Electronic Supplementary Information: Spectroscopic Detection of Gas-Phase $HOSO_2$

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List of Contents

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Table S-I: Observed line frequencies of $HOSO_2$ and their assignments.

N'	K'_a	K'_c	J'	F'	N''	K''_a	K''_c	J''	F''	obs. freq.[a] (MHz)	o.−c. (kHz)
$0^- \leftarrow 0^+$											
1	0	1	1.5	1	0	0	0	0.5	0	14040.362	1
			1.5	2				0.5	1	14041.186	−1
			1.5	1				0.5	1	14047.273	−0
			0.5	0				0.5	1	14068.138	−3
			0.5	1				0.5	0	14071.815	−0
			0.5	1				0.5	1	14078.727	−2
$0^+ \leftarrow 0^-$											
1	0	1	1.5	1	0	0	0	0.5	0	14000.242	2
			1.5	2				0.5	1	14001.116	−0
			1.5	1				0.5	1	14007.153	1
			0.5	0				0.5	1	14032.247	3
			0.5	1				0.5	0	14035.743	1
			0.5	1				0.5	1	14042.654	1
$0^+ \leftarrow 0^+$											
1	1	0	1.5	1	0	0	0	0.5	0	18490.943	−2
			1.5	2				0.5	1	18494.666	−0
			1.5	1				0.5	1	18497.856	−2
			0.5	1				0.5	0	18524.771	1
			0.5	1				0.5	1	18531.688	5
			0.5	0				0.5	1	18533.505	2
$0^- \leftarrow 0^-$											
1	1	0	1.5	1	0	0	0	0.5	0	18490.923	0
			1.5	2				0.5	1	18494.646	−0
			1.5	1				0.5	1	18497.835	−1
			0.5	1				0.5	0	18524.750	−0
			0.5	1				0.5	1	18531.658	−6
			0.5	0				0.5	1	18533.485	2
$0^+ \leftarrow 0^+$											
1	1	1	0.5	1	0	0	0	0.5	0	14294.803[b]	−4
			1.5	2				0.5	1	14301.727[c]	−3
			0.5	1				0.5	1	14301.727[c]	7
			1.5	1				0.5	0	14302.518	2
			0.5	0				0.5	1	14306.723	−1

Table S-I (*continue*)

N'	K'_a	K'_c	J'	F'	N''	K''_a	K''_c	J''	F''	obs. freq.[a] (MHz)	o.−c. (kHz)
$0^- \leftarrow 0^-$											
1	1	1	0.5	1	0	0	0	0.5	1	14290.696	−1
			1.5	1				0.5	0	14292.530	2
			1.5	2				0.5	1	14293.195	−1
			0.5	0				0.5	1	14294.018	−0
$0^+ \leftarrow 0^+$											
1	1	0	1.5	2	1	0	1	1.5	2	4469.240[d]	2
			1.5	1				1.5	2	4472.429[d]	0
			0.5	1				1.5	2	4506.256[d]	1
$0^- \leftarrow 0^-$											
1	1	0	1.5	2	1	0	1	1.5	2	4477.772[d]	0
			1.5	1				1.5	2	4480.963[d]	2
			0.5	1				1.5	2	4514.788[d]	−0
$0^+ \leftarrow 0^+$											
2	0	2	2.5	3	1	1	1	1.5	2	23838.367	0
			2.5	2				1.5	1	23835.740	2
			2.5	2				1.5	2	23843.456[c]	18
			2.5	2				0.5	1	23843.456[c]	8
			1.5	1				0.5	0	23853.588	1
			1.5	2				1.5	1	23856.791	−3
			1.5	1				1.5	2	23858.595[c]	13
			1.5	1				0.5	1	23858.595[c]	3
			1.5	2				1.5	2	23864.501[c]	8
			1.5	2				0.5	1	23864.501[c]	−2
$0^- \leftarrow 0^-$											
2	0	2	2.5	2	1	1	1	1.5	1	23848.683	−3
			2.5	3				1.5	2	23849.910	−2
			2.5	2				1.5	2	23854.930	0
			2.5	2				0.5	1	23857.430	1
			1.5	1				0.5	0	23868.320	2
			1.5	2				1.5	1	23868.771	−2
			1.5	1				0.5	1	23871.643	3
			1.5	2				1.5	2	23875.015	−2
			1.5	2				0.5	1	23877.519	2
$0^- \leftarrow 0^+$											

Table S-I (*continue*)

