Supporting Information for

Formation of Thiocarbonic Acid (H_2CS_3) – the Sulfur Counterpart of Carbonic Acid (H_2CO_3) – in Interstellar Analog Ices

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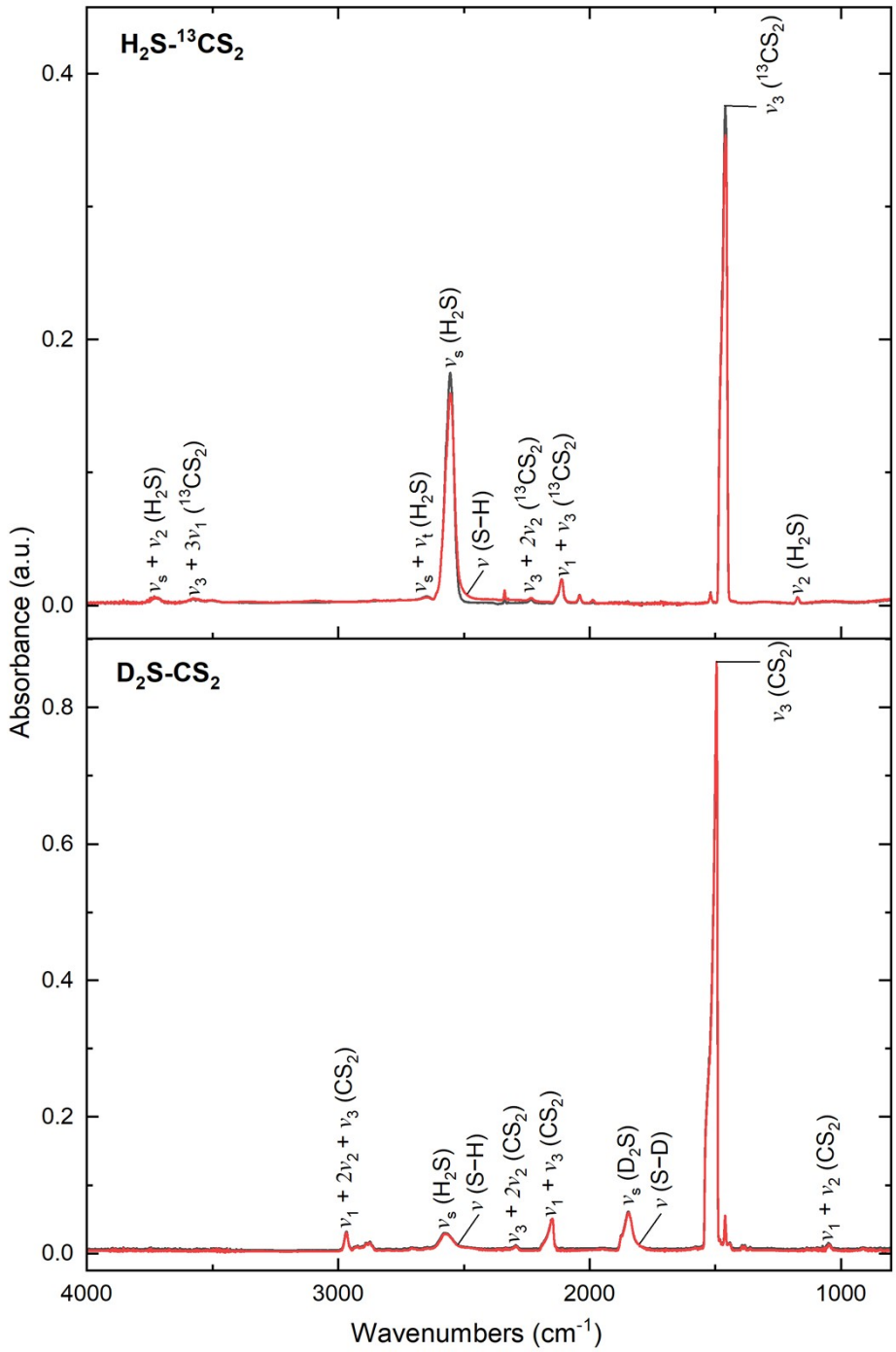


Fig. S1 IR spectrum of pristine (black) and irradiated (red) 6.1:1 H_2S–$^{13}CS_2$ ice (top) and 0.5:1 D_2S–CS_2 ice (bottom) at 5 K. Assignments were given based on detailed wavenumbers listed in Table S3.

