Supporting Information for

Formation of Thioformic Acid (HCOSH) – the Simplest Thioacid – in Interstellar Ice Analogues

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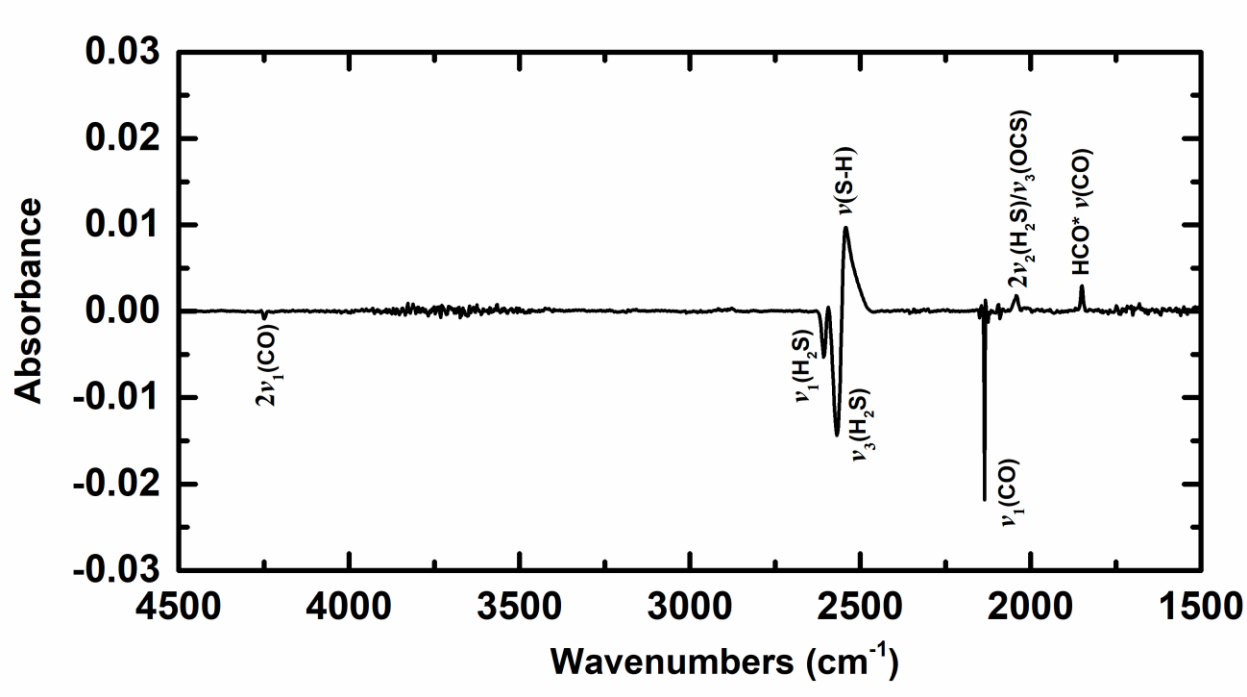

Figure S1. Difference infrared spectrum (baseline corrected) between the irradiated and pristine carbon monoxide (CO) – hydrogen sulfide (H_2S) ice at 5 K.