N'	K'_a	K'_c	J'	F'	N''	K''_a	K''_c	J''	F''	obs. freq.[a] (MHz)	o.−c. (kHz)
2	1	2	2.5	2	1	1	1	1.5	1	23860.820	−0
			2.5	3				1.5	2	23863.482	−2
			2.5	2				0.5	1	23868.537	7
			1.5	1				0.5	0	23875.868	−2
			1.5	2				1.5	1	23879.173	−1
$0^+ \leftarrow 0^+$											
2	1	2	1.5	1	1	0	1	0.5	1	24089.312	2
			1.5	2				0.5	1	24095.353	1
			1.5	1				0.5	0	24099.721	−0
			2.5	2				1.5	1	24111.537	−1
			2.5	3				1.5	2	24112.478	−3
			2.5	2				1.5	2	24117.571	−3
			1.5	1				1.5	1	24124.812	−0
			1.5	2				1.5	2	24136.893	3
$0^- \leftarrow 0^-$											
2	1	2	1.5	1	1	0	1	0.5	1	24103.866	1
			1.5	2				0.5	1	24109.875	0
			1.5	1				0.5	0	24114.451	−2
			2.5	2				1.5	1	24122.976	1
			2.5	3				1.5	2	24124.023	−4
			2.5	2				1.5	2	24129.063	1
			1.5	1				1.5	1	24135.323	2
			1.5	2				1.5	2	24147.416	−1
$0^+ \leftarrow 0^-$											
2	0	2	1.5	2	1	0	1	0.5	1	24087.495	1
			2.5	2				1.5	1	24097.895	1
			2.5	3				1.5	2	24098.908	−1
$0^+ \leftarrow 0^+$											
2	1	1	2.5	3	1	0	1	1.5	2	36730.629[d]	9
			2.5	2				1.5	2	36735.491[d]	6
			1.5	1				1.5	2	36809.840[d]	0
			1.5	2				1.5	2	36814.715[d]	−2
$0^- \leftarrow 0^-$											
2	1	1	2.5	3	1	0	1	1.5	2	36730.254[d]	−5
			2.5	2				1.5	2	36735.137[d]	−9

Table S-I (*continue*)

N'	K_a'	K_c'	J'	F'	N''	K_a''	K_c''	J''	F''	obs. freq.[a] (MHz)	o.−c. (kHz)
			1.5	1				1.5	2	36807.299[d]	0
			1.5	2				1.5	2	36812.222[d]	−1
$0^- \leftarrow 0^+$											
2	2	0	2.5	3	1	0	1	1.5	2	41506.713[d]	5
			2.5	2				1.5	2	41509.260[d]	5
			1.5	1				0.5	1	41524.184[d]	3
			1.5	2				0.5	1	41524.308[d]	1
			1.5	2				1.5	2	41565.848[d]	3
$0^+ \leftarrow 0^-$											
2	2	0	2.5	3	1	0	1	1.5	2	41466.716[d]	−3
			2.5	2				1.5	2	41469.264[d]	−4
			1.5	1				0.5	1	41488.188[d]	−1
			1.5	2				0.5	1	41488.311[d]	−3
			1.5	2				1.5	2	41525.849[d]	−7
$0^+ \leftarrow 0^+$											
2	2	1	2.5	3	1	1	1	1.5	2	37267.319[e]	35
			2.5	2				1.5	2	37268.240[d]	−1
			1.5	2				1.5	2	37289.471[d]	−6
			1.5	1				1.5	2	37290.396[e]	19
$0^- \leftarrow 0^-$											
2	2	1	2.5	3	1	1	1	1.5	2	37266.958[d]	−6
			2.5	2				1.5	2	37267.822[d]	1
			1.5	2				1.5	2	37287.151[d]	5
			1.5	1				1.5	2	37287.884[d]	7

[a] Lines without superscript letter were observed by FTMW spectroscopy, and estimated error of 3 kHz are given in the least-squares analysis uisng the spfit program.

[b] Observed by the FTMW-MW double resonance technique. Estimated error of 20 kHz is given in the least-squares analysis.

[c] Overlapping peak. Not included in the least-squares analysis.

[d] Observed by the FTMW-MW double resonance technique. Estimated error of 6 kHz is given in the least-squares analysis.

[e] Not included in the least-squares analysis.

Table S-II: Observed line frequencies of $DOSO_2$ and their assignments.

