Electronic Supplementary Information

Role of spin-orbit coupling, Duschinsky rotation and displacement vector on the rate of intersystem crossing of benzophenone and its fused analog fluorenone : A time dependent correlation function based approach

Pijush Karak and Swapan Chakrabarti*

Department of Chemistry,
University of Calcutta,
92, A.P.C. Road, Kolkata-700 009, India

* e-mail:swcchem@caluniv.ac.in

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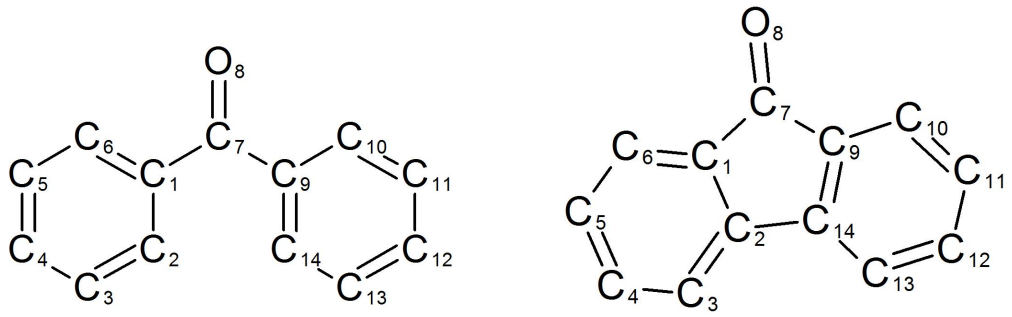
1. Figure of optimized geometries of benzophenone and fluorenone.



(a) (b)

Fig. S1: Optimized structures of (a) benzophenone and (b) fluorenone without depicting the H atoms.

2. Co-ordinates of the optimized geometries of benzophenone and fluorenone .

Table S1: **Coordinates of optimized geometry of S_0 state of benzophenone.**

C	0.000000	3.703275	0.350895
C	0.621763	3.761979	-0.897266
C	1.040271	2.589250	-1.521073
C	0.820333	1.356462	-0.910880
C	0.191815	1.288440	0.338884
C	-0.200248	2.476477	0.970487
H	-0.320379	4.615593	0.841152
H	0.785375	4.720154	-1.377770
H	1.540954	2.633162	-2.481635
H	1.162323	0.450420	-1.395472
H	-0.656614	2.412904	1.950607
C	-1.040271	-2.589250	-1.521073
C	-0.621763	-3.761979	-0.897266
C	0.000000	-3.703275	0.350895
C	0.200248	-2.476477	0.970487
C	-0.191815	-1.288440	0.338884
C	-0.820333	-1.356462	-0.910880
H	-1.540954	-2.633162	-2.481635
H	-0.785375	-4.720154	-1.377770
H	0.320379	-4.615593	0.841152
H	0.656614	-2.412904	1.950607
H	-1.162323	-0.450420	-1.395472
C	0.000000	0.000000	1.085719
O	0.000000	0.000000	2.304918

Table S2: **Coordinates of optimized geometry of S_1 state of benzophenone.**

C	-0.000000	3.717324	0.477178
C	0.461465	3.850816	-0.832900
C	0.784684	2.704437	-1.566508
C	0.644227	1.442818	-1.012142
C	0.145899	1.291301	0.304654
C	-0.156854	2.462452	1.045333
H	-0.245902	4.599540	1.057734
H	0.577525	4.832927	-1.275566
H	1.169341	2.799171	-2.575997
H	0.955516	0.573962	-1.575594
H	-0.540017	2.368867	2.053441
C	-0.784684	-2.704437	-1.566508
C	-0.461465	-3.850816	-0.832900
C	-0.000000	-3.717324	0.477178
C	0.156854	-2.462452	1.045333
C	-0.145899	-1.291301	0.304654
C	-0.644227	-1.442818	-1.012142
H	-1.169341	-2.799171	-2.575997
H	-0.577525	-4.832927	-1.275566
H	0.245902	-4.599540	1.057734
H	0.540017	-2.368867	2.053441
H	-0.955516	-0.573962	-1.575594
C	-0.000000	-0.000000	0.936989
O	-0.000000	-0.000000	2.252832

Table S3: **Coordinates of optimized geometry of T_1 state of benzophenone.**

C	0.000000	3.721763	0.461498
C	0.526232	3.854396	-0.824419
C	0.886838	2.706879	-1.541855
C	0.728474	1.447144	-0.989573
C	0.161472	1.295747	0.299279
C	-0.181894	2.467137	1.022842
H	-0.280297	4.604475	1.025521
H	0.661498	4.836190	-1.262505
H	1.311668	2.803004	-2.535028
H	1.055380	0.572481	-1.537215
H	-0.614453	2.365698	2.010018
C	-0.886838	-2.706879	-1.541855
C	-0.526232	-3.854396	-0.824419
C	-0.000000	-3.721763	0.461498
C	0.181894	-2.467137	1.022842
C	-0.161472	-1.295747	0.299279
C	-0.728474	-1.447144	-0.989573
H	-1.311668	-2.803004	-2.535028
H	-0.661498	-4.836190	-1.262505
H	0.280297	-4.604475	1.025521
H	0.614453	-2.365698	2.010018
H	-1.055380	-0.572481	-1.537215
C	0.000000	0.000000	0.919339
O	0.000000	0.000000	2.243640

