Supporting Information for:

Conformer Specific Excited-state Structure of 3-methylthioanisole

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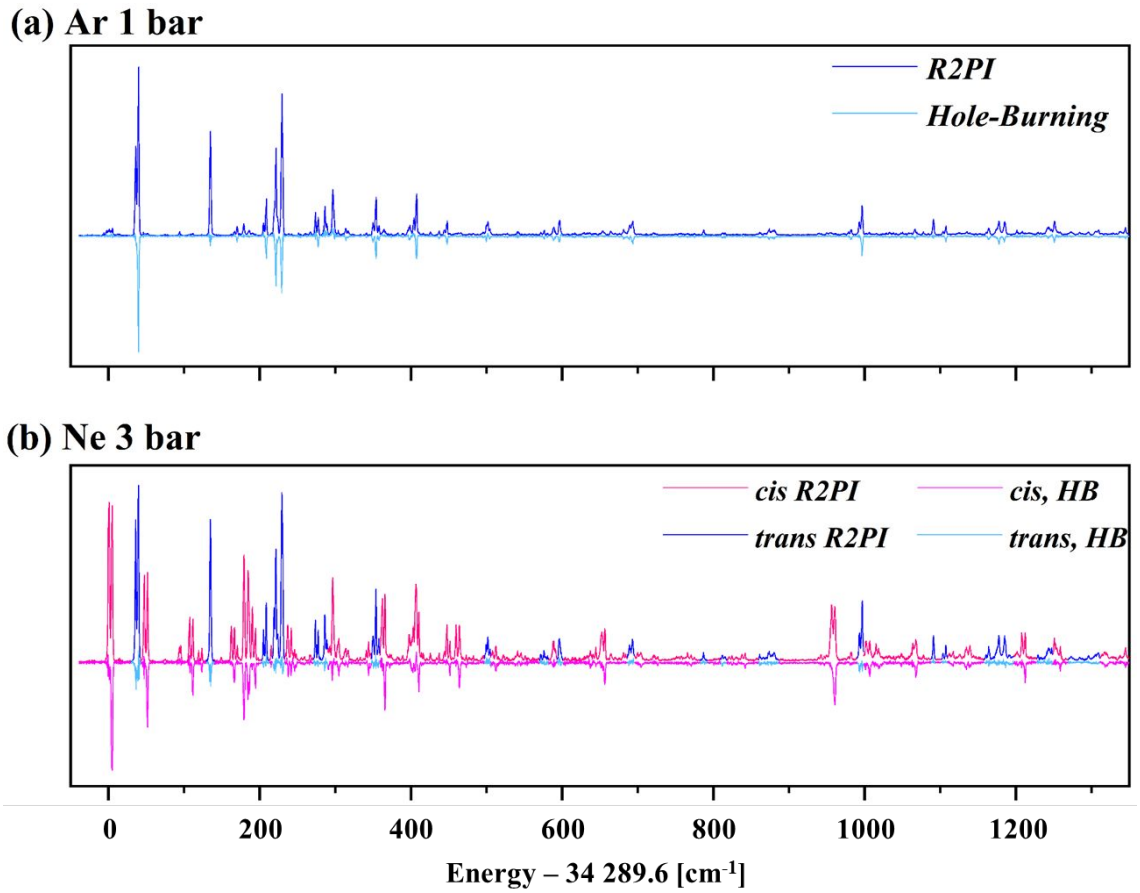

Figure S1. Full R2PI spectra for m-methylthioanisole (3MTA) backed by (a) Ar 1 bar and (b) Ne 3 bar, respectively. (a) Light-blue shows UV-UV hole-burning (HB) R2PI spectrum in which the burning laser beam was fixed at the $0a_1'$-$0a_1''$ transition of conformer 1 (trans). (a) blue represents the vibronic transitions of trans-3MTA where (b) pink depicts conformer 2 (cis). (b) (lower) magenta and light-blue lines come from the UV-UV HB R2PI spectra in which the burning laser beam was fixed at the $0a_1'$-$0a_1''$ transition of cis-3MTA.