N'	K'_a	K'_c	J'	F'	N''	K''_a	K''_c	J''	F''	obs. freq.[a] (MHz)	o.−c. (kHz)
$0^+ \leftarrow 0^+$											
1	0	1	1.5	1.5	0	0	0	0.5	0.5	13329.790[b]	2
			1.5	2.5				0.5	1.5	13330.285	1
			1.5	0.5				0.5	0.5	13330.470[b]	4
			1.5	1.5				0.5	1.5	13331.519[c]	1
			1.5	0.5				0.5	1.5	13332.195[c]	−1
			0.5	0.5				0.5	0.5	13334.197	−3
			0.5	0.5				0.5	1.5	13335.927[c]	−3
			0.5	1.5				0.5	0.5	13336.382	−1
			0.5	1.5				0.5	1.5	13338.080[b]	−33
$0^- \leftarrow 0^-$											
1	0	1	1.5	2.5	0	0	0	0.5	1.5	13330.228	−1
			1.5	1.5				0.5	1.5	13331.463[c]	0
			1.5	0.5				0.5	1.5	13332.138[c]	−4
			0.5	0.5				0.5	0.5	13334.147	2
			0.5	0.5				0.5	1.5	13335.879[c]	4
			0.5	1.5				0.5	0.5	13336.332	3
			0.5	1.5				0.5	1.5	13338.080[b]	22
$0^+ \leftarrow 0^+$											
1	1	0	1.5	2.5	1	1	1	0.5	1.5	3828.473[d]	1
			1.5	2.5				1.5	1.5	3856.959[d]	−4
			1.5	2.5				1.5	2.5	3857.794[d]	−1
$0^- \leftarrow 0^-$											
1	1	0	1.5	2.5	1	1	1	0.5	1.5	3828.519[d]	−1
			1.5	2.5				1.5	1.5	3857.021[d]	10
			1.5	2.5				1.5	2.5	3857.845[d]	2
$0^+ \leftarrow 0^+$											
2	0	2	2.5	2.5	1	0	1	1.5	1.5	23416.465[c]	−18
			2.5	1.5				1.5	0.5	23416.500[c]	−4
			2.5	3.5				1.5	2.5	23416.634[c]	4
			2.5	1.5				1.5	1.5	23417.184[c]	2
			2.5	2.5				1.5	2.5	23417.719[c]	2
			1.5	1.5				0.5	1.5	23425.528[c]	3
			1.5	2.5				0.5	1.5	23426.715[c]	6

Table S-II (*continue*)

N'	K_a'	K_c'	J'	F'	N''	K_a''	K_c''	J''	F''	obs. freq.[a] (MHz)	o.−c. (kHz)
			1.5	0.5				0.5	0.5	23426.894[c]	3
			1.5	1.5				0.5	0.5	23427.709[c]	1
			1.5	1.5				1.5	1.5	23432.070[b]	−51
			1.5	2.5				1.5	2.5	23434.500[b]	−39
$0^- \leftarrow 0^-$											
2	0	2	2.5	2.5	1	0	1	1.5	1.5	23416.390[c]	−3
			2.5	1.5				1.5	0.5	23416.416[c]	2
			2.5	3.5				1.5	2.5	23416.541[c]	1
			2.5	1.5				1.5	1.5	23417.094[c]	2
			2.5	2.5				1.5	2.5	23417.630[c]	3
			1.5	1.5				0.5	1.5	23425.435[c]	0
			1.5	2.5				0.5	1.5	23426.617[c]	−2
			1.5	0.5				0.5	0.5	23426.801[f]	−1
			1.5	1.5				0.5	0.5	23427.620[c]	1
			1.5	1.5				1.5	1.5	23432.070[b]	39
			1.5	2.5				1.5	2.5	23434.500[b]	51
$0^+ \leftarrow 0^+$											
2	1	2	1.5	0.5	1	1	1	0.5	0.5	22796.190	1
			1.5	1.5				0.5	1.5	22796.850[e]	4
			1.5	1.5				0.5	0.5	22796.945	−1
			1.5	2.5				0.5	1.5	22797.949	2
			2.5	3.5				1.5	2.5	22806.675[c]	1
			2.5	2.5				1.5	1.5	22806.891	0
			2.5	1.5				1.5	0.5	22807.030[c]	1
			2.5	1.5				1.5	1.5	22807.569	−2
			2.5	2.5				1.5	2.5	22807.724	1
			1.5	2.5				1.5	2.5	22827.256[f]	−14
$0^- \leftarrow 0^-$											
2	1	2	1.5	0.5	1	1	1	0.5	0.5	22796.095	−1
			1.5	1.5				0.5	1.5	22796.754	0
			1.5	1.5				0.5	0.5	22796.850[e]	−3
			1.5	2.5				0.5	1.5	22797.855	0
			2.5	3.5				1.5	2.5	22806.581	0
			2.5	2.5				1.5	1.5	22806.799[c]	0
			2.5	1.5				1.5	0.5	22806.936[c]	0

Table S-II (*continue*)

