFT level of theory within the LVC approach. All parameters are given in eV.

MECI		
	TD-B3LYP/6-311++G	TD-M06/6-311++G
T_1-T_2	3.05	3.28
T_1-T_3	3.58	3.92
T_1-T_4	3.89	3.66
T_2-T_3	3.15	3.36
T_2-T_4	3.16	3.35
T_3-T_4	3.20	3.39
State-minimum		
	TD-B3LYP/6-311++G	TD-M06/6-311++G
$T_{1,min.}$	2.34	2.37
$T_{2,min.}$	2.95	3.13
$T_{3,min.}$	3.15	3.36
$T_{4,min.}$	3.16	3.35

Table SI21: MCTDH details with normal mode combination and size of the primitive and single particle basis employed in the S_1-S_2 vibronic dynamics of apigenin at different level of theory.

	Normal modes	Primitive basis	SPF basis
TD-B3LYP/ 6-311++G	(ν_1, ν_2, ν_3, ν_{23}, ν_{24})	(7,6,7,10,6)	[8,8]
	(ν_4, ν_5, ν_6, ν_{25}, ν_{26})	(9,8,8,8,6)	[8,7]
	(ν_7, ν_8, ν_9, ν_{27}, ν_{28})	(10,6,5,6,6)	[7,6]
	(ν_{10}, ν_{11}, ν_{12}, ν_{13}, ν_{29})	(6,6,6,7,5)	[6,6]
	(ν_{14}, ν_{15}, ν_{16}, ν_{17}, ν_{18}, ν_{30})	(7,7,8,8,8,6)	[6,6]
	(ν_{19}, ν_{20}, ν_{21}, ν_{22}, ν_{31}, ν_{32})	(9,8,7,6,6,5)	[7,7]
	Normal modes	Primitive basis	SPF basis
TD-M06/ 6-311++G	(ν_1, ν_2, ν_3, ν_{23}, ν_{24})	(8,7,7,10,8)	[8,8]
	(ν_4, ν_5, ν_6, ν_{25}, ν_{26})	(9,8,8,8,5)	[8,7]
	(ν_7, ν_8, ν_9, ν_{27}, ν_{28})	(10,6,6,5,5)	[7,6]
	(ν_{10}, ν_{11}, ν_{12}, ν_{13}, ν_{29})	(7,6,7,8,5)	[6,5]
	(ν_{14}, ν_{15}, ν_{16}, ν_{17}, ν_{18}, ν_{30})	(7,8,5,8,9,5)	[6,5]
	(ν_{19}, ν_{20}, ν_{21}, ν_{22}, ν_{31}, ν_{32})	(8,8,7,8,5,8)	[7,8]

Table SI22: MCTDH details with normal mode combination and size of the primitive and single particle basis employed in the T_1-T_2-T_3-T_4 vibronic dynamics of apigenin at different levels of theory.

	Normal modes	Primitive basis	SPF basis
TD-B3LYP/ 6-311++G	(ν_1, ν_2, ν_3, ν_{21}, ν_{22})	(9,8,7,10,10)	[8,8,8,8]
	(ν_4, ν_5, ν_6, ν_{23}, ν_{24})	(7,8,7,9,10)	[6,8,7,7]
	(ν_7, ν_8, ν_9, ν_{25}, ν_{26})	(7,7,7,7,8)	[7,7,7,5]
	(ν_{10}, ν_{11}, ν_{12}, ν_{27}, ν_{28})	(6,7,8,7,7)	[7,6,7,6]
	(ν_{13}, ν_{14}, ν_{15}, ν_{16}, ν_{29}, ν_{30})	(7,7,6,7,7,6)	[7,7,7,6]
	(ν_{17}, ν_{18}, ν_{19}, ν_{20}, ν_{31}, ν_{32})	(7,7,9,8,6,7)	[6,7,7,8]
	Normal modes	Primitive basis	SPF basis
TD-M06/ 6-311++G	(ν_1, ν_2, ν_3, ν_{21}, ν_{22})	(8,8,7,10,10)	[8,8,8, 8]
	(ν_4, ν_5, ν_6, ν_{23}, ν_{24})	(7,6,8,10,9)	[7,8,7,7]
	(ν_7, ν_8, ν_9, ν_{25}, ν_{26})	(7,7,7,9,8)	[7,7,7,6]
	(ν_{10}, ν_{11}, ν_{12}, ν_{27}, ν_{28})	(6,6,7,8,9)	[8,8,7,7]
	(ν_{13}, ν_{14}, ν_{15}, ν_{16}, ν_{29}, ν_{30})	(8,7,7,9,8,8)	[7,7,7,8]
	(ν_{17}, ν_{18}, ν_{19}, ν_{20}, ν_{31}, ν_{32})	(9,9,6,8,7,7)	[8,5,6,5]

Table SI23: Vertical energies (FC energies) of apigenin in different solvent environments computed at different TDDFT levels of theory. All values are in eV.

	TD-B3LYP			TD-M06		
	Toluene	DCM	Acetonitrile	Toluene	DCM	Acetonitrile
S_1	3.50 (A′, 0.36)	3.51 (A′, 0.42)	3.51 (A′, 0.42)	3.66 (A′, 0.48)	3.65 (A′, 0.53)	3.66 (A′, 0.53)
T_1	2.65 (A′)	2.65 (A′)	2.65 (A′)	2.69 (A′)	2.70 (A′)	2.70 (A′)
T_2	3.20 (A′)	3.21 (A′)	3.21 (A′)	3.32 (A′)	3.32 (A′)	3.32 (A′)
T_3	3.34 (A′)	3.36 (A′)	3.36 (A′)	3.53 (A′)	3.55 (A′)	3.55 (A′)
T_4	3.55 (A″)	3.65 (A″)	3.69 (A″)	3.72 (A″)	3.82 (A″)	3.85 (A″)

Table SI24: ISC pathway associated with the S_1 and corresponding triplet states of apigenin. The energy gap of the involved electronic states (ΔE_{ST} in cm^{-1}), SOC parameter (in cm^{-1}) and the ISC rate (K_{ISC} in s^{-1}) of those pathways estimated at the TD-M06/6-311++G level of theory.

ISC pathway	ΔE_{ST}	SOC	K_{ISC}
Gas phase			
S_1-T_2	3146	0.02	0.01 10^0
S_1-T_3	1613	0.05	6.28 x 10^2
S_1-T_4	726	5.62	3.12 x 10^8
Toluene			
S_1-T_2	2742	0	0
S_1-T_3	1049	0.04	4.76 x 10^3
S_1-T_4	484	2.38	1.24 x 10^8
DCM			
S_1-T_2	2662	0.01	0.07 x 10^0
S_1-T_3	807	0.03	6.67 x 10^3
S_1-T_4	1371	1.53	1.80 x 10^6
ACN			
S_1-T_2	2742	0.02	0.17 x 10^0
S_1-T_3	887	0.03	4.97 x 10^3
S_1-T_4	1532	1.47	7.96 x 10^5

Table SI25: The S_1-T_2 energy gap (ΔE_{ST} in cm^{-1}) along the each O-H bond length elongation (Å) and the corresponding SOCME (in cm^{-1}) and the ISC rate (K_{ISC} in s^{-1}) of apigenin tautomer in gas phase computed at the TD-B3LYP/6-311++G level of theory.