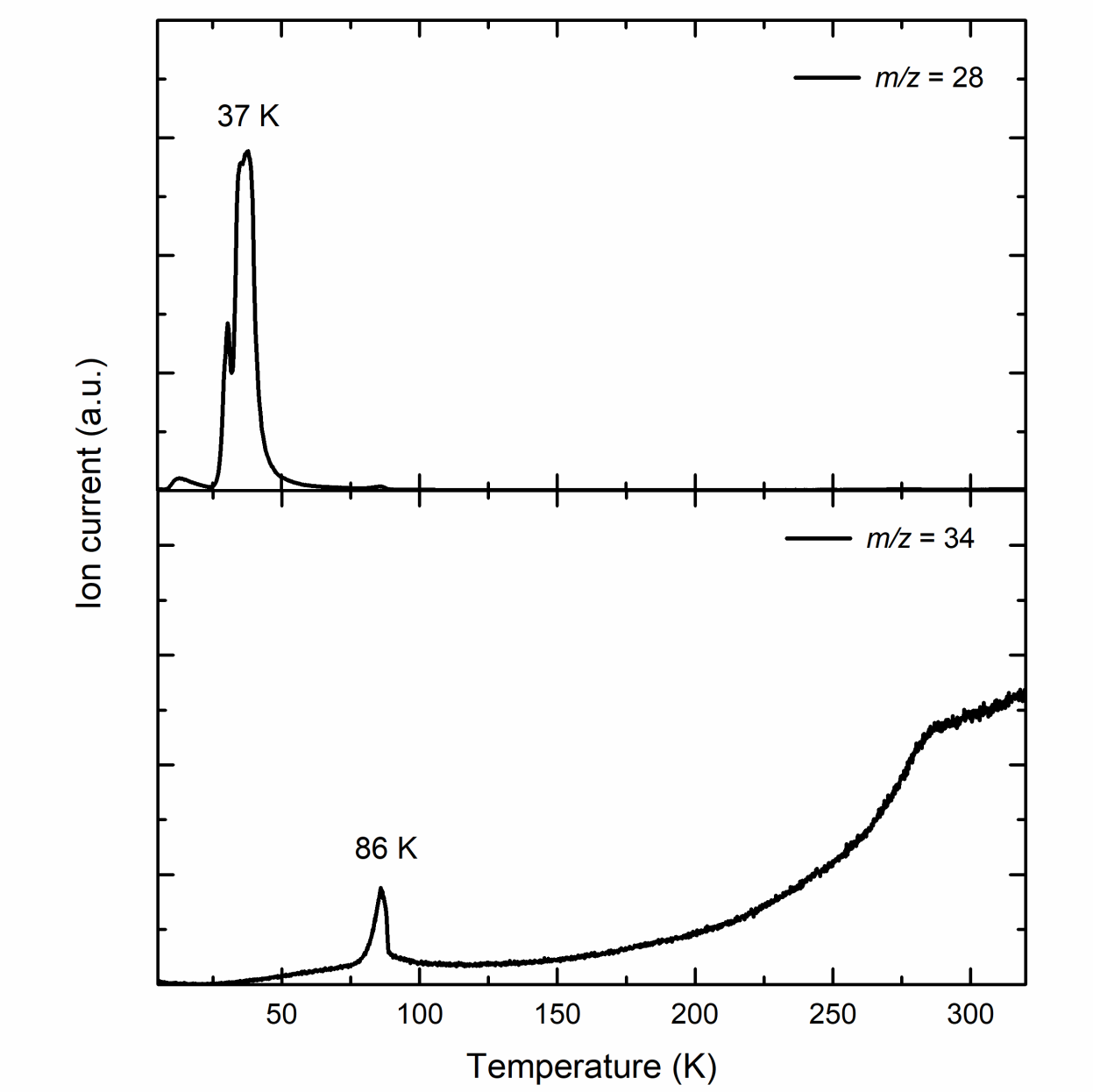

Figure S2. QMS ion signals of carbon monoxide (top) at *m/z* = 28 and hydrogen sulfide (bottom) at *m/z* = 34 in irradiated CO–H_2S ice.