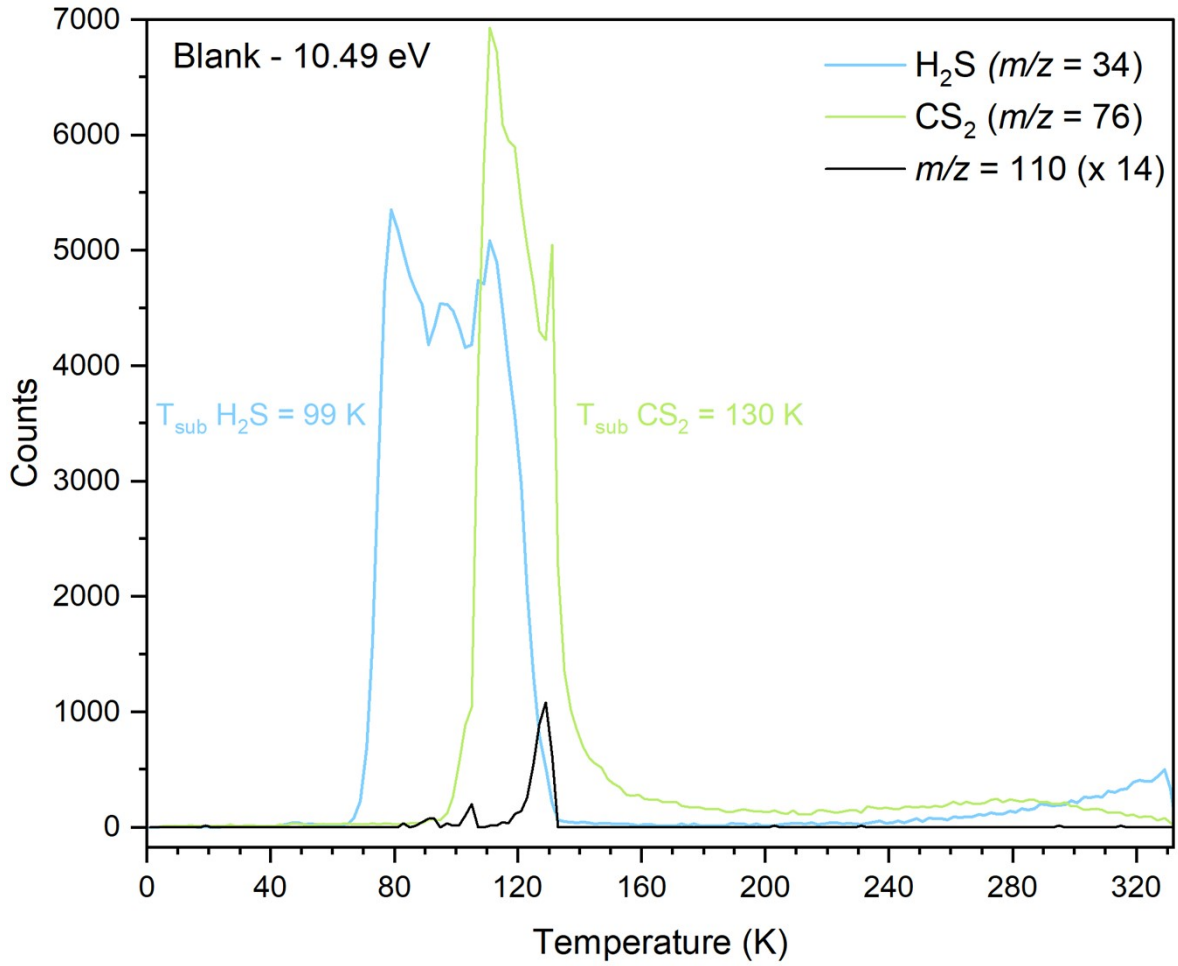


Fig. S2 TPD profiles of hydrogen sulfide (blue) at *m/z* = 34, carbon disulfide (green) at *m/z* = 76 and the co-desorption features at *m/z* = 110 (black) in unirradiated (blank) H_2S–CS_2 ice at 10.49 eV. For the TPD profiles of hydrogen sulfide and carbon disulfide, the unusual shape is caused by the saturation of the detector upon sublimation.

