Photophysics of uracil: an explicit time-dependent generating function based method combining both the nonadiabatic and spin-orbit coupling effects Supporting Information

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1 Coordinates of the optimized geometries

The ground (S_0 and T_1) as well as the excited states (S_1, S_2(nonplanar), S_3 and T_2) were optimized using Gaussian16 software at the b3lyp/6-311g(d,p) level of theory. The S_2(planar) geometry was optimized at the EOMCCSD/aug-cc-pVDZ method and then the computation of frequencies on that geometry was performed using b3lyp/6-311g(d,p) level of theory.

S_0 geometry (Å)

C	-0.00265	1.70623	-0.00002
N	0.03200	-0.98737	-0.00100
C	-1.22403	-0.40708	-0.00005
C	1.29335	-0.34939	0.00003
C	1.20320	1.10676	-0.00026
N	-1.17303	0.98699	0.00014
H	-2.0705	1.44675	0.00085
H	-0.11976	2.78267	-0.00006
O	-2.26452	-1.02451	0.00038
H	0.04529	-1.99933	-0.00088
H	2.12235	1.67196	-0.00030
O	2.31335	-1.0053	0.00065

S_1 geometry (Å)

C	0.032740	1.757817	-0.000175
N	-0.060502	-0.985326	0.000222
C	1.216860	-0.396503	-0.000060
C	-1.247574	-0.259245	0.000141
C	-1.215897	1.108750	-0.000022
N	1.193200	0.967383	-0.000186
H	2.104323	1.398991	-0.000396
H	0.168423	2.824454	-0.000179
O	2.218547	-1.080260	-0.000167
H	-0.077194	-1.993824	0.000147
H	-2.136715	1.669525	-0.000033
O	-2.306609	-1.049547	0.000281

S_2 non-planar geometry (Å)

C	0.009522	1.757763	0.103009
N	-0.003620	-0.921013	0.383717
C	1.164930	-0.359868	0.032357
C	-1.321598	-0.293532	0.030373
C	-1.225217	1.104324	-0.004919
N	1.190697	0.968118	-0.123935
H	2.007938	1.351040	-0.578555
H	0.168592	2.777659	0.414025
O	2.202672	-1.079883	-0.135253
H	-0.004408	-1.928775	0.495917
H	-2.141102	1.662010	-0.157191
O	-2.215971	-1.100591	-0.234446

S_2 planar geometry (Å)

```
C -0.009792   -1.796899   -0.000000
N -0.000000    1.033774    0.000000
C -1.202487    0.399608   -0.000000
C  1.289343    0.371462    0.000000
C  1.265720   -1.048198    0.000000
N -1.128638   -1.028809   -0.000000
H -2.055757   -1.452678   -0.000000
H -0.120795   -2.879872   -0.000000
O -2.317409    0.913143   -0.000000
H  0.005084    2.047878    0.000000
H  2.212593   -1.587931    0.000000
O  2.292738    1.122107    0.000000
```

S_3 geometry (Å)

```
C  0.031279    1.765075   -0.068155
N -0.033404   -0.986934   -0.009409
C  1.157288   -0.382881    0.007636
C -1.292277   -0.283762    0.002174
C -1.206805    1.103515   -0.004822
N  1.208248    0.944996    0.019757
H  2.121954    1.365086   -0.036040
H  0.183479    2.785321    0.248852
O  2.256388   -1.062632    0.000482
H -0.070877   -1.995075    0.000165
H -2.127332    1.665772    0.011932
O -2.314893   -1.029770    0.009724
```

T_1 geometry (Å)

```
C  0.118839    1.764810    0.234955
N -0.064959   -0.979118    0.246411
C  1.187978   -0.438929    0.001387
C -1.295728   -0.313282    0.009016
C -1.187396    1.109579   -0.069956
N  1.193625    0.953043   -0.110231
H  2.115503    1.340610   -0.258420
H  0.258733    2.826836    0.098356
O  2.201087   -1.094477   -0.105471
H -0.102853   -1.989338    0.264597
H -2.043490    1.666277   -0.425517
O -2.334925   -0.954889   -0.105115
```

T_2 geometry (Å)

```
C  0.013514    1.752768   -0.000155
N -0.045304   -0.994018    0.000419
C  1.221110   -0.394703   -0.000046
C -1.240040   -0.271686    0.000143
```

```
C -1.217526    1.099866   -0.000062
N  1.187139    0.973756   -0.000154
H  2.093724    1.413267   -0.000505
H  0.137630    2.821188   -0.000144
O  2.233562   -1.061519   -0.000260
H -0.048461   -2.002071    0.000086
H -2.142344    1.655487   -0.000132
O -2.320529   -1.046419    0.000206
```

T_3 geometry (Å)

```
C  0.076019    1.759496   -0.000125
N -0.073030   -0.965530    0.000272
C  1.230858   -0.386587   -0.000038
C -1.334025   -0.249681    0.000121
C -1.183636    1.139099   -0.000016
N  1.240459    0.950156   -0.000157
H  2.154591    1.375434   -0.000480
H  0.241337    2.821330    0.000044
O  2.199354   -1.145744   -0.000231
H -0.116071   -1.980836    0.000415
H -2.079305    1.742399   -0.000032
O -2.337836   -1.032339    0.000179
```

2 Normal mode frequencies

S_0	S_1	S_2	S_3	T_2	T_1	T_3
149.39	103.48	117.90	154.82	93.45	119.74	69.19
167.92	179.21	181.60	242.11	147.42	172.16	204.74
388.55	255.52	286.88	333.65	302.82	213.99	223.14
397.34	341.22	328.96	350.15	334.64	379.02	348.12
521.29	356.27	350.66	416.82	381.60	470.96	352.14
542.59	386.51	474.27	452.73	385.62	498.75	469.34
560.59	498.16	485.20	516.66	494.20	518.08	504.80
570.32	534.74	514.95	532.06	502.90	536.35	513.64
687.48	542.71	548.43	554.45	528.76	546.30	550.72
733.03	555.63	610.87	570.33	560.72	597.82	581.34
768.38	605.19	683.34	621.95	562.50	647.72	615.96
773.78	732.57	756.57	761.24	738.11	716.23	748.70
820.75	753.45	765.08	771.82	775.80	746.23	765.64
962.89	780.78	773.77	782.61	794.66	764.85	774.75
972.44	945.93	880.11	966.96	947.37	933.14	830.75
991.32	1010.87	967.26	980.37	1004.41	959.21	945.58
1085.18	1037.54	1048.11	1055.75	1045.73	1009.20	995.09
1187.11	1141.90	1152.72	1160.22	1150.49	1142.96	1054.57
1225.24	1216.36	1182.00	1264.25	1236.24	1234.69	1159.55
1381.46	1268.89	1314.83	1332.47	1283.78	1356.66	1275.01
1405.07	1356.55	1359.69	1399.10	1363.02	1387.99	1323.28
1420.50	1427.51	1398.97	1421.85	1428.96	1397.41	1374.88
1502.41	1445.95	1432.89	1464.84	1477.41	1416.89	1420.50
1675.98	1486.60	1505.41	1544.62	1487.78	1480.09	1523.03
1789.30	1653.55	1617.88	1667.48	1618.76	1625.29	1658.43
1826.93	1805.28	2243.14	2537.95	1813.84	1795.11	1926.49
3199.54	3242.38	3183.29	3214.95	3235.93	3213.54	3228.24
3242.67	3278.50	3229.85	3238.55	3273.58	3223.93	3282.44
3600.59	3641.27	3581.29	3634.10	3647.87	3605.10	3563.66
3641.67	3644.15	3586.71	3652.66	3651.50	3611.31	3643.59

Table S1. Frequencies(in cm^{-1}) as computed at (u)b3lyp/6-311g(d,p) level of theory using Gaussian16 software.