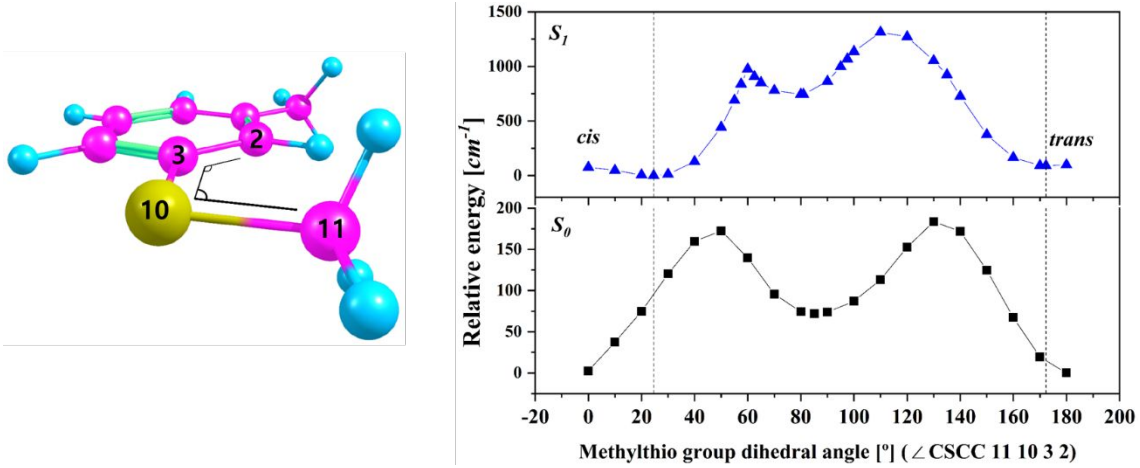

Figure S2. Relaxed scan for m-methylthioanisole with respect to the methylthio group (SCH_3) torsional coordinates. Turbomole 7.0. was used with RICC2 method and aug-cc-pVDZ basis set. 7.7° (trans) and 24.6° (cis) are the minimum methylthio group dihedral angles (i.e. ∠CSCC (11 10 3 2)), respectively.

Table S1. Selective vibrational peak assignment (unit is cm^{-1})

	***trans*-3MTA**			***cis*-3MTA**		
	Calculation[a]		Experiment	Calculation[a]		Experiment
Selected vibration mode	S_0	S_1	$h\nu$-34 325.7	S_0	S_1	$h\nu$-34 289.6
$\tau CH_3 + \tau$	58	116		42	119	
$\tau + \tau CH_3$	41	48		48	84	
SCH_3 out-of-plane (oop)	169	85		163	178	
CH_3 oop	207	238		213	194	
Ring Bending	384	364	367.7	370	364	362.1
β_S **(Scissoring)**	419	412		419	393	
ν_S **(Sym. S-C Stretching)**	672	648	653.1	674	649	652.3
$\gamma_S SCH_3$ **(oop Rocking)**	959	930		959	921	
$\beta_{as} SCH_3$ **(Wagging)**	971	983	957.1	975	946	956.0
***Bz*-CH_3 Stretching**	1237	1224	1210.9	1236	1217	1207.7

[a] Calculations were done by Turbomole 7.0. using RICC2 method and aug-cc-pVDZ basis set

Table S2. Methyl-group-internal rotation and methylthio-torsional vibration assignments