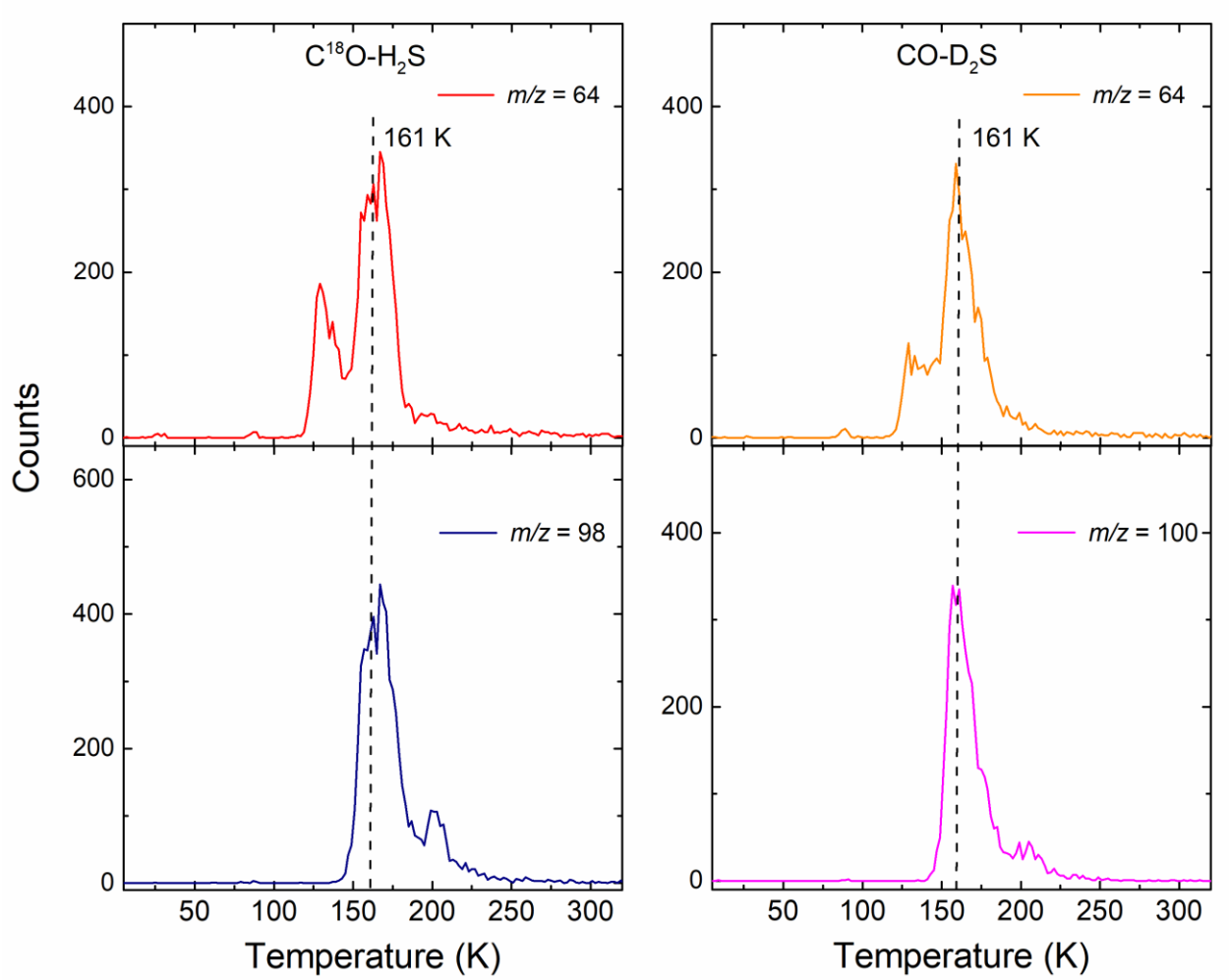

Figure S3. TPD profiles for S_2^+ (*m/z* = 64), H_2S_3 (*m/z* = 98) and D_2S_3 (*m/z* = 100) in the irradiated $C^{18}O$–H_2S (left) and CO–D_2S (right) ices at a photon energy of 10.82 eV. The dashed lines indicate the sublimation peak at 161 K, suggesting the S_2^+ signal (top) originates from the photofragment of H_2S_3 or D_2S_3 (bottom).

Table S1. Parameters for the generation of vacuum ultraviolet (VUV) light. The uncertainty for VUV photon energies is less than 0.005 eV.

VUV	Photoionization energy (eV)	10.82 ($2\omega_1 - \omega_2$)	10.39 ($2\omega_1 - \omega_2$)
	Wavelength (nm)	114.588	119.330
ω_1	Wavelength (nm)	202.316	202.316
Nd:YAG	Wavelength (nm)	532	532
Dye laser	Wavelength (nm)	606.948	606.948
Dye		Rhodamine 610 and 640	Rhodamine 610 and 640
ω_2	Wavelength (nm)	863.117	664.271
Nd:YAG	Wavelength (nm)	532	532
Dye laser	Wavelength (nm)	863.117	664.271
Dye		LDS 867	DCM in DMSO
	Nonlinear medium	Krypton	Krypton

Table S2. Absorption peaks observed in CO−H_2S ice before and after electron irradiation at 5 K.

