

Supplementary information

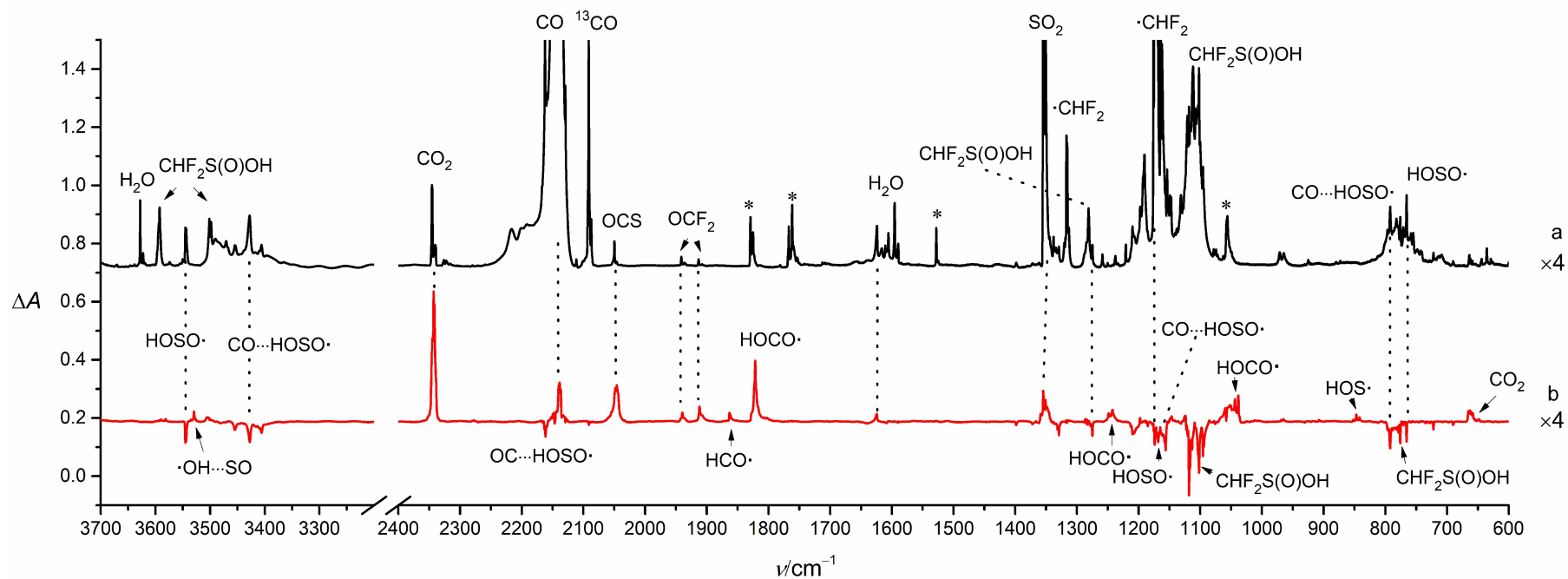
Unraveling Sulfur Chemistry in Interstellar Carbon Oxide Ices

