Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

THz Spectroscopy of Weakly Bound Cluster Molecules in Solid *para*-Hydrogen: A Sensitive Probe of van der Waals Interactions

D. Mihrin and R. Wugt Larsen*

[a]*Department of Chemistry, Technical University of Denmark, Kemitorvet 206, 2800 Kgs. Lyngby, Denmark*

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Supplementary Information

Table S1. Optimized Geometries, Harmonic Vibrational Band Origins and Electronic Energies of CS_2 and H_2O and Selected Binary and Ternary $(CS_2)_m\cdot\cdot(H2O)_n$ van der Waals Cluster Molecules at the RI-MP2/aug-pCVXZ (X = Q, 5) Level of Theory.

CS_2

Cartesian Coordinates (Angstrom)

C	0.000000000	0.000000000	0.000000000
S	0.000000000	0.000000000	-1.549576863
S	0.000000000	0.000000000	1.549576863

E(RI-MP2 ACV5Z) = −910.832463836750 E_h

Vibrational Band Origins (cm^{-1}) and Band Intensities (km/mol) [CCSD(T)-F12]

403.0 [399.0]	5.0
403.0 [399.0]	5.0
683.4 [672.3]	0
1631.1 [1560.4]	561.3

H_2O

Cartesian Coordinates (Angstrom)

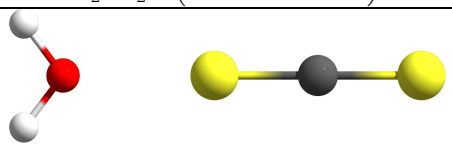
S	0.000000000	0.000000000	2.540744000
S	0.000000000	0.000000000	-0.561321000
C	0.000000000	0.000000000	0.988190000
O	0.000000000	0.000000000	-3.684576000
H	0.000000000	0.757589000	-4.270772000
H	0.000000000	-0.757589000	-4.270772000

E(RI-MP2 ACV5Z) = −910.832463836750 E_h

Vibrational Band Origins (cm^{-1}) and Band Intensities (km/mol) [CCSD(T)-F12]

1630.8 [1649.4]	74.8
3849.3 [3833.8]	6.6
3976.4 [3944.3]	81.2

$CS_2\cdot\cdot H_2O$ (Conformation 1)



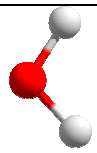
Cartesian coordinates (Angstrom)

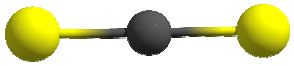
S	0.000000000	0.000000000	2.561030000
S	0.000000000	0.000000000	-0.551944000
C	0.000000000	0.000000000	1.003044000
O	0.000000000	0.000000000	-3.699001000
H	0.000000000	0.757139000	-4.285818000
H	0.000000000	-0.757139000	-4.285818000

E(RI-MP2 ACV5Z) = −910.832463836750 E_h, D_e (CCSD(T)/CBS)= 6.96 kJ/mol,
D_e (CCSD(T)-F12b/AV5Z)= 7.05 kJ/mol

Vibrational Band Origins (cm^{-1}) and Band Intensities (km/mol) [CCSD(T)-F12]							
	CS_2··H_2O			CS_2··HDO		CS_2··D_2O	
in-plane CS_2 lib.	19.0	[24.8]	8.1	18.2	7.5	17.5	6.9
out-of-plane CS_2 lib	27.0	[26.6]	3.0	26.7	3.2	26.1	3.7
inter. O··S str.	78.2	[75.9]	1.1	75.2	5.7	75.0	0.97
H_2O wag (lib)	90.8	[56.8]	223	81.0	172.5	69.9	121.6
H_2O rock (lib)	95.8	[96.2]	56.6	84.4	32.2	74.8	26.3
x-axis C-S-C bend	410.2	[406.1]	5.1	410.2	5.0	410.2	5.0
y-axis C-S-C bend	411.4	[407.4]	6.1	411.4	5.7	411.3	5.5
C-S sym. str.	680.4	[669.3]	1.2	680.4	1.2	680.4	1.2
C-S asym. str.	1623.4	[1552.7]	629	1623.6	574.8	1623.6	576.3
H_2O bend.	1631.8	[1650.0]	23.5	1432.0	66.3	1198.1	43.3
H_2O sym. str.	3842.6	[3831.2]	12.3	2845.1	24.6	2778.9	9.2
H_2O asym. str.	3968.7	[3941.1]	86.1	3908.7	54.2	2917.0	49.9