O-H bond length (Å)	$\Delta(E_{ST})$	SOCME (cm^{-1})	K_{ISC} x 10^6
1.00	2724.54	0.01944	0.0000002
1.04	2479.35	0.01142	0.0000003
1.08	2177.70	0.00022	0
1.12	1804.26	0.01478	0.0000215
1.16	1338.88	0.03284	0.0009558
1.20	815.430	0.05157	0.0191090
1.24	304.070	0.06851	0.1758200
1.28	139.530	0.08297	0.4038700
1.32	503.290	0.09515	0.1866600
1.36	791.230	0.10547	0.0871855
1.40	1022.71	0.11417	0.0429330
1.44	1210.64	0.12163	0.0227340
1.48	1364.69	0.12821	0.0130030
1.52	1496.16	0.13396	0.0078324
1.56	1597.78	0.13910	0.0052400
1.60	1694.57	0.14406	0.0035170
1.64	1764.74	0.14829	0.0026298
1.68	1832.49	0.15251	0.0019729
1.72	1876.85	0.15610	0.0016445
1.76	1931.70	0.15928	0.0012854
1.80	1969.61	0.16241	0.0010934
1.84	2005.09	0.16544	0.0009383

Table SI26: The S_1-T_3 energy gap (ΔE_{ST} in cm^{-1}) along the each O-H bond length elongation (Å) and the corresponding SOCME (in cm^{-1}) and the ISC rate (K_{ISC} in s^{-1}) of apigenin tautomer in gas phase computed at the TD-B3LYP/6-311++G level of theory.

O-H bond length (Å)	$\Delta(E_{ST})$	SOCME (cm^{-1})	K_{ISC} x 10^6
1.00	1496.16	0.07064	0.002180
1.04	1040.46	0.07778	0.018600
1.08	458.12	0.08627	0.177000
1.12	255.68	0.09587	0.395000
1.16	1083.20	0.10642	0.029300
1.20	1947.83	0.11665	0.000632
1.24	2776.16	0.12600	0.000006
1.28	3509.32	0.13411	0
1.32	4133.59	0.14212	0
1.36	4651.40	0.15143	0
1.40	5082.10	0.16640	0
1.44	5432.95	0.19785	0
1.48	5681.37	0.26530	0
1.52	5778.16	0.28358	0
1.56	5808.00	0.27558	0
1.60	5829.78	0.26880	0
1.64	5838.65	0.26341	0
1.68	5847.52	0.25894	0
1.72	5846.71	0.25504	0
1.76	5857.20	0.25156	0
1.80	5858.00	0.24837	0
1.84	5858.00	0.24542	0

Table SI27: The S_1-T_4 energy gap (ΔE_{ST} in cm^{-1}) along the each O-H bond length elongation (Å) and the corresponding SOCME (in cm^{-1}) and the ISC rate (K_{ISC} in s^{-1}) of apigenin tautomer in gas phase computed at the TD-B3LYP/6-311++G level of theory.

O-H bond length (Å)	$\Delta(E_{ST})$	SOCME (cm^{-1})	K_{ISC} x 10^{10}
1.00	628.31	8.05595	0.089300
1.04	287.94	10.0982	0.400000
1.08	1356.62	12.57463	0.012900
1.12	2501.13	15.43390	0.000047
1.16	3572.23	18.51866	0
1.2	4399.75	21.43561	0
1.24	4916.76	23.84933	0
1.28	5166.79	25.62430	0
1.32	5249.06	26.85096	0
1.36	5243.41	27.66998	0
1.40	5188.56	28.20613	0
1.44	5106.30	28.55262	0
1.48	5011.12	28.78739	0
1.52	4910.30	28.90723	0
1.56	4797.39	28.99296	0
1.60	4693.34	29.00030	0
1.64	4578.00	28.98678	0
1.68	4465.09	28.95228	0
1.72	4354.59	28.86390	0
1.76	4241.67	28.81620	0
1.80	4138.43	28.70869	0
1.84	4019.87	28.64655	0

Table SI28: The S_1-T_2 energy gap (ΔE_{ST} in cm^{-1}) along the each O-H bond length elongation (Å) and the corresponding SOCME (in cm^{-1}) and the ISC rate (K_{ISC} in s^{-1}) of apigenin tautomer in acetonitrile computed at the TD-B3LYP/6-311++G level of theory.

O-H bond length (Å)	$\Delta(E_{ST})$	SOCME (cm^{-1})	K_{ISC} x 10^6
1.00	2364.01	0.02525	0.000003
1.04	2262.39	0.02447	0.000005
1.08	2126.08	0.02513	0.000011
1.12	1950.25	0.02835	0.000037
1.16	1739.74	0.03457	0.000162
1.20	1496.16	0.04316	0.000813
1.24	1241.29	0.05235	0.003701
1.28	990.45	0.06116	0.013969
1.32	756.55	0.06899	0.042200
1.36	546.04	0.07588	0.104000
1.40	360.53	0.08160	0.211860
1.44	192.77	0.08679	0.383900
1.48	41.13	0.09136	0.628200
1.52	93.56	0.09552	0.602440
1.56	216.96	0.09951	0.472740
1.60	325.04	0.10311	0.375030
1.64	431.51	0.10618	0.290210
1.68	522.65	0.10930	0.231700
1.72	609.76	0.11230	0.184470
1.76	683.96	0.11510	0.151040
1.80	749.29	0.11777	0.126110
1.84	815.43	0.12044	0.104230

Table SI29: The S_1-T_3 energy gap (ΔE_{ST} in cm^{-1}) along the each O-H bond length elongation (Å) and the corresponding SOCME (in cm^{-1}) and the ISC rate (K_{ISC} in s^{-1}) of apigenin tautomer in acetonitrile computed at the TD-B3LYP/6-311++G level of theory.