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Xiaoqing Zeng

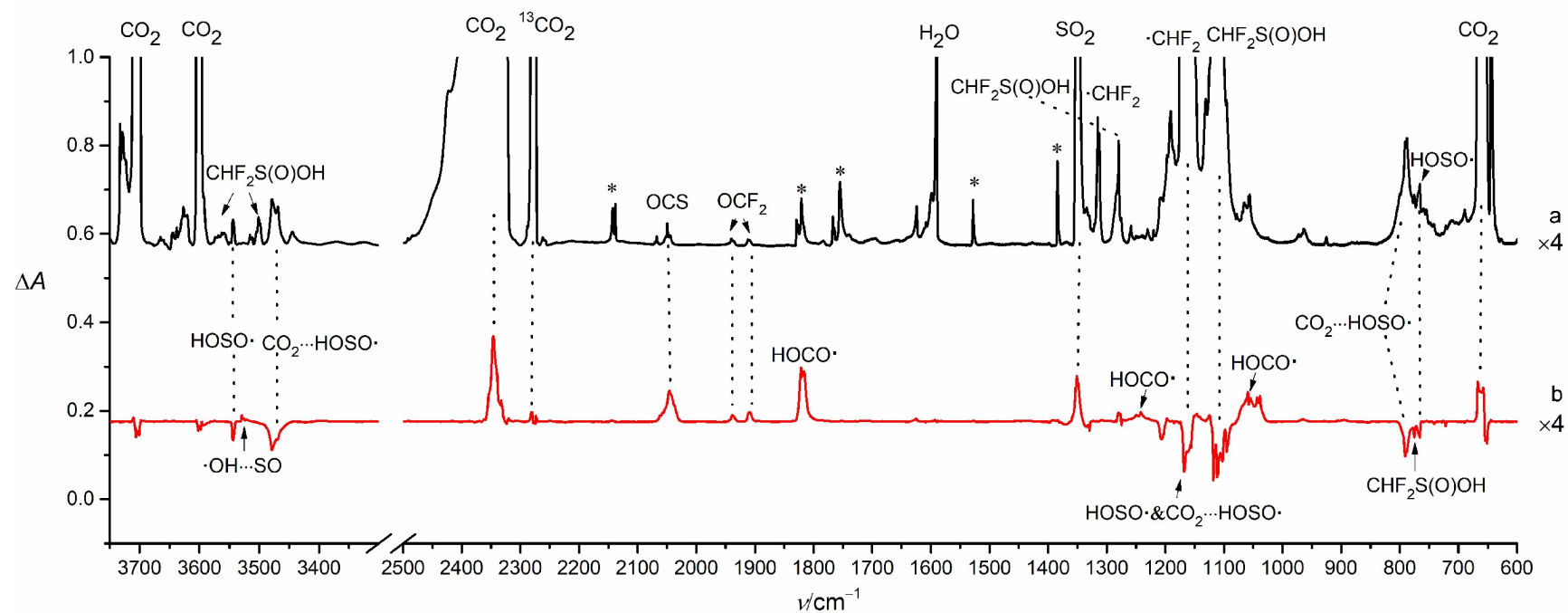
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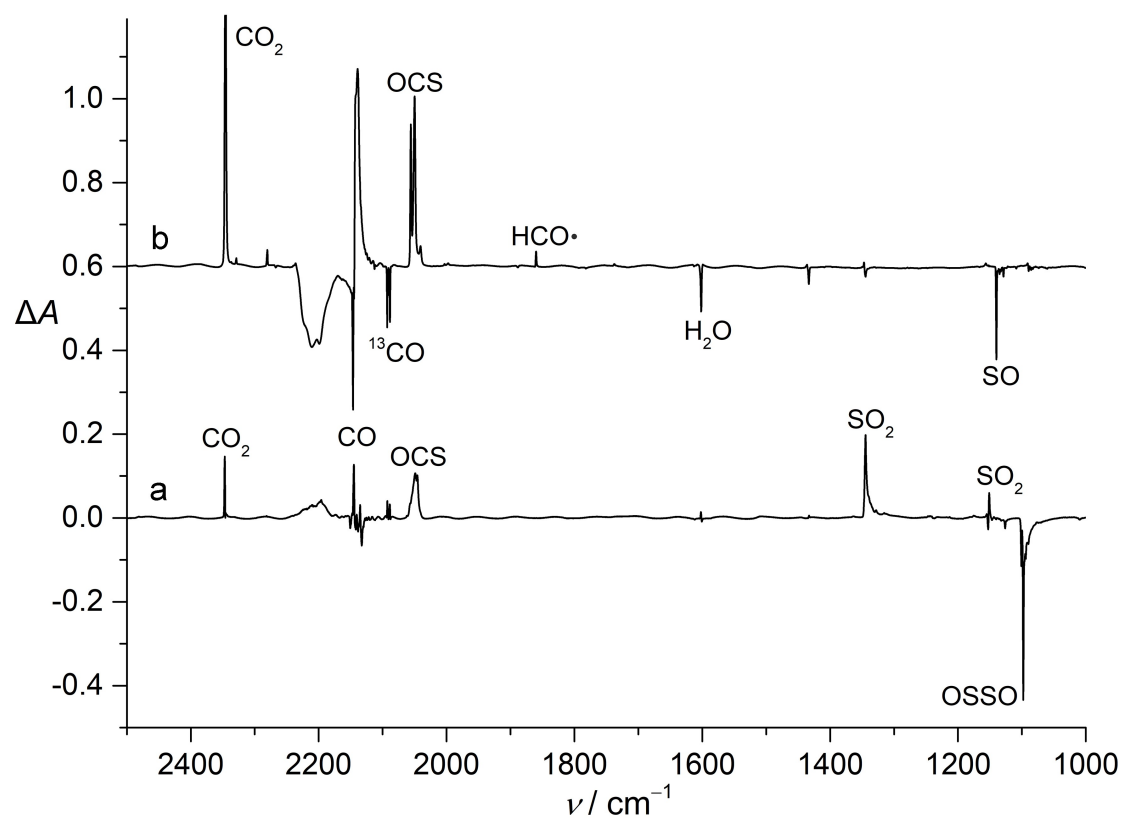
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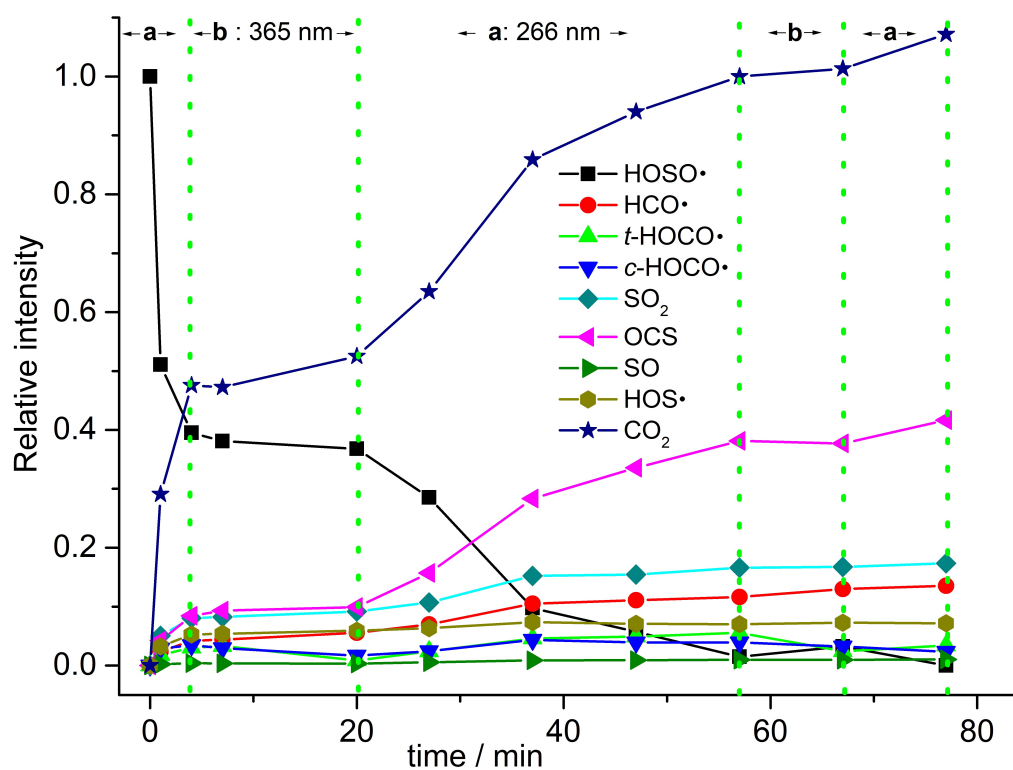
Supplementary Fig. 1 | The radical complexes and photochemistry of HOSO• in CO-doped Ar-matrix. **a** Infrared (IR) spectrum ($3700\text{--}600\text{ cm}^{-1}$) for the high-vacuum flash pyrolysis (HVFP, ca. $700\text{ }^\circ\text{C}$) products of $\text{CHF}_2\text{S(O)OH}$ in CO-doped Ar-matrix (1:50) at 16 K. **b** IR difference spectrum ($3700\text{--}600\text{ cm}^{-1}$) reflecting the changes of the HFVP products of $\text{CHF}_2\text{S(O)OH}$ in CO-doped Ar-matrix (20 : 1000) at 16 K upon 30 min 266 nm laser irradiation. Unknown species (*) are marked.