CS_2··H_2O (Conformation 2)





Cartesian Coordinates (Angstrom)

C	-0.000514000	0.697628000	0.000000000
S	-1.541005000	0.809681000	0.000000000
S	1.549332000	0.573760000	0.000000000
O	-0.127840000	-2.605274000	0.000000000
H	0.304745000	-3.459743000	0.000000000
H	0.592004000	-1.970648000	0.000000000

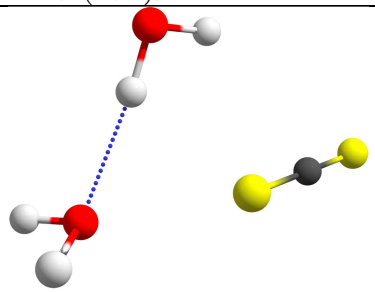
E(RI-MP2 ACV5Z) = −910.832372421122 Eh, D_e (CCSD(T)/CBS)= 5.65 kJ/mol

D_e (CCSD(T)-F12b/AV5Z)= 5.65 kJ/mol

Vibrational Band Origins (cm^{-1}) and Band Intensities (km/mol)

CS_2··H_2O		CS_2··HDO (D-bound (left), H-bound right))				CS_2··D_2O	
37.5	4.0	37.4	3.8	36.5	4.1	36.5	4.0
74.3	134.0	73.5	10.6	55.2	72.7	55.1	72.7
75.2	9.2	74.2	135.3	74.3	9.1	72.6	10.9
152.2	115.3	125.4	75.1	127.5	75.1	110.3	52.6
187.2	49.8	135.7	19.5	186.7	59.6	134.8	30.7
401.1	5.1	401.1	5.1	401.1	5.0	401.1	5.0
407.0	8.1	406.7	6.6	406.8	6.6	406.6	5.9
683.1	0.4	683.1	0.4	683.1	0.4	683.1	0.4
1627.6	422.9	1426.0	54.2	1435.1	77.4	1196.1	38.1
1633.2	165.6	1631.0	517.0	1631.0	516.0	1630.9	519.1
3821.1	25.1	2816.7	59.0	2846.3	20.4	2764.5	10.2
3952.3	143.1	3910.1	56.6	3869.3	129.2	2904.1	87.0

$CS_2\cdot\cdot(H_2O)_2$ Conformation 1



Cartesian Coordinates (Angstrom)

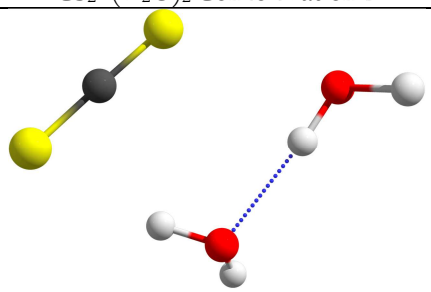
C	1.519807000	0.270721000	0.000000000
S	0.016173000	0.655724000	-0.000002000
S	3.022441000	-0.115120000	0.000003000
O	-2.530935000	-1.991581000	0.000000000
H	-2.684795000	-1.039240000	0.000000000
H	-1.577068000	-2.077583000	-0.000002000
H	-3.739730000	1.065106000	0.760064000
H	-3.739738000	1.065102000	-0.760062000
O	-3.192221000	0.857873000	-0.000001000

E(RI-MP2 ACVQZ) = −987.186381818758 E_h

Vibrational Band Origins (cm^{-1}) and Band Intensities (km/mol)