O-H bond length (Å)	$\Delta(E_{ST})$	SOCME (cm^{-1})	K_{ISC} x 10^6
1.00	1269.52	0.05815	0.00404
1.04	873.50	0.06536	0.02480
1.08	347.62	0.07514	0.18700
1.12	309.72	0.08743	0.28200
1.16	1060.62	0.10127	0.02910
1.20	1843.78	0.11561	0.00107
1.24	2578.55	0.12938	0.00002
1.28	3222.99	0.14218	0
1.32	3773.06	0.15396	0
1.36	4224.73	0.16542	0
1.40	4599.78	0.17721	0
1.44	4916.76	0.19157	0
1.48	5186.14	0.20959	0
1.52	5410.37	0.23412	0
1.56	5591.84	0.26618	0
1.60	5727.34	0.30339	0
1.64	5824.94	0.33032	0
1.68	5878.98	0.34337	0
1.72	5910.43	0.34698	0
1.76	5924.95	0.34668	0
1.80	5925.76	0.34498	0
1.84	5928.98	0.34298	0

Table SI30: The S_1-T_4 energy gap (ΔE_{ST} in cm^{-1}) along the each O-H bond length elongation (Å) and the corresponding SOCME (in cm^{-1}) and the ISC rate (K_{ISC} in s^{-1}) of apigenin tautomer in acetonitrile computed at the TD-B3LYP/6-311++G level of theory.

O-H bond length (Å)	$\Delta(E_{ST})$	SOCME (cm^{-1})	K_{ISC} x 10^{10}
1.00	1400.98	3.57861	0.000861
1.04	2201.89	5.73591	0.000038
1.08	3147.98	8.42023	0
1.12	4152.95	11.55379	0
1.16	5087.75	14.83005	0
1.20	5827.36	17.96080	0
1.24	6320.97	20.61193	0
1.28	6593.58	22.70074	0
1.32	6736.34	24.26773	0
1.36	6779.90	25.43450	0
1.40	6781.51	26.30980	0
1.44	6741.18	26.97001	0
1.48	6687.14	27.47548	0
1.52	6612.94	27.85994	0
1.56	6531.48	28.14828	0
1.60	6443.56	28.34951	0
1.64	6346.78	28.55346	0
1.68	6250.80	28.66071	0
1.72	6144.33	28.77444	0
1.76	6043.51	28.81576	0
1.80	5939.47	28.85883	0
1.84	5835.42	28.88062	0

Table SI31: The S_1-T_2 energy gap (ΔE_{ST} in cm^{-1}) along the each O-H bond length elongation (Å) and the corresponding SOCME (in cm^{-1}) and the ISC rate (K_{ISC} in s^{-1}) of apigenin tautomer in gas phase computed at the TD-M06/6-311++G level of theory.

O-H bond length (Å)	$\Delta(E_{ST})$	SOCME (cm^{-1})	K_{ISC} x 10^6
0.99	3110.07	0.01883	0
1.03	2882.63	0.01651	0
1.07	2606.78	0.01101	0
1.11	2257.55	0.00060	0
1.15	1781.68	0.01865	0.000038
1.19	1290.49	0.04192	0.001920
1.23	913.83	0.06060	0.018400
1.27	586.37	0.07627	0.091900
1.31	290.36	0.09005	0.316000
1.35	22.58	0.10255	0.829000
1.39	204.86	0.11370	0.638000
1.43	390.37	0.12321	0.442000
1.47	541.20	0.13127	0.315000
1.51	662.99	0.13835	0.234000
1.55	759.77	0.14454	0.183000
1.59	842.85	0.15003	0.146000
1.63	913.83	0.15505	0.120000
1.67	970.28	0.15979	0.103000
1.71	1030.78	0.16383	0.085600
1.75	1070.30	0.16789	0.076900
1.79	1108.21	0.17124	0.068700
1.83	1143.69	0.17482	0.061900

Table SI32: The S_1-T_3 energy gap (ΔE_{ST} in cm^{-1}) along the each O-H bond length elongation (Å) and the corresponding SOCME (in cm^{-1}) and the ISC rate (K_{ISC} in s^{-1}) of apigenin tautomer in gas phase computed at the TD-M06/6-311++G level of theory.

O-H bond length (Å)	$\Delta(E_{ST})$	SOCME (cm^{-1})	K_{ISC} x 10^6
0.99	1551.00	0.04718	0.000751
1.03	1106.59	0.05559	0.007290
1.07	533.13	0.06695	0.084100
1.11	233.90	0.08354	0.318000
1.15	1296.13	0.11007	0.012900
1.19	2359.98	0.14260	0.000094
1.23	3110.07	0.17245	0.000001
1.27	3702.08	0.20674	0
1.31	4174.73	0.24909	0
1.35	4522.35	0.28948	0
1.39	4745.77	0.30972	0
1.43	4885.30	0.31289	0
1.47	4980.47	0.31002	0
1.51	5049.84	0.30573	0
1.55	5098.23	0.30116	0
1.59	5140.17	0.29675	0
1.63	5173.24	0.29257	0
1.67	5198.24	0.28869	0
1.71	5229.70	0.28480	0
1.75	5245.83	0.28127	0
1.79	5265.99	0.27789	0
1.83	5278.90	0.27477	0

Table SI33: The S_1-T_4 energy gap (ΔE_{ST} in cm^{-1}) along the each O-H bond length elongation (Å) and the corresponding SOCME (in cm^{-1}) and the ISC rate (K_{ISC} in s^{-1}) of apigenin tautomer in gas phase computed at the TD-M06/6-311++G level of theory.

O-H bond length (Å)	$\Delta(E_{ST})$	SOCME (cm^{-1})	K_{ISC} x 10^{10}
0.99	704.93	5.61228	0.03340
1.03	105.66	7.35123	0.34600
1.07	1104.17	9.50911	0.02150
1.11	2338.20	12.30562	0.00008
1.15	3779.51	16.05917	0
1.19	4835.29	19.49661	0
1.23	5363.59	21.68649	0
1.27	5636.20	23.28788	0
1.31	5766.06	24.48799	0
1.35	5742.67	25.40804	0
1.39	5650.72	26.02279	0
1.43	5531.35	26.40749	0
1.47	5408.75	26.65299	0
1.51	5291.80	26.78813	0
1.55	5174.85	26.8783	0
1.59	5070.81	26.88659	0
1.63	4962.73	26.92983	0
1.67	4862.72	26.89233	0
1.71	4760.28	26.89071	0
1.75	4654.63	26.84149	0
1.79	4558.65	26.78792	0
1.83	4459.44	26.72612	0

Table SI34: The S_1-T_2 energy gap (ΔE_{ST} in cm^{-1}) along the each O-H bond length elongation (Å) and the corresponding SOCME (in cm^{-1}) and the ISC rate (K_{ISC} in s^{-1}) of apigenin tautomer in acetonitrile computed at the TD-M06/6-311++G level of theory.