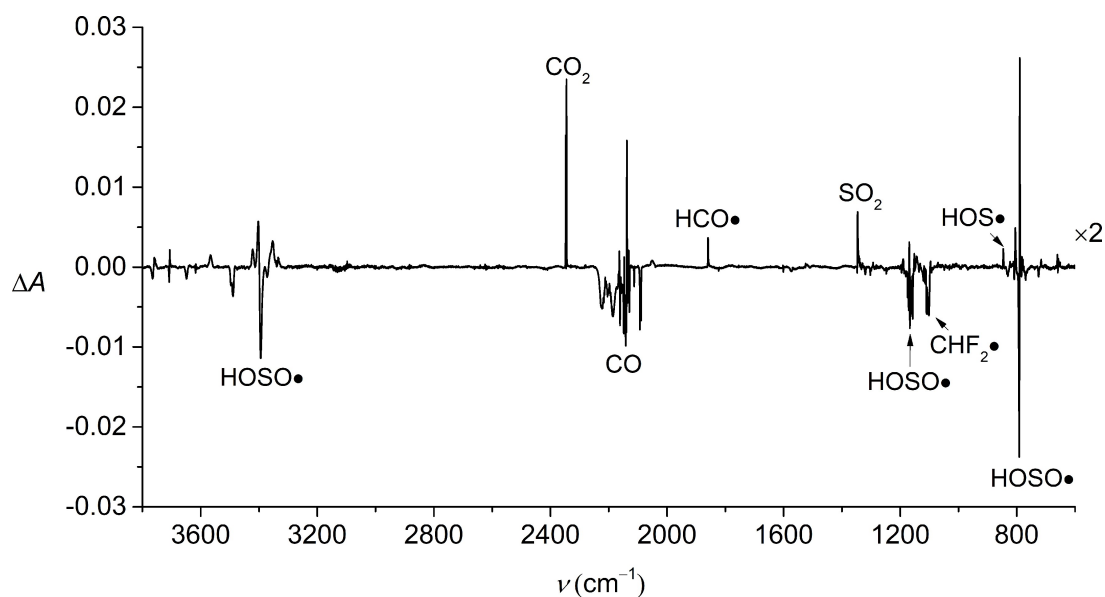
Supplementary Fig. 2 | The radical complexes and photochemistry of HOSO in CO_2 -doped Ar-matrix. **a** Infrared (IR) spectrum (3750–600 cm^{-1}) for the HVFP products of $\text{CHF}_2\text{S(O)OH}$ in CO_2 -doped Ar-matrix (50:1000) at 16 K. **b** IR difference spectrum (3750–600 cm^{-1}) reflecting the changes of the HFVP products of $\text{CHF}_2\text{S(O)OH}$ in CO_2 -doped Ar-matrix (20 : 100) at 16 K upon 30 min 266 nm laser irradiation. Unknown species (*) are also marked.



