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

Supporting Information for:

Conformer specific nonadiabatic reaction dynamics in photodissociation of partially deuterated thioanisoles (C_6H_5S-CH_2D and C_6H_5S-CHD_2)

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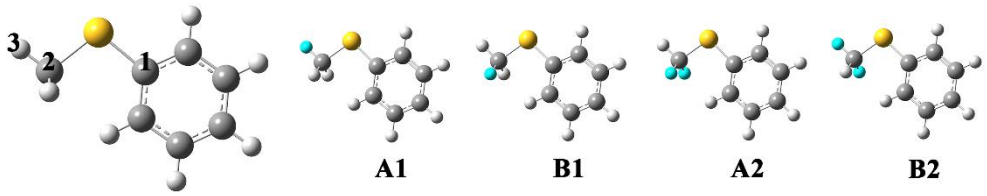
Table S1. Calculated molecular structural parameters and energetics for the ground (S_0), first excited (S_1), cationic ground (D_0) states, and S_1/S_2 MECI for thioanisole. The positions of D atom(s) are presented for each isotopomers.



	Equilibrium				S_1/S_2 MECI
	S_0	S_1[a](adiabatic)	S_1(vertical)	D_0	
Relative E. / (cm^{-1})	-	+37 134	+38 794	+55 098	+39 751
	(-)	(+35 091)[c]	(+36 467)[c]	(+61 634)[c]	(+38 817)[c]
d(S-Me) / (Å)	1.86	1.87	-	1.87	2.13
d(C-SMe) / (Å)	1.82	1.79	-	1.72	1.78
$\gamma(H_{(3)}\text{-}C_{(2)}\text{-}S)$ / (˚)	105.02	104.91	-	104.30	101.24
$\gamma(C_{(2)}\text{-}S\text{-}C_{(1)})$ / (˚)	102.34	103.13	-	106.13	102.63
d(C-C)[b] / (Å)	1.40	1.43	-	1.40	1.42

[a] imaginary frequency with ring and –SMe torsional mode
[b] averaged values for the phenyl moiety
[c] The values in parentheses are obtained with CASPT2 correction.

TABLE S2. Assignments of vibrational frequencies of TA-d_1-A1 in the cationic state (D_0) appeared in (1+1′) SEVI spectra shown in Fig. 6 (a), (b).

TA-d_1-A1	Ion internal energy (cm^{-1})	Assignment
Via ν_S (659 cm^{-1} on S_1)	666	ν_S^1
	775	$15^1 6b^1/\tau^4 6a^1$
	802	$15^2 6a^1/\tau CH3^1 \nu_S^1$
	835	$\tau CH3^2 16a^1 15^1/\tau^2 \tau CH3^2 16a^1$
	898	$\tau^1 CH_3^1 \nu_s^1/\tau^2 \tau CH_3^1 6b^1$
Via 7a (712 cm^{-1} on S_1)	663	ν_S^1
	693	$\tau^4 \beta s^1/ \tau^3 6a^1$
	727	$7a^1$
	757	$\tau^1 \nu_S^1/\beta s^1 6a^1$
	784	$15^1 6b^1/\tau^4 6a^1$

TABLE S3. Assignments of vibrational frequencies of TA-d_1-B1 in the cationic state (D_0) appeared in (1+1′) SEVI spectra shown in Fig. 6 (c), (d).

TA-d_1-B1	Ion internal energy (cm^{-1})	Assignment
Via ν_S (678 cm^{-1} on S_1)	680	ν_S^1
	763	$\tau^1 \nu_S^1/15^1 6b^1$
	847	$6a^2$
	895	$\tau^2 \tau CH3^1 6b^1/ \tau^2 \tau CH3^1 \nu_S^1$
	921	$15^1 16a^2/\beta s^1 6b^1$
	979	12^1
	998	$\tau^1 \tau CH3^1 15^1 6b^1/ \tau^3 16a^2$
Via 7a (708 cm^{-1} on S_1)	685	ν_S^1
	719	$7a^1$
	745	$\tau^1 \tau CH3^1 15^1 \beta s^1/ \tau CH3^1 15^1 6a^1$ or $\tau^1 \nu_S^1/ \beta s^1 6a^1$ of TA-d_1-A1
	772	$\tau^1 \nu_S^1/15^1 6b^1$

TABLE S4. Assignments of vibrational frequencies of TA-d_2-A2 in the cationic state (D_0) appeared in (1+1′) SEVI spectra shown in Fig. 7 (a), (b).

TA-d_1-A2	Ion internal energy (cm^{-1})	Assignment
Via ν_S (676 cm^{-1} on S_1)	682	ν_S^1
	752	$\beta s^1 6a^1$
	775	$\tau^1\nu_S^1/15^1 6b^1$
	844	$6a^2/15^1\beta s^2$
Via 7a (707 cm^{-1} on S_1)	659	βs^2
	725	$7a^1$
	758	$\beta s^1 6a^1$
	835	$\tau^2\beta s^1/15^1\beta s^2$

TABLE S5. Assignments of vibrational frequencies of TA-d_2-B2 in the cationic state (D_0) appeared in (1+1′) SEVI spectra shown in Fig. 7 (c), (d).

TA-d_1-B2	Ion internal energy (cm^{-1})	Assignment
Via ν_S (658 cm^{-1} on S_1)	665	ν_S^1
Via 7a (706 cm^{-1} on S_1)	663	ν_S^1
	718	$7a^1$
	754	$\tau^1\nu_S^1/\beta s^1 6a^1$

Table S6. Experimental and calculated vibrational frequencies (cm^{-1}) of S_0 and D_0 minima for thioanisole-h_3, -d_3, -d_1-A1/B1, and -d_2-A2/B2. The frequencies are obtained from the B3LYP/6-311^{++}G(3df,3pd) level of calculation, whereas the values in parentheses were obtained using the SA4-CASSCF(12(11 for D_0),11)/6-311^{++}G(d,p) calculation.