3 Position of the singlet and triplet energy levels in eV at CASSCF method.

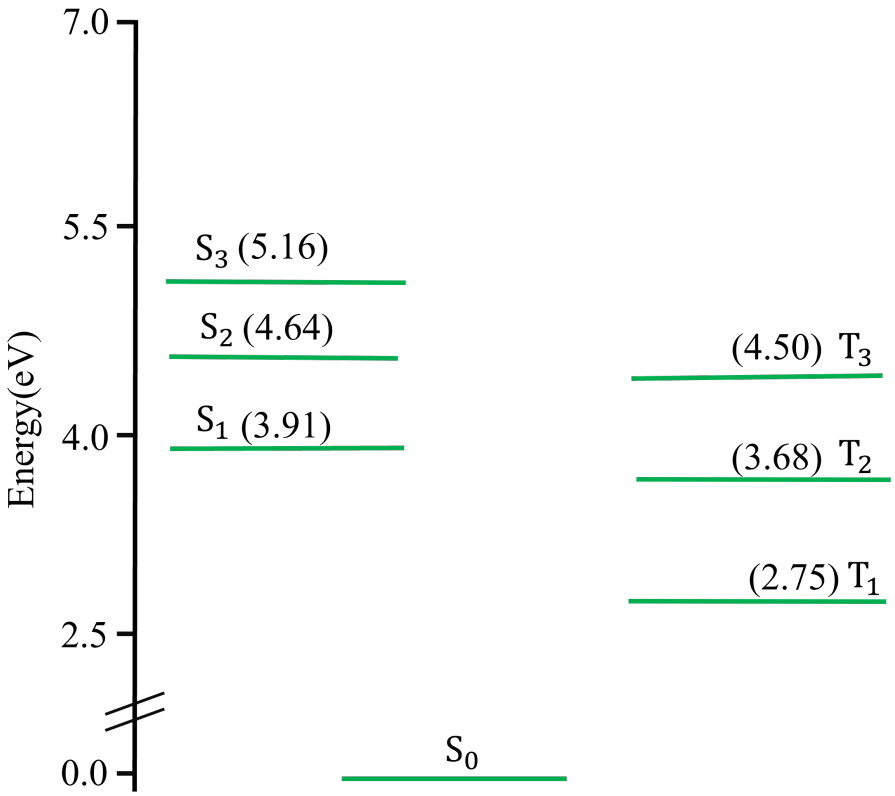


Fig. S1. Pictorial representation of the energy levels obtained with the S_2 geometry of uracil at the CASSCF(14e,10o) level of theory. The energy values are in eV given in parenthesis.

CASSCF orbitals of the singlet and the triplet states computed at the S_2 geometry

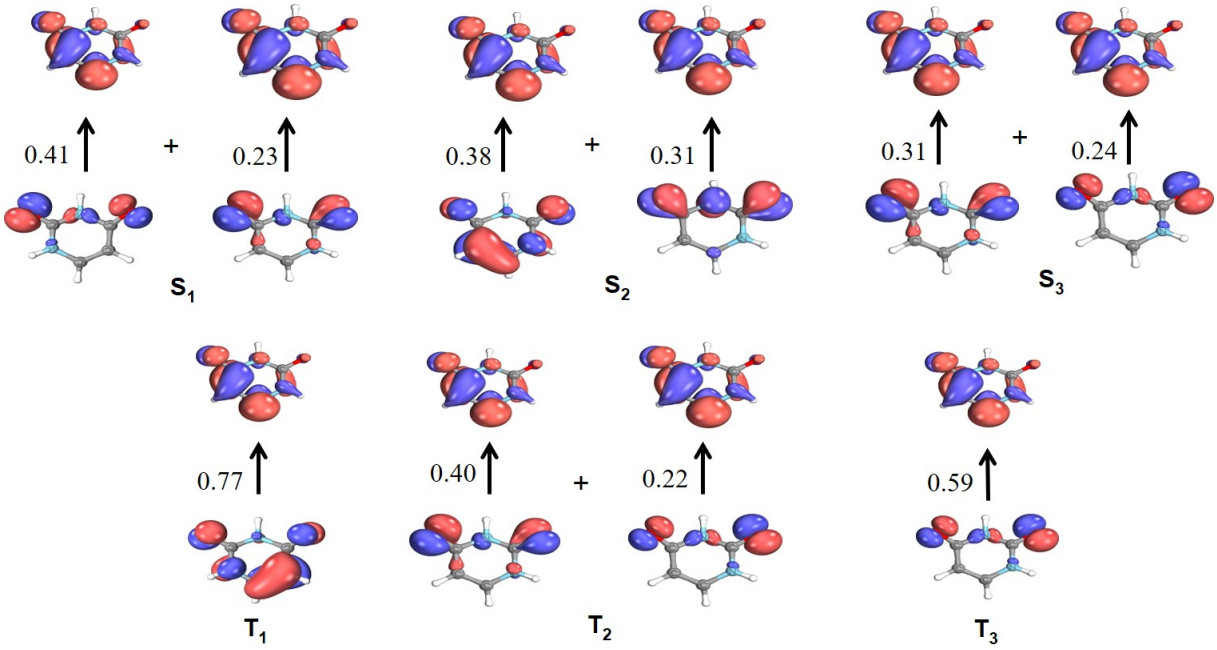


Fig. S2. Singlet and triplet electronic state character obtained at CASSCF(14e,10o)/def2-TZVP level of theory using S_2 optimized geometry.

Intersystem crossing between the singlet and triplet states is mainly governed by two important factors, namely, energy gap and SOCME between them. Among them the SOCME in the rate expresion appears as a square term and hence it dominates over the energy gap factor. To explain qualitatively, how SOC facilitates ISC, the nature of the orbitals comprising the electronic states involved in the transition should be considered. To study this, we look at the CASSCF orbitals comprising the excited states in Fig.S2. The S_1 electronic state has major contributions from the p_z, p_x, p_y atomic orbitals of the O_9 and O_{12} atoms and also the p_z orbital of the C_1, C_4 and C_5 atoms. In contrast, only the p_z orbital of the O_9, O_{12}, C_1 and C_5 atoms has large contributions in the T_1 state. From this picture, we can estimate that the $\hat{L}_z$ operator connecting the p_z orbitals of C as well as O atoms of the S_1 and T_1 states and also the $\hat{L}_{+/-}$ operator coupling the p_z orbital of T_1 state with that of the p_y and p_x orbitals of the S_1 state for both C and O atoms, leads to the significant SOC value of 53.10 cm^{-1} between S_1 and T_1 states. Similar analysis is also true for for S_3–T_3, S_2–T_2 and S_2–T_1, which have corresponding SOC of 56.18, 19.44 and 15.28 cm^{-1} respectively. The higher values of SOC between S_1-T_1 and S_3-T_3 arise due to the larger contribution of the atomic orbitals (p_z, p_y, p_x) of O and C atoms in the former pathway and contribution of p_x and p_z of N_2 in the latter transition.