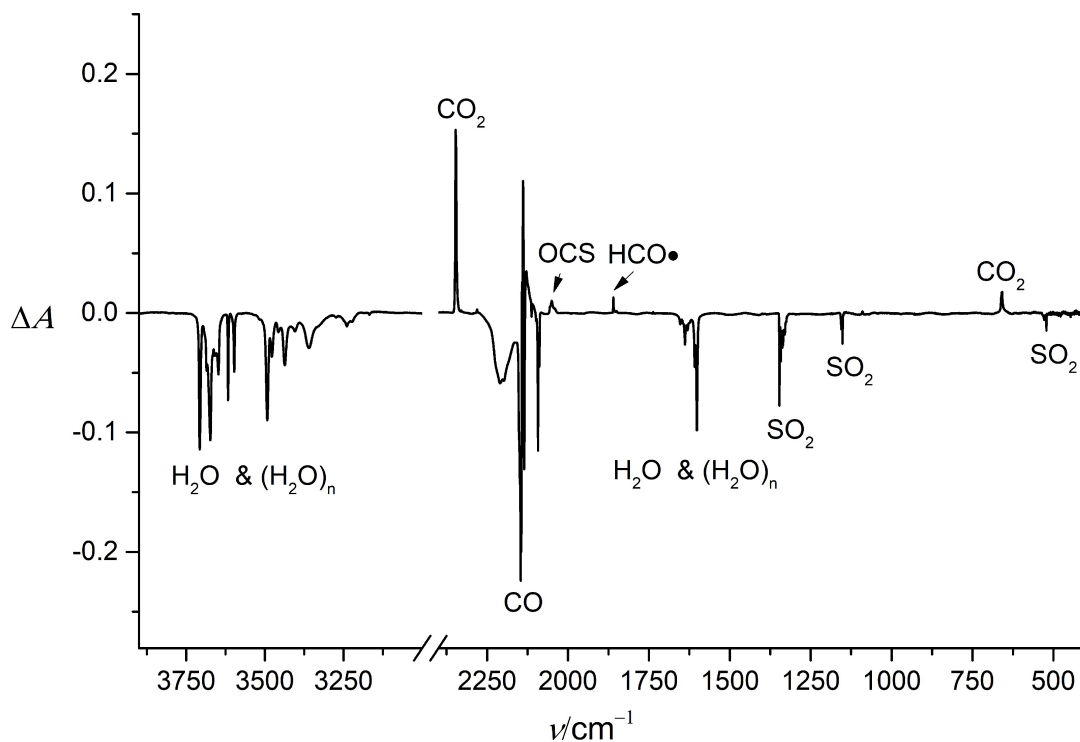
Supplementary Fig. 3 | Reactions of OSSO and SO in matrixes upon irradiation. a Infrared (IR) difference spectrum reflecting the change of the CO-matrix isolated OSSO upon irradiation at 365 nm (15 min). **b** IR difference spectrum reflecting the change of the CO-matrix isolated SO upon irradiation at 193 nm (3 min).