Before Irradiation (cm^{-1})		New Absorption After Irradiation (cm^{-1})	Assignment	Reference
CO	H_2S			
4249			$2\nu_1$ (CO)	(1)
	3760		$\nu_1 + \nu_2$ (H_2S)	
	3735		$\nu_2 + \nu_3$ (H_2S)	
	2603		ν_1 (H_2S)	(2, 3, 4)
	2566		ν_3 (H_2S)	(2, 3, 4)
		2518	ν(S–H)	(3)
2136			ν_1 (CO)	(1)
2090			ν_1 (^{13}CO)	(1)
2045			$2\nu_2$ (H_2S)	
		2045	ν_3 (OCS)	(5)
		1840	HĊO ν_3(CO)	(6)
	1175		ν_2 (H_2S)	

Table S3. Cartesian coordinates (Å) and vibrational frequencies (cm^{-1}) of neutral CH_2SO molecules as well as their respective monoatomic cations computed at the ωB97XD/cc-pVTZ level.

Isomer	Vibration frequencies (cm^{-1})			Cartesian coordinates (Å)			
				Atom	X	Y	Z
1a	384.8827	425.6787	727.8784	C	-0.672749	0.426250	0.000000
	946.6177	977.9956	1379.9966	S	1.007304	-0.168256	0.000000
	1827.4883	2721.7288	2972.4970	O	-1.612801	-0.304750	0.000010
				H	-0.754426	1.525297	0.000000
				H	1.576473	1.047289	0.000000
$1a^+$	386.7397	483.3919	798.1573	C	-0.611212	0.399359	0.000000
	825.1137	1007.6620	1116.1018	S	0.993050	-0.167362	0.000000
	1463.0218	2665.0406	2897.2321	O	-1.617462	-0.285400	0.000000
				H	-0.806538	1.492718	0.000000
				H	1.524709	1.072128	0.000000
1b	423.6185	440.6100	689.3846	C	-0.675991	0.432682	0.000000
	958.0273	960.8829	1391.9165	S	1.047092	-0.008687	0.000000
	1822.4035	2717.8583	2975.8493	O	-1.590777	-0.331488	0.000000
				H	-0.796524	1.528521	0.000000
				H	0.825214	-1.333717	0.000000
$1b^+$	351.4069	495.8969	768.2837	C	0.000000	0.762154	0.000000
	866.3154	960.8667	1174.9299	S	-0.580286	-0.838987	0.000000
	1478.6819	2640.3722	2950.4491	O	1.174529	1.088013	0.000000
				H	-0.748553	1.576849	0.000000
				H	0.636897	-1.430087	0.000000
2a	472.7303	699.2686	972.0482	C	0.437926	0.492896	0.000000
	981.5653	1243.0431	1331.8842	S	-1.066764	-0.105589	0.000000
	1475.5101	3160.1338	3767.8675	O	1.557457	-0.209676	0.000000
				H	0.661136	1.556381	0.000000
				H	1.319876	-1.146930	0.000000
$2a^+$	404.5802	681.6114	844.5200	C	0.469550	0.463512	0.000000
	987.3522	1209.6461	1410.6936	S	-1.088863	-0.105047	0.000000
	1517.2980	3108.7993	3728.6380	O	1.564740	-0.186810	0.000000
				H	0.596309	1.549133	0.000000
				H	1.490281	-1.154980	0.000000
2b	482.8624	523.6250	941.9017	C	-0.426426	0.442784	0.000000
	975.7310	1272.3529	1285.1597	S	1.092000	-0.095503	0.000000
	1495.2124	3092.3317	3855.6392	O	-1.494054	-0.351325	0.000000
				H	-0.661974	1.508304	0.000000
				H	-2.299029	0.173640	0.000000
$2b^+$	408.6172	628.9618	856.9429	C	0.000000	0.645677	0.000000
	967.2229	1226.4180	1362.2013	S	-0.683237	-0.861068	0.000000
	1567.7114	3092.8428	3746.4985	O	1.261906	0.830403	0.000000
				H	-0.688922	1.495718	0.000000