Mode specific nonadiabatic coupling vectors (NACMEs)

$\omega_{S_2}(cm^{-1})$	NACME$_{S_3-S_2}$ (a.u.)	NACME$_{S_2-S_1}$ (a.u.)	NACME$_{T_2-T_1}$ (a.u.)
$\omega_1 = 117.90$	7.76002998E-04	1.48363074E-03	1.58658717E-04
$\omega_2 = 181.60$	3.65964865E-04	5.57537656E-04	2.86894559E-04
$\omega_3 = 286.88$	2.20003352E-03	1.78145000E-03	2.16550427E-03
$\omega_4 = 328.95$	2.01355177E-03	3.46044032E-03	6.31499104E-04
$\omega_5 = 350.66$	5.66056138E-03	1.05705962E-03	7.10672408E-04
$\omega_6 = 474.26$	3.03356373E-03	1.99337373E-03	7.18050636E-04
$\omega_7 = 485.20$	1.94071431E-03	1.19192339E-03	7.22190016E-04
$\omega_8 = 514.95$	8.01453367E-04	2.47899583E-03	4.92417661E-04
$\omega_9 = 548.42$	2.02249037E-03	3.54057108E-03	3.00675689E-04
$\omega_{10} = 610.86$	6.99708296E-04	5.99646801E-03	2.48900591E-03
$\omega_{11} = 683.34$	1.55475701E-03	2.56310729E-03	7.58672133E-04
$\omega_{12} = 756.57$	3.45308450E-03	1.52230030E-04	4.81726660E-04
$\omega_{13} = 765.08$	2.13766447E-03	3.93654360E-03	8.85971713E-06
$\omega_{14} = 773.77$	2.43262039E-03	3.33694229E-03	3.73851867E-06
$\omega_{15} = 880.10$	5.30165248E-03	2.86960183E-03	4.54266672E-04
$\omega_{16} = 967.26$	9.96061368E-04	1.43948375E-04	1.72205939E-04
$\omega_{17} = 1048.10$	2.31651240E-03	4.99785063E-04	1.66662867E-05
$\omega_{18} = 1152.71$	4.91754571E-03	3.72572249E-05	7.81253766E-05
$\omega_{19} = 1182.00$	6.61430124E-04	1.24236406E-03	4.17539792E-04
$\omega_{20} = 1314.82$	4.54468699E-03	4.68172785E-03	9.64349485E-04
$\omega_{21} = 1359.68$	4.42613289E-03	2.07221508E-03	2.42709386E-04
$\omega_{22} = 1398.96$	9.22293693E-04	3.31485673E-04	5.07181045E-04
$\omega_{23} = 1432.89$	1.75175853E-02	3.20402300E-03	2.17730785E-03
$\omega_{24} = 1505.41$	1.10596120E-02	8.03841464E-03	2.02693813E-03
$\omega_{25} = 1617.88$	1.28597207E-02	9.69238952E-03	2.04378885E-04
$\omega_{26} = 2243.13$	1.70365553E-02	2.14493163E-02	1.45300210E-03
$\omega_{27} = 3183.29$	1.62241806E-04	4.11651767E-04	2.95502250E-04
$\omega_{28} = 3229.85$	6.53257652E-04	7.72324333E-04	1.97583242E-04
$\omega_{29} = 3581.29$	3.50671029E-03	3.68964043E-03	3.88095621E-04
$\omega_{30} = 3586.70$	3.87876108E-03	2.73942039E-03	4.56529342E-05

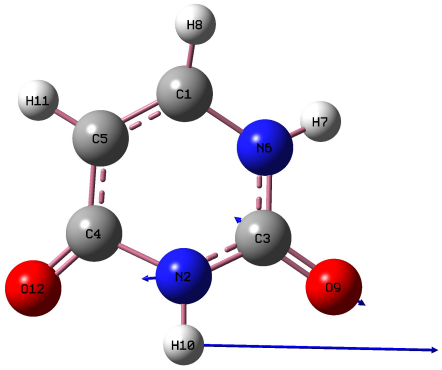
Table S2. Magnitude of the normal mode specific nonadiabatic coupling vector elements(NACMEs) in a.u. at the MS-CASPT2 method.

Mode specific nonadiabatic coupling vectors (NACMEs)

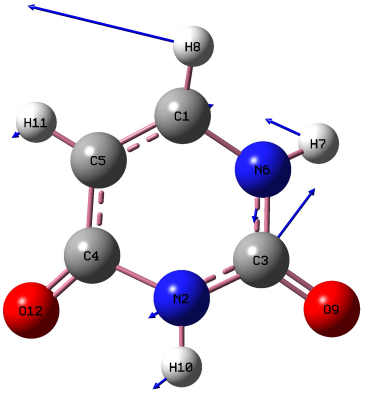
$\omega_{S_2}(cm^{-1})$	NACME$_{S_3-S_2}$ (a.u.)	NACME$_{S_2-S_1}$ (a.u.)	NACME$_{T_2-T_1}$ (a.u.)
$\omega_1 = 117.90$	1.54766371E-03	9.29847592E-04	4.55901900E-04
$\omega_2 = 181.60$	1.02340989E-03	5.80630498E-04	5.98930579E-04
$\omega_3 = 286.88$	7.28939369E-04	5.20423055E-04	1.41302403E-03
$\omega_4 = 328.95$	2.79358681E-03	7.63351389E-04	3.92654270E-04
$\omega_5 = 350.66$	2.56412255E-04	7.32114888E-04	4.69044084E-04
$\omega_6 = 474.26$	1.37780036E-03	1.06989499E-03	4.05569561E-04
$\omega_7 = 485.20$	1.66766206E-03	5.87386719E-04	3.72241426E-04
$\omega_8 = 514.95$	2.00414052E-03	6.22883672E-04	3.81047605E-04
$\omega_9 = 548.42$	2.57060892E-04	9.13765281E-04	8.54200625E-05
$\omega_{10} = 610.86$	1.03873224E-03	2.06200965E-03	1.76598551E-03
$\omega_{11} = 683.34$	3.91924893E-03	1.84379649E-04	5.61052933E-04
$\omega_{12} = 756.57$	4.05502564E-04	5.43058675E-04	8.25963682E-04
$\omega_{13} = 765.08$	7.54590146E-04	1.41738099E-03	9.38816593E-05
$\omega_{14} = 773.77$	1.05116027E-03	3.75249103E-04	4.22314071E-04
$\omega_{15} = 880.10$	3.89976369E-04	3.77891032E-04	9.61042388E-05
$\omega_{16} = 967.26$	2.03027832E-03	1.15339302E-04	7.45022990E-05
$\omega_{17} = 1048.10$	1.37136655E-03	1.75646448E-03	2.57568900E-06
$\omega_{18} = 1152.71$	2.66946666E-03	2.46330840E-03	1.73045642E-04
$\omega_{19} = 1182.00$	5.05485979E-04	7.55292829E-04	2.27730314E-04
$\omega_{20} = 1314.82$	2.02403706E-03	1.46492047E-03	7.84475356E-04
$\omega_{21} = 1359.68$	8.25345982E-04	1.06079294E-03	9.81510238E-05
$\omega_{22} = 1398.96$	3.90865328E-03	3.39966246E-05	1.11657382E-05
$\omega_{23} = 1432.89$	4.98720584E-03	7.20016367E-04	2.12274434E-04
$\omega_{24} = 1505.41$	6.95940945E-03	2.01314013E-03	1.06031192E-03
$\omega_{25} = 1617.88$	7.82380719E-03	2.99172313E-03	6.79792895E-04
$\omega_{26} = 2243.13$	1.29351104E-02	1.07276207E-02	2.70361919E-03
$\omega_{27} = 3183.29$	2.61915149E-04	2.93150573E-04	2.05844539E-04
$\omega_{28} = 3229.85$	2.09113423E-04	1.42673263E-04	5.65051087E-05
$\omega_{29} = 3581.29$	1.07411388E-03	1.90662162E-03	3.27802933E-04
$\omega_{30} = 3586.70$	2.14625616E-03	6.95662806E-04	1.21082783E-04

Table S3. Magnitude of the normal mode specific nonadiabatic coupling vector elements(NACMEs) in a.u. at the CASSCF method.