Table S4: **Coordinates of optimized geometry of T_2 state of benzophenone.**

C	-0.000383	3.743808	0.667130
C	-0.000000	4.022076	-0.699065
C	0.000622	2.945012	-1.611294
C	0.000683	1.637798	-1.177437
C	0.000146	1.314843	0.213224
C	-0.000233	2.437186	1.119652
H	-0.000719	4.555001	1.386484
H	-0.000069	5.043407	-1.060231
H	0.001125	3.149529	-2.676386
H	0.001365	0.865771	-1.927195
H	-0.000371	2.221891	2.175219
C	-0.000622	-2.945012	-1.611294
C	-0.000000	-4.022076	-0.699065
C	0.000383	-3.743808	0.667130
C	0.000233	-2.437186	1.119652
C	-0.000146	-1.314843	0.213224
C	-0.000683	-1.637798	-1.177437
H	-0.001125	-3.149529	-2.676386
H	0.000069	-5.043407	-1.060231
H	0.000719	-4.555001	1.386484
H	0.000371	-2.221891	2.175219
H	-0.001365	-0.865771	-1.927195
C	0.000000	-0.000000	0.818131
O	0.000000	-0.000000	2.143615

Table S5: **Coordinates of optimized geometry of S_0 state of fluorenone**

C	1.391551	0.000033	3.026515
C	1.707718	0.000015	1.662161
C	0.668900	-0.000028	0.741582
C	-0.664894	-0.000053	1.188840
C	-0.981140	-0.000030	2.536605
C	0.066373	0.000012	3.463132
H	2.192630	0.000068	3.757377
H	2.744123	0.000041	1.343628
H	-2.018219	-0.000053	2.852866
H	-0.148882	0.000027	4.525367
C	1.707718	0.000015	-1.662161
C	1.391551	0.000033	-3.026515
C	0.066373	0.000012	-3.463132
C	-0.981140	-0.000030	-2.536605
C	-0.664894	-0.000053	-1.188840
C	0.668900	-0.000028	-0.741582
H	2.744123	0.000041	-1.343628
H	2.192630	0.000068	-3.757377
H	-0.148882	0.000027	-4.525367
H	-2.018219	-0.000053	-2.852866
C	-1.579437	-0.000124	0.000000
O	-2.790596	0.000149	0.000000

Table S6: **Coordinates of optimized geometry of S_1 state of fluorenone.**

C	-1.429431	-0.000194	2.987586
C	-1.742917	0.000103	1.648913
C	-0.687886	0.000250	0.704190
C	0.704003	0.000309	1.151458
C	0.988625	-0.000143	2.516485
C	-0.066528	-0.000275	3.416400
H	-2.215314	-0.000360	3.733093
H	-2.776380	0.000351	1.321472
H	2.019593	-0.000246	2.849365
H	0.138409	-0.000538	4.481547
C	-1.742917	0.000103	-1.648913
C	-1.429431	-0.000194	-2.987586
C	-0.066528	-0.000275	-3.416400
C	0.988625	-0.000143	-2.516485
C	0.704003	0.000309	-1.151458
C	-0.687886	0.000250	-0.704190
H	-2.776380	0.000351	-1.321472
H	-2.215314	-0.000360	-3.733093
H	0.138409	-0.000538	-4.481547
H	2.019593	-0.000246	-2.849365
C	1.606480	0.000206	0.000000
O	2.854764	-0.000032	0.000000

Table S7: **Coordinates of optimized geometry of T_1 state of fluorenone.**

C	0.000000	-1.426460	2.989101
C	-0.000001	-1.747490	1.660847
C	-0.000002	-0.694120	0.699114
C	0.000000	0.699669	1.155115
C	0.000003	0.993664	2.517808
C	0.000003	-0.052328	3.423800
H	0.000001	-2.208647	3.738978
H	-0.000001	-2.783587	1.341559
H	0.000003	2.027525	2.843534
H	0.000003	0.154160	4.488146
C	-0.000001	-1.747490	-1.660847
C	0.000000	-1.426460	-2.989101
C	0.000003	-0.052328	-3.423800
C	0.000003	0.993664	-2.517808
C	0.000000	0.699669	-1.155115
C	-0.000002	-0.694120	-0.699114
H	-0.000001	-2.783587	-1.341559
H	0.000001	-2.208647	-3.738978
H	0.000003	0.154160	-4.488146
H	0.000003	2.027525	-2.843534
C	-0.000005	1.603303	-0.000000
O	-0.000001	2.840755	-0.000000

Table S8: **Coordinates of optimized geometry of T_2 state of fluorenone.**

C	0.000082	-1.388779	3.029347
C	0.000040	-1.704651	1.665281
C	-0.000007	-0.680379	0.733187
C	-0.000120	0.671895	1.171394
C	0.000035	0.990758	2.538104
C	0.000082	-0.055188	3.449395
H	0.000139	-2.183345	3.765847
H	0.000127	-2.740595	1.344498
H	-0.000005	2.019242	2.874983
H	0.000072	0.167252	4.510727
C	0.000040	-1.704651	-1.665281
C	0.000082	-1.388779	-3.029347
C	0.000082	-0.055188	-3.449395
C	0.000035	0.990758	-2.538104
C	-0.000120	0.671895	-1.171394
C	-0.000007	-0.680379	-0.733187
H	0.000127	-2.740595	-1.344498
H	0.000139	-2.183345	-3.765847
H	0.000072	0.167252	-4.510727
H	-0.000005	2.019242	-2.874983
C	-0.000387	1.519680	0.000000
O	0.000041	2.794117	0.000000