				H	1.525461	1.764078	0.000000
3a	224.2192	331.7791	663.2456	C	-1.443085	0.370812	0.000000
	717.0811	842.9734	1079.9812	S	-0.137921	-0.449301	0.000000
	1224.0644	3208.3389	3845.9663	O	1.294167	0.459138	0.000000
				H	-1.517895	1.452928	0.000000
				H	2.029806	-0.162095	0.000000
3a$^+$	192.7578	220.9912	421.6589	C	1.355520	0.382416	0.000000
	705.4453	819.4116	1144.7277	S	0.072469	-0.480278	0.000000
	1224.4426	3280.7576	3731.8955	O	-1.174709	0.526819	0.000000
				H	2.109735	1.155404	0.000000
				H	-2.004686	0.019990	0.000000
3b	287.3560	339.2302	664.5053	O	-1.378909	0.276552	0.000000
	705.7462	836.1251	1054.2569	C	1.421858	0.400836	0.000000
	1231.6052	3206.5504	3846.4649	S	0.141413	-0.458299	0.000000
				H	-1.275240	1.233713	0.000000
				H	1.512752	1.481645	0.000000
3b$^+$	285.9440	345.1817	447.6532	O	-1.288752	0.316518	0.000000
	702.3319	856.2647	1134.7985	C	1.294253	0.513473	0.000000
	1162.0919	3253.2591	3732.0156	S	0.087430	-0.470992	0.000000
				H	-1.223783	1.286131	0.000000
				H	2.369397	0.636757	0.000000
3c	182.2929	412.6166	703.8033	S	-0.134535	-0.447862	0.000000
	820.4649	830.6388	1107.5866	C	-1.286506	0.628677	0.000000
	1175.0423	3110.9526	3857.2929	O	1.263853	0.438589	0.000000
				H	-2.231931	0.074954	0.000000
				H	1.992707	-0.189929	0.000000
3c$^+$	234.4319	370.7098	485.7183	S	0.082792	-0.463451	0.000000
	718.5574	864.6328	1144.3427	C	1.307940	0.500485	0.000000
	1205.9330	3258.1066	3743.5818	O	-1.194432	0.490065	0.000000
				H	2.389264	0.535942	0.000000
				H	-2.006120	-0.044157	0.000000
4	252.5645	326.0635	587.2990	S	-0.968919	-0.061845	-0.000044
	666.1486	812.8868	1260.2073	C	0.725164	-0.465885	-0.000109
	1710.9582	1942.8774	2213.7285	O	1.694661	0.242482	0.000116
				H	-1.203426	0.921980	0.966907
				H	-1.202134	0.922991	-0.966468
5a	262.3069	433.2906	587.6787	S	-1.010265	0.007928	0.000000
	739.5903	979.7257	1337.8250	C	1.545597	0.430679	0.000000
	1381.7348	2647.9006	2875.4185	O	0.641499	-0.482656	0.000000
				H	-0.720417	1.325382	0.000000
				H	2.479089	-0.175052	0.000000
5a$^+$	214.9682	319.1425	486.4431	S	-1.055483	0.003591	0.000000
	608.6326	997.5039	1100.3002	C	1.614949	-0.332453	0.000000
	1730.5748	2649.1581	3042.1470	O	0.671834	0.411169	0.000000
				H	-0.846432	-1.331522	0.000000