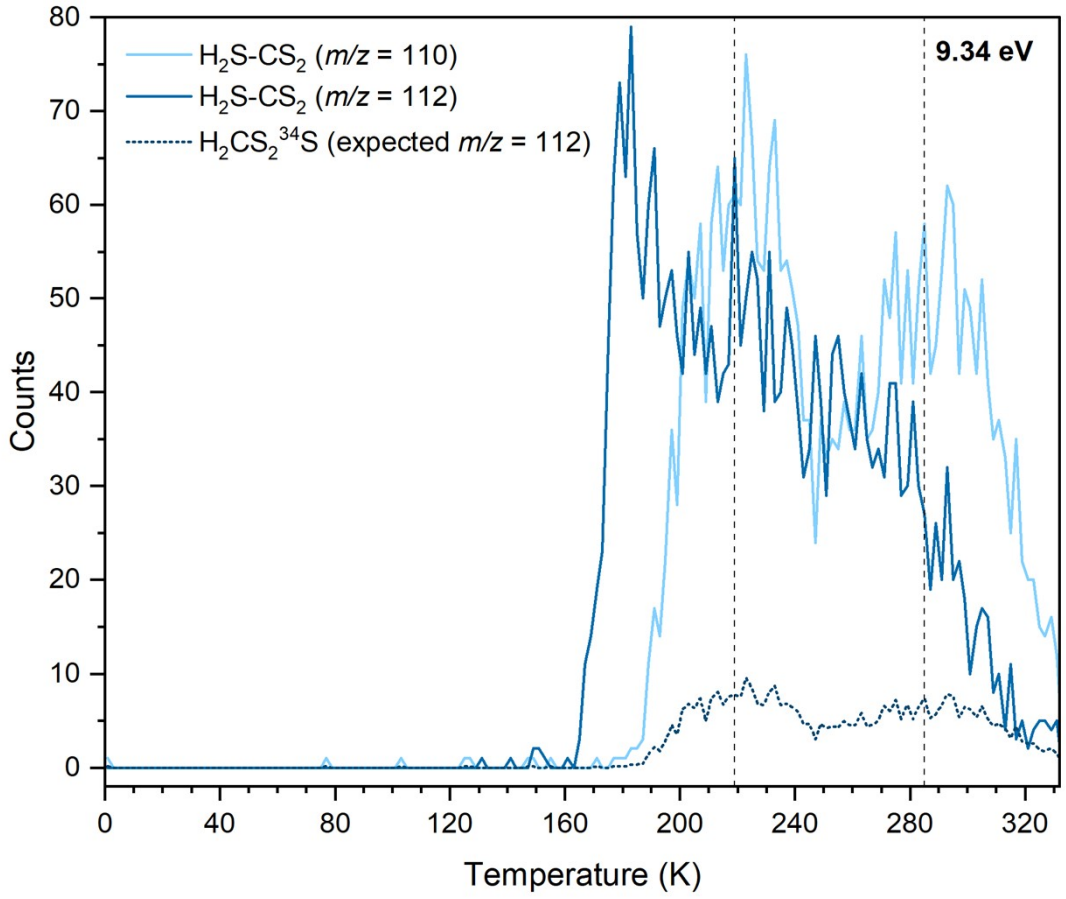


Fig. S3 TPD profiles at 9.34 eV for : $H_2S{-}CS_2$ (*m/z* = 110), $H_2S{-}CS_2$ (*m/z* = 112), and expected signal for $H_2CS_2{}^{34}S$ (*m/z* = 112). The dashed lines indicate sublimation peaks II (219 K) and III (285 K).

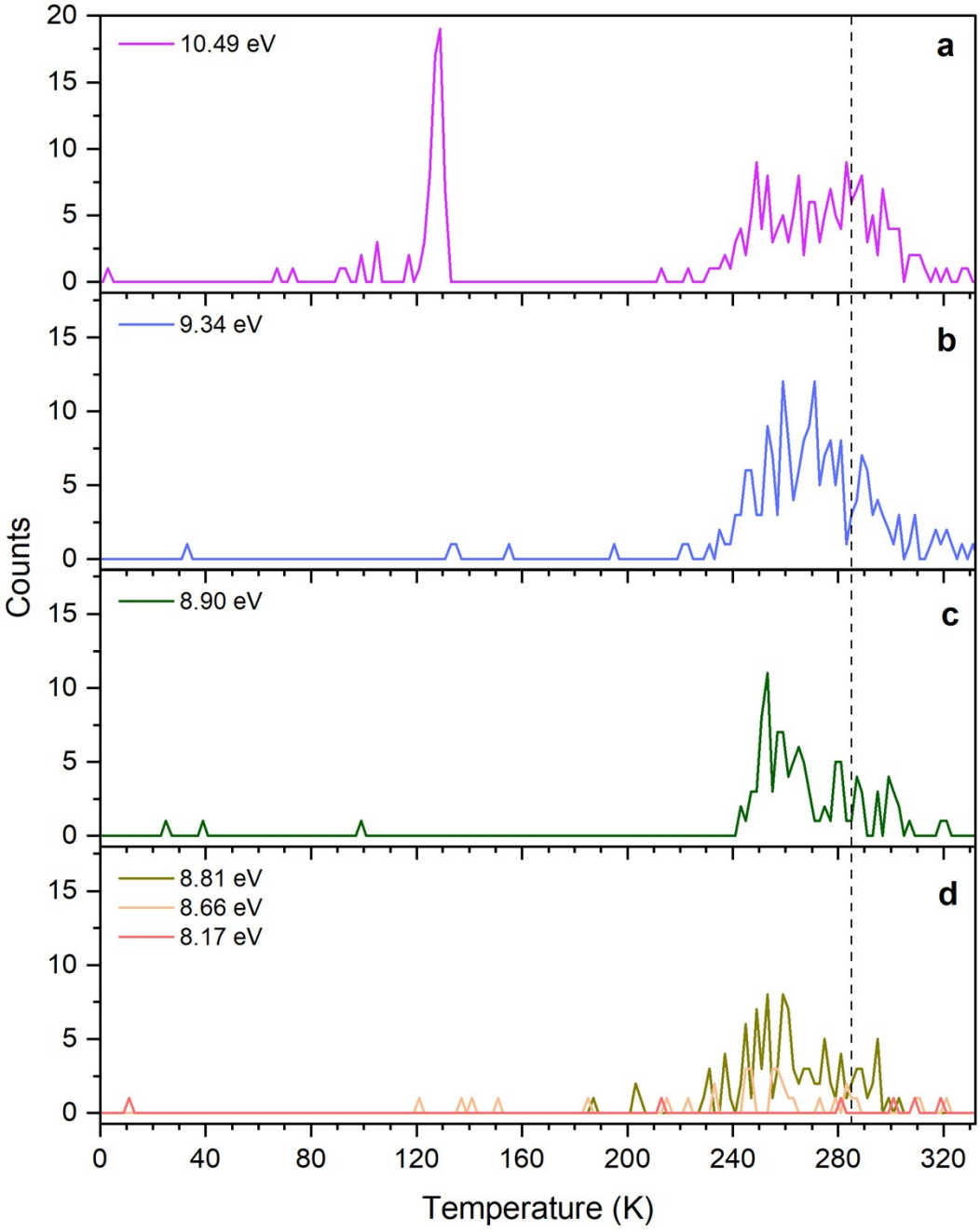


Fig. S4 TPD profiles of *m/z* = 220 from the irradiated $H_2S{-}CS_2$ ice at (a) 10.49 eV, (b) 9.34 eV, (c) 8.90 eV, (d) 8.81, 8.66, and 8.17 eV. The dashed black line indicates the sublimation peak at 285 K.