O-H bond length (Å)	$\Delta(E_{ST})$	SOCME (cm^{-1})	K_{ISC} x 10^6
0.99	2632.59	0.02259	0.0000004
1.03	2523.71	0.01930	0.0000006
1.07	2377.72	0.01699	0.0000012
1.11	2173.66	0.01680	0.0000038
1.15	1893.79	0.02162	0.0000288
1.19	1634.08	0.03122	0.0002210
1.23	1434.86	0.04139	0.0009890
1.27	1254.19	0.05137	0.0033700
1.31	1075.14	0.06101	0.0099600
1.35	900.11	0.07040	0.0261000
1.39	736.38	0.07897	0.0593000
1.43	591.20	0.08637	0.1160000
1.47	462.96	0.09290	0.2020000
1.51	350.85	0.09864	0.3190000
1.55	248.42	0.10380	0.4720000
1.59	163.73	0.10863	0.6500000
1.63	77.43	0.11269	0.8740000
1.67	3.23	0.11676	1.1300000
1.71	62.91	0.12059	1.0400000
1.75	125.02	0.12424	0.9410000
1.79	180.67	0.12742	0.8550000
1.83	239.55	0.13064	0.7660000

Table SI35: The S_1-T_3 energy gap (ΔE_{ST} in cm^{-1}) along the each O-H bond length elongation (Å) and the corresponding SOCME (in cm^{-1}) and the ISC rate (K_{ISC} in s^{-1}) of apigenin tautomer in acetonitrile computed at the TD-M06/6-311++G level of theory.

O-H bond length (Å)	$\Delta(E_{ST})$	SOCME (cm^{-1})	K_{ISC} x 10^6
0.99	859.79	0.03051	0.005690
1.03	524.26	0.03901	0.029400
1.07	71.78	0.05107	0.182000
1.11	567.01	0.06940	0.081000
1.15	1455.02	0.09766	0.005020
1.19	2286.58	0.12669	0.000114
1.23	2899.56	0.15064	0.000003
1.27	3408.50	0.17442	0
1.31	3849.68	0.20070	0
1.35	4227.15	0.23179	0
1.39	4531.22	0.26774	0
1.43	4756.25	0.30267	0
1.47	4915.14	0.33044	0
1.51	5023.22	0.34770	0
1.55	5099.04	0.35669	0
1.59	5147.43	0.36067	0
1.63	5194.21	0.36177	0
1.67	5223.25	0.36161	0
1.71	5245.02	0.36070	0
1.75	5261.15	0.35924	0
1.79	5266.80	0.35799	0
1.83	5275.67	0.35627	0

Table SI36: The S_1-T_4 energy gap (ΔE_{ST} in cm^{-1}) along the each O-H bond length elongation (Å) and the corresponding SOCME (in cm^{-1}) and the ISC rate (K_{ISC} in s^{-1}) of apigenin tautomer in acetonitrile computed at the TD-M06/6-311++G level of theory.

O-H bond length (Å)	$\Delta(E_{ST})$	SOCME (cm^{-1})	K_{ISC} x 10^6
0.99	1526.00	1.35793	0.700000
1.03	2225.28	2.93617	0.087100
1.07	3109.27	5.13107	0.000959
1.11	4233.60	8.19573	0
1.15	5511.99	12.28282	0
1.19	6388.72	15.77990	0
1.23	6864.58	18.18829	0
1.27	7145.27	20.08418	0
1.31	7285.61	21.63571	0
1.35	7320.29	22.88487	0
1.39	7278.35	23.83127	0
1.43	7201.72	24.53801	0
1.47	7113.81	25.04927	0
1.51	7021.86	25.43618	0
1.55	6930.72	25.72231	0
1.59	6838.77	25.92747	0
1.63	6741.18	26.13300	0
1.67	6645.20	26.26117	0
1.71	6539.54	26.37934	0
1.75	6447.60	26.43476	0
1.79	6346.78	26.51660	0
1.83	6258.06	26.54159	0

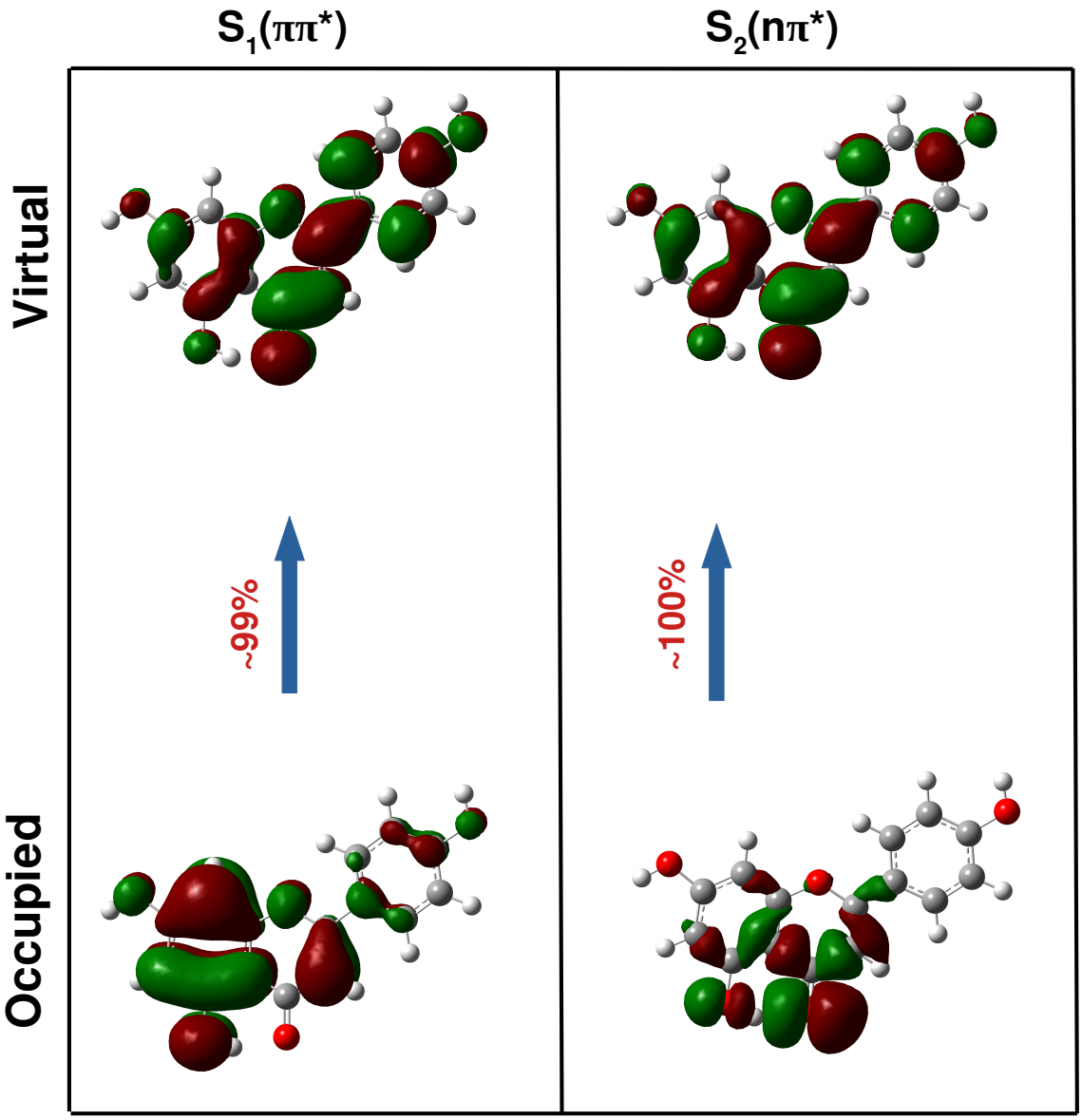

Figure S1: Natural transition orbitals (NTOs) associated with the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions of apigenin.