Thioanisole-h_3						**Thioanisole-d_3**					
mode	sym.	S_0	D_0	R2PI	MATI	mode	sym.	S_0	D_0	R2PI	MATI
τ	a″	48 (19)	94 (93)	37	89	τ	a″	44 (18)	88 (87)	35	87
10b	a″	168 (178)	157 (161)	66	150	10b	a″	142 (159)	167 (170)		
15	a′	197 (205)	192 (202)	204	200	15	a′	180 (189)	123 (186)	185	184
τCH_3	a″	230 (257)	185 (195)		178	τCD_3	a″	195 (205)	176 (132)	63	124
β_s	a′	333 (330)	340 (347)		337	β_s	a′	321 (319)	328 (336)	320	327
16a	a″	412 (432)	383 (403)		369	16a	a″	412 (431)	383 (403)		
6a	a′	420 (405)	434 (441)	392	426	6a	a′	412 (397)	426 (434)	384	423
16b	a″	485 (499)	438 (460)			16b	a″	484 (499)	438 (460)		
6b	a′	631 (663)	598 (631)	524	589	6b	a′	630 (663)	597 (630)	522	590
ν_S	a′	698 (616)	688 (816)	687	690	ν_S	a′	667 (588)	657 (769)	656	664
4	a″	700 (716)	644 (622)			4	a″	699 (715)	644 (622)		
7a	a′	730 (715)	734 (736)	724	732	7a	a′	714 (708)	727 (717)	705	726
11	a″	754 (765)	780 (768)			11	a″	754 (765)	780 (768)		
10a	a″	850 (864)	831 (850)			10a	a″	849 (864)	832 (851)		
17b	a″	913 (922)	965 (963)			17b	a″	913 (922)	965 (963)		
$\gamma_s CH_3$	a″	972 (1011)	934 (999)			$\gamma_s CD_3$	a″	734 (1152)	706 (749)		
$\beta_{as} CH_3$	a′	981 (1036)	991 (1055)			$\beta_{as} CD_3$	a′	775 (808)	778 (817)	755	775
17a	a″	989 (994)	1015 (1023)			17a	a″	989 (994)	1015 (1023)		
12	a′	998 (1088)	978 (1075)	956	981	12	a′	996 (1087)	980 (1073)	952	983
5	a″	1003 (1007)	1029 (1031)			5	a″	1003 (1009)	965 (1031)		
1	a′	1045 (1045)	1023 (1033)			1	a′	1045 (1045)	1022 (1033)		
19a	a′	1102 (1144)	1123 (1178)			19a	a′	1103 (1149)	1121 (1168)		

19b	a′	1107 (1153)	1103 (1162)
9b	a′	1183 (1217)	1192 (1239)
9a	a′	1210 (1277)	1222 (1288)
14	a′	1311 (1325)	1318 (1385)
$\beta_s CH_3$	a′	1349 (1460)	1360 (1497)
3	a′	1365 (1436)	1372 (1439)
18a	a′	1467 (1556)	1454 (1549)
$\gamma_{as} CH_3$	a″	1469 (1590)	1460 (1580)
$\beta_s CH_2$	a′	1487 (1604)	1458 (1576)
18b	a′	1512 (1614)	1488 (1596)
8b	a′	1607 (1667)	1546 (1657)
8a	a′	1625 (1723)	1605 (1697)
$\nu_s CH_3$	a′	3040 (3197)	3051 (3215)
$\nu_{as} CH_2$	a″	3119 (3294)	3146 (3328)
$\nu_{as} CH_3$	a′	3133 (3282)	3154 (3336)
13	a′	3165 (3313)	3191 (3345)
7b	a′	3172 (3320)	3197 (3353)
20a	a′	3182 (3333)	3207 (3362)
2	a′	3195 (3345)	3215 (3372)
20b	a′	3210 (3365)	3225 (3386)

19b	a′	1107 (1151)	1104 (1158)
9b	a′	1183 (1217)	1192 (1239)
9a	a′	1210 (1277)	1222 (1288)
14	a′	1310 (1324)	1320 (1386)
$\beta_s CD_3$	a′	1034 (1096)	1030 (1186)
3	a′	1357 (1440)	1372 (1440)
18a	a′	1468 (1556)	1455 (1549)
$\gamma_{as} CD_3$	a″	1062 (1152)	1054 (1144)
$\beta_s CD_2$	a′	1075 (1164)	1050 (1139)
18b	a′	1512 (1613)	1487 (1595)
8b	a′	1607 (1667)	1546 (1657)
8a	a′	1625 (1723)	1604 (1696)
$\nu_s CD_3$	a′	2177 (2288)	2183 (2299)
$\nu_{as} CD_2$	a″	2315 (2435)	2334 (2472)
$\nu_{as} CD_3$	a′	2321 (2447)	2339 (2479)
13	a′	3165 (3313)	3191 (3345)
7b	a′	3172 (3320)	3197 (3353)
20a	a′	3182 (3333)	3207 (3362)
2	a′	3195 (3345)	3215 (3372)
20b	a′	3209 (3365)	3225 (3386)

* Partially revised from our previous work[38,52]

Thioanisole-d_1-A1						**Thioanisole-d_1-B1**					
mode	sym.	S_0	D_0	R2PI	SEVI	mode	sym.	S_0	D_0	R2PI	SEVI
τ	a″	47 (19)	92 (90)	37	89	τ	a″	47 (19)	92 (91)	36	91
10b	a″	161 (173)	149 (157)			10b	a″	160 (173)	145 (152)		
15	a′	190	185	196	188	15	a′	190	190	199	188