3. Geometrical parameters of ground and excited electronic states of benzophenone and fluorenone.

Table S9: **Geometrical parameters of ground and excited electronic states of benzophenone and fluorenone. Angles, dihedral angles and bond lengths are in degree, degree and angstrom unit respectively.**

geometrical parameters of benzophenone	S_0(expt.)	S_0	S_1	T_1	T_2
$C_7 - 0_8$	1.24	1.21	1.31	1.32	1.32
$C_7 - C_9$	1.49	1.50	1.44	1.44	1.44
$C_2 - C_1$	1.37	1.40	1.41	1.41	1.42
$C_1 - C_6$	1.39	1.40	1.41	1.41	1.44
$< C_1 - C_7 - C_9$	122.4	120.3	128.1	129.1	130.5
$< C_2 - C_1 - C_7$	117.3	122.8	122.5	122.0	127.7
$< C_1 - C_7 - O_8$	120.0	119.8	115.9	115.4	114.7
$< C_2 - C_1 - C_7 - O_8$	---	148.6	156.3	153.0	179.9
$< C_6 - C_1 - C_7 - O_8$	---	27.0	20.4	23.1	0.022
$< C_1 - C_7 - C_9 - C_{14}$	---	31.13	23.6	26.9	0.025

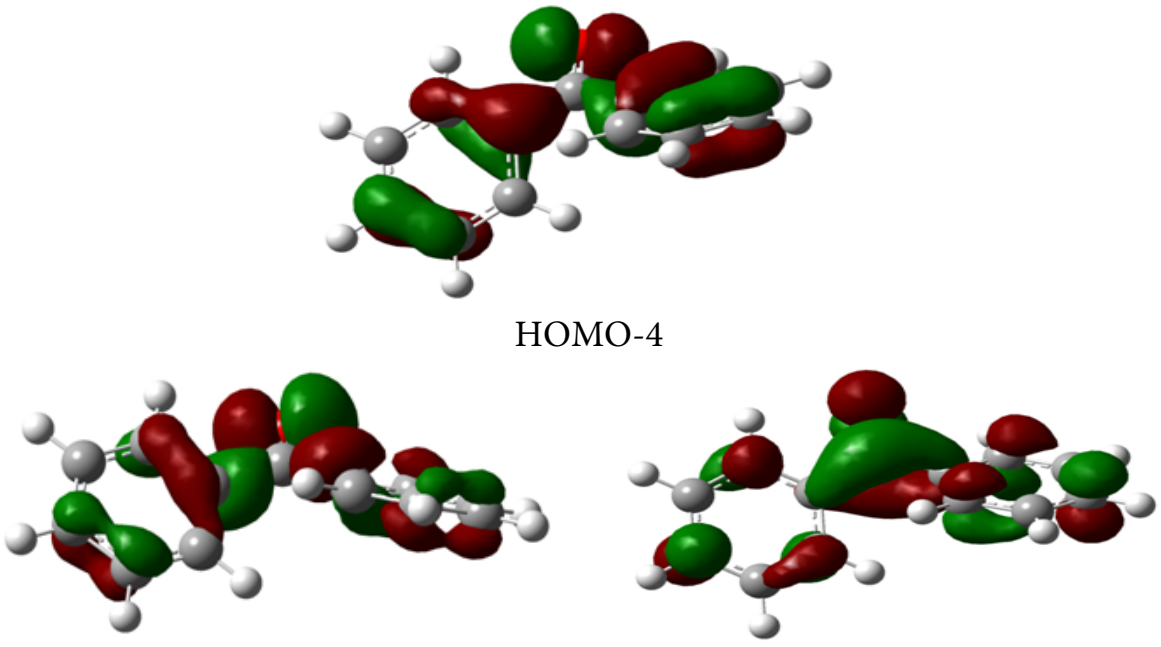
geometrical parameters of fluorenone	S_0(expt.)	S_0	S_1	T_1	T_2
$C_7 - 0_8$	1.21	1.21	1.24	1.23	1.27
$C_2 - C_{14}$	1.44	1.48	1.40	1.39	1.46
$C_1 - C_2$	1.40	1.40	1.46	1.46	1.42
$C_9 - C_{10}$	1.40	1.40	1.46	1.46	1.42
$C_1 - C_7$	1.38	1.38	1.39	1.39	1.40
$< C_1 - C_7 - C_9$	106.5	104.8	103.8	103.9	108.2
$< C_1 - C_7 - O_8$	126.7	127.5	128.08	128.03	125.8
$< C_3 - C_2 - C_{14}$	131.2	131.5	131.8	132.3	132.2
$< C_2 - C_1 - C_7$	109.1	109.03	110.2	109.9	107.9
$< C_3 - C_2 - C_{14} - C_{13}$	0.011	0.00	0.00	0.00	0.00
$< C_2 - C_1 - C_7 - O_8$	179.95	179.98	179.98	180.0	180.0
$< C_3 - C_2 - C_1 - C_7$	179.98	179.96	179.97	179.97	179.98

4. Electronic states and character of the orbitals involved with the transition process of benzophenone and fluorenone.

Table S10: **Electronic states and character of the orbitals involved with the transition process of benzophenone and fluorenone.**

system	electronic transition	transition orbital	nature of transition orbital
benzophenone	$S_0 \rightarrow S_1$	H-4→L	$n-\pi^*$
	$S_0 \rightarrow T_1$	H-4→L	$n-\pi^*$
	$S_0 \rightarrow T_1$	H→L	$\pi-\pi^*$
	$S_0 \rightarrow T_2$	H→L	$\pi-\pi^*$
fluorenone	$S_0 \rightarrow S_1$	H-4→L	$n-\pi^*$
	$S_0 \rightarrow T_1$	H→L	$\pi-\pi^*$
	$S_0 \rightarrow T_2$	H→L+1	$\pi-\pi^*$
	$S_0 \rightarrow T_2$	H-1→L	$n-\pi^*$

5. Molecular orbitals associated with transition process for each molecule.



HOMO-4

HOMO LUMO

Fig. S2: Molecular orbital pictures of benzophenone (isovalue=0.04).