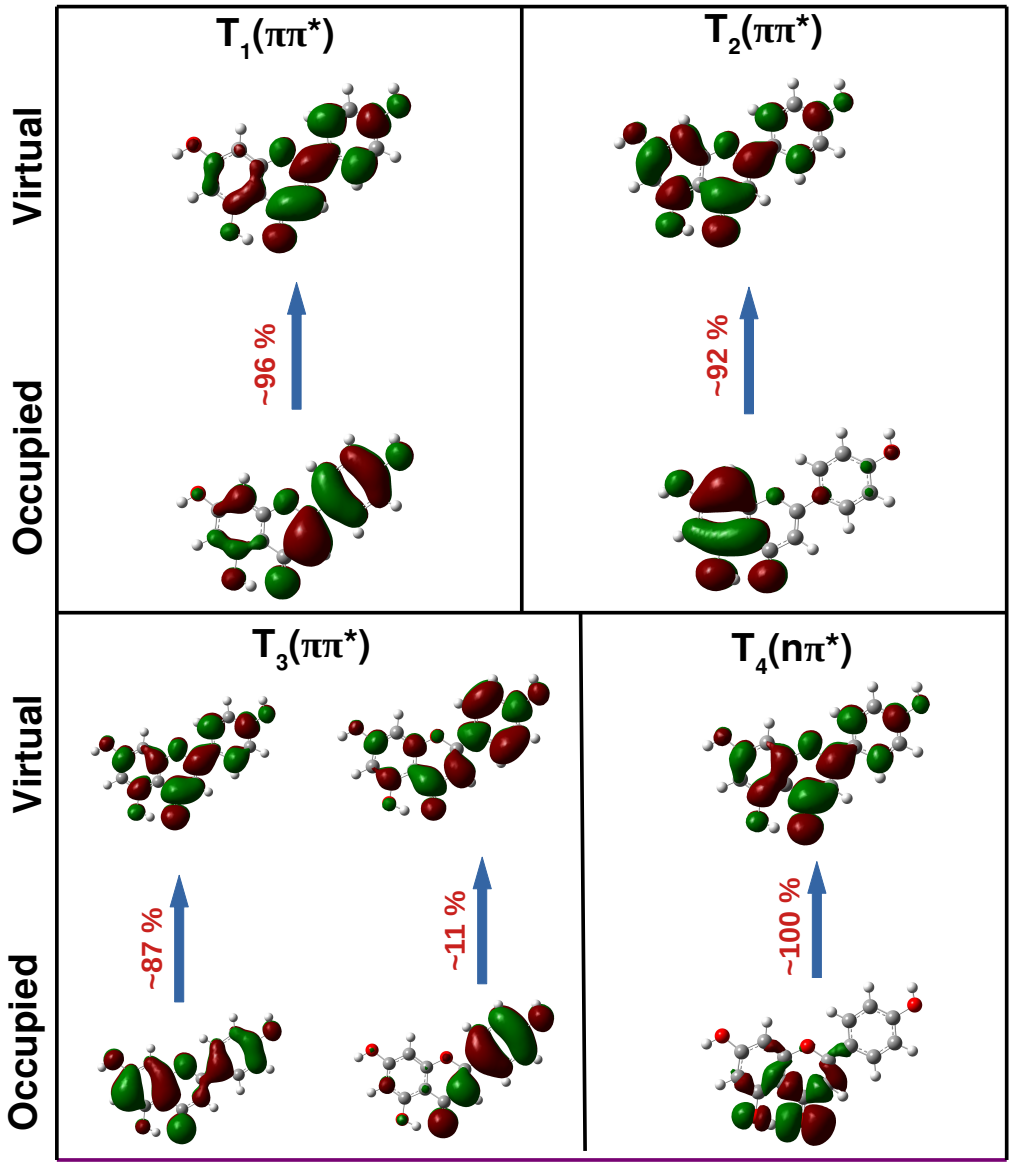

Figure S2: Natural transition orbitals (NTOs) associated with the $S_0 \rightarrow T_n$ transitions of apigenin.

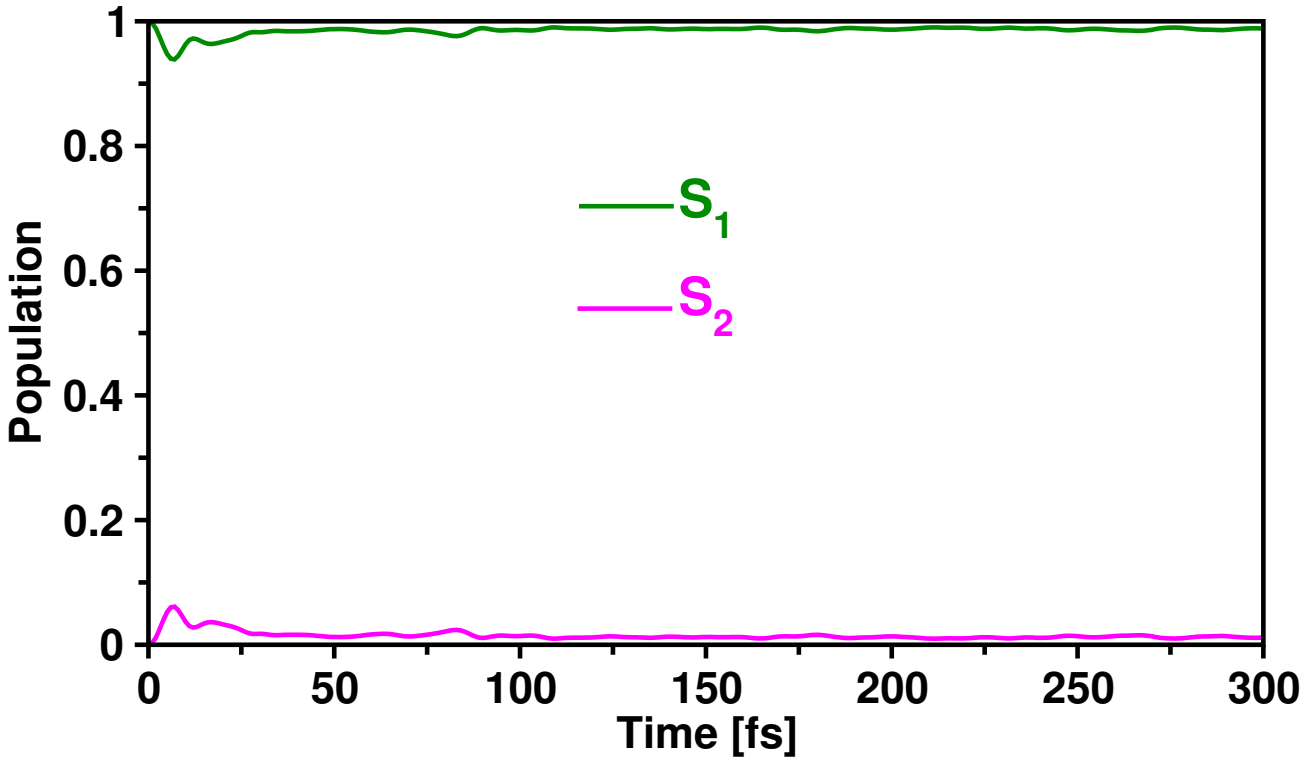

Figure S3: Diabatic electronic populations of S_1 and S_2 states obtained during the wavepacket propagation on S_1 state of apigenin. The vibronic coupling of the TD-M06 method is employed in these simulations.