$CS_2\cdot\cdot(H_2O)_2$		$CS_2\cdot\cdot(HDO)_2$		$CS_2\cdot\cdot(D_2O)_2$	
16.8	1.0	16.6	1.1	16.3	2.5
17.3	3.3	16.8	2.8	16.4	0.9
52.9	1.8	52.5	1.7	50.8	1.9
64.9	0.0	63.0	0.1	61.9	0.1
100.5	1.7	87.4	3.0	76.0	0.3
126.4	0.5	100.2	5.4	91.3	0.1
157.8	72.4	144.1	96.0	119.1	67.9
163.8	124.3	159.7	107.1	124.8	101.8
188.6	184.0	177.8	89.5	168.0	35.7
354.3	50.8	302.3	44.3	263.2	30.9
407.7	5.4	407.4	3.5	407.1	1.9
408.5	7.1	408.5	6.7	408.5	6.3
604.9	79.8	451.8	51.1	437.0	47.8
680.4	0.3	680.4	0.3	680.4	0.3
1620.5	750.3	1420.5	140.2	1197.9	64.3
1631.7	6.7	1433.4	53.9	1207.4	65.1
1651.6	62.9	1625.4	577.8	1625.0	587.0
3752.0	227.0	2750.2	150.1	2720.8	108.3
3830.1	20.3	2834.3	30.1	2769.8	14.6
3930.1	90.1	3893.1	70.7	2882.2	68.8
3951.2	102.9	3911.6	33.6	2904.3	58.1

$CS_2\cdot\cdot(H_2O)_2$ Conformation 2



Cartesian Coordinates (Angstrom)

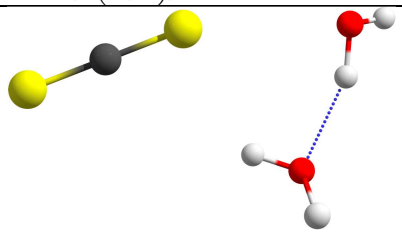
C	-3.502078000	1.070241000	-0.231999000
S	-2.411534000	1.941840000	-0.929511000
S	-4.571497000	0.222921000	0.489431000
O	-2.850970000	3.171273000	2.357338000
H	-2.633892000	2.957795000	1.443990000
H	-3.291451000	4.021725000	2.310277000
O	-4.423561000	1.091675000	3.591707000
H	-3.862197000	1.794728000	3.235551000
H	-4.156430000	1.008262000	4.507486000

E(RI-MP2 ACVQZ) = −987.186109544898 E_h

Vibrational Band Origins (cm^{-1}) and Band Intensities (km/mol)

$CS_2\cdot\cdot(H_2O)_2$		$CS_2\cdot\cdot(HDO)_2$		$CS_2\cdot\cdot(D_2O)_2$	
16.2	2.1	16.1	2.0	15.6	1.8
39.5	0.6	39.3	0.6	38.9	0.5
72.3	17.1	71.8	16.3	69.1	20.8
99.0	5.4	96.7	5.7	86.0	21.6
117.2	48.3	110.9	34.7	95.3	5.2
151.4	95.1	146.1	96.9	112.7	54.2
185.0	20.6	177.7	43.1	148.5	23.2
207.1	53.1	179.2	9.9	176.4	6.7
296.1	129.1	229.7	100.0	213.3	72.5
393.6	49.6	320.6	64.5	293.3	47.6
402.8	11.5	402.4	5.5	402.4	5.4
414.1	43.5	408.7	7.5	408.6	6.7
643.3	105.7	480.1	70.5	464.4	60.2
680.0	2.0	680.0	1.5	679.0	1.5
1623.5	469.9	1422.8	49.3	1198.7	26.3
1632.2	52.6	1428.1	39.0	1212.8	26.2
1656.4	69.9	1623.8	497.4	1623.8	495.5
3700.9	235.5	2710.3	155.1	2686.7	114.3
3787.6	109.9	2782.0	105.5	2742.3	49.5
3926.8	166.7	3898.7	73.9	2877.9	73.5
3927.7	93.6	3913.5	43.6	2883.6	104.2

$CS_2\cdot\cdot(H_2O)_2$ Conformation 3



Cartesian Coordinates (Angstrom)