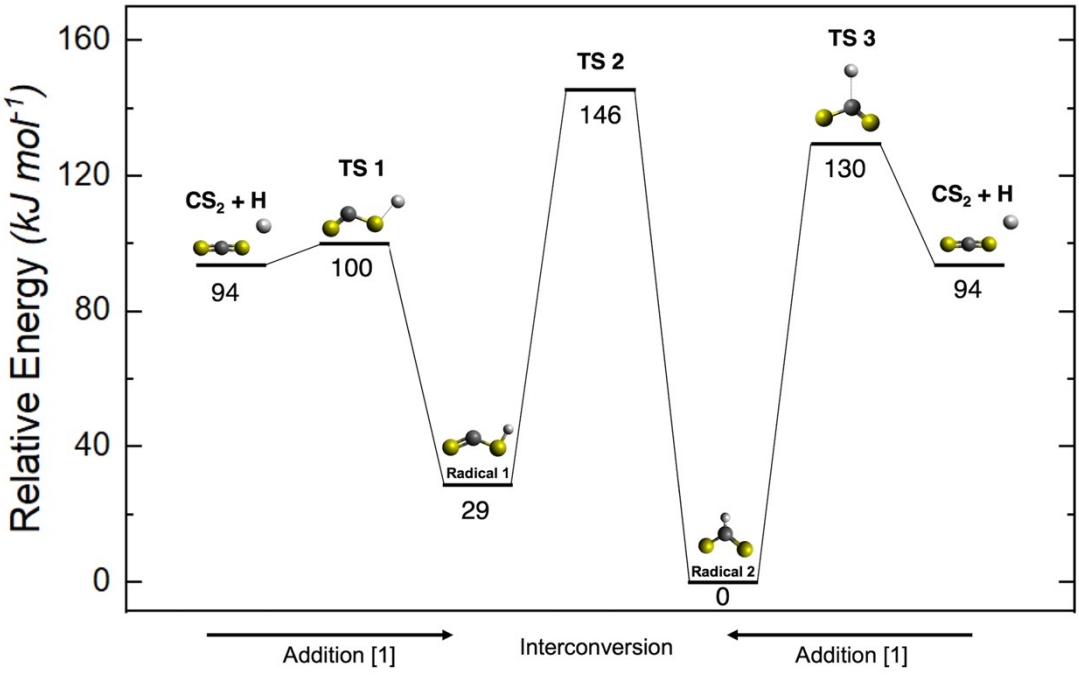


Fig. S5 CCSD(T)-F12/cc-pVTZ-F12 potential energy surface for the formation and interconversion of radical 1 (HSĊS) and radical 2 (HC(S)Ṡ).

Table S1 Experimental parameters of the ices : composition, ratio, thickness, irradiation dose (current and irradiation time), and photon energy used during TPD.

Experiment	Composition	Ratio	Thickness (nm)	Current (nA)	Time (min)	Dose, H_2S (eV molecule^{-1})	Dose, CS_2 (eV molecule^{-1})	Photon energy (eV)
1	H_2S:CS_2	2.7 : 1	850 ± 50	0	0	0	0	10.49
2	H_2S:CS_2	3.7 : 1	850 ± 50	20 ± 1	10	0.24	0.83	10.49
3	H_2S:CS_2	3.5 : 1	850 ± 50	20 ± 1	10	0.24	0.78	9.34
4	H_2S:CS_2	3.5 : 1	850 ± 50	20 ± 1	10	0.25	0.83	8.17
5	H_2S:CS_2	4.1 : 1	850 ± 50	20 ± 1	10	0.25	0.96	8.90
6	H_2S:CS_2	3.7 : 1	850 ± 50	20 ± 1	10	0.23	0.79	8.66
7	H_2S:CS_2	4.3 : 1	850 ± 50	20 ± 1	10	0.25	1.0	8.81
8	D_2S:CS_2	0.5 : 1	850 ± 50	20 ± 1	10	1.9	0.94	9.34
9	H_2S:$^{13}CS_2$	6.1 : 1	850 ± 50	20 ± 1	10	0.38	2.2	9.34

Table S2 Parameters for the generation of vacuum ultraviolet (VUV) photons via four-wave mixing schemes.