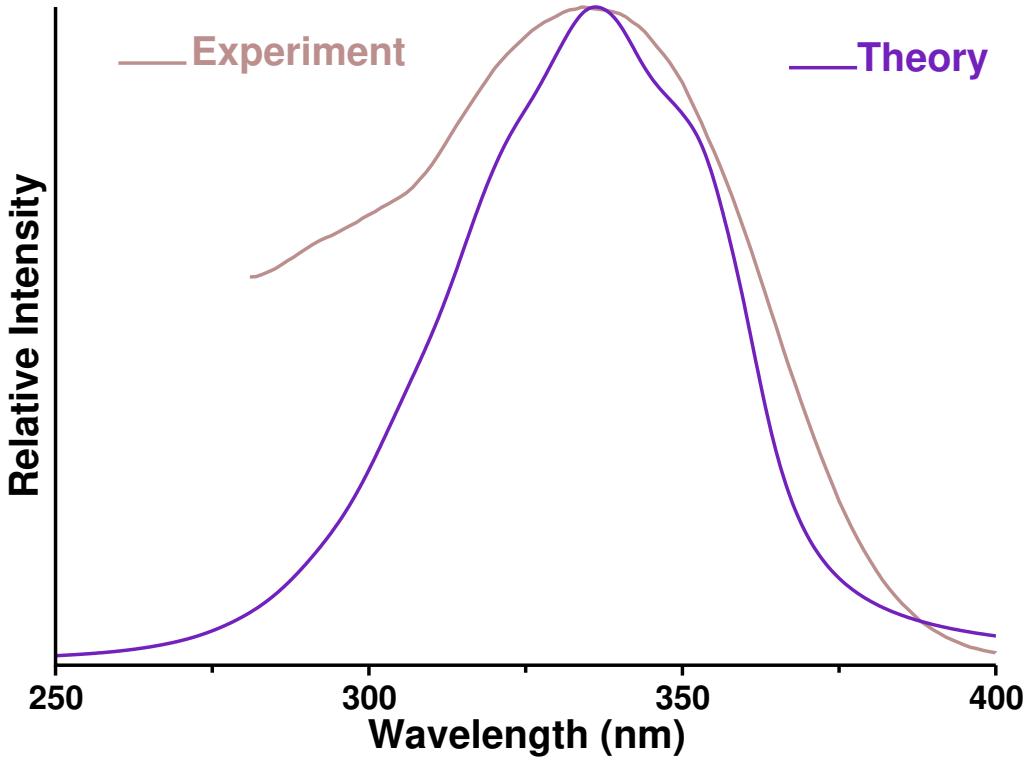

Figure S4: The low-energy absorption band of apigenin. The experimental band is reproduced from Ref. [34]. The theoretical band is obtained from the MCTDH wavepacket simulations using the vibronic coupling parameters of the TD-M06/6-311++G level of theory.

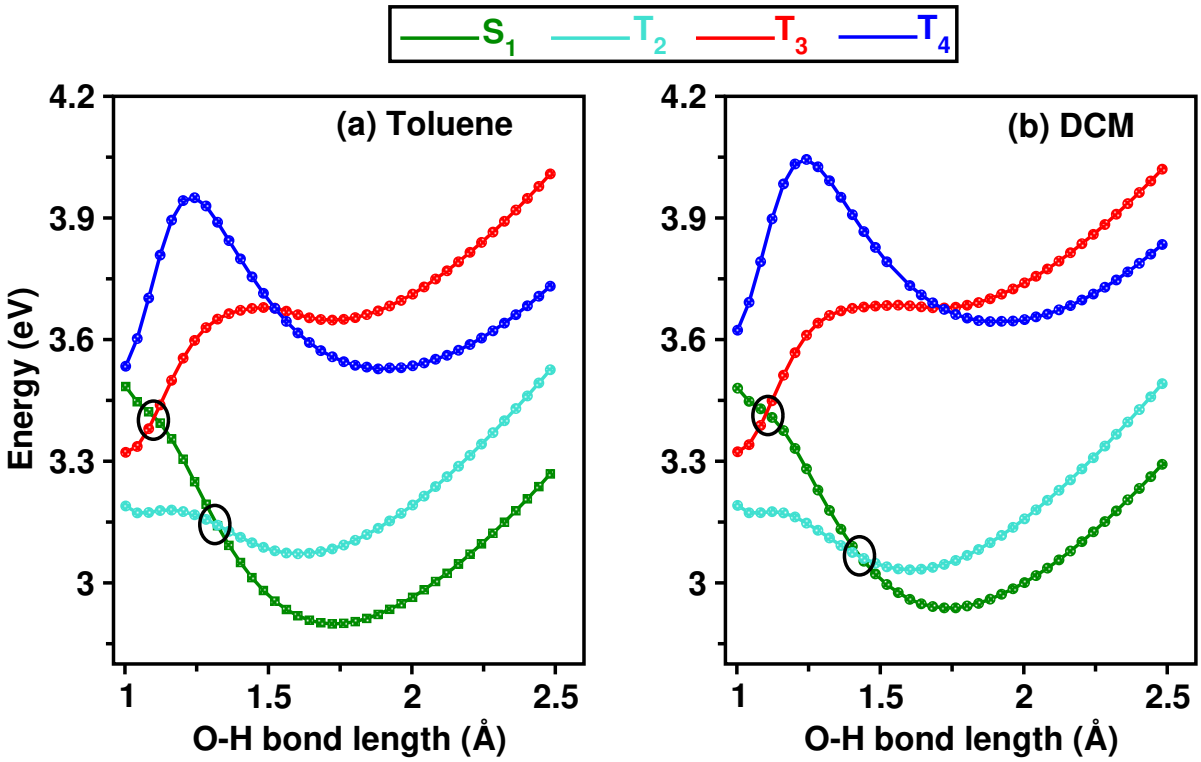

Figure S5:Relaxed scan profiles of S_1, T_2, T_3 and T_4 states along the O-H bond elongation of apigenin computed at TD-B3LYP/6-311++G level of theory in different solvents. Singlet-triplet crossings are shown open circle.