				H	2.669795	-0.020571	0.000000
				O	0.641021	0.476182	0.000000
	205.8567	378.9360	608.2326	C	1.569468	-0.414369	0.000000
5b	744.9271	1006.8550	1335.2136	S	-0.969325	-0.162938	0.000000
	1391.0649	2703.0159	2876.0433	H	2.483178	0.220644	0.000000
				H	-1.518953	1.063131	0.000000
				O	0.666687	0.394966	0.000000
	222.1913	335.2219	493.3694	C	1.636299	-0.315162	0.000000
5b^{+}	608.7400	1009.0211	1101.5841	S	-1.025181	-0.152548	0.000000
	1728.9331	2693.6194	3049.5429	H	2.677343	0.038118	0.000000
				H	-1.425737	1.133894	0.000000
				S	1.086221	0.083308	0.000000
	386.6563	571.5204	574.7063	C	-1.532362	0.246246	0.000000
6	1050.3160	1251.3348	1456.0550	O	-0.533958	-0.486332	0.000000
	1610.9604	3094.7244	3240.4757	H	-1.415599	1.327784	0.000000
				H	-2.498107	-0.247525	0.000000
				S	-1.092543	0.078275	0.000000
	306.5158	565.7962	603.6957	C	1.565597	0.214079	0.000000
6^{+}	1166.5435	1242.6006	1492.7293	O	0.505050	-0.432432	0.000000
	1635.4073	3096.6563	3244.3834	H	1.570641	1.303090	0.000000
				H	2.476067	-0.380504	0.000000
				O	1.264969	0.457405	0.000000
	403.2011	659.4771	817.8391	C	-1.321891	0.337568	0.000000
7	896.8820	1041.9766	1237.9957	S	0.088629	-0.425540	0.000000
	1423.6112	3162.9327	3287.4813	H	-1.405514	1.415358	0.000000
				H	-2.200953	-0.291365	0.000000
				O	-1.286210	0.479644	0.000000
	300.1830	679.2829	819.6986	C	1.286144	0.392392	0.000000
7^{+}	888.5069	1083.0920	1090.6454	S	-0.057786	-0.466460	0.000000
	1403.5777	3129.7845	3263.0036	H	1.303896	1.476769	0.000000
				H	2.193502	-0.204918	0.000000
				O	1.481958	-0.292924	0.000000
	421.5374	501.7781	717.0577	C	0.555051	0.644538	0.000000
8a	741.8793	958.5302	1291.6012	S	-0.989430	-0.165710	0.000000
	1338.1184	2752.4600	3851.3254	H	2.334015	0.150993	0.000000
				H	-1.689100	0.976528	0.000000
				O	1.586715	-0.211453	0.000000
	390.4152	396.0715	557.1725	C	0.514673	0.421805	0.000000
8a^{+}	820.7189	973.4702	1177.3768	S	-1.037664	-0.141083	0.000000
	1640.8316	2634.2284	3670.2690	H	2.403411	0.321999	0.000000
				H	-1.582549	1.096125	0.000000
				O	1.461039	0.310948	0.000000
	424.3974	542.7269	700.7254	C	0.554373	-0.644830	0.000000
8b	718.3773	918.2280	1291.8200	S	-1.033891	0.009306	0.000000
	1337.9587	2569.5964	3837.7449	H	2.323786	-0.113625	0.000000