Experiment	Medium	ω_{VUV}	YAG 1 Wavelength (nm)	ω_1 Dye	ω_1 (nm)	YAG 2 Wavelength (nm)	ω_2 Dye	ω_2 (nm)	Energy (eV)
1, 2	Xenon	$3\omega_1$	355	-	355[a]	-	-	-	10.49
3, 8, 9	Krypton	$2\omega_1 - \omega_2$	355	Stilbene 420	212.556	532	-	532[b]	9.34
4	Krypton	$2\omega_1 - \omega_2$	355	Stilbene 420	212.556	355	-	355[a]	8.17
5	Krypton	$2\omega_1 - \omega_2$	355	Stilbene 420	212.556	355	Coumarin 450	448.239	8.90
6	Xenon	$2\omega_1 - \omega_2$	355	Coumarin 450	222.566	355	Coumarin 503	500	8.66
7	Xenon	$2\omega_1 - \omega_2$	355	Coumarin 450	222.566	532	-	532[b]	8.81

[a]Nd :YAG third harmonic
[b]Nd :YAG second harmonic

Table S3 Absorption peaks observed in H_2S−CS_2 ice and isotopic mixtures before and after electron irradiation at 5 K.

H_2S (cm^{-1})	D_2S (cm^{-1})	CS_2 (cm^{-1})	$^{13}CS_2$ (cm^{-1})	Assignment	Reference
3721				$\nu_s + \nu_2$ (H_2S)	[50], [51]
			3570	$\nu_3 + 3\nu_1$ ($^{13}CS_2$)	-
		3485		$\nu_3 + 3\nu_1$ (CS_2)	[52]
		2967		$\nu_1 + 2\nu_2 + \nu_3$ (CS_2)	[52], [53]
2644				$\nu_s + \nu_t$ (H_2S)	[50], [51]
2546				ν_s (ν_1 and ν_3) (H_2S)	[50], [51]
		2295		$\nu_3 + 2\nu_2$ (CS_2)	[52]
			2232	$\nu_3 + 2\nu_2$ ($^{13}CS_2$)	-
		2153		$\nu_1 + \nu_3$ (CS_2)	[52], [53]
			2112	$\nu_1 + \nu_3$ ($^{13}CS_2$)	[54]
	1847			ν_s (ν_1 and ν_3) (D_2S)	[51]
		1499		ν_3 (CS_2)	[52],[53],[54]
			1460	ν_3 ($^{13}CS_2$)	[54]
1166				ν_2 (H_2S)	[50], [51]
		1043		$\nu_1 + \nu_2$ (CS_2)	[52]

Table S4 Adiabatic ionization energies (IEs) and relative energies (Rel. E) of thiocarbonic acid dimers ($H_4C_2S_6$) (*m/z* = 220) were computed at the CCSD(T)-F12/cc-pVTZ-F12 + ZPVE(ωB97XD/aug-cc-pVTZ) level of theory. The calculated energies were corrected for the combined error limits of ± 0.04 eV and the thermal and Stark effect by −0.03 eV.

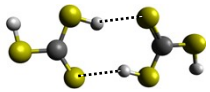
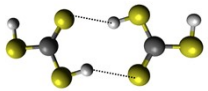
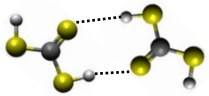
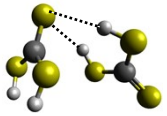
	Conformer	Structure	Rel. E (kJ/mol)	IE (eV)	IE range with error (eV)	Corrected IE with Stark effect (eV)
1a-1a	ct-ct		1	7.93	7.89–7.97	7.86–7.94
1b-1a	cc-ct		0	7.93	7.89–7.97	7.86–7.94
1b-1b	cc-cc		0	8.93	8.89–8.97	8.86–8.94
1c-1c	tt-tt		14	8.32	8.28–8.36	8.25–8.33

Table S5 CCSD(T)-F12/cc-pVTZ-F12 optimized geometries (in Å).

Isomer 1b+
CCSD(T)-F12/CC-PVTZ-F12 ENERGY=-1232.19956925

S	0.0000000000	0.0000000000	-1.7145548140
C	0.0000000000	0.0000000000	-0.0439406003
S	0.0000000000	1.4492020350	0.8711853682
S	0.0000000000	-1.4492020350	0.8711853682
H	0.0000000000	2.2902587959	-0.1805702321
H	0.0000000000	-2.2902587959	-0.1805702321

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Isomer 1b
CCSD(T)-F12/CC-PVTZ-F12 ENERGY=-1232.52616031

S	0.0000000000	0.0000000000	-1.7432588191
C	0.0000000000	0.0000000000	-0.1138924571
S	0.0000000000	1.4353460125	0.8972765856
S	0.0000000000	-1.4353460125	0.8972765856
H	0.0000000000	2.2870389749	-0.1371781177
H	0.0000000000	-2.2870389749	-0.1371781177

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Isomer 1a+
CCSD(T)-F12/CC-PVTZ-F12 ENERGY=-1232.19889542

S	0.0000000000	1.6948034708	-0.1714993834
C	0.0000000000	0.0273015591	0.0021159258
S	0.0000000000	-0.6420152461	1.5749912679
S	0.0000000000	-1.0014060275	-1.3687275219
H	0.0000000000	-1.9281281904	1.1734458466
H	0.0000000000	-0.0315442791	-2.3044257168

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Isomer 1a
CCSD(T)-F12/CC-PVTZ-F12 ENERGY=-1232.52586362