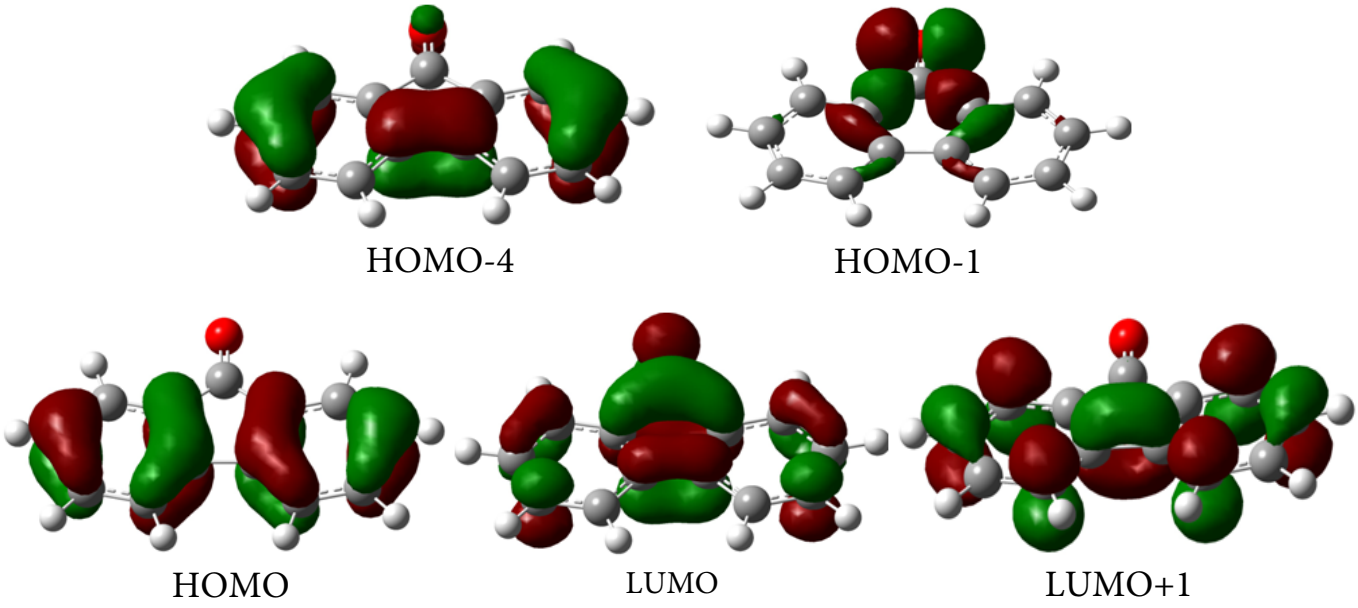


Fig. S3: Molecular orbital pictures of fluorenone (isovalue=0.04)

6. Nature of the real part of time dependent correlation function.

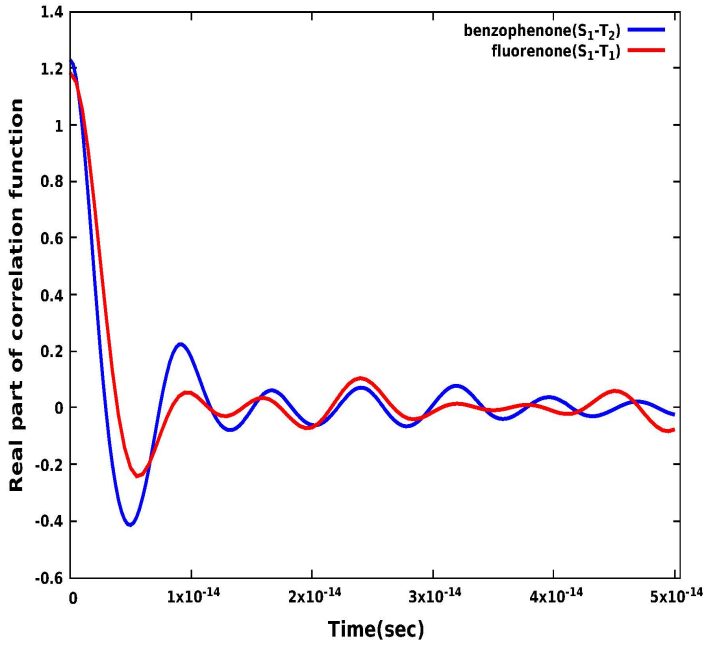


Fig. S4: Real part of the time dependent correlation function for the first 50 fs of benzophenone and fluorenone.

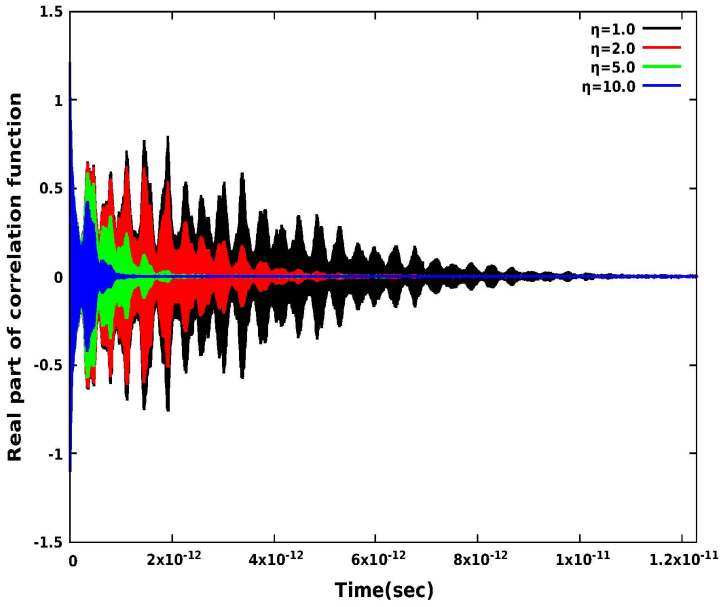


Fig. S5: Real part of the time dependent correlation function for the first 12 ps of benzophenone for S_1 - T_1 pathway.