				H	-0.796076	1.346124	0.000000
				O	1.580633	0.226354	0.000000
	375.5409	406.9643	535.5873	C	0.515734	-0.420434	0.000000
8b^{+}	788.7755	956.8206	1190.6046	S	-1.078033	-0.019973	0.000000
	1641.2122	2564.1463	3659.6639	H	2.404117	-0.297850	0.000000
				H	-0.895059	1.329199	0.000000
				O	-1.558059	0.166562	0.000000
	444.1547	503.5148	664.5160	C	-0.558333	-0.669342	0.000000
8c	733.8809	926.1372	1301.4494	S	1.021237	0.013366	0.000000
	1351.4821	2474.6653	3573.3575	H	-1.310403	1.108812	0.000000
				H	0.785078	1.360893	0.000000
				O	-1.662537	0.039498	0.000000
	363.9306	381.2394	533.7163	C	-0.513127	-0.416998	0.000000
8c^{+}	760.0719	960.6853	1098.7509	S	1.079206	-0.010218	0.000000
	1694.1131	2555.3480	3585.4323	H	-1.814303	1.006374	0.000000
				H	0.926062	1.343121	0.000000
				C	0.888834	-0.547519	-0.000001
	663.6797	745.1911	908.8982	O	0.654026	0.817460	0.000002
9	1146.6856	1153.2505	1190.3916	S	-0.820549	-0.083671	-0.000001
	1515.0727	3106.3386	3207.9456	H	1.281801	-0.957909	-0.924405
				H	1.281771	-0.957923	0.924411
				C	-0.972872	-0.481602	0.000007
	598.0428	860.3661	918.7969	O	-0.472188	0.858659	-0.000041
9^{+}	1121.4136	1138.8538	1164.6303	S	0.775510	-0.147490	0.000013
	1495.9026	3134.3217	3270.3913	H	-1.396802	-0.809701	0.941820
				H	-1.396633	-0.810125	-0.941740
				C	1.400888	-0.480099	0.000000
	362.4860	430.7614	723.1338	S	0.011961	0.228836	0.000000
10	779.2916	1017.0384	1070.1714	O	-1.332594	-0.332541	0.000000
	1354.3275	2459.5330	3151.1839	H	2.177155	0.287765	0.000000
				H	-0.113111	1.591783	0.000000
				C	-1.397010	-0.375583	0.000000
	220.5517	228.6450	430.7178	S	0.022587	0.246371	0.000000
10^{+}	592.4396	1015.9082	1087.8502	O	1.312831	-0.375977	0.000000
	1399.4229	2525.8961	3261.2331	H	-2.475158	-0.291916	0.000000
				H	-0.006814	1.611296	0.000000
				C	1.699323	-0.469160	0.000000
	327.0930	383.2291	475.8183	O	0.646495	0.324457	0.000000
11	922.2904	1205.3433	1231.4449	S	-1.166146	-0.082162	0.000000
	1460.2799	2900.3931	3674.2275	H	2.552691	0.242879	0.000000
				H	0.737751	1.291012	0.000000
				C	-1.620849	-0.514368	0.000000
	378.8079	407.7669	607.7152	O	-0.587335	0.397201	0.000000
11^{+}	840.1971	923.8502	1266.4633	S	1.103540	-0.100553	0.000000
	1436.8539	2977.0741	3536.8266	H	-2.509998	0.147493	0.000000

H	-0.722877	1.369963	0.000000

References

(1) Abplanalp, M. J.; Góbi, S.; Kaiser, R. I. On the Formation and the Isomer Specific Detection Of Methylacetylene (CH_3CCH), Propene (CH_3CHCH_2), Cyclopropane (c-C_3H_6), Vinylacetylene (CH_2CHCCH), and 1,3-butadiene ($CH_2CHCHCH_2$) from interstellar Methane Ice Analogues. *Phys. Chem. Chem. Phys.* **2019**, *21*, 5378-5393.

(2) Jiménez-Escobar, A.; Muñoz Caro, G. M. Sulfur Depletion in Dense Clouds and Circumstellar Regions. *Astron. Astrophys.* **2011**, *536*, A91.

(3) Jiménez-Escobar, A.; Muñoz Caro, G. M.; Chen, Y.-J. Sulphur Depletion in Dense Clouds and Circumstellar Regions. Organic Products Made from UV Photoprocessing of Realistic Ice Analogs Containing H_2S. *Mon. Not. R. Astron. Soc.* **2014**, *443*, 343-354.

(4) Cazaux, S.; Carrascosa, H.; Muñoz Caro, G. M.; Caselli, P.; Fuente, A.; Navarro-Almaida, D.; Riviére-Marichalar, P. Photoprocessing of H_2S on Dust Grains. *Astron. Astrophys.* **2022**, *657*, A100.

(5) Ferrante, R. F.; Moore, M. H.; Spiliotis, M. M.; Hudson, R. L. Formation of Interstellar OCS: Radiation Chemistry and IR Spectra of Precursor Ices. *Astrophys. J.* **2008**, *684*, 1210-1220.

(6) Milligan, D. E.; Jacox, M. E. Infrared Spectrum of HCO. *J. Chem. Phys.* **1964**, *41*, 3032-3036.