S	0.0000000000	-0.8505122958	-1.5045643799

C 0.0000000000 -0.0599788464 -0.0805845634
S 0.0000000000 1.6894984492 -0.0424168882
S 0.0000000000 -0.8095794868 1.5040147091
H 0.0000000000 1.8447624359 1.2927365261
H 0.0000000000 -2.0653825182 1.0341966965
--
Isomer 1c+
CCSD(T)-F12/CC-PVTZ-F12 ENERGY=-1232.19509331
S 0.0000000000 0.0000000000 -1.6763592443
C 0.0000000000 0.0000000000 0.0122769986
S 0.0000000000 1.5330832235 0.7718421125
S 0.0000000000 -1.5330832235 0.7718421125
H 0.0000000000 1.0787894060 2.0368782293
H 0.0000000000 -1.0787894060 2.0368782293
--
Isomer 1c
CCSD(T)-F12/CC-PVTZ-F12 ENERGY=-1232.52260092
S 0.0000000000 0.0000000000 -1.6952802937
C 0.0000000000 0.0000000000 -0.0644317538
S 0.0000000000 1.5233731627 0.7951612429
S 0.0000000000 -1.5233731627 0.7951612429
H 0.0000000000 1.0573915280 2.0531168102
H 0.0000000000 -1.0573915280 2.0531168102
--
Isomer 2
CCSD(T)-F12/CC-PVTZ-F12 ENERGY=-1232.52287668
C -0.4994182041 0.0105456054 -0.7998519934
S 0.7314460846 -0.0006957421 0.4333527124
S -0.3512915563 0.0406688955 2.1801167605
H -0.4400204307 -1.2868863505 2.3616495903
S -0.1315482009 -0.0045412512 -2.3752388730
H -1.5162535602 0.0342224531 -0.4078137881

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Isomer 2+
CCSD(T)-F12/CC-PVTZ-F12 ENERGY=-1232.19269359

C	-0.0312986086	0.4248265444	-0.7692794964
S	0.0017504368	-0.7434498963	0.4496916159
S	0.0460232672	0.3795060987	2.1673957052
H	-1.2646756719	0.2260241880	2.4306608034
S	0.0057996201	0.1513708207	-2.3909553884
H	-0.0663888595	1.4729837058	-0.4563108767

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Isomer 3
CCSD(T)-F12/CC-PVTZ-F12 ENERGY=-1232.51419855

C	-0.6341251965	0.0552773704	0.2548849922
S	0.1473157026	-0.0018935805	1.8589566590
H	-0.4675843834	1.0875855125	2.3441496827
S	0.0610465097	-1.0675413969	-0.9513349380
S	0.0978918383	1.0119183054	-1.0852698020
H	-1.7170963790	0.0831667209	0.2690751480

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Isomer 3+
UCCSD(T)-F12/CC-PVTZ-F12 ENERGY=-1232.20148490

H	-1.7253041733	0.0000000000	0.3272367236
C	-0.6399171524	0.0000000000	0.3089378699
S	0.0984193555	0.0000000000	1.9014232601
H	1.3681913560	0.0000000000	1.4604537018
S	0.0762736849	-0.9952431134	-1.0366838297
S	0.0762736849	0.9952431134	-1.0366838297

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Isomer 4
CCSD(T)-F12/CC-PVTZ-F12 ENERGY=-1232.51226316

S	0.1337369104	-1.2516685987	0.0000000000
C	0.4100442389	1.3569833922	0.0000000000

H	1.4965535728	1.4385392904	0.0000000000
H	-0.0676580399	2.3341323277	0.0000000000
S	-0.1661398575	0.3123384454	1.3823403838
S	-0.1661398575	0.3123384454	-1.3823403838

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Isomer 4+

CCSD(T)-F12/CC-PVTZ-F12 ENERGY=-1232.21813879

S	0.0000000000	0.0000000000	-1.2071086634
C	0.0000000000	0.0000000000	1.4314023631
H	-0.9005760448	0.0000000000	2.0465772197
H	0.9005760448	0.0000000000	2.0465772197
S	0.0000000000	1.4028232890	0.2710804099
S	0.0000000000	-1.4028232890	0.2710804099

Table S6 CCSD(T)-F12/cc-pVTZ-F12 harmonic frequencies (in cm^{-1}).

Isomer 1b+

1	77.08
2	227.86
3	247.87
4	385.58
5	470.20
6	519.06
7	842.63
8	876.13
9	1037.24
10	1140.98
11	2658.45
12	2658.60

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Isomer 1b

1	212.54
2	253.94

3	295.35
4	406.83
5	464.33
6	504.56
7	765.63
8	915.60
9	997.34
10	1170.62
11	2705.82
12	2707.50

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Isomer 1a+

1	146.35
2	233.82
3	255.23
4	376.16
5	465.68
6	517.27
7	837.15
8	896.73
9	1029.51
10	1137.00
11	2650.29
12	2654.56

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Isomer 1a

1	245.88
2	256.38
3	280.47
4	370.86
5	468.54
6	499.46

7	815.22
8	901.21
9	1021.29
10	1170.04
11	2671.13
12	2699.75

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Isomer 1c

1	143.78
2	259.18
3	284.05
4	286.24
5	475.64
6	489.53
7	833.34
8	927.54
9	1013.56
10	1157.49
11	2682.47
12	2698.92