N'	K'_a	K'_c	J'	F'	N''	K''_a	K''_c	J''	F''	obs. freq.[a] (MHz)	o.−c. (kHz)
			2.5	1.5				1.5	1.5	22807.479	0
			2.5	2.5				1.5	2.5	22807.632	1
			1.5	2.5				1.5	2.5	22827.184[f]	7
$0^+ \leftarrow 0^+$											
2	1	1	1.5	0.5	1	1	0	0.5	0.5	30519.244	1
			1.5	1.5				0.5	0.5	30519.761	0
			1.5	1.5				0.5	1.5	30520.270	−3
			1.5	2.5				0.5	1.5	30521.112	0
			2.5	3.5				1.5	2.5	30524.810	1
			2.5	2.5				1.5	1.5	30525.007	2
			2.5	1.5				1.5	0.5	30525.115[c]	2
			2.5	2.5				1.5	2.5	30525.716[g]	2
$0^- \leftarrow 0^-$											
2	1	1	1.5	0.5	1	1	0	0.5	0.5	30519.191	2
			1.5	1.5				0.5	0.5	30519.707	0
			1.5	1.5				0.5	1.5	30520.220	1
			1.5	2.5				0.5	1.5	30521.058	0
			2.5	3.5				1.5	2.5	30524.754	−2
			2.5	2.5				1.5	1.5	30524.953[c]	3
			2.5	1.5				1.5	0.5	30525.056	−3
			2.5	2.5				1.5	2.5	30525.655[g]	−5
$0^+ \leftarrow 0^+$											
2	2	1	2.5	1.5	2	0	2	2.5	1.5	13757.533	1
			2.5	2.5				2.5	2.5	13757.821	0
			2.5	1.5				2.5	2.5	13758.229	−2
			2.5	3.5				2.5	3.5	13758.499	−1
			1.5	2.5				1.5	2.5	13808.465	0
			1.5	1.5				1.5	2.5	13808.656	−2
			1.5	2.5				1.5	1.5	13809.649	0
			1.5	1.5				1.5	1.5	13809.844	2
$0^- \leftarrow 0^-$											
2	2	1	2.5	1.5	2	0	2	2.5	1.5	13757.625	−1
			2.5	2.5				2.5	2.5	13757.916	0
			2.5	1.5				2.5	2.5	13758.327	1
			2.5	3.5				2.5	3.5	13758.594	0

Table S-II (*continue*)

N'	K'_a	K'_c	J'	F'	N''	K''_a	K''_c	J''	F''	obs. freq.[a] (MHz)	o.−c. (kHz)
			1.5	2.5				1.5	2.5	13808.558	−1
			1.5	1.5				1.5	2.5	13808.753	0
			1.5	2.5				1.5	1.5	13809.744	1
			1.5	1.5				1.5	1.5	13809.937	1
$0^+ \leftarrow 0^+$ & $0^- \leftarrow 0^-$ [h]											
1	1	0	1.5	1.5	0	0	0	0.5	0.5	17883.584[f]	−1
			1.5	0.5				0.5	0.5	17884.135[f]	−1
			1.5	2.5				0.5	1.5	17884.606	−1
			1.5	1.5				0.5	1.5	17885.316	1
			1.5	0.5				0.5	1.5	17885.866[f]	−1
			0.5	1.5				0.5	0.5	17918.854	−1
			0.5	0.5				0.5	0.5	17919.366	−1
			0.5	1.5				0.5	1.5	17920.584[f]	−1
			0.5	0.5				0.5	1.5	17921.097[f]	0
$0^+ \leftarrow 0^+$ & $0^- \leftarrow 0^-$ [h]											
2	1	1	2.5	1.5	1	0	1	1.5	0.5	35078.778[e]	−6
			2.5	2.5				1.5	1.5	35078.804	1
			2.5	3.5				1.5	2.5	35079.132	0
			2.5	2.5				1.5	2.5	35080.039	2
			1.5	0.5				0.5	1.5	35102.228[i]	1
			1.5	1.5				0.5	1.5	35102.746	2
			1.5	2.5				0.5	1.5	35103.583	−1
			1.5	0.5				0.5	0.5	35104.412	2
			1.5	1.5				0.5	0.5	35104.926	−2
			1.5	2.5				1.5	2.5	35111.414[i,j]	−2
$0^- \leftarrow 0^+$											
1	1	1	1.5	1.5	0	0	0	0.5	0.5	14025.948[g]	1
			1.5	2.5				0.5	1.5	14026.847	1
			1.5	1.5				0.5	1.5	14027.672[g]	−4
$0^+ \leftarrow 0^-$											
1	1	1	1.5	1.5	0	0	0	0.5	0.5	14025.829[g]	−2
			1.5	2.5				0.5	1.5	14026.731	1
			1.5	1.5				0.5	1.5	14027.562[g]	1

[a] Lines without superscript letter were observed by FTMW spectroscopy, and estimated error of 3 kHz are given in the least-squares analysis uisng the spfit program.