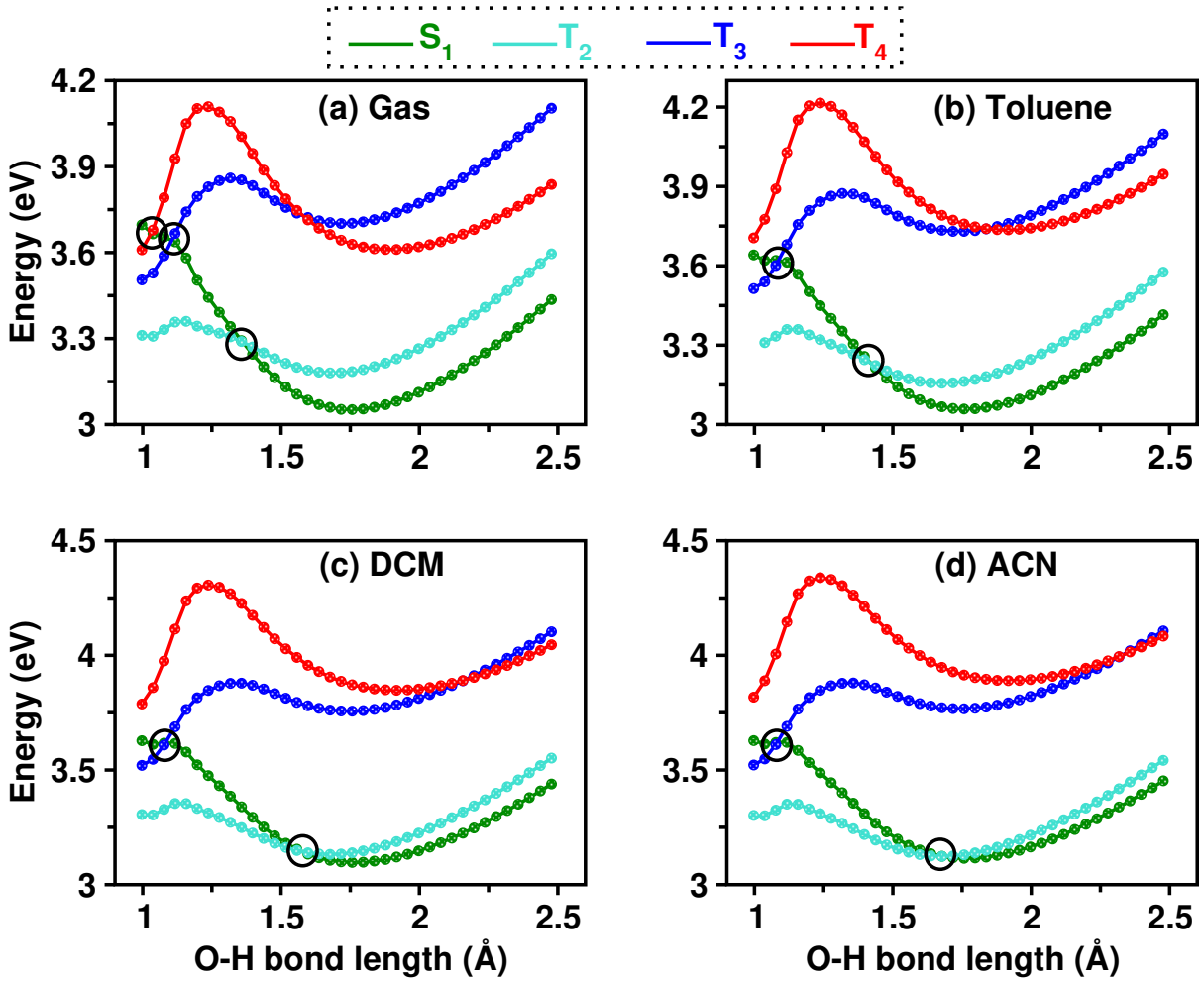

Figure S6: Relaxed scan profiles of S_1, T_2, T_3 and T_4 states along the O-H bond elongation of apigenin computed at TD-M06/6-311++G level of theory in different solvents. Singlet-triplet crossings are shown open circle.

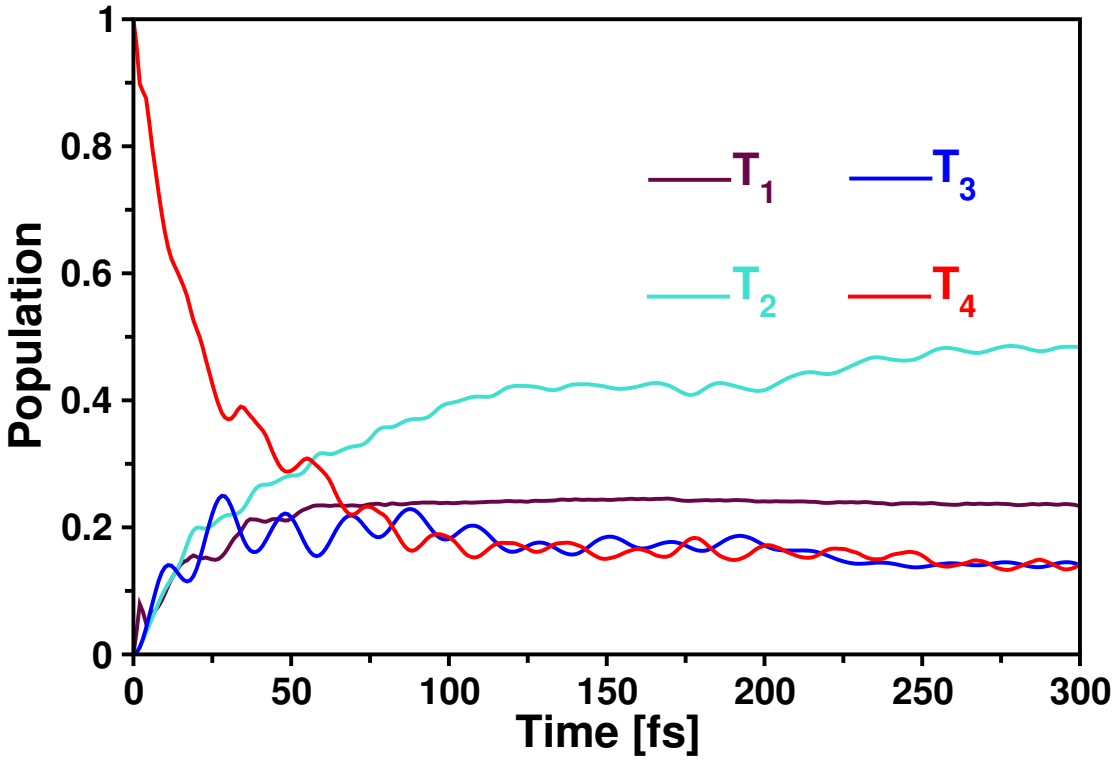

Figure S7: The MCTDH diabatic population of triplet states obtained by propagating the initial wavepacket on T_4 state. The vibronic coupling parameters estimated at the TD-M06/6-311++G level of theory were employed.