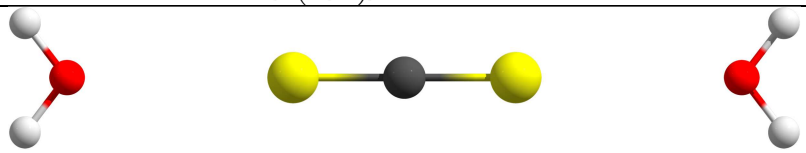
C	-3.702111000	0.465998000	-0.161994000
S	-2.155164000	0.327904000	-0.313646000
S	-5.227231000	0.634541000	0.004035000
O	-2.796886000	2.932482000	1.996627000
H	-2.543955000	2.578389000	2.850982000
H	-2.467405000	2.291556000	1.358703000
O	-5.612066000	3.404411000	1.591420000
H	-4.663117000	3.309605000	1.755288000
H	-5.792636000	4.332754000	1.741655000

E(RI-MP2 ACVQZ) = −987.186122050447 E_h

Vibrational Band Origins (cm^{-1}) and Band Intensities (km/mol)

$CS_2\cdot\cdot(H_2O)_2$		$CS_2\cdot\cdot(HDO)_2$		$CS_2\cdot\cdot(D_2O)_2$	
21.4	0.6	21.2	0.6	20.8	0.6
29.0	0.2	28.7	0.2	28.0	0.1
74.2	25.4	72.9	22.6	69.2	29.7
83.8	0.2	81.7	0.2	80.0	4.5
109.9	47.0	100.1	28.1	84.2	15.3
140.9	95.2	129.8	99.1	102.7	49.9
180.2	64.7	161.5	22.1	131.5	25.6
181.2	3.1	168.9	81.3	158.6	66.5
228.0	217.5	192.9	105.2	181.7	57.6
401.9	40.2	331.9	51.8	303.4	40.4
410.5	8.9	409.9	3.9	409.8	3.4
424.3	38.2	415.1	7.7	414.6	8.7
620.7	140.7	467.5	98.9	449.5	76.5
678.2	0.5	678.2	0.8	678.2	0.8
1617.0	401.5	1418.2	62.4	1195.3	27.4
1630.0	255.5	1425.9	22.7	1207.8	33.2
1650.7	31.4	1619.8	583.5	1619.8	580.5
3714.8	235.6	2721.8	155.8	2695.9	110.2
3805.5	74.6	2800.7	90.1	2753.7	36.0
3931.6	109.7	3900.0	73.5	2881.9	84.7
3936.3	168.6	3915.6	52.1	2891.9	101.5

$CS_2\cdot\cdot(H_2O)_2$ Conformation 4



Cartesian Coordinates (Angstrom)

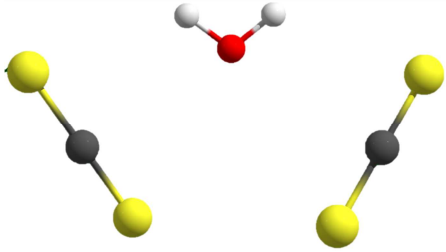
C	0.000000000	0.000000000	0.000000000
S	0.000000000	0.000000000	1.553491000
S	0.000000000	0.000000000	-1.553491000
O	0.000000000	0.000000000	-4.706660000
H	-0.757633000	0.000000000	-5.293610000
H	0.757633000	0.000000000	-5.293610000
H	0.757633000	0.000000000	5.293610000
H	-0.757633000	0.000000000	5.293610000
O	0.000000000	0.000000000	4.706660000

E(RI-MP2 ACVQZ) = −987.180269345504 E_h

Vibrational Band Origins (cm^{-1}) and Band Intensities (km/mol)