		(199)	(196)					(198)	(200)		
τCH_3	a″	210 (230)	172 (178)	65	143	τCH_2D	a″	213 (232)	172 (177)	65	136
β_s	a′	331 (328)	338 (346)	330	336	β_s	a′	328 (325)	335 (342)	329	333
16a	a″	412 (432)	383 (403)			16a	a″	412 (432)	383 (403)		
6a	a′	415 (402)	428 (436)	386	423	6a	a′	419 (402)	433 (440)	388	428
16b	a″	485 (499)	438 (460)			16b	a″	485 (499)	438 (460)		
6b	a′	631 (663)	598 (631)	523	585	6b	a′	631 (663)	958 (631)	522	584
ν_S	a′	671 (594)	663 (791)	659	666	ν_S	a′	694 (609)	678 (765)	678	680
4	a″	700 (716)	644 (622)			4	a″	700 (716)	644 (622)		
7a	a′	718 (709)	733 (721)	712	727	7a	a′	718 (714)	727 (731)	708	719
11	a″	754 (765)	780 (768)			11	a″	754 (765)	780 (768)		
10a	a″	849 (864)	831 (850)			10a	a″	850 (864)	832 (849)		
17b	a″	913 (922)	965 (963)			17b	a″	913 (923)	965 (964)		
$\gamma_s CH_2D$	a″	952 (991)	908 (977)			$\gamma_s CH_2D$	a″	797 (820)	777 (863)		
$\beta_{as} CH_2D$	a′	840 (864)	838 (888)			$\beta_{as} CH_2D$	a′	949 (1004)	947 (1017)		
17a	a″	989 (995)	1015 (1023)			17a	a″	989 (994)	1015 (1023)		
12	a′	996 (1088)	980 (1074)	953	982	12	a′	996 (1088)	980 (1074)	953	982
5	a″	1003 (1009)	1029 (1031)			5	a″	1003 (1009)	1029 (1031)		
1	a′	1045 (1045)	1022 (1033)			1	a′	1045 (1045)	1023 (1034)		
19a	a′	1102 (1144)	1121 (1174)			19a	a′	1102 (1144)	1122 (1176)		
19b	a′	1105 (1151)	1103 (1162)			19b	a′	1107 (1152)	1103 (1162)		
9b	a′	1183 (1217)	1192 (1239)			9b	a′	1183 (1217)	1192 (1239)		
9a	a′	1209 (1276)	1221 (1287)			9a	a′	1210 (1277)	1222 (1287)		
14	a′	1311 (1322)	1320 (1384)			14	a′	1312 (1323)	1325 (1383)		
$\beta_s CH_2D$	a′	1256 (1353)	1255 (1392)			$\beta_s CH_2D$	a′	1265 (1359)	1255 (1400)		
3	a′	1357 (1441)	1372 (1441)			3	a′	1357 (1441)	1372 (1441)		

18a	a′	1469 (1556)	1455 (1549)			18a	a′	1469 (1556)	1455 (1549)
$\gamma_s CH_2$	a″	1277 (1377)	1268 (1364)			$\gamma_s CH_2$	a″	1449 (1571)	1441 (1562)
$\gamma_{as} CH_2D$	a′	1465 (1583)	1429 (1558)			$\gamma_{as} CH_2D$	a′	1291 (1385)	1276 (1361)
18b	a′	1512 (1613)	1487 (1596)			18b	a′	1512 (1613)	1487 (1596)
8b	a′	1607 (1667)	1546 (1657)			8b	a′	1607 (1667)	1546 (1657)
8a	a′	1625 (1723)	1605 (1697)			8a	a′	1625 (1723)	1605 (1697)
$\nu_s CD$	a′	3063 (3232)	3080 (3255)			$\nu_s CD$	a″	3075 (3229)	3091 (3261)
$\nu_{as} CH_2$	a″	3119 (3294)	3146 (3336)			$\nu_{as} CH_2$	a″	3130 (3285)	3153 (3330)
$\nu_s CH$	a′	2280 (2381)	2291 (2413)			$\nu_s CH$	a″	2263 (2390)	2277 (2412)
13	a′	3165 (3313)	3191 (3345)			13	a′	3165 (3313)	3191 (3345)
7b	a′	3172 (3320)	3197 (3353)			7b	a′	3172 (3320)	3197 (3353)
20a	a′	3182 (3333)	3207 (3362)			20a	a′	3182 (3333)	3207 (3362)
2	a′	3195 (3345)	3215 (3372)			2	a′	3195 (3345)	3215 (3372)
20b	a′	3209 (3365)	3225 (3386)			20b	a′	3209 (3365)	3225 (3386)

* Partially revised from our previous work[38,52]

Thioanisole-d_2-A2						**Thioanisole-d_2-B2**					
mode	sym.	S_0	D_0	R2PI	SEVI	mode	sym.	S_0	D_0	R2PI	SEVI
τ	a″	45 (19)	90 (89	35	90	τ	a″	45 (19)	90 (88)	36	89
10b	a″	152 (168)	133 (141)			10b	a″	151 (166)	134 (144)		
15	a′	186 (194)	181 (191)	191	185	15	a′	185 (193)	182 (192)	192	187
τCHD_2	a″	199 (214)	169 (173)	64	128	τCHD_2	a″	201 (216)	168 (171)	64	130
β_s	a′	322 (320)	329 (337)			β_s	a′	326 (324)	333 (341)	326	332
16a	a″	412 (499)	383 (403)			16a	a″	412 (431)	383 (403)		
6a	a′	417 (400)	431 (439)	386	426	6a	a′	413 (399)	427 (435)	385	422
16b	a″	485 (499)	438 (460)			16b	a″	485 (499)	438 (460)		
6b	a′	631	598	523	586	6b	a′	631	598	523	587

		(663)	(631)					(663)	(631)		
ν_S	a′	691 (605)	676 (769)	676	682	ν_S	a′	668 (590)	659 (764)	658	665
4	a″	699 (715)	644 (622)			4	a″	700 (716)	644 (622)		
7a	a′	716 (714)	728 (730)	707	725	7a	a′	715 (708)	723 (718)	706	718
11	a″	754 (766)	780 (768)			11	a″	754 (765)	780 (768)		
10a	a″	850 (864)	832 (851)			10a	a″	849 (864)	830 (850)		
17b	a″	913 (923)	965 (964)			17b	a″	913 (923)	965 (963)		
$\gamma_s CD_2$	a″	737 (759)	711 (752)			γ_s CHD_2	a″	857 (885)	754 (903)		
β_{as} CHD_2	a′	846 (891)	849 (933)			β_{as} CHD_2	a′	764 (793)	841 (806)		
17a	a″	989 (994)	1015 (1023)			17a	a″	989 (994)	1015 (1023)		
12	a′	996 (1087)	980 (1073)	953	982	12	a′	996 (1087)	980 (1074)	953	982
5	a″	1003 (1009)	1029 (1031)			5	a″	1003 (1009)	1029 (1031)		
1	a′	1045 (1045)	1022 (1033)			1	a′	1045 (1045)	1022 (1033)		
19a	a′	1102 (1140)	1121 (1179)			19a	a′	1103 (1150)	1121 (1175)		
19b	a′	1107 (1151)	1103 (1165)			19b	a′	1106 (1153)	1104 (1162)		
9b	a′	1183 (1217)	1192 (1239)			9b	a′	1183 (1217)	1192 (1239)		
9a	a′	1210 (1277)	1222 (1288)			9a	a′	1210 (1277)	1222 (1287)		
14	a′	1312 (1320)	1327 (1394)			14	a′	1310 (1323)	1321 (1385)		
β_s CHD_2	a′	1254 (1344)	1264 (1361)			β_s CHD_2	a′	1252 (1336)	1239 (1359)		
3	a′	1357 (1441)	1372 (1442)			3	a′	1357 (1442)	1372 (1441)		
18a	a′	1468 (1556)	1455 (1549)			18a	a′	1468 (1556)	1455 (1549)		
γ_{as} CHD	a″	1303 (1415)	1297 (1410)			γ_s CHD	a″	1051 (1130)	1291 (1149)		
β_sCHD	a′	1070 (1155)	1041 (1148)			β_s CHD	a′	1321 (1431)	1048 (1409)		
18b	a′	1512 (1613)	1487 (1595)			18b	a′	1512 (1613)	1487 (1595)		
8b	a′	1607 (1667)	1546 (1657)			8b	a′	1607 (1667)	1546 (1657)		
8a	a′	1625 (1723)	1604 (1696)			8a	a′	1625 (1723)	1604 (1696)		