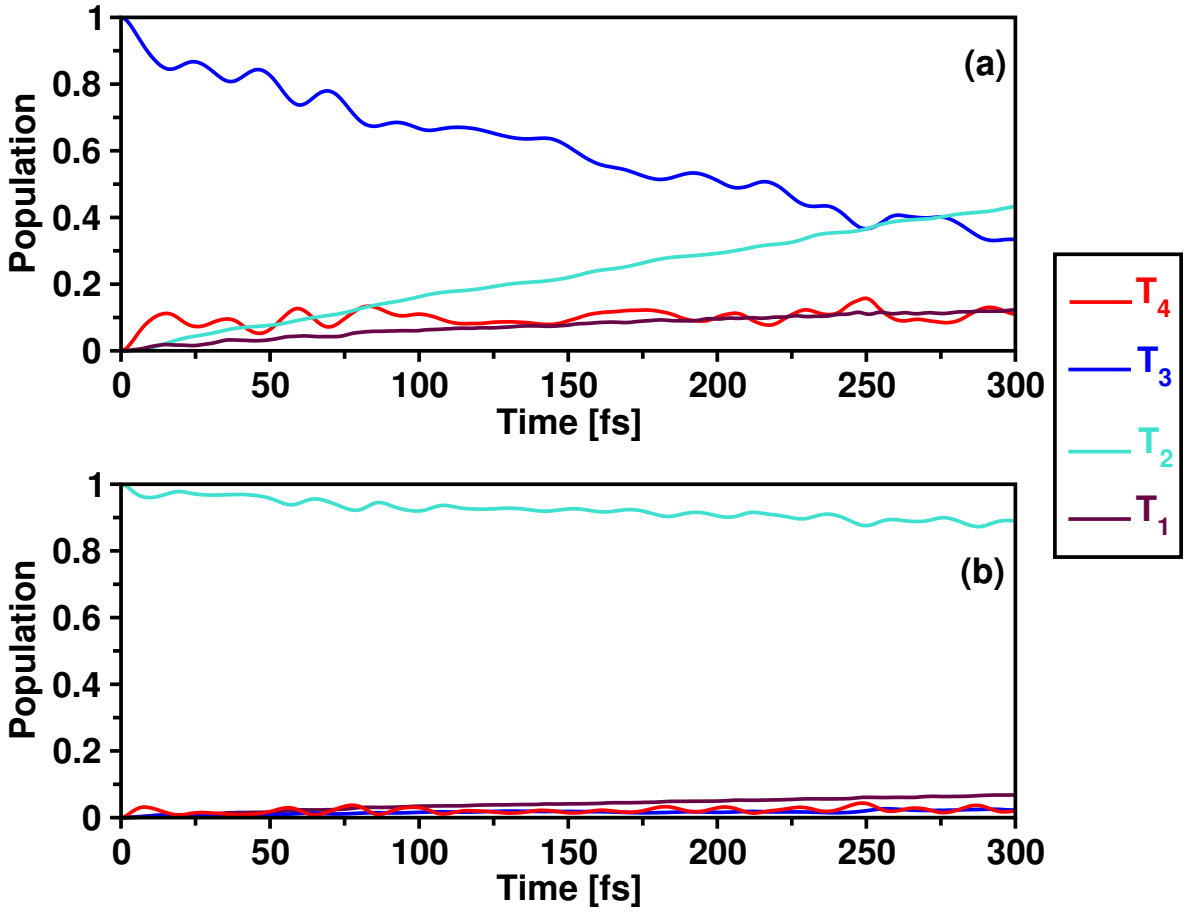

Figure S8: The MCTDH diabatic population of triplet states obtained by propagating the initial wavepacket on (a) T_3 and (b) T_2 states. The vibronic coupling parameters estimated at the TD-B3LYP/6-311++G level of theory were employed.

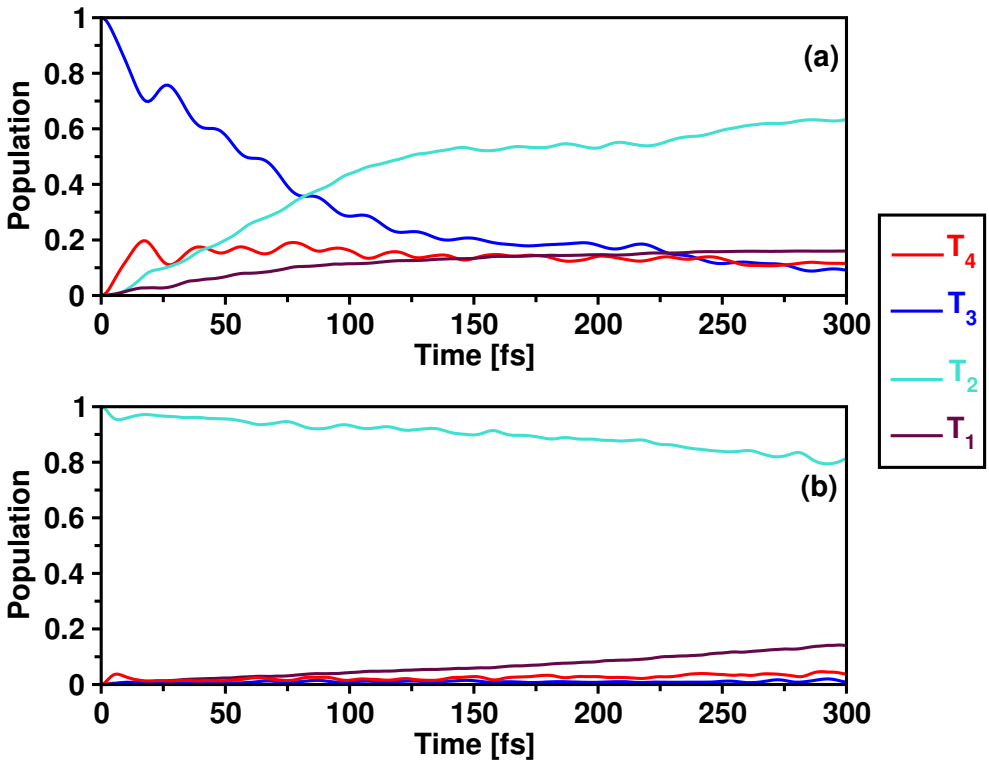

Figure S9: The MCTDH diabatic population of triplet states obtained by propagating the initial wavepacket on (a) T_3 and (b) T_2 states. The vibronic coupling parameters estimated at the TD-M06/6-311++G level of theory were employed.