[b] Very broad line. Not included in the least-squares analysis.

[c] Doppler component(s) of the line is(are) overlapping with other(s). Estimated error of 6 kHz is given in the least-squares analysis.

[d] Observed by the FTMW-MW double resonance technique. Estimated error of 6 kHz is given in the least-squares analysis.

[e] The line is overlapping with other. Estimated error of 6 kHz is given in the least-squares analysis.

[f] Broader line observed. Estimated error of 6 kHz is given in the least-squares analysis.

[g] Very weak line observed. Estimated error of 6 kHz is given in the least-squares analysis.

[h] Tunnel splitting is not observed in c-type transitions. The observed line frequency is processed as the averaged frequencies for the $0^+ \leftarrow 0^+$ & $0^- \leftarrow 0^-$ components in the least squares fit.

[i] Observed by the FTMW-MW double resonance technique. Estimated error of 20 kHz is given in the least-squares analysis.

[j] Only the $0^+ \leftarrow 0^+$ component is observed by monitoring 1_{01}–0_{00} ($J = 1.5$–0.5, $F = 2.5$–1.5, $0^+ \leftarrow 0^+$) line @ 13330.285 MHz.

A model calculation for the C constant of $HOSO_2$

For a simplification, we made following assumptions.

- The structure of the SO_3 frame is invariant during the OH torsional motion.
- The c-axis is fixed to the SO_3 frame, paerpendicular to the plane involving three O atoms, through the S atom, as illustrated in Fig. S-I.

The inertial moment of the proton with respect to the fixed c-axis is written as a function of the torsional coordinate α,

$$I_{\mathrm{H}}^{C}(\alpha)/M_{\mathrm{H}} = \left\{(R_{\mathrm{SO}} + R_{\mathrm{OH}}\cos(\pi-\gamma))\cdot\cos\left(\beta-\frac{\pi}{2}\right) + R_{\mathrm{OH}}\sin(\pi-\gamma)\sin\left(\beta-\frac{\pi}{2}\right)\cos\alpha\right\}^2 + \left\{R_{\mathrm{OH}}\sin(\pi-\gamma)\sin\alpha\right\}^2, \tag{1}$$

where M_{H} is the mass of proton. The values of R_{SO}, R_{OH}, β, and γ are fixed to those at the theoretical equilibrium structure in Fig. 1 of the main text, 1.607 Å, 0.968 Å, 102.92°, and 107.69°, respectively. Then, eq. (1) is rewritten as

$$I_{\mathrm{H}}^{C}(\alpha) = M_{\mathrm{H}}\left\{(1.853 + 0.206\cos\alpha)^2 + (0.922\sin\alpha)^2\right\}. \tag{2}$$

The contribution of the SO_3 frame, $I_{\mathrm{SO_3}}^{C}$, is constant from the above assumptions, fixed to 98.65 uÅ^2 in the present calculation in order to reproduce the experimental C constant well.

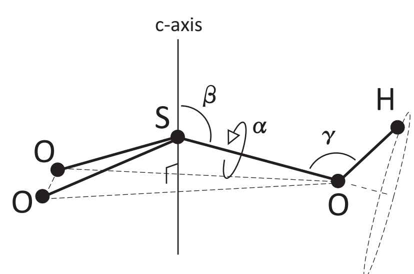

Figure S-I: Structural parameters for a model caluculation of the C constant. α is the torsional coordinate. The OH bond is paralell to the c-axis and the proton is above the plane involing three O atoms at $\alpha = 0$. β and γ are fixed to 102.92° and 107.69°, respectively.

The total $I^C(\alpha)$ value is the sum of $I^C_{\mathrm{H}}(\alpha)$ and $I^C_{\mathrm{SO_3}}$. The rotational constant C is then obtained by calculating the expectation value of the inverse of $I^C(\alpha)$ using the wavefunction obtained from the tunnel splitting calculation described in the discussion of the main text. The C constant of $HOSO_2$ is then calculated to be 4910.69577 and 4910.69558 MHz for the 0^+ and 0^- sublevels, respectively, assuming the potential barrier of 1150 cm^{-1} (V_1=0 and V_2 = 1150 cm^{-1}). For $DOSO_2$, a similar calculation gives a much smaller difference in the C constant, 8×10^{-4} kHz (the C constant of 0^+ is larger).