$\nu_s CD_2$	a′	2214 (2336)	2225 (2350)	ν_s CD_2	a″	2225 (2336)	2234 (2356)
$\nu_{as} CD_2$	a″	2315 (2447)	2334 (2479)	$\nu_{as} CD_2$	a″	2320 (2438)	2338 (2474)
$\nu_s CH$	a′	3115 (3252)	3132 (3296)	$\nu_s CH$	a″	3092 (3264)	3115 (3298)
13	a′	3165 (3313)	3191 (3345)	13	a′	3165 (3313)	3191 (3345)
7b	a′	3172 (3320)	3197 (3353)	7b	a′	3172 (3320)	3197 (3353)
20a	a′	3182 (3333)	3207 (3362)	20a	a′	3182 (3333)	3207 (3362)
2	a′	3195 (3345)	3215 (3372)	2	a′	3195 (3345)	3215 (3372)
20b	a′	3209 (3365)	3225 (3386)	20b	a′	3209 (3365)	3225 (3386)

* Partially revised from our previous work[38,52]

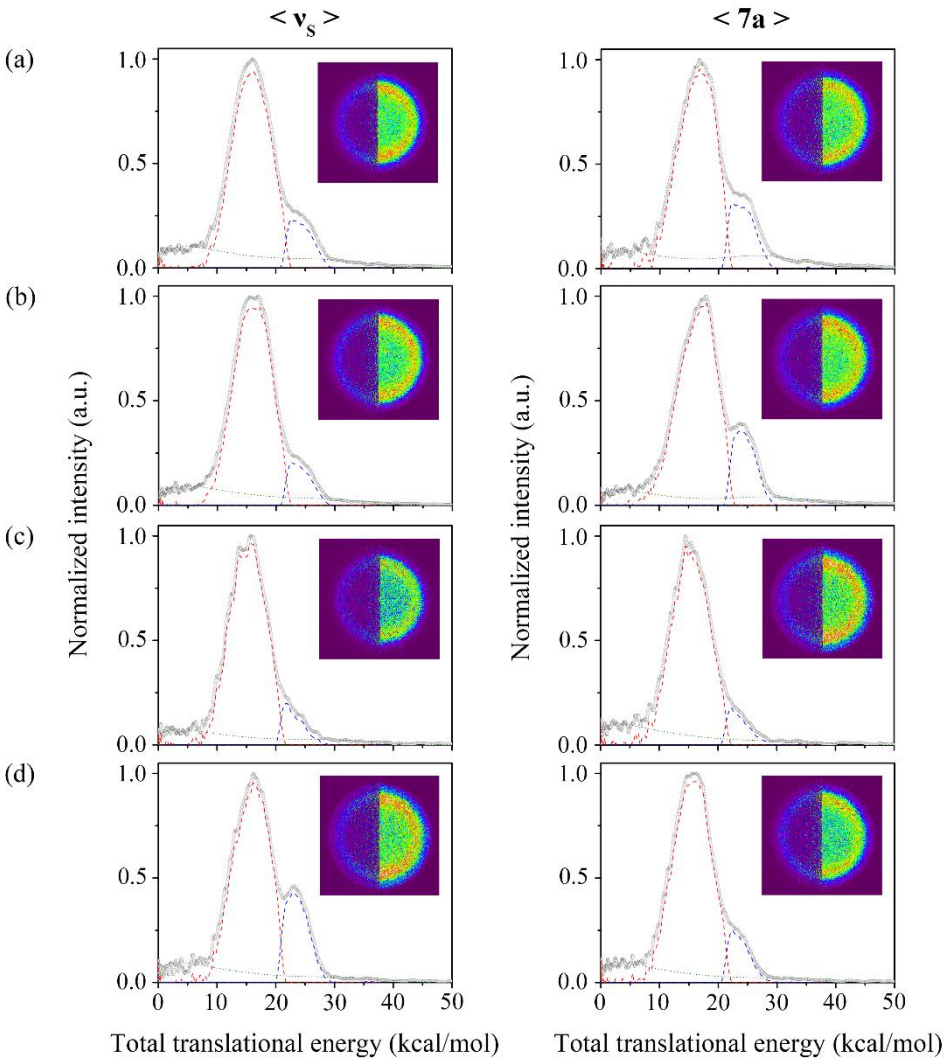


Figure S1. Dynamic resonances of the S_1 excited for TA-d_1/-d_2. Total translational energy distributions deduced from ·CH_2D and ·CHD_2 (υ=0) images obtained via the ν_S and 7a levels of the S_1 excited states for (a) A1, (B) B1, (c) A2, and (d) B2. Corresponding images are given in insets with the raw images on the right and the reconstructed images on the left.

Table S7. $\tilde{X}/\tilde{A}$ product branching ratio with errors obtained via S_1-S_0 origin, ν_S, 7a, and 12 for TA-d1/-d2 isotopomers. Corresponding total translational energy distributions deduced from $\cdot CH_2D$ and $\cdot CHD_2$ (υ=0) images are shown in Figure S1.