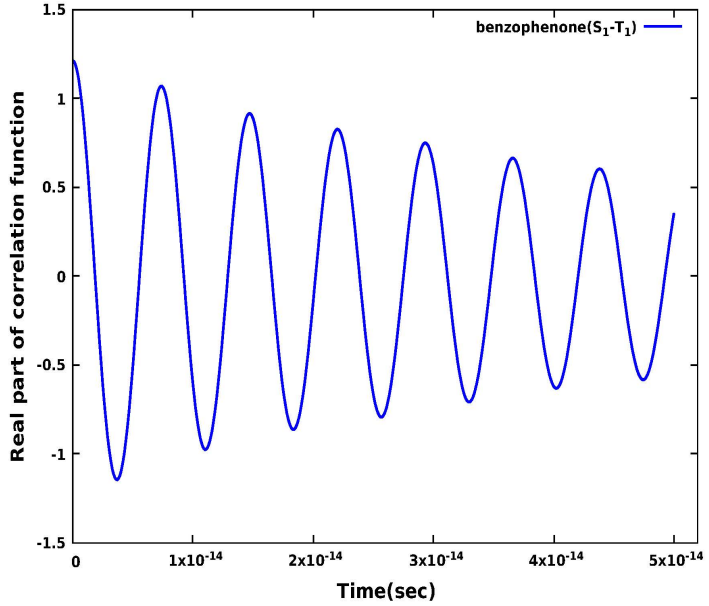


Fig. S6: Real part of the time dependent correlation function for the first 50 fs of benzophenone for S_1 -T_1 pathway.

7. k_{ISC} data of S_1 - T_1 pathway of benzophenone.

Table S21: k_{ISC} data of $S_1 \rightsquigarrow T_1$ pathway of benzophenone

Temparature(K)	**Time interval(ps)**	**#points**	$\eta(\mathbf{cm}^{-1})$	$\mathbf{k_{ISC}}\,(s^{-1})$
0	20	20000	1.0	1.28×10^8
0	20	20000	2.0	2.41×10^8
0	20	20000	5.0	3.55×10^8
0	20	20000	10.0	3.39×10^7
0	20	20000	100	2.74×10^8

8. SEPARATION OF THE INTERSYSTEM CROSSING RATE FORMULA INTO REAL AND IMAGINARY PART FOR FINITE TEMPARATURE CASE

The final form of intersystem crossing rate formula after using Mehler's generating formula is

$$\begin{aligned} \mathrm{k_{ISC}} = \quad & \frac{1}{Z}|\left\langle S_a|\hat{H}_{so}|T_b\right\rangle|^2 \int_{-\infty}^{\infty} \sqrt{\frac{det(\mathbf{S_S^{-1}S_T^{-1}\Omega_S\Omega_T})}{det(\mathbf{J^\dagger\Omega_T B_T J+\Omega_S B_S})det(\mathbf{J^\dagger\Omega_T B_T^{-1}J+\Omega_S B_S^{-1}})}} \\ & \times e^{\mathbf{D^\dagger}\left(\mathbf{\Omega_T B_T J(J^\dagger\Omega_T B_T}J+\mathbf{\Omega_S B_S})^{-1}\mathbf{J^\dagger\Omega_T B_T-\Omega_T B_T}\right)\mathbf{D}} \times e^{it\Delta E}dt, \end{aligned} \tag{1}$$

where the form of is generating function is

$$\begin{aligned} G(t) = \sqrt{\frac{det(\mathbf{S}_S^{-1}\mathbf{S}_T^{-1}\mathbf{\Omega}_S\mathbf{\Omega}_T)}{det(\mathbf{J^\dagger\Omega}_T\mathbf{B}_T\mathbf{J}+\mathbf{\Omega}_S\mathbf{B}_S)det(\mathbf{J^\dagger\Omega}_T\mathbf{B}_T^{-1}\mathbf{J}+\mathbf{\Omega}_S\mathbf{B}_S^{-1})}} \\ \times e^{\mathbf{D^\dagger}\left(\mathbf{\Omega}_T\mathbf{B}_T\mathbf{J}(\mathbf{J^\dagger\Omega}_T\mathbf{B}_T\mathbf{J}+\mathbf{\Omega}_S\mathbf{B}_S)^{-1}\mathbf{J^\dagger\Omega}_T\mathbf{B}_T-\mathbf{\Omega}_T\mathbf{B}_T\right)\mathbf{D}}, \end{aligned} \tag{2}$$

where, $(\mathbf{S}_S)_{ii} = \sinh\left((\beta - it)(\boldsymbol{\omega}_S)_i\right)$,$(\mathbf{S}_T)_{ii} = \sinh(i(\boldsymbol{\omega}_T)_i t)$,$(\mathbf{B}_T)_{ii} = \tanh(\frac{i(\boldsymbol{\omega}_T)_i t}{2})$, $(\mathbf{B}_S)_{ii} = \tanh\left(\frac{(\beta-it)(\boldsymbol{\omega}_S)_i}{2}\right)$. These all are diagonal matrix.
$(\mathbf{S}_T)_{ii} = \sinh(i(\boldsymbol{\omega}_T)_i t) = i\sin((\boldsymbol{\omega}_T)_i t), (\mathbf{B}_T)_{ii} = \tanh(\frac{i(\boldsymbol{\omega}_T)_i t}{2}) = i\tan(\frac{(\boldsymbol{\omega}_T)_i t}{2})$,
$(\mathbf{S}_S)_{ii} = \sinh\left((\beta - it)(\boldsymbol{\omega}_S)_i\right) = \sinh(2x)\cos(2y) - i\sin(2y)\cosh(2x)$ where $y = \frac{i(\boldsymbol{\omega}_S)_i t}{2}, x = \frac{\beta(\boldsymbol{\omega}_S)_i}{2}$
$(\mathbf{B}_S)_{ii} = \tanh\left(\frac{(\beta-it)(\boldsymbol{\omega}_S)_i}{2}\right) = \frac{\sinh(2x)}{\cosh(2x)+\cos(2y)} - i\frac{\sin(2y)}{\cosh(2x)+\cos(2y)}$