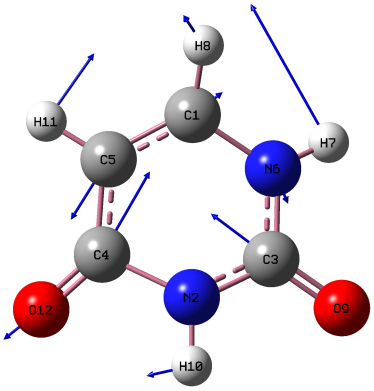
4 Displacement vectors of a few selected normal modes of the S_2-non-planar state having dominant contribution to the NACMEs between two different singlet or triplet levels.



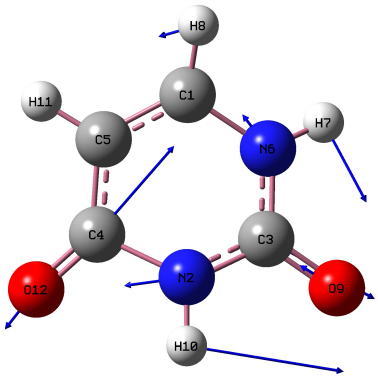
(a) ω_{20} =1314.82 cm^{-1}



(b) ω_{24} =1505.41 cm^{-1}



(c) ω_{25} =1617.88 cm^{-1}



(d) ω_{26} =2243.13 cm^{-1}

Fig. S3. Displacement vector of a few selected normal modes of S_2 geometry having significant NACMEs.

5 Potential energy surfaces of a few selected normal modes

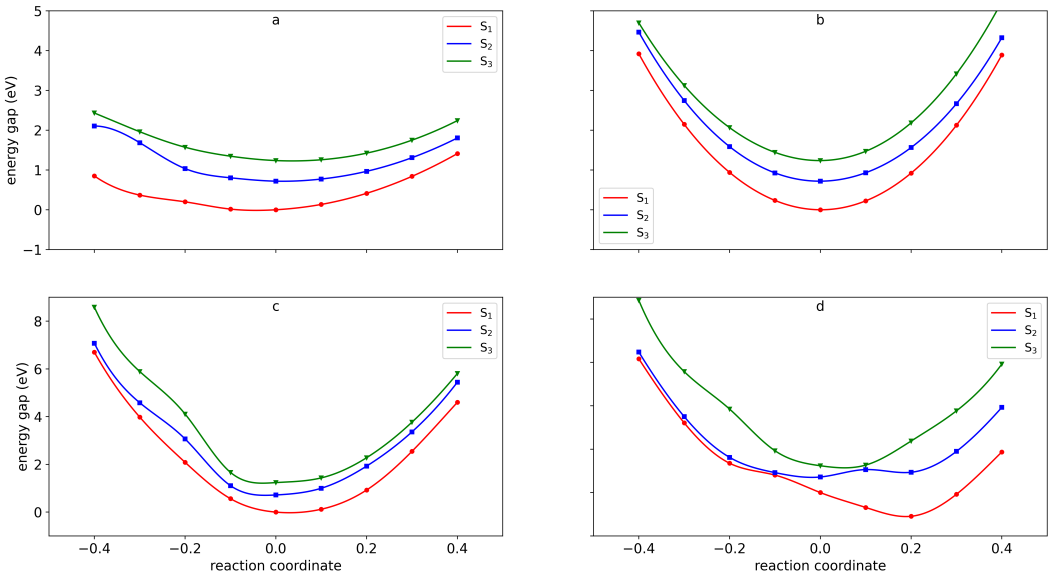


Fig. S4. Potential energy surfaces of normal modes obtained using CASSCF/(14e,10o) method. Here the reaction coordinate indicate the manual displacement of the normal mode coordinate along the direction of the displacement vector of the respective normal mode. a, b, c and d denotes the potential energy surface for normal mode 20, 24, 25 and 26 with frequencies 1314, 1505, 1617 and 2243 cm^{-1}, respectively.

6 Normal mode specific internal conversion rate constants.

Table S4. Internal conversion(IC) rate constant computed using the energy gap taken from the MS-CASPT2 method obtained at the S_2-nonplanar geometry of e few selected normal modes having dominant NAC values.

Normal mode	$k_{IC}^{S_3-S_2}$ (s^{-1})	$k_{IC}^{S_2-S_1}$ (s^{-1})	$k_{IC}^{T_2-T_1}$ (s^{-1})
ω_{20}	3.29×10^{10}	6.60×10^{9}	1.94×10^{9}
ω_{24}	2.35×10^{11}	1.85×10^{10}	1.52×10^{10}
ω_{25}	3.45×10^{11}	4.40×10^{10}	1.42×10^{8}
ω_{26}	9.31×10^{11}	2.11×10^{11}	9.92×10^{9}