	Mode	Excitation energy (cm^{-1})	$\tilde{X}/\tilde{A}$ branching ratio	Error (±, cm^{-1})
A1	S_1-S_0 org.	0	0.0412	0.0051
	ν_S	687	0.1331	0.0118
	7a	724	0.1929	0.0119
	12	956	0.0815	0.0059
B1	S_1-S_0 org.	0	0.0427	0.0075
	ν_S	656	0.1065	0.0117
	7a	705	0.1745	0.0110
	12	952	0.0856	0.0087
A2	S_1-S_0 org.	0	0.0396	0.0051
	ν_S	659	0.1052	0.0122
	7a	712	0.1055	0.0068
	12	953	0.0767	0.0053
B2	S_1-S_0 org.	0	0.0428	0.0076
	ν_S	678	0.3019	0.0173
	7a	708	0.1365	0.0153
	12	953	0.0797	0.0069

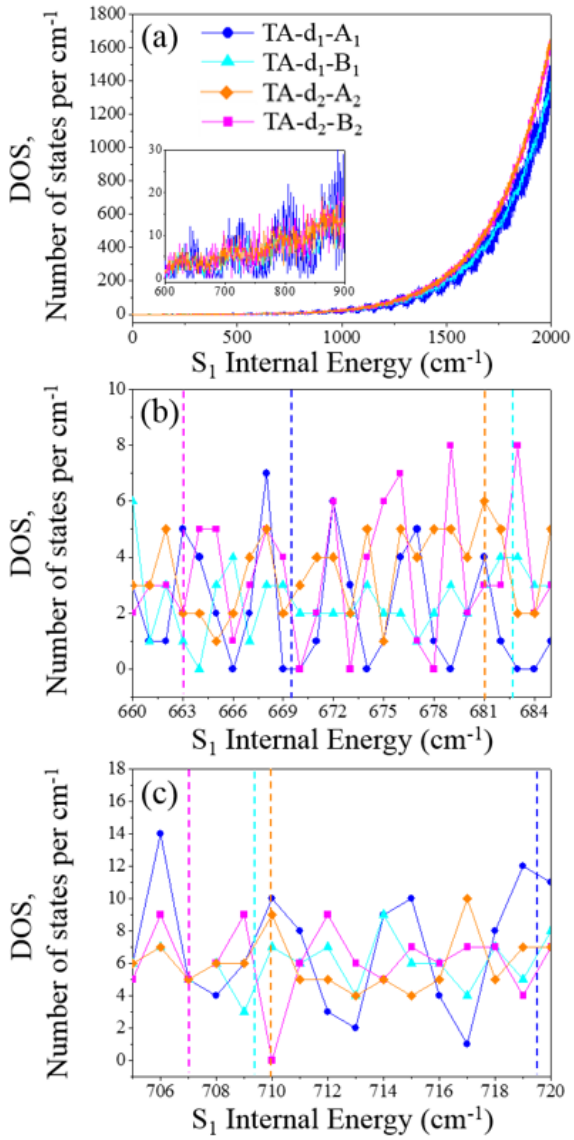


FIGURE S2. Calculated density of states on S_1 state for TA-d_1-A1 (blue dot), -B1 (light blue triangle) and TA-d_2-A2 (orange rhombic), -B2 (magenta square). (a) up to 2000cm^{-1} (b) symmetric stretching (ν_S) region. The vertical dashed lines represent the ν_S vibrational frequencies for each isomers. (c) asymmetric stretching (7a) region. The vertical dashed lines represent the 7a vibrational frequencies for each isomers.

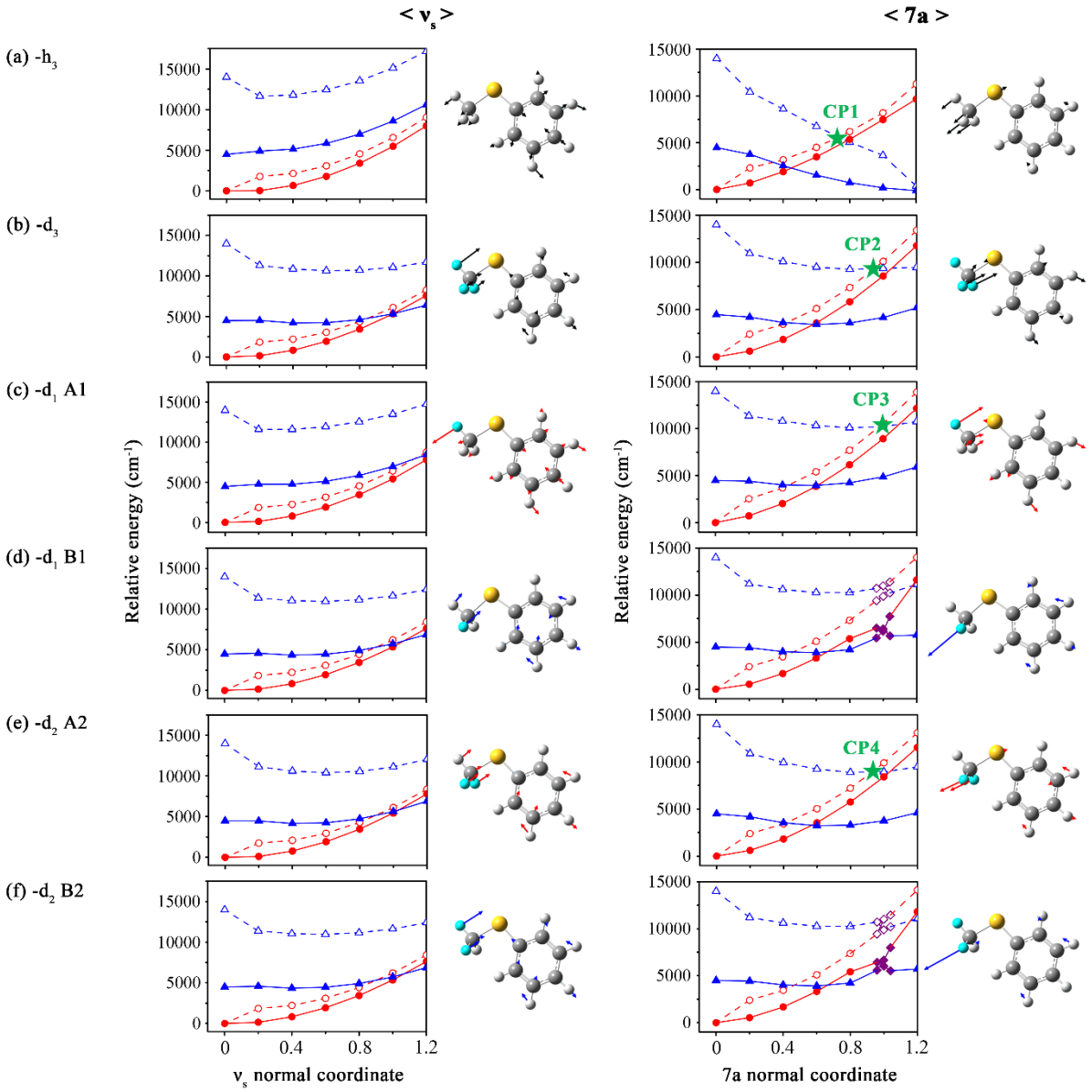
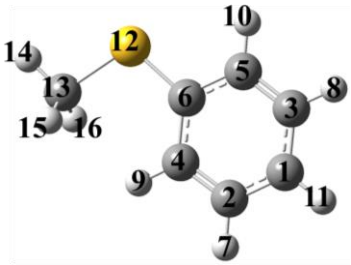