$CS_2\cdot\cdot(H_2O)_2$		$CS_2\cdot\cdot(HDO)_2$		$CS_2\cdot\cdot(D_2O)_2$	
5.0	0.0	4.7	0.0	4.4	0
5.0	0.0	4.7	0.0	4.4	0
8.8	0.0	7.3	0.0	6.2	0
16.2	6.6	25.1	1.1	23.9	2.1
33.5	0.0	25.1	1.1	23.9	2.1
65.0	0.0	58.3	174.4	50.9	129.7
67.7	0.0	58.4	174.9	50.9	129.7
70.0	109.6	65.5	15.0	62.9	15.6
72.1	443.0	67.4	29.0	62.9	15.6
77.8	0.0	71.6	15.6	67.2	0.0
80.0	2.4	83.1	4.3	81.0	2.2
416.2	5.2	417.7	5.8	417.7	5.5
418.7	7.2	417.7	5.8	417.7	5.5
676.8	0.0	673.6	0.0	673.6	0.0
1615.5	660.5	1428.4	124.4	1195.1	84.1
1629.7	0.0	1428.5	4.7	1195.2	0.0
1629.8	82.4	1611.5	577.6	1611.4	580.7
3839.7	21.7	2827.0	26.2	2761.9	15.4
3839.7	0.0	2827.0	18.6	2761.9	0.0
3966.1	0.0	3883.6	54.7	2897.6	46.7
3966.1	165.8	3883.64	54.7	2897.6	46.7

$(CS_2)_2 \cdot\cdot H_2O$



Cartesian Coordinates (Angstrom)

C	-0.942861000	-0.017323000	0.125739000
S	0.267046000	0.950245000	0.244472000
S	-2.160601000	-0.987567000	0.004571000
O	-2.914552000	2.413092000	-0.257634000
H	-3.385904000	1.581095000	-0.349616000
H	-3.577842000	3.091521000	-0.407078000
S	-2.848003000	5.896532000	-0.184623000
S	-0.270054000	4.484427000	0.847437000
C	-1.555410000	5.189340000	0.332083000

E(RI-MP2-FC AVQZ) = −1743.387004395677 E_h

D_e ($(CS_2)_2 H_2O \rightarrow (CS_2)_2 + H_2O$) = 2,75 kJ/mol

Vibrational Band Origins (cm^{-1}) and Band Intensities (km/mol)

$CS_2 \cdot\cdot (H_2O)_2$		$CS_2 \cdot\cdot (D_2O)_2$	
5.2	0.0	5.2	0.0
8.3	0.7	8.2	0.7
36.0	0.6	35.7	1.2
43.2	0.0	43.1	0.0
48.3	1.2	46.7	28.5
64.5	100.7	49.4	29.2
78.7	5.9	75.4	2.4
110.1	34.7	86.0	84.8
117.9	123.1	105.3	0.8
214.9	0.2	152.7	0.1
393.9	14.8	393.6	12.9
395.5	0.2	395.5	0.2
396.4	4.2	396.4	4.0
396.7	7.4	396.7	7.2
676.9	0.3	676.9	0.3
677.1	0.2	677.1	0.2
1604.6	611.9	1184.2	100.0
1617.0	433.1	1616.9	429.8
1633.3	179.3	1624.5	611.8
3806.8	0.8	2753.2	0.1
3935.0	68.2	2892.3	44.0

Table S2. Total Electronic Energies Calculated at the CCSD(T) and CCSD(T)-F12b Levels (with and without Scaling of Triples) for CS_2 and H_2O and the Two Different Conformations of the Binary $CS_2 \cdot\cdot H_2O$ System.

	Total energy, E_h						
	CCSD(T)				CCSD(T)-F12b-scaled		CCSD(T)-F12b
Structure	AVTZ	AVQZ	AV5Z	AV6Z	AV5Z	VQZ-F12	VQZ-F12
CS_2	-833.51651077	-833.55744648	-833.57230472	-833.57766924	-833.5788534	-833.5814286	-833.5793665
H_2O	-76.34229272	-76.36358311	-76.37029631	-76.37255691	-76.37443923	-76.37437824	-76.37394551
$CS_2 - H_2O$, C_{2v}	-909.86193015	-909.92385560	-909.94531634	-909.95290518	-909.9559764	-909.95841	-909.95594713
$CS_2 - H_2O$, C_s	-909.86147740	-909.92337827	-909.94482795	-909.952905181	-909.95544453	-909.9579380	-909.95547975

Table S3. Electronic Interaction Energies D_e (kJ·mol^{-1}) at the CCSD(T) and CCSD(T)-F12b Levels (with and without scaling of Triples) and the CCSD(T) Complete Basis Set (CBS) Limits for the Two Different Conformations of the Binary $CS_2 \cdot\cdot H_2O$ System.