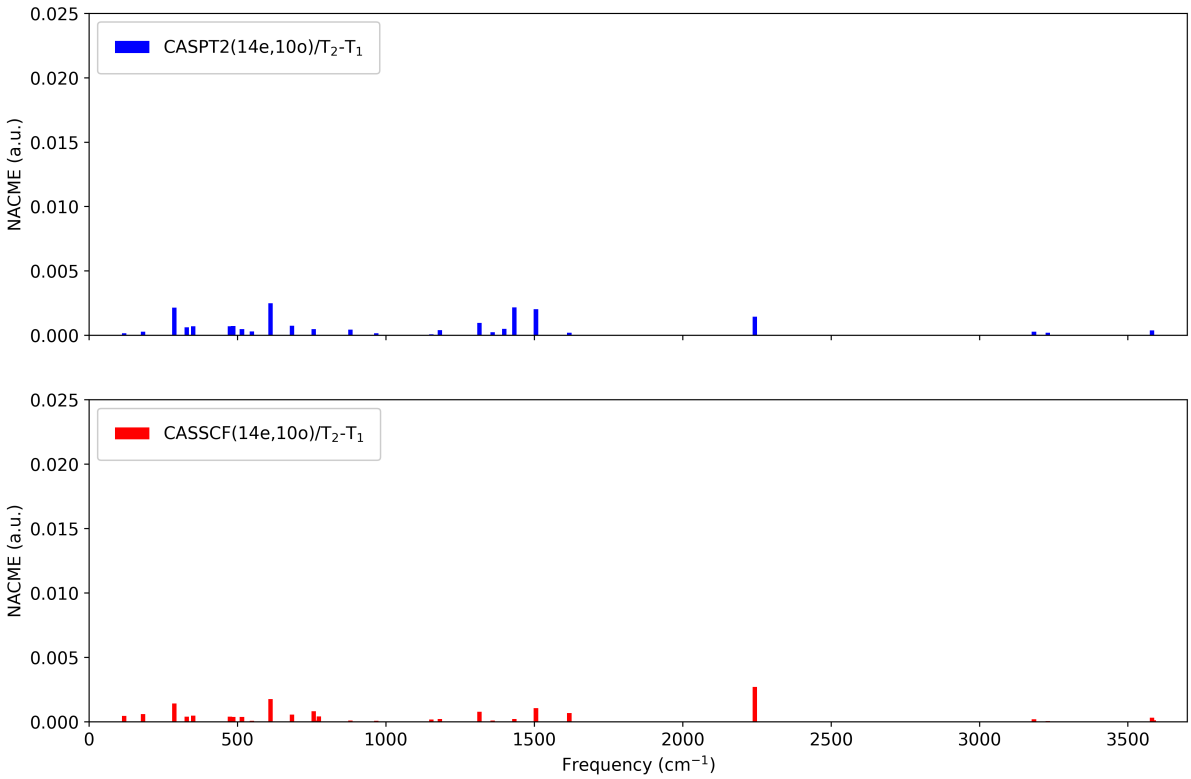


Fig. S5. Mode specific NACMEs between the T_2 and T_1 states..

7 Linear interpolation between S_2 and S_2-S_1 conical intersection (CI) geometry at the MS-CASPT2 method

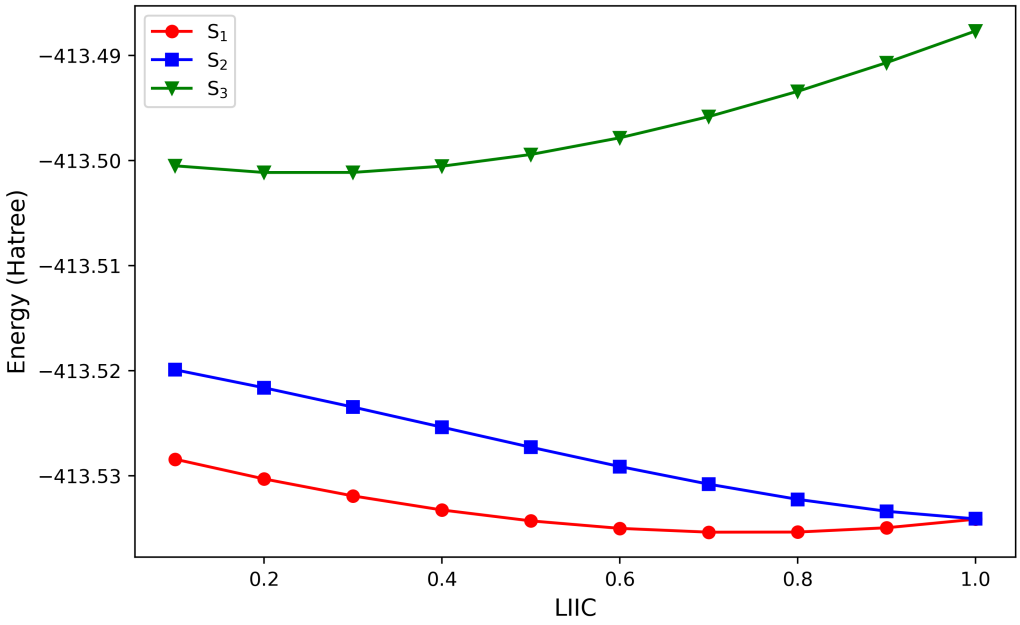


Fig. S6. Potential energy surfaces generated by linear interpolation in internal coordinate (LIIC) technique between S_2 and S_2-S_1 conical intersection (CI) geometry at the MS-CASPT2 level of theory using (14e,10o) active space.

8 Variation of k_{IC} in s^{-1} with energy gap in eV at CASSCF method.

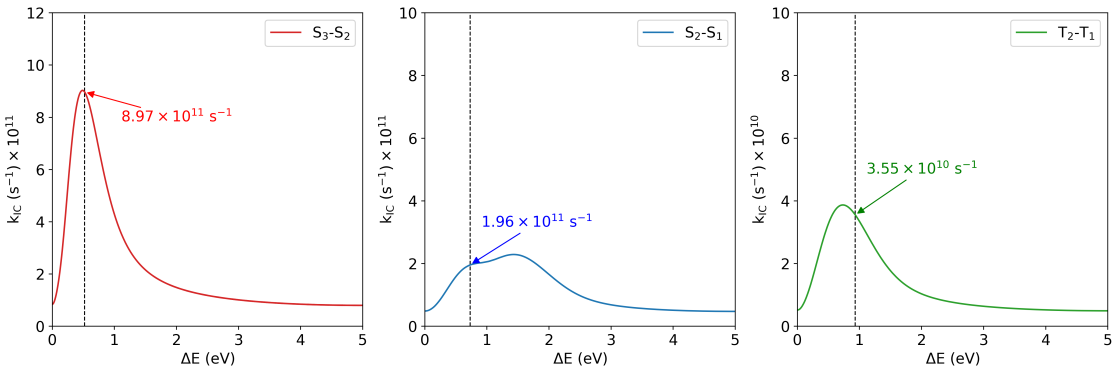


Fig. S7. Variation of k_{IC} with the energy gap obtained by Fourier transforming the generating function.

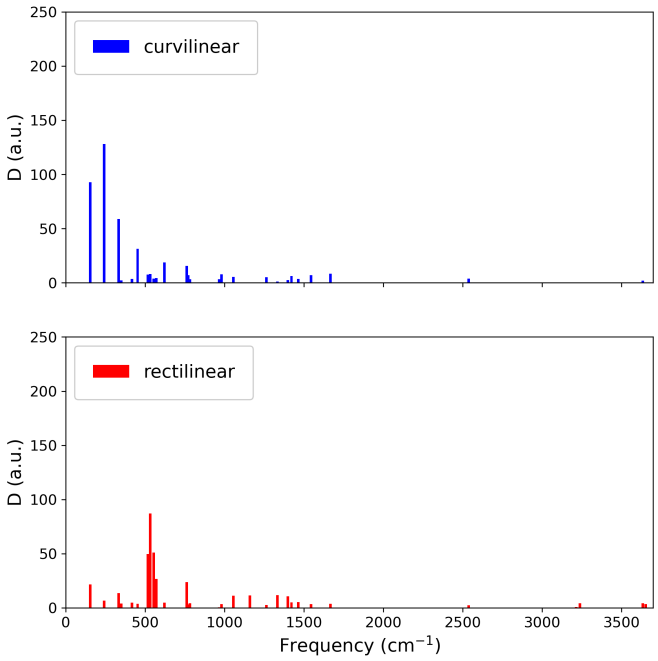
9 Internal conversion rate constants between the singlet or triplet levels at the CASSCF(14e,10o) level of theory

Table S5. Internal conversion rate constant calculated using the energy gap and NACME obtained at the S_2 geometry using the CASSCF level of theory with (14e,10o) active space. Here a and b denotes the rate constant evaluated involving the J and D computed in curvilinear and rectilinear coordinates, respectively.