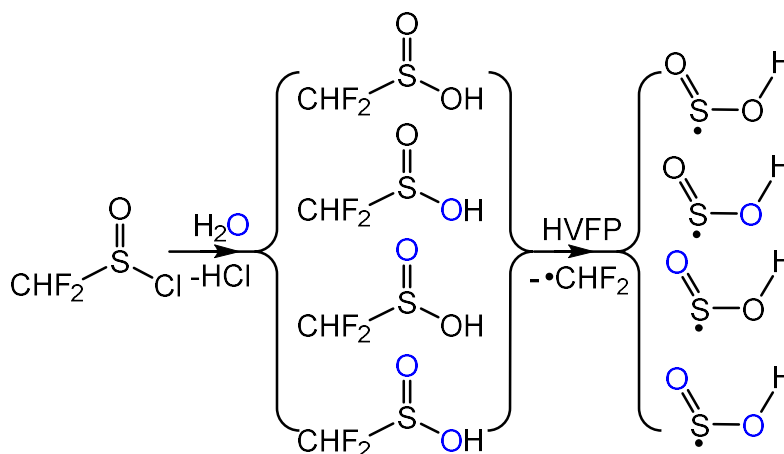
Supplementary Fig. 4 | The integrated infrared band intensities during the irradiation of HOSO• in CO-matrix. For clarity, the initial intensity of HOSO• was normalized. Panel **a** corresponds to the irradiation the matrix at 266 nm, and panel **b** corresponds to the irradiation of the matrix at 365 nm.



Supplementary Fig. 5 | The photochemistry of HOSO• in CO-matrix. Infrared (IR) difference spectrum reflecting the change of the CO-matrix isolated HOSO• upon irradiation at 365 nm (7 min).



Supplementary Fig. 6 | The photochemistry of a SO₂/H₂O/CO (1 : 10 : 1000) mixture. Infrared (IR) difference spectrum reflecting the change of the CO-matrix isolated H₂O and SO₂ upon irradiation at 193 nm (14 min).



Supplementary Fig. 7 | Pathway for the synthesis of ¹⁸O-labeled HOSO• by using ¹⁸O-labeled H₂O (97%) as the starting material.

Supplementary Table 1 | Calculated and observed Infrared (IR) spectra of HOCO•/SO/SO₂ and their complexes.

Mode	<i>t</i> -HOCO•/SO/SO ₂ ^[a]			<i>t</i> -HOCO••••SO			<i>t</i> -HOCO••••SO ₂		
	Obs. ^[a]	B3LYP ^[b]	CCSD(T) ^[c]	Obs. ^[d]	B3LYP ^[b]	CCSD(T) ^[c]	Obs. ^[e]	B3LYP ^[b]	CCSD(T) ^[c]
$\nu(\text{O-H})$	3456	3779 (119)	3804	3311.0	3607 (633)	3861	3529.1	3615 (597)	3686
$\nu(\text{C=O})$	1833	1902 (230)	1882	1831.7/1795.2	1888 (271)	1870	1818.9	1890 (274)	1871
$\delta(\text{COH})$	1261	1235 (244)	1254	1273.8	1306 (190)	1319	1278.7	1313 (193)	1358
$\nu_{\text{asym}}(\text{SO}_2)$	1355.0	1376 (215)	1365	-	-	-	1350.9	1368 (210)	13221
$\nu_{\text{sym}}(\text{SO}_2)$	1152.2	1179 (32)	1156	-	-	-	1146.4	1176 (53)	1157
$\nu(\text{SO})$	1139.5	1157 (15)	1144	1140.0	1164 (45)	1149	-	-	-