		Electronic dissociation energy (D_e), kJ/mol							
Structure/Component		CCSD(T)					CCSD(T)-F12b-scaled		CCSD(T)-F12b
		AVTZ	AVQZ	AV5Z	AV6Z	CBS	AV5Z	VQZ-F12	VQZ-F12
$CS_2 - H_2O$, C_{2v}	Ref.	-1.501	-1.088	-1.008	-0.990	-0.984			
$CS_2 - H_2O$, C_s		3.684	3.894	3.952	3.963	4.010			
$CS_2 - H_2O$, C_{2v}	Correlation	-6.708	-6.332	-6.121	-6.044	-5.971			
$CS_2 - H_2O$, C_s		-10.704	-10.061	-9.799	-9.704	-9.448			
$CS_2 - H_2O$, C_{2v}	Total	-8.209	-7.420	-7.129	-7.034	-6.955	-7.046	-6.826	-6.919
$CS_2 - H_2O$, C_s		-7.020	-6.166	-5.847	5.741	-5.655		-5.595	-5.691

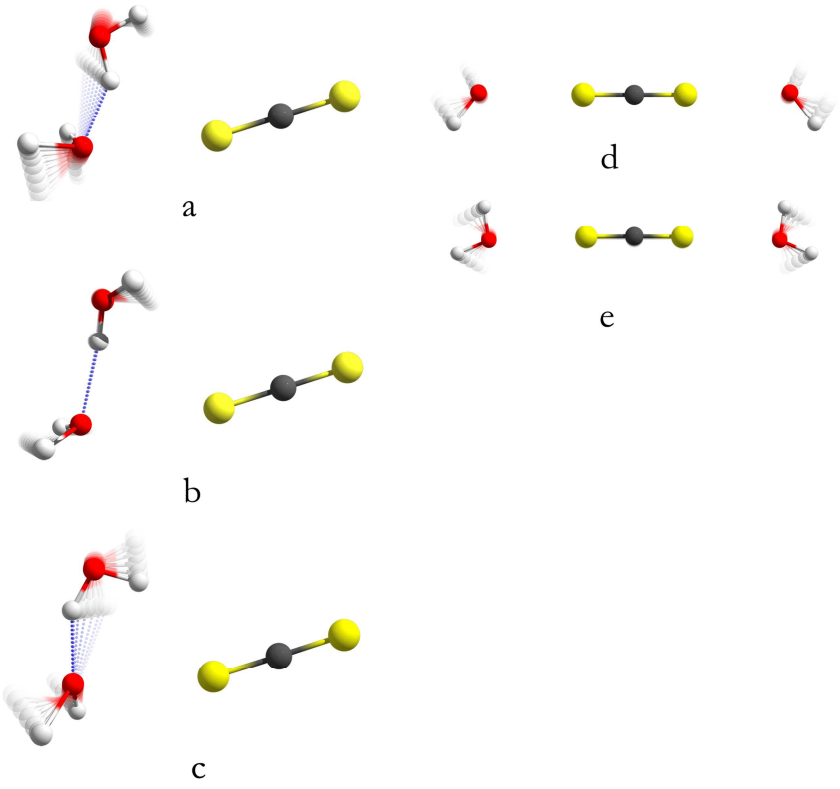


Figure S1. Normal Mode Animations of the Most Active Large-Amplitude Intermolecular Vibrations for the Two Different Observed Conformations of the Ternary $CS_2 \cdot\cdot (H_2O)_2$ System (Left: Conformation 1, Right: Conformation 4).