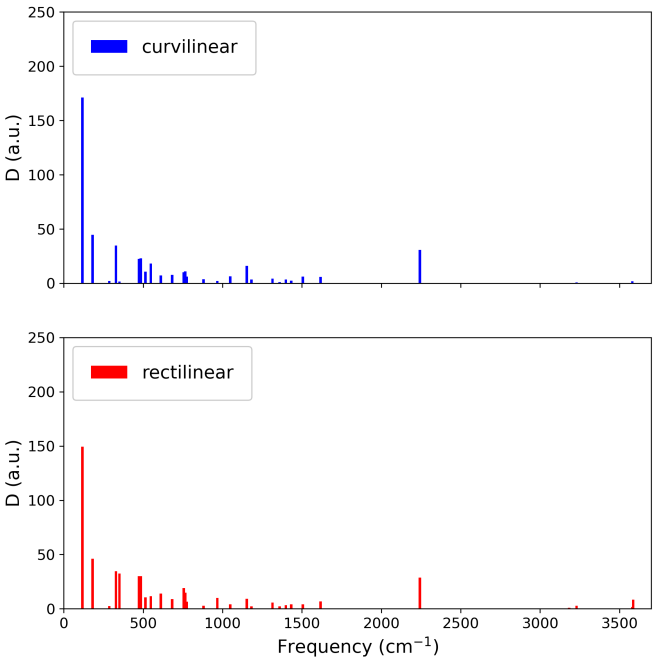
Transition	ΔE (eV)	norm (Bohr^{-1})	k^a_{IC} (s^{-1})	k^b_{IC} (s^{-1})
$S_3 \rightarrow S_2$	0.52	2.88	8.97×10^{11}	3.73×10^{11}
$S_2 \rightarrow S_1$	0.73	1.88	1.96×10^{11}	2.20×10^{11}
$T_2 \rightarrow T_1$	0.93	0.63	3.55×10^{10}	2.70×10^{10}