Methyl Internal Rotation (M.I.R.)	***trans*-3MTA [cm^{-1}]**		***cis*-3MTA [cm^{-1}]**		*SCH_3*	
	FC simulation[a]	Experiment	FC Simulation[b]	Experiment	oop	M.I.R
Origin						
$1e'$-$1e''$	0	0	0	0	τ_0^0	$1e'$-$1e''$
$0a_1'$-$0a_1''$	3.8	3.8	4.1	4.1		$0a_1'$-$0a_1''$
$2e'$-$1e''$	97.3	98.8	47.6	47.6	τ_0^2	$1e'$-$1e''$
$3a_1'$-$0a_1''$	185.9	185.7	51.7	51.7		$0a_1'$-$0a_1''$
$4e'$-$1e''$	190.2	193.4	107.5	107.5	τ_0^4	$1e'$-$1e''$
$5e'$-$1e''$	253.5	252.7	111.6	111.9		$0a_1'$-$0a_1''$
$6a_1'$-$0a_1''$	312.3	313.7				
Ring Bending						
$1e'$-$1e''$	367.7	367.7	362.1	362.1	τ_0^0	$1e'$-$1e''$
$0a_1'$-$0a_1''$	371.5	371.6	366.2	365.4		$0a_1'$-$0a_1''$
$2e'$-$1e''$	465	465.6	409.7	406.5	τ_0^2	$1e'$-$1e''$
$3a_1'$-$0a_1''$	553.6	552.9	413.8	410.8		$0a_1'$-$0a_1''$
$4e'$-$1e''$	557.9	561.7	469.6	459.5	τ_0^4	$1e'$-$1e''$
$5e'$-$1e''$	621.2	619.5	473.7	464.0		$0a_1'$-$0a_1''$
$6a_1'$-$0a_1''$	680	684.8				
ν_S **(S-C Sym. Stretching)**						
$1e'$-$1e''$	653.7	653.7	652.3	652.3	τ_0^0	$1e'$-$1e''$
$0a_1'$-$0a_1''$	657.5	657.3	656.4	656.2		$0a_1'$-$0a_1''$
$2e'$-$1e''$	751	751.1	699.9	699.9	τ_0^2	$1e'$-$1e''$
$3a_1'$-$0a_1''$	839.6	837.9	704	703.9		$0a_1'$-$0a_1''$
$4e'$-$1e''$	843.9	845.9	759.8	765.7	τ_0^4	$1e'$-$1e''$
$5e'$-$1e''$	907.2	906.5	763.9	770.6		$0a_1'$-$0a_1''$
$6a_1'$-$0a_1''$	966	969.8				
$\beta_{as}SCH_3$ **(Wagging)**						

$1e'$-$1e''$	957.1	957.1	956	956.0	τ_0^0	$1e'$-$1e''$
$0a_1'$-$0a_1''$	960.9	960.8	960.1	960.3		$0a_1'$-$0a_1''$
$2e'$-$1e''$	1054.4	1054.9	1003.6	1002.3	τ_0^2	$1e'$-$1e''$
$3a_1'$-$0a_1''$	1143	1141.4	1007.7	1006.9		$0a_1'$-$0a_1''$
$4e'$-$1e''$	1147.3	1148.9	1063.5	1063.6	τ_0^4	$1e'$-$1e''$
$5e'$-$1e''$	1210.6	1210.9	1067.6	1067.7		$0a_1'$-$0a_1''$
$6a_1'$-$0a_1''$	1269.4	1273.4				
***Bz*–CH_3 Stretching**						
$1e'$-$1e''$	1210.9	1210.9	1207.7	1207.7	τ_0^0	$1e'$-$1e''$
$0a_1'$-$0a_1''$	1214.7	1215	1211.8	1212.4		$0a_1'$-$0a_1''$
$2e'$-$1e''$	1308.2	1308.6	1255.3	1254.0	τ_0^2	$1e'$-$1e''$
$3a_1'$-$0a_1''$	1396.8		1259.4	1258.7		$0a_1'$-$0a_1''$
$4e'$-$1e''$	1401.1		1315.2	1314.3	τ_0^4	$1e'$-$1e''$
$5e'$-$1e''$	1464.4		1319.3	1317.2		$0a_1'$-$0a_1''$
$6a_1'$-$0a_1''$	1523.2					

[a]Fitted parameters were $V_3'' = 33.856$, $V_6'' = -10$, $F'' = 5.343_1$ cm^{-1} for S_0 state and $V_3' = 304$, $V_6' = -25.4$, $F' = 5.330_6$ cm^{-1} for S_1 state, respectively. Anchor points are the vibrational $1e'$-$1e''$ transitions.

[b]Fitted parameters were k'=0.0002419 (0.00016) [hartree/a_0^2] and reduced mass of 2.797 (2.998) [amu] for S_0 (S_1) state, A′=0.00058 [hartree] and a'=0.667 [a_0^{-2}] for S_1 state, respectively. Methyl internal rotation parameters were $F = 5.317_7$ (5.301_6) cm^{-1} and V_3 = 27 (300) cm^{-1} for S_0 (S_1).