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Isomer 2

1	116.21
2	171.45
3	303.60
4	325.14
5	528.67
6	770.41
7	807.62
8	894.45
9	1068.81
10	1253.18

11	2674.23
12	3100.85

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Isomer 2+

1	129.75
2	173.02
3	277.96
4	296.50
5	528.11
6	763.67
7	796.76
8	903.48
9	964.13
10	1170.54
11	2667.93
12	3072.66

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Isomer 3

1	210.67
2	235.45
3	285.75
4	510.94
5	588.66
6	688.70
7	901.49
8	960.65
9	1025.98
10	1229.22
11	2689.14
12	3163.27

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Isomer 3+

1	229.54
2	243.113
3	316.61
4	511.81
5	569.44
6	676.51
7	885.28
8	997.27
9	1028.37
10	1269.94
11	2689.00
12	3176.66

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Isomer 4

1	184.17
2	366.56
3	477.81
4	507.78
5	717.24
6	722.33
7	880.62
8	1080.15
9	1205.70
10	1457.18
11	3064.43
12	3148.31

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Isomer 4+

1	125.61
2	385.27
3	524.62
4	568.06

5	713.51
6	762.24
7	795.20
8	1033.63
9	1193.65
10	1426.33
11	3063.89
12	3139.85

Table S7 ωB97XD/aug-cc-pVTZ optimized geometries (in Å).

1b-1b+
C,0.0279409892,0.0504624027,-0.1365042332
S,0.0667939071,0.2556774992,1.5691441155
H,1.2484636109,-0.3591342705,1.7631233554
S,1.1107735419,-0.8555184921,-0.9997462673
S,-1.2700681065,0.9026898111,-0.8998545459
H,-1.1924817922,0.3026001448,-2.1223943173
H,0.9757172388,-0.1204310858,-3.3044095348
S,1.2626371264,0.3909995791,-4.5361812652
C,-0.2592386589,0.0592062084,-5.2898478109
S,-0.2242192381,0.2345769867,-6.9990205667
H,-1.5495621083,0.0932385437,-7.1872711849
S,-1.5961246484,-0.3725233694,-4.4156432814
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1b-1b
C,-0.0883001682,0.,0.2690574527
S,-0.0944549542,0.,2.0225195742
H,1.240901691,0.,2.1499132481
S,1.2732659201,0.,-0.6384946517
H,0.8953502126,0.,-3.2008014158
S,-1.7251670985,0.,-0.329533054
H,-1.7597637054,0.,-6.9956526686

S,-0.4244070601,0.,-6.8682589947
C,-0.4305618461,0.,-5.1147968732
S,-1.7921279344,0.,-4.2072447688
H,-1.4142122269,0.,-1.6449380048
S,1.2063050842,0.,-4.5162063665
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1a-1a+
C,0.0649026198,0.3186385038,-0.4508512476
S,0.0324935955,0.3153995576,1.2704448423
H,1.0832559942,-0.5051918757,1.4673489578
S,-1.0917755796,1.2673648136,-1.2039935598
S,1.2705270292,-0.6387123193,-1.2168980515
H,0.9579292452,-0.3024049949,-2.4837501237
H,-2.3565125743,-0.5252944324,-2.552174163
S,-2.6171341308,-0.9804645676,-3.7934142734
C,-1.5458758945,0.0768884305,-4.6247630534
S,-1.5068249094,-0.032052636,-6.3424642166
H,-2.4388970675,-0.9954508819,-6.481592581
S,-0.52757764,1.2163183234,-3.9391676615
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1a-1a
C,0.100026044,0.,0.2621752163
S,-0.0303130602,0.,2.0059230083
H,1.2823031748,0.,2.3022705475
S,-1.2719848597,0.,-0.6284185974
H,-0.9069956274,0.,-3.1851199114
S,1.7318864798,0.,-0.3429099567
H,-0.7634411565,0.,-7.1480099674
S,0.5491750784,0.,-6.8516624282
C,0.4188359743,0.,-5.1079146362
S,1.790846878,0.,-4.2173208225
H,1.4258576457,0.,-1.6606195085

S,-1.2130244616,0.,-4.5028294632
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1c-1c+
C,0.0912036514,-0.0856492217,-0.2221036585
S,0.1672618493,-0.5467770946,1.4017888325
S,1.0984266069,1.2104403885,-0.6940766693
H,0.7209392053,1.2283829451,-2.0172585557
S,-0.9862308463,-0.9644515835,-1.2140551789
H,-0.7231128363,-0.2782758595,-2.3774861658
H,1.9842122922,-0.2758973563,-7.0363621871
S,1.0055236892,0.5819391242,-6.6990784232
C,0.9245908433,0.2585065627,-5.0101205555
S,-0.1904356051,1.1167111361,-4.1223595399
S,1.9295803739,-0.8967756703,-4.2018845895
H,2.656223524,-1.3481533698,-5.2380534281
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1c-1c
C,0.1772794396,0.5890534913,-1.4664295486
S,0.3643423713,1.8774078116,-0.4834042639
S,1.4790306387,-0.5627488238,-1.6386012269
H,0.9788515486,-1.3389595769,-2.6209793249
S,-1.3384381838,0.381048334,-2.3171701942
H,-1.0970749475,-0.7884356214,-2.9374662544
H,-1.2538905431,1.041364041,-6.6660849072
S,-1.516745015,-0.2435284422,-6.3745890071
C,-0.0039305755,-0.6956884969,-5.6375706589
S,0.1765631214,-2.2309823216,-5.0896075894
S,1.3117045965,0.4290815957,-5.4627997266
H,0.7223075525,1.5423880514,-5.9295103469
--
1b-1a+