1 Simplification of the determinant part within square root

$$
\begin{aligned}
&(\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{B}_T\mathbf{J}+\mathbf{\Omega}_S\mathbf{B}_S)(\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{B}_T^{-1}\mathbf{J}+\mathbf{\Omega}_S\mathbf{B}_S^{-1})\\
&=\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{B}_T\mathbf{J}\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{B}_T^{-1}\mathbf{J}+\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{B}_T\mathbf{J}\mathbf{\Omega}_S\mathbf{B}_S^{-1}+\mathbf{\Omega}_S\mathbf{B}_S\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{B}_T^{-1}\mathbf{J}+\mathbf{\Omega}_S\mathbf{B}_S\mathbf{\Omega}_S\mathbf{B}_S^{-1}\\
&=\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{B}_T\mathbf{\Omega}_T\mathbf{B}_T^{-1}\mathbf{J}+\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{B}_T\mathbf{J}\mathbf{\Omega}_S\mathbf{B}_S^{-1}+\mathbf{\Omega}_S\mathbf{B}_S\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{B}_T^{-1}\mathbf{J}+\mathbf{\Omega}_s^2\\
&=\mathbf{J}^\dagger\mathbf{\Omega}_T^2\mathbf{J}+\mathbf{\Omega}_S^2+\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{B}_T\mathbf{J}\mathbf{\Omega}_S\mathbf{B}_S^{-1}+\mathbf{\Omega}_S\mathbf{B}_S\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{B}_T^{-1}\mathbf{J}\\
&=\mathbf{J}^\dagger\mathbf{\Omega}_T^2\mathbf{J}+\mathbf{\Omega}_S^2+\mathbf{J}^\dagger\mathbf{\Omega}_T i\mathbf{b}_T\mathbf{J}\mathbf{\Omega}_S(\mathbf{A}'+i\mathbf{B}')+\frac{\mathbf{\Omega}_S(\mathbf{A}+i\mathbf{B})\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T^{-1}\mathbf{J}}{i},
\end{aligned}
\tag{3}
$$

where, $\mathbf{B}_S=\mathbf{A}+i\mathbf{B},\mathbf{B}_S^{-1}=(\mathbf{A}'+i\mathbf{B}'),\mathbf{B}_T=i\mathbf{b}_T,\mathbf{b}_T=\tan(\frac{\boldsymbol{\omega}_{T_i}t}{2}),\mathbf{B}_T^{-1}=-i\mathbf{b}_T^{-1},\mathbf{b}_T^{-1}=\frac{1}{\tan(\frac{\boldsymbol{\omega}_{T_i}t}{2})}$.

$$
\begin{aligned}
&=\mathbf{J}^\dagger\mathbf{\Omega}_T^2\mathbf{J}+\mathbf{\Omega}_s^2+i\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T\mathbf{J}\mathbf{\Omega}_S\mathbf{A}'+\mathbf{J}^\dagger\mathbf{\Omega}_T i\mathbf{b}_T\mathbf{J}\mathbf{\Omega}_S i\mathbf{B}'+\frac{\mathbf{\Omega}_S\mathbf{A}\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T^{-1}\mathbf{J}}{i}+\frac{\mathbf{\Omega}_S i\mathbf{B}\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T^{-1}\mathbf{J}}{i}\\
&=(\mathbf{J}^\dagger\mathbf{\Omega}_T^2\mathbf{J}+\mathbf{\Omega}_S^2+\mathbf{\Omega}_S\mathbf{B}\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T^{-1}\mathbf{J}-\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T\mathbf{J}\mathbf{\Omega}_S\mathbf{B}')+i(\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T\mathbf{J}\mathbf{\Omega}_S\mathbf{A}'-\mathbf{\Omega}_S\mathbf{A}\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T^{-1}J).
\end{aligned}
\tag{4}
$$

Therefore,

$$
\begin{aligned}
&det(\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{B}_T\mathbf{J}+\mathbf{\Omega}_S\mathbf{B}_S)det(\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{B}_T^{-1}\mathbf{J}+\mathbf{\Omega}_S\mathbf{B}_S^{-1})\\
&=det(\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{B}_T\mathbf{J}+\mathbf{\Omega}_S\mathbf{B}_S)(\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{B}_T^{-1}\mathbf{J}+\mathbf{\Omega}_S\mathbf{B}_S^{-1})\\
&=det((\mathbf{J}^\dagger\mathbf{\Omega}_T^2\mathbf{J}+\mathbf{\Omega}_S^2+\mathbf{\Omega}_S\mathbf{B}\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T^{-1}\mathbf{J}-\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T\mathbf{J}\mathbf{\Omega}_S\mathbf{B}')+i(\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T J\Omega_S\mathbf{A}'-\mathbf{\Omega}_S\mathbf{A}\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T^{-1}\mathbf{J}))\\
&=det(\mathbf{C}+i\mathbf{E}),
\end{aligned}
\tag{5}
$$

where,

$$
\begin{aligned}
&\mathbf{C}=(\mathbf{J}^\dagger\mathbf{\Omega}_T^2\mathbf{J}+\mathbf{\Omega}_S^2+\mathbf{\Omega}_S\mathbf{B}\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T^{-1}\mathbf{J}-\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T\mathbf{J}\mathbf{\Omega}_S\mathbf{B}'),\\
&\mathbf{E}=(\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T\mathbf{J}\mathbf{\Omega}_S\mathbf{A}'-\mathbf{\Omega}_S\mathbf{A}\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T^{-1}\mathbf{J}),\\
&(\mathbf{C}+i\mathbf{E})^{-1}=\mathbf{C}'+i\mathbf{D}'.
\end{aligned}
\tag{6}
$$