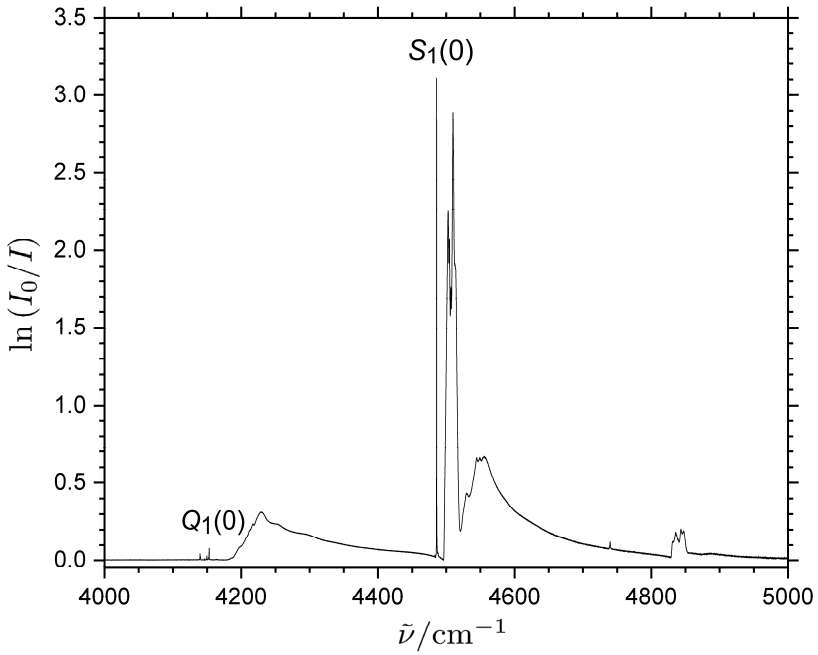


Figure S2. Mid-Infrared Absorption Spectrum of Solid *para*-H_2 obtained at 3 K with Assignments of the Solid-State Induced $Q_1(0)$ and $S_1(0)$ Transitions Employed for the Estimation of the *ortho-para* Conversion Efficiency.

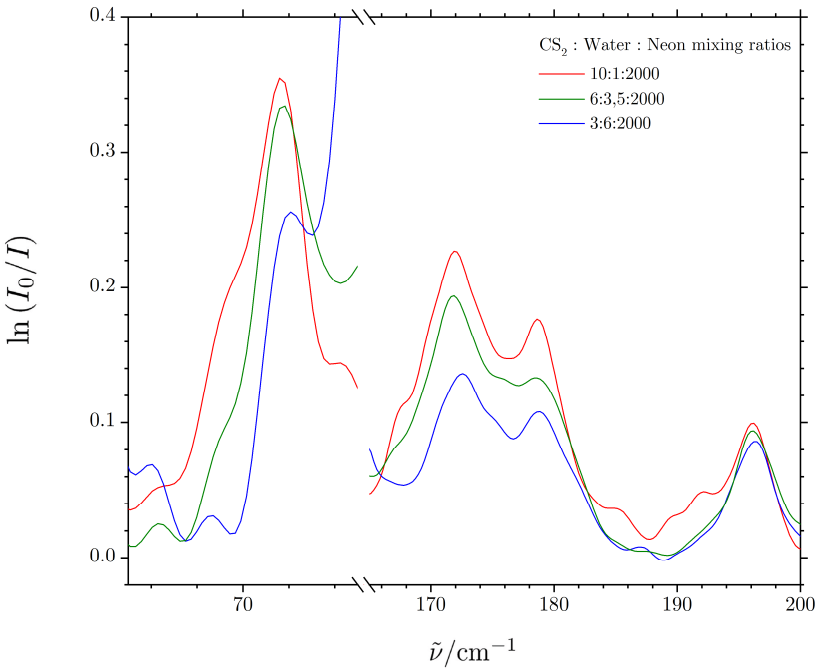


Figure S3. Stacked THz Absorption Spectra of *para*-H_2 Matrices doped with CS_2/H_2O Mixtures with Varying Mixing Ratios. The Spectra Are Normalized Relative to the Band Assigned to the H_2O Wagging Mode of the Weakly Bound Binary $CS_2 \cdot\cdot H_2O$ Complex.