[a] Observed IR frequencies in CO-matrix.^[1] [b] Calculated harmonic IR frequencies and intensities (km mol^{-1} , in parentheses) at the B3LYP-D3(BJ)/def2-TZVP level of theory. [c] Calculated harmonic IR frequencies at the CCSD(T)/aug-cc-pV(T+d)Z level of theory. [d] Observed IR frequencies in CO-matrix. [e] Observed IR frequencies in CO₂-doped Ar-matrix.

Supplementary Table 2 | Calculated and observed Infrared (IR) spectra of HCO•/SO₂ and their complex.

Mode	HCO•/SO ₂			HCO•⋯SO ₂		
	Obs. ^[a]	B3LYP ^[b]	CCSD(T) ^[c]	Obs. ^[d]	B3LYP ^[b]	CCSD(T) ^[c]
$\nu(\text{C-H})$	2488	2645 (81)	2703	2493.8	2727 (18)	2750
$\nu(\text{C=O})$	1861	1935 (96)	1876	1859.9	1922 (87)	1868
$\delta(\text{COH})$	1090	1108 (36)	1108	1076.5	1101 (101)	1120
$\nu_{\text{asym}}(\text{SO}_2)$	1355.0	1376 (215)	1365	1346.8	1358 (204)	1358
$\nu_{\text{sym}}(\text{SO}_2)$	1152.2	1179 (32)	1156	1151.9	1160 (50)	1156

[a] Observed IR frequencies in CO-matrix.^[2] [b] Calculated harmonic IR frequencies and intensities (km mol^{-1} , in parentheses) at the B3LYP-GD3(BJ)/def2-TZVP level of theory. [c] Calculated harmonic IR frequencies at the CCSD(T)/aug-cc-pV(T+d)Z level of theory. [d] Observed IR frequencies in CO-matrix.

Supplementary Table 3 | Calculated and observed Infrared (IR) spectra of HOS•/CO₂ and their complex.

Mode	HOS•/CO ₂			CO ₂ ⋯HOS•		
	Obs. ^[a]	B3LYP ^[b]	CCSD(T) ^[c]	Obs. ^[d]	B3LYP ^[b]	CCSD(T) ^[c]
$\nu(\text{O-H})$	3605.7	3722 (91)	3765	3451.4	3644 (213)	3703
$\delta(\text{SOH})$	1156.5	1167 (46)	1185	1166.2	1224 (85)	1238
$\nu(\text{S-O})$	837.3	845 (68)	843	846.2	859 (55)	854
$\nu_{\text{asym}}(\text{CO}_2)$	2346.7	2411 (650)	2372	2345.1	2409 (594)	2372
$\delta(\text{CO}_2)$	659.3	677 (64)	664	652.1	671 (27)/648 (85)	660/650

[a] Observed IR frequencies in *para*-H₂ matrix.^[3] [b] Calculated harmonic IR frequencies and intensities (km mol^{-1} , in parentheses) at the B3LYP-GD3(BJ)/def2-TZVP level of theory. [c] Calculated harmonic IR frequencies at the CCSD(T)/aug-cc-pV(T+d)Z level of theory. [d] Observed IR frequencies in CO-matrix.

Supplementary References

1. Milligan, D. E. & Jacox, M. E. Infrared spectrum and structure of intermediates in the reaction of OH with CO. *J. Chem. Phys.* **54**, 927–942 (1971).
2. Ewing, G. E., Thompson, W. E. & Pimentel, G. C. Infrared detection of the formyl radical HCO. *J. Chem. Phys.* **32**, 927–932 (1960).
3. Góbi, S., Csonka, I. P., Bazsó, G. & Tarczay, G. Successive hydrogenation of SO and SO₂ in Solid *para*-H₂: Formation of elusive small oxoacids of sulfur. *ACS Earth Space Chem.* **5**, 1180–1195 (2021).