FIGURE S3. Calculated potential energy profiles of the first (S_1, red) and second (S_2, blue) electronically excited states along the asymmetric stretching (ν_S, left) and the symmetric stretching (7a, right) normal coordinates. SA4/CASSCF(dashed line) and CASPT2 corrected (solid line) values are calculated for thioanisole -h_3(a), -d_3(b), A1(c), B1(d), A2(e) and B2(f). S_1/S_2 crossing points are presented with green star. The geometrical parameters and energetics of each crossing point are shown in Table S7.

Table S8. Normalized cationic vibrational normal mode vectors of vs and 7a modes for TA-h_3, d_3, A1, B1, A2, and B2 isotopes corresponding to the (1.0) coordinate on x axes. Vs and 7a normal mode coordinates on S_1 and S_2 electronic states adopted in the CASSCF calculations in Fig. 5 (or Fig. S3) are developed with cationic vibrational normal modes.



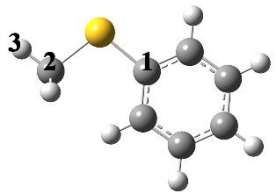
h3		ν_S^+ (736cm^{-1})			7a$^+$ (816cm^{-1})			d3		ν_S^+ (717cm^{-1})			7a$^+$ (769cm^{-1})		
		X	Y	Z	X	Y	Z			X	Y	Z	X	Y	Z
1	C	-0.02	0.00	0.10	0.00	0.00	-0.03	1	C	0.02	0.00	-0.08	-0.01	0.00	0.06
2	C	0.10	0.00	-0.02	-0.04	0.00	0.01	2	C	-0.08	0.00	0.01	0.06	0.00	0.00
3	C	-0.09	0.00	-0.05	0.04	0.00	0.04	3	C	0.07	0.00	0.03	-0.06	0.00	-0.06
4	C	0.11	0.00	-0.01	-0.04	0.00	0.00	4	C	-0.08	0.00	0.01	0.07	0.00	0.00
5	C	-0.08	0.00	-0.05	0.04	0.00	0.03	5	C	0.06	0.00	0.03	-0.06	0.00	-0.05
6	C	0.02	0.00	-0.09	0.00	0.00	0.01	6	C	-0.02	0.00	0.08	0.01	0.00	-0.04
7	H	0.06	0.00	-0.15	-0.02	0.00	0.05	7	H	-0.05	0.00	0.11	0.03	0.00	-0.09
8	H	-0.01	0.00	-0.14	0.00	0.00	0.09	8	H	0.00	0.00	0.10	0.00	0.00	-0.13
9	H	0.06	0.00	0.05	-0.04	0.00	0.00	9	H	-0.04	0.00	-0.04	0.05	0.00	0.03
10	H	-0.05	0.00	0.04	0.04	0.00	0.01	10	H	0.04	0.00	-0.04	-0.05	0.00	0.00
11	H	-0.02	0.00	0.10	-0.01	0.00	-0.03	11	H	0.03	0.00	-0.08	0.01	0.00	0.07
12	S	-0.05	0.00	0.03	-0.08	0.00	-0.07	12	S	0.07	0.00	0.01	0.06	0.00	0.07
13	C	0.07	0.00	0.05	0.16	0.00	0.09	13	C	-0.08	0.00	-0.08	-0.10	0.00	-0.02
14	H	0.12	0.00	0.06	0.15	0.00	0.09	14	**D**	-0.22	0.00	-0.13	-0.03	0.00	0.00
15	H	0.06	0.00	0.02	0.18	-0.01	0.11	15	**D**	-0.10	0.02	-0.05	-0.18	0.01	-0.15
16	H	0.06	0.00	0.02	0.18	0.01	0.11	16	**D**	-0.10	-0.02	-0.05	-0.18	-0.01	-0.15