C,0.3072158574,0.0230598745,-0.2140299169
S,0.1533786923,0.2840896506,1.4843615875
H,1.1251179306,-0.5687316103,1.8553180549
S,1.4269705864,-1.0586118731,-0.8264120584
S,-0.7995237066,0.9803475099,-1.122142575
H,-0.456788468,0.4914662908,-2.3291973763
H,2.7924083406,0.5479969637,-2.3275035975
S,3.10234199,0.8591929606,-3.6011902747
C,2.019955554,-0.2495752021,-4.3476214764
S,2.0315950249,-0.3244592635,-6.0676607431
H,2.9968473245,0.5917708168,-6.2799656785
S,0.9455706889,-1.2754333189,-3.5751190905
--
1b-1a
C,-0.0061105525,0.,0.0120383898
S,-0.0315432545,0.,1.7655348141
H,1.3023664354,0.,1.9074085694
S,1.3658217295,0.,-0.8799742473
S,-1.6365476986,0.,-0.6032226011
H,-1.3143591095,0.,-1.9158466884
H,1.0143927371,0.,-3.4443441173
S,1.3282841193,0.,-4.7599007317
C,-0.3019313908,0.,-5.3711063681
S,-0.4267864578,0.,-7.1150681201
H,0.8867836388,0.,-7.4072776425
S,-1.6757221794,0.,-4.4839600692
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Table S8 ωB97XD/aug-cc-pVTZ harmonic frequencies (in cm^{-1}).

1b-1b+

18.5307	29.7458	30.0679
80.8118	100.5116	142.9459

265.5364 272.2777 281.9558
298.7356 304.8669 323.9614
423.2035 441.3259 491.8949
492.9076 520.6841 521.3102
847.1706 859.6900 891.6135
893.2739 1038.0228 1039.7495
1124.8123 1139.6126 2640.3277
2642.6754 2672.8778 2673.1062
--
1b-1b
8.2305 22.2712 42.2176
58.9013 67.7510 67.8920
266.7585 271.6124 290.9944
292.0502 294.3931 302.3161
455.0379 467.5630 489.2924
491.4814 510.4836 512.1090
834.2916 842.4711 910.9077
912.8579 1034.2885 1047.6164
1149.3785 1177.2484 2569.4219
2581.3890 2685.2864 2685.3372
--
1a-1a+
18.3792 27.1749 30.6116
64.7460 87.0656 87.8176
240.8414 255.9695 268.9879
278.7507 294.2423 295.4832
411.9800 429.5198 486.1727
487.8027 526.2787 539.0409
836.9602 857.0105 890.2226
913.6431 1018.7690 1032.2962
1135.4775 1526.7386 2441.9734
2685.5869 2690.0285 3145.4012

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1a-1a
4.7446 20.3643 39.6565
58.8847 67.3269 68.1730
265.7640 269.4264 278.4840
291.6400 302.6775 307.5393
468.5227 476.2556 485.7182
491.4223 515.3748 517.2369
789.4682 798.9745 925.3830
929.4426 1015.6072 1027.3306
1154.1340 1181.5233 2583.0586
2594.0960 2716.3113 2716.3233
--
1c-1c+
13.9973 24.9560 33.4417
54.2421 61.8702 100.8790
233.3201 241.7456 279.0486
292.9059 301.5336 350.5808
406.0829 475.5232 507.7207
510.6439 523.3673 563.6742
865.2415 885.0992 901.4396
955.0570 1030.0992 1044.6865
1137.2777 1164.8096 2211.0755
2337.6638 2695.3091 2710.5737
--
1c-1c
21.7823 28.1278 33.3438
59.9063 69.0598 76.3137
206.6954 266.4122 268.3040
276.5791 293.1274 308.6826
324.0383 368.6651 494.0415
498.3774 500.5160 510.2012

845.1309 850.3192 921.7841
942.7146 1025.5307 1026.6727
1149.7002 1162.0264 2633.4153
2680.4334 2698.8155 2714.7402
--
1b-1a+
18.7213 29.0706 32.2258
79.3278 98.5487 145.5564
261.9690 269.5592 273.7202
284.7491 302.4987 327.0370
427.8314 458.7572 491.5881
496.0215 520.8561 522.8622
830.4714 851.4062 889.5578
895.2007 1034.0504 1038.2910
1127.4932 1143.7305 2644.9978
2648.9123 2676.6184 2692.2880
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1b-1a
7.5003 21.1930 40.8970
58.9805 67.1149 68.3629
266.2786 270.5664 282.2196
292.5812 301.9914 305.2832
458.2187 474.2449 487.5152
491.5185 510.8966 516.4654
793.8405 838.9219 912.4641
927.6718 1019.5019 1043.5763
1151.7538 1179.6834 2577.5728
2592.5363 2683.1324 2717.3533