10 Displacement vectors and Duschinsky rotation matrices

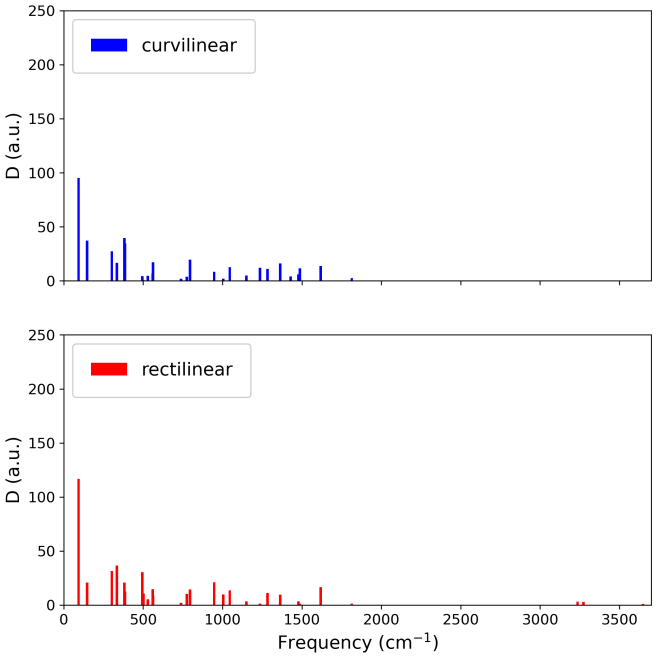
Displacement vectors



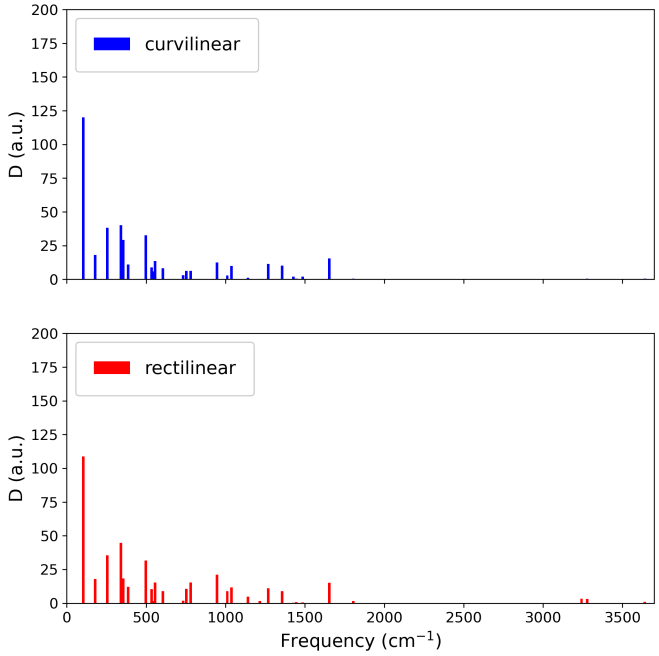
$S_3 \rightarrow S_2$



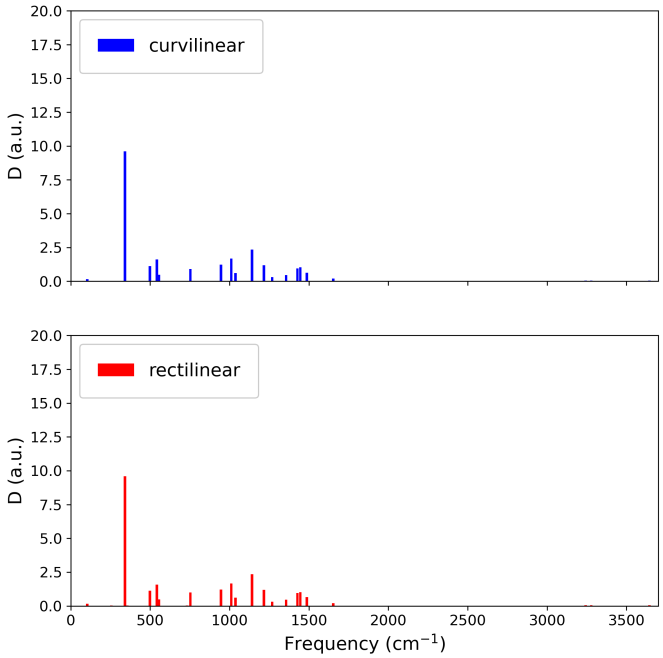
$S_2 \rightarrow S_1$



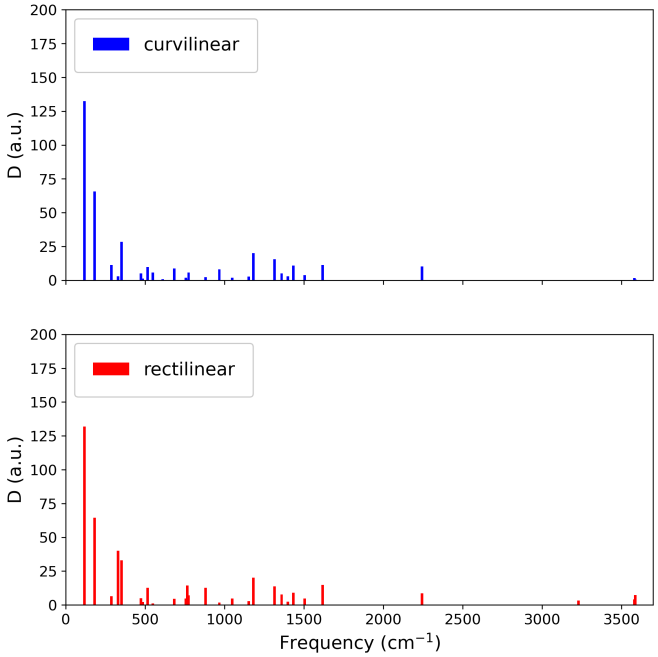
$T_2 \rightarrow T_1$



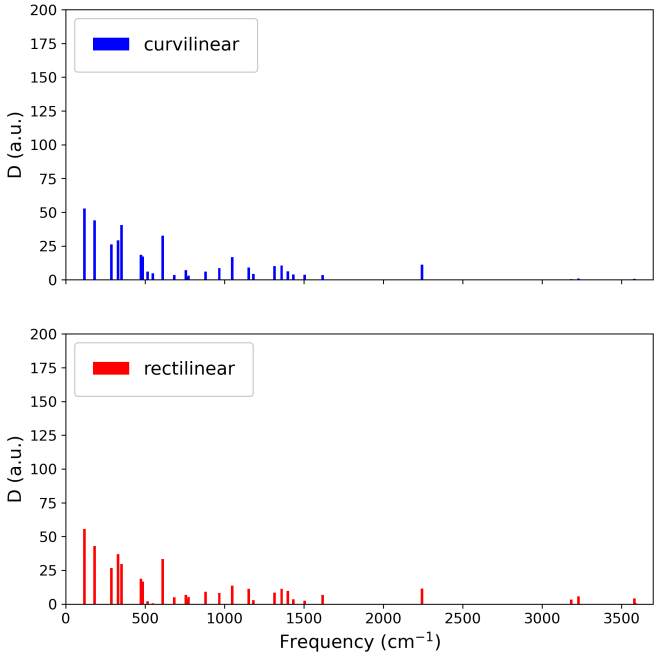
$S_1 \rightarrow T_1$



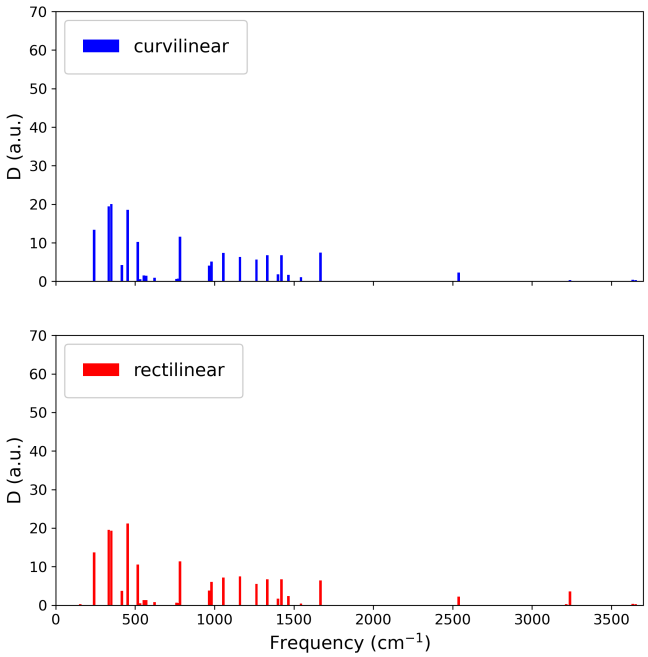
$S_1 \rightarrow T_2$



$S_2 \rightarrow T_2$

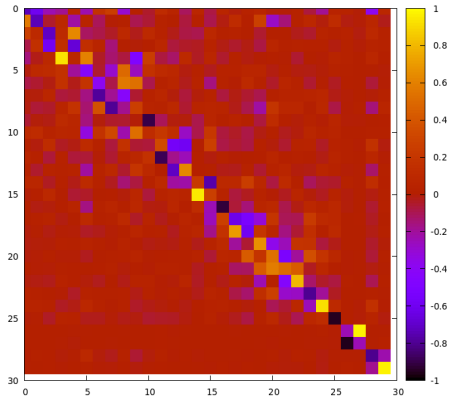


$S_2 \rightarrow T_1$

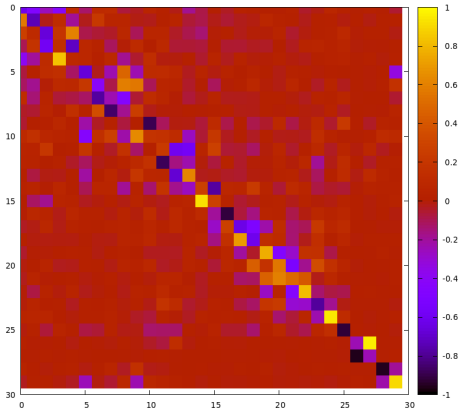


$S_3 \rightarrow T_3$

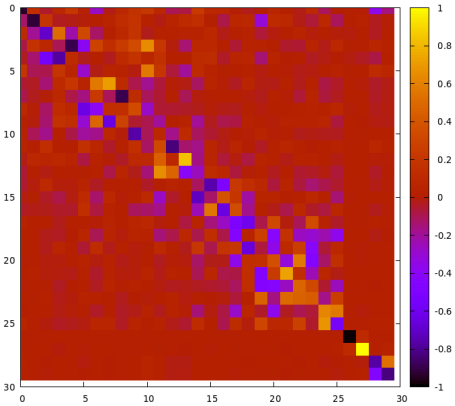
Duschinsky rotation matrices



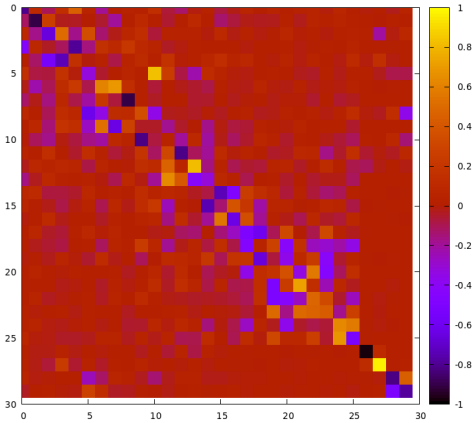
$S_3 \rightarrow S_2$ (curvilinear)



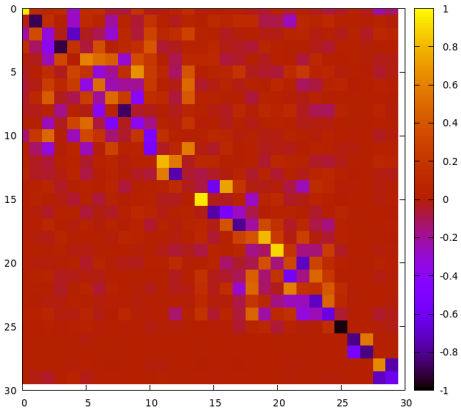
$S_3 \rightarrow S_2$ (rectilinear)



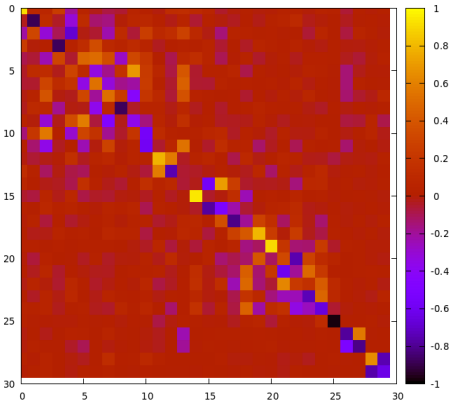
$S_2 \rightarrow S_1$ (curvilinear)