d_1-A1		ν_S^+ (721cm^{-1})			7a$^+$ (791cm^{-1})			d_1-B1		ν_S^+ (731cm^{-1})			7a$^+$ (765cm^{-1})		
		X	Y	Z	X	Y	Z			X	Y	Z	X	Y	Z
1	C	-0.02	0.00	0.09	-0.01	0.00	0.05	1	C	0.02	0.00	-0.09	0.01	-0.01	-0.05
2	C	0.09	0.00	-0.01	0.06	0.00	-0.01	2	C	-0.09	0.00	0.02	-0.05	0.00	0.00
3	C	-0.08	0.00	-0.03	-0.06	0.00	-0.05	3	C	0.07	0.00	0.03	0.06	-0.01	0.05
4	C	0.09	0.00	-0.01	0.07	0.00	-0.01	4	C	-0.10	0.00	0.01	-0.06	-0.01	0.00
5	C	-0.07	0.00	-0.04	-0.05	0.00	-0.04	5	C	0.07	0.00	0.04	0.06	-0.01	0.04
6	C	0.02	0.00	-0.09	0.01	0.00	-0.03	6	C	-0.02	0.00	0.08	-0.01	0.01	0.04
7	H	0.05	0.00	-0.12	0.03	0.00	-0.10	7	H	-0.05	0.00	0.13	-0.03	0.03	0.08
8	H	0.00	0.00	-0.12	-0.01	0.00	-0.11	8	H	0.01	-0.01	0.11	0.00	0.06	0.11
9	H	0.04	0.00	0.05	0.06	0.00	0.01	9	H	-0.05	0.01	-0.04	-0.04	0.03	-0.02
10	H	-0.05	0.00	0.04	-0.04	0.00	0.00	10	H	0.04	-0.01	-0.04	0.04	0.08	0.00
11	H	-0.02	0.00	0.09	0.00	0.00	0.05	11	H	0.03	0.00	-0.09	-0.01	0.06	-0.06
12	S	-0.05	0.00	0.00	0.04	0.00	0.08	12	S	0.07	0.01	-0.01	-0.05	-0.02	-0.05
13	C	0.06	0.00	0.08	-0.08	0.00	-0.09	13	C	-0.09	-0.02	-0.05	0.08	0.05	0.01
14	**D**	0.24	0.00	0.14	-0.26	0.00	-0.16	14	H	-0.12	0.03	-0.06	0.00	-0.05	-0.01
15	H	0.05	-0.01	0.01	-0.09	0.02	-0.04	15	**D**	-0.19	0.02	-0.12	0.35	-0.05	0.26
16	H	0.05	0.01	0.01	-0.09	-0.02	-0.04	16	H	-0.03	0.00	0.00	-0.04	-0.02	-0.01

d_2-A2		ν_S^+ (730cm^{-1})			7a$^+$ (769cm^{-1})			d_2-B2		ν_S^+ (718cm^{-1})			7a$^+$ (764cm^{-1})		
		X	Y	Z	X	Y	Z			X	Y	Z	X	Y	Z
1	C	0.02	0.00	-0.09	0.01	0.00	-0.06	1	C	0.02	0.00	-0.09	0.01	0.00	-0.05

2	C	-0.09	0.00	0.02	-0.06	0.00	0.00	2	C	-0.08	0.00	0.01	-0.05	0.00	0.00
3	C	0.07	0.00	0.03	0.06	0.00	0.06	3	C	0.07	0.00	0.03	0.06	-0.01	0.05
4	C	-0.10	0.00	0.01	-0.06	0.00	0.00	4	C	-0.08	0.00	0.01	-0.06	0.00	0.00
5	C	0.06	0.00	0.04	0.06	0.00	0.04	5	C	0.07	0.00	0.03	0.06	0.00	0.04
6	C	-0.02	0.00	0.08	-0.01	0.00	0.04	6	C	-0.02	0.00	0.08	-0.01	0.00	0.04
7	H	-0.05	0.00	0.13	-0.03	0.00	0.08	7	H	-0.05	0.00	0.11	-0.03	0.00	0.08
8	H	0.00	0.00	0.11	0.00	0.00	0.13	8	H	0.00	0.00	0.10	0.00	0.03	0.11
9	H	-0.05	0.00	-0.04	-0.04	0.00	-0.02	9	H	-0.04	0.00	-0.04	-0.04	-0.01	-0.02
10	H	0.04	0.00	-0.04	0.05	0.00	0.00	10	H	0.04	-0.01	-0.04	-0.04	0.05	0.00
11	H	0.03	0.00	-0.09	-0.01	0.00	-0.06	11	H	0.03	0.00	-0.08	-0.01	0.02	-0.06
12	S	0.07	0.00	-0.01	-0.06	0.00	-0.07	12	S	0.07	0.00	0.01	-0.05	-0.02	-0.05
13	C	-0.09	0.00	-0.05	0.11	0.00	0.02	13	C	-0.08	-0.02	-0.08	0.08	0.06	0.01
14	H	-0.12	0.00	-0.06	0.02	0.00	-0.01	14	**D**	-0.23	0.02	-0.13	-0.01	-0.05	-0.02
15	**D**	-0.13	0.01	-0.07	0.19	-0.01	0.15	15	**D**	-0.14	0.02	-0.08	0.37	-0.06	0.25
16	**D**	-0.13	-0.01	-0.07	0.19	0.01	0.15	16	H	-0.03	-0.01	0.00	-0.06	-0.02	0.00

Table S9. Calculated molecular structural parameters for S_1/S_2 crossing (seam) points obtained via the 7a normal coordinate scan (Fig. S3) including S_1/S_2 MECI. The crossing points (CP) 1~4 are from $-h_3$, $-d_3$, $-d_1$-A1, and $-d_1$-A2 isomers. The values in parentheses are obtained with CASPT2 correction.



	Equilibrium.	Crossing points in Figure S3.				S_1/S_2
	S_1 min.	CP1	CP2	CP3	CP4	MECI
Relative E. / (cm^{-1})	-	+5595	+9375	+10170	+8867	+2617
	-	(+1721)	(+8595)	(+5526)	(+4280)	(+3726)
d(S-CH_3) / (Å)	1.87	2.08	2.05	2.07	2.05	2.13
d(C-SCH_3) / (Å)	1.79	1.68	1.63	1.63	1.64	1.78
γ(S-$C_{(2)}$- $H_{(3)}$-) / (˚)	104.91	104.06	100.12	116.34	99.19	101.24
γ($C_{(2)}$-S-$C_{(1)}$) / (˚)	103.13	104.21	103.35	106.30	103.10	102.63
d(C-C)[a] / (Å)	1.43	1.39	1.38	1.38	1.39	1.42