Here,

$$
(\mathbf{S}_T)_{ii}=\sinh(i(\boldsymbol{\omega}_T)_i t)=i\sin((\boldsymbol{\omega}_T)_i t)=i\boldsymbol{s_T},\boldsymbol{s_T}=\sin((\boldsymbol{\omega}_T)_i t),(S_T)_{ii}^{-1}=\frac{1}{i\sin((\boldsymbol{\omega}_T)_i t)}=-i\boldsymbol{s}_{\boldsymbol{T}}^{-1}. \tag{7}
$$

Now,

$$
\begin{aligned}
&(\mathbf{S}_S)_{ii}=\sinh\left((\beta-it)(\boldsymbol{\omega}_S)_i\right)=\sinh(2x)\cos(2y)-i\sin(2y)\cosh(2x),(\mathbf{S}_S)_{ii}^{-1}=\mathbf{F}+i\mathbf{M}.\\
&(\mathbf{S}_S)_{ii}^{-1}(\mathbf{S}_T)_{ii}^{-1}\mathbf{\Omega}_S\mathbf{\Omega}_T=(\mathbf{F}+i\mathbf{M})(-i\mathbf{s}_T^{-1})\mathbf{\Omega}_S\mathbf{\Omega}_T\\
&=-i\mathbf{F}\boldsymbol{s}_{\boldsymbol{T}}^{-1}\mathbf{\Omega}_S\mathbf{\Omega}_T+\mathbf{M}\boldsymbol{s}_{\boldsymbol{T}}^{-1}\mathbf{\Omega}_S\mathbf{\Omega}_T=\mathbf{P}+i\mathbf{Q},\mathbf{P}=\mathbf{M}\boldsymbol{s}_T^{-1}\mathbf{\Omega}_S\mathbf{\Omega}_T,\mathbf{Q}=-\mathbf{F}\boldsymbol{s}_{\boldsymbol{T}}^{-1}\mathbf{\Omega}_S\mathbf{\Omega}_T.
\end{aligned}
\tag{8}
$$

The simplified form of the determinant within square root becomes

$$\begin{aligned}
&\sqrt{det(\mathbf{P}+i\mathbf{Q})det(\mathbf{C}'+i\mathbf{D}')} \\
&= \sqrt{(U+iV)} \\
&= \sqrt{Amp(U+iV)e^{i\theta}}, \\
&= \sqrt{\sqrt{(U^2+V^2)}e^{i\theta}} \\
&= \sqrt{\sqrt{(U^2+V^2)}}(\cos(\frac{\theta}{2})+i\sin(\frac{\theta}{2})),
\end{aligned} \tag{9}$$

where,

$$\theta = \tan^{-1}(\frac{V}{U}) \tag{10}$$

2 Simplification of the exponential part

$e^{\mathbf{D}^\dagger\left(\mathbf{\Omega}_T\mathbf{B}_T\mathbf{J}(\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{B}_T\mathbf{J}+\mathbf{\Omega}_S\mathbf{B}_S)^{-1}\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{B}_T-\mathbf{\Omega}_T\mathbf{B}_T\right)\mathbf{D}} \times e^{it\Delta E}dt$
Therefore,

$$\begin{aligned}
&\mathbf{D}^\dagger\left(\mathbf{\Omega}_T\mathbf{B}_T\mathbf{J}(\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{B}_T\mathbf{J}+\mathbf{\Omega}_S\mathbf{B}_S)^{-1}\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{B}_T-\mathbf{\Omega}_T\mathbf{B}_T\right)\mathbf{D} \\
&= \mathbf{D}^\dagger\left(\mathbf{\Omega}_T i\mathbf{b}_T\mathbf{J}(\mathbf{J}^\dagger\mathbf{\Omega}_T i\mathbf{b}_T\mathbf{J}+\mathbf{\Omega}_S(\mathbf{A}+i\mathbf{B}))^{-1}\mathbf{J}^\dagger\mathbf{\Omega}_T i\mathbf{b}_T-\mathbf{\Omega}_T i\mathbf{b}_T\right)\mathbf{D} \\
&= \mathbf{D}^\dagger\left(-\mathbf{\Omega}_T\mathbf{b}_T\mathbf{J}(\mathbf{J}^\dagger\mathbf{\Omega}_T i\mathbf{b}_T\mathbf{J}+\mathbf{\Omega}_S\mathbf{A}+i\mathbf{\Omega}_S\mathbf{B})^{-1}\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T-\mathbf{\Omega}_T i\mathbf{b}_T\right)\mathbf{D} \\
&= \mathbf{D}^\dagger\left(-\mathbf{\Omega}_T\mathbf{b}_T\mathbf{J}(\mathbf{\Omega}_S\mathbf{A}+i(\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T\mathbf{J}+\mathbf{\Omega}_S\mathbf{B}))^{-1}\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T-\mathbf{\Omega}_T i\mathbf{b}_T\right)\mathbf{D} \\
&= \mathbf{D}^\dagger\left(-\mathbf{\Omega}_T\mathbf{b}_T\mathbf{J}(\mathbf{L}+i\mathbf{H})\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T-\mathbf{\Omega}_T i\mathbf{b}_T\right)\mathbf{D} \\
&= -\mathbf{D}^\dagger\mathbf{\Omega}_T\mathbf{b}_T\mathbf{J}\mathbf{L}\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T-i\mathbf{D}^\dagger\mathbf{\Omega}_T\mathbf{b}_T\mathbf{J}\mathbf{H}\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T-i\mathbf{D}^\dagger\mathbf{\Omega}_T\mathbf{b}_T\mathbf{D} \\
&= -\mathbf{D}^\dagger\mathbf{\Omega}_T\mathbf{b}_T\mathbf{J}\mathbf{L}\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T\mathbf{D}+i(-\mathbf{D}^\dagger\mathbf{\Omega}_T\mathbf{b}_T\mathbf{J}\mathbf{H}\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T\mathbf{D}-\mathbf{D}^\dagger\mathbf{\Omega}_T\mathbf{b}_T\mathbf{D}) \\
&= K_1+iK_2,
\end{aligned} \tag{11}$$