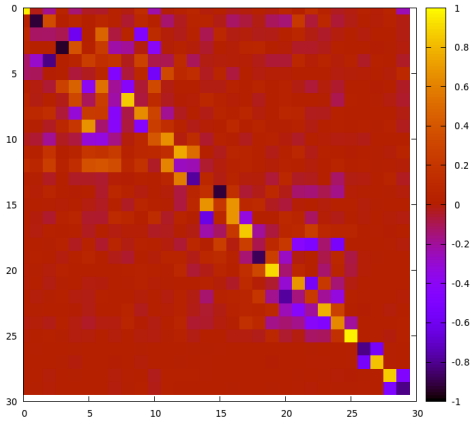
$S_2 \rightarrow S_1$ (rectilinear)



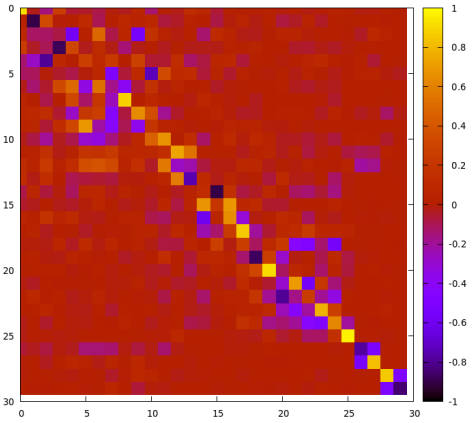
$T_2 \rightarrow T_1$ (curvilinear)



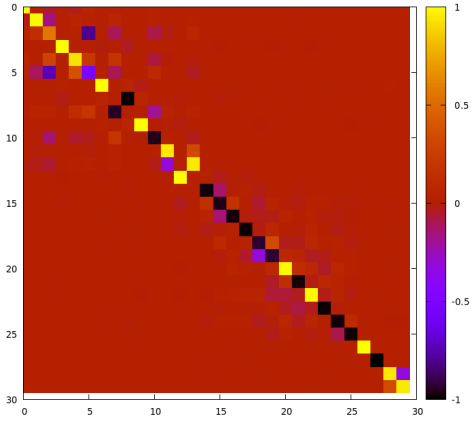
$T_2 \rightarrow T_1$ (rectilinear)



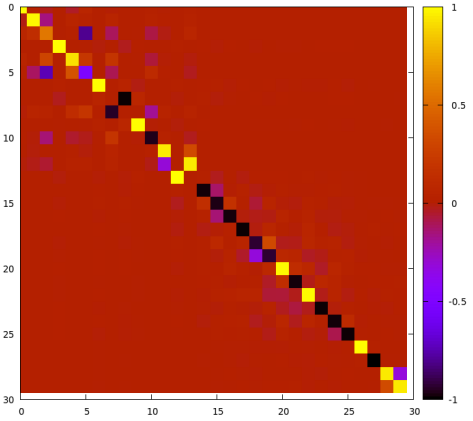
$S_1 \rightarrow T_1$ (curvilinear)



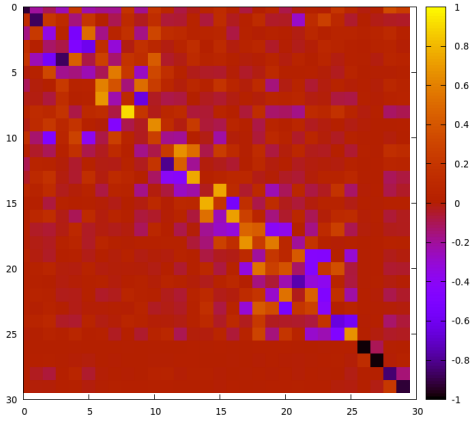
$S_1 \rightarrow T_1$ (rectilinear)



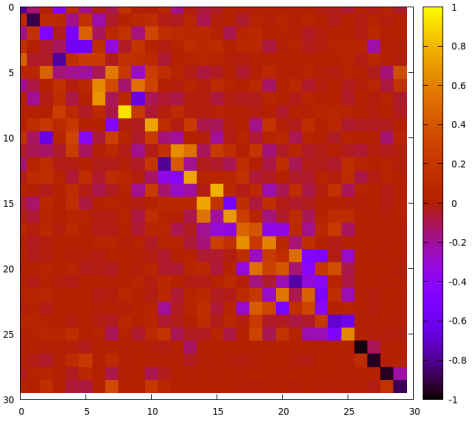
$S_1 \rightarrow T_2$ (curvilinear)



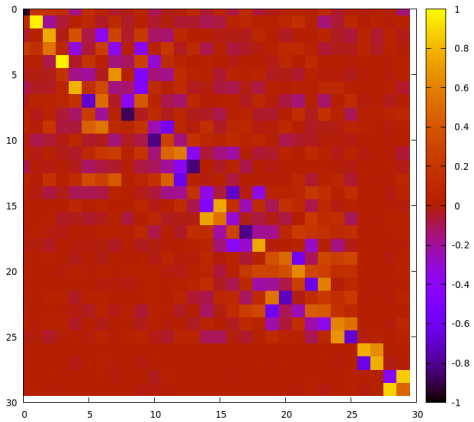
$S_1 \rightarrow T_2$ (rectilinear)



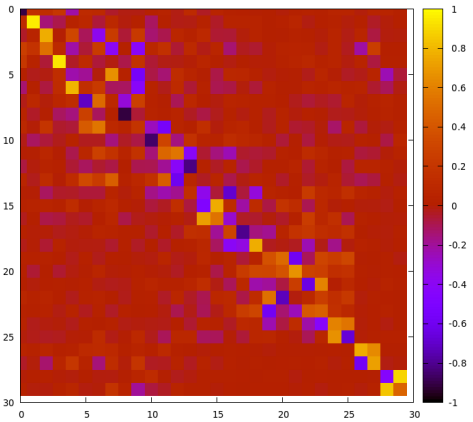
$S_2 \rightarrow T_2$ (curvilinear)



$S_2 \rightarrow T_2$ (rectilinear)



$S_1 \rightarrow T_1$ (curvilinear)



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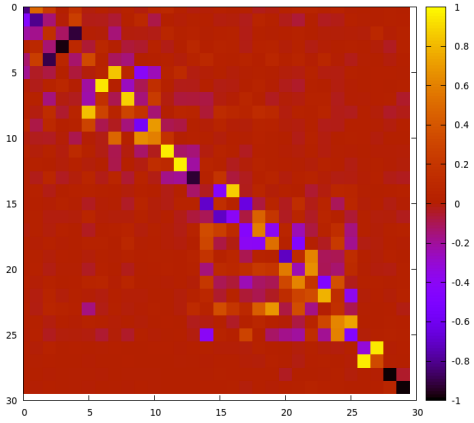
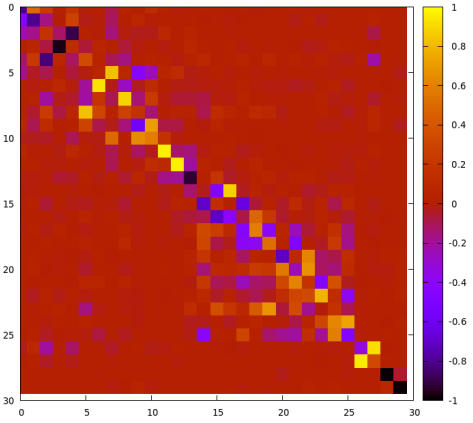


$S_3 \rightarrow T_3$ (curvilinear)



$S_3 \rightarrow T_3$ (rectilinear)