[a] averaged values for the phenyl moiety

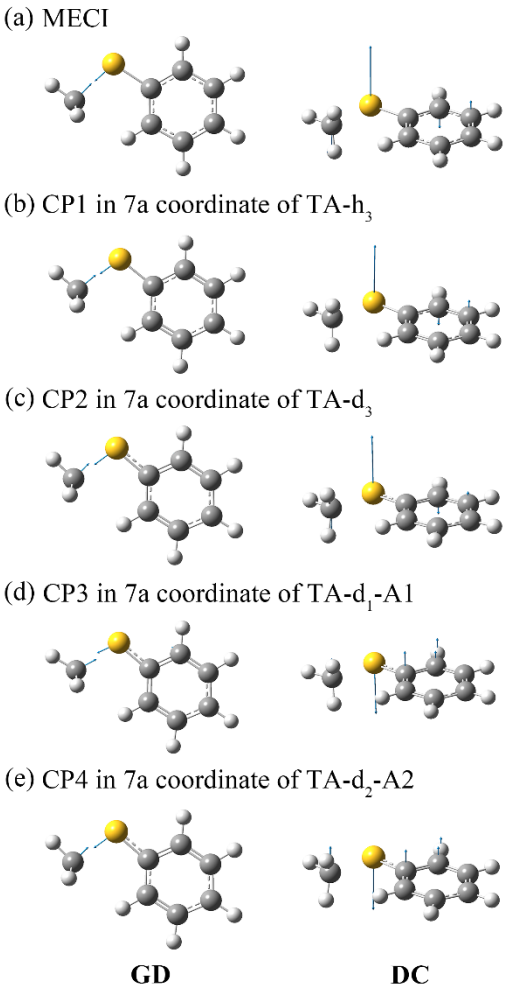


Figure S4. Gradient difference (h) and derivative coupling (g) vectors for each crossing points (CP1~4) depicted in Fig. S3 and S_1/S_2 MECI.

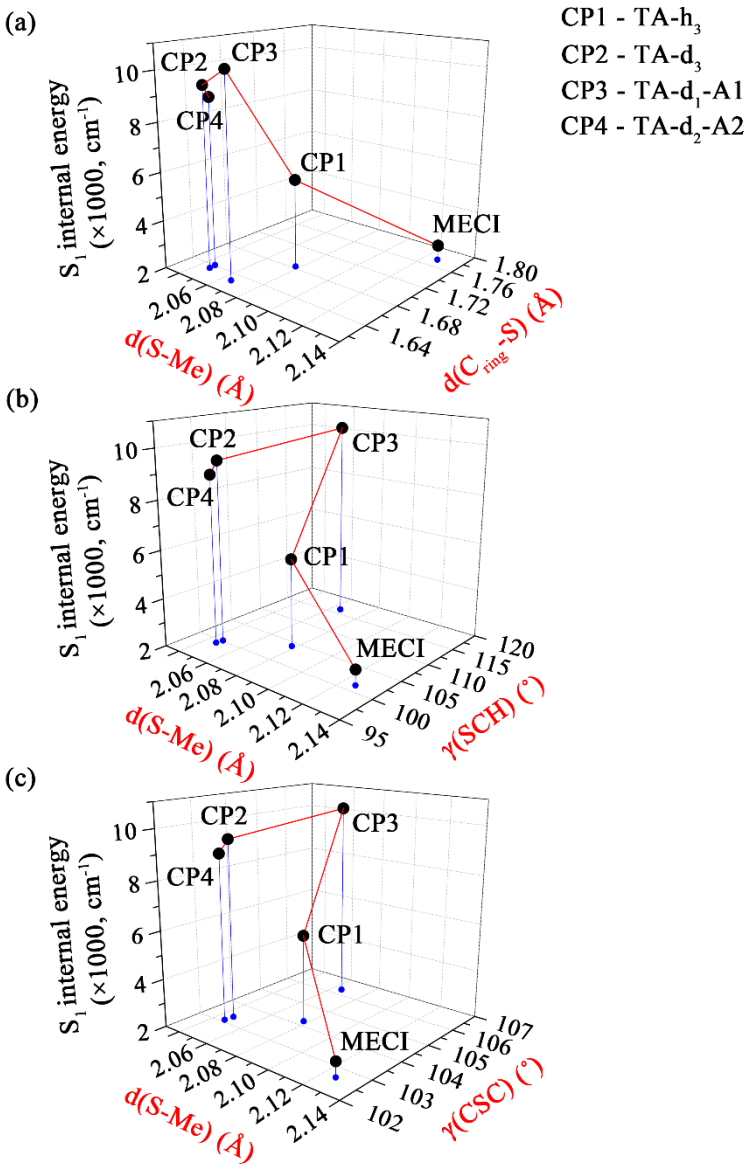


FIGURE S5. CI seam plotted along the S-Me bond length and (a) C_{ring}-SMe bond length, (b) S-C-H bond angle, and (c) C-S-C bond angle. CI seam is build up with the crossing points in Fig. S3 and MECI.

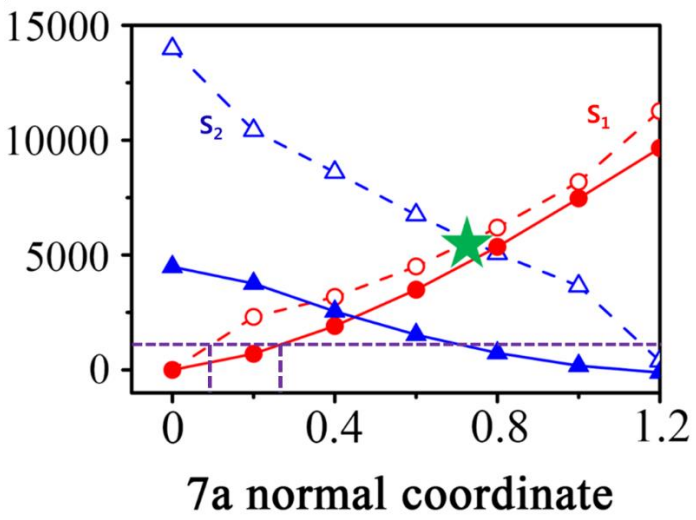


FIGURE S6. Calculated potential energy profiles of the first (S_1, red) and second (S_2, blue) electronically excited states along 7a asymmetric stretching normal coordinates, obtained by SA4/CASSCF (dashed line) and CASPT2 (solid line) level of theory for thianisole-h3. The green star indicates CASSCF S_1/S_2 crossing point. Corresponding 7a normal mode coordinates on S_1 and S_2 electronic states are developed with cationic vibrational normal modes, and x axis coordinate starts with from the cationic minimum geometry and covers 7a normal coordinates with the directions of stretched S-CH3 bond length. Purple dashed line represents energy for one quantum of 7a vibrational mode with zero-point energy correction.