where, $(\mathbf{\Omega}_S\mathbf{A}+i(\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T\mathbf{J}+\mathbf{\Omega}_S\mathbf{B}))^{-1}=\mathbf{L}+i\mathbf{H}$ and the form of K_1 and K_2 are

$$K_1 = -\mathbf{D}^\dagger\mathbf{\Omega}_T\mathbf{b}_T\mathbf{J}\mathbf{L}\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T\mathbf{D}, K_2 = (-\mathbf{D}^\dagger\mathbf{\Omega}_T\mathbf{b}_T\mathbf{J}\mathbf{H}\mathbf{J}^\dagger\mathbf{\Omega}_T\mathbf{b}_T\mathbf{D}-\mathbf{D}^\dagger\mathbf{\Omega}_T\mathbf{b}_T\mathbf{D}). \tag{12}$$

3 Complete form of correlation function and its separation into real and imaginary part

So the final form of correlation function becomes

$$\begin{aligned}
&\sqrt{\sqrt{(U^2+V^2)}}(\cos\frac{\theta}{2}+i\sin\frac{\theta}{2})\times e^{(K_1+iK_2)}\times e^{it\Delta E_{ab}}\\
&=\sqrt{\sqrt{(U^2+V^2)}}(\cos\frac{\theta}{2}+i\sin\frac{\theta}{2})\times e^{K_1}\times e^{i(K_2+t\Delta E_{ab})}\\
&=\sqrt{\sqrt{(U^2+V^2)}}(\cos\frac{\theta}{2}+i\sin\frac{\theta}{2})\times e^{K_1}\times(\cos\phi+i\sin\phi),\\
&=\sqrt{\sqrt{(U^2+V^2)}}e^{K_1}(\cos\frac{\theta}{2}\cos\phi+i\cos\frac{\theta}{2}\sin\phi+i\sin\frac{\theta}{2}\cos\phi-\sin\frac{\theta}{2}\sin\phi)\\
&=\sqrt{\sqrt{(U^2+V^2)}}e^{K_1}\cos(\frac{\theta}{2}+\phi)+i\sqrt{\sqrt{(U^2+V^2)}}e^{K_1}\sin(\frac{\theta}{2}+\phi),
\end{aligned}\tag{13}$$

$\phi=(K_2+t\Delta E_{ab})$,

here the cosine term is a real function of time and sine term is an imaginary function of time.

4 Final form of ISC rate equation after separation into real and imaginary part

Therefore the form of intersystem crossing rate formula after separation into real and imaginary part becomes

$$\begin{aligned}
\mathrm{k_{ISC}}=\ &\frac{1}{Z}|\langle S_a|\hat{H}_{so}|T_b\rangle|^2\int_{-\infty}^{\infty}\sqrt{\sqrt{(U^2+V^2)}}e^{K_1}\cos(\frac{\theta}{2}+\phi)\\
&+i\frac{1}{Z}|\langle S_a|\hat{H}_{so}|T_b\rangle|^2\int_{-\infty}^{\infty}\sqrt{\sqrt{(U^2+V^2)}}e^{K_1}\sin(\frac{\theta}{2}+\phi).
\end{aligned}\tag{14}$$

9. Variation of k_{ISC} with temperature of benzophenone and fluorenone.

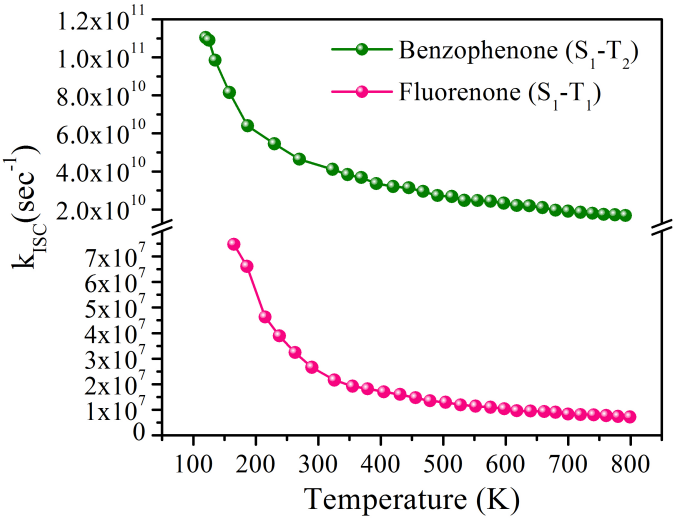


Fig. S7: Variation of k_{ISC} of benzophenone and fluorenone with temperature.

For benzophenone(S_1-T_2):

Ground state to ground state FC factor: 0.1625794967E-03
Average sum of Franck-Condon factors for the first state(S_1): 0.8931266883E-07

For fluorenone(S_1-T_1):

Ground state to ground state FC factor: 0.0441309348
Average sum of Franck-Condon factors for the first state(S_1): 0.1231235500E-05