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Chalcogen Bond and Internal Dynamics of the 2,2,4,4-Tetrafluoro-1,3-dithietane···Water Complex

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Electronic Supplementary Information

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S1. Theoretical and Experimental Procedures

S1.1. Theoretical Calculations

The molecular electrostatic surface potential (MESP) of $C_2F_4S_2$ was calculated at the MP2/6-311++G(d,p) level of theory to show how the potential energy varies over the isosurface at an electron density of 0.0004 electrons Bohr^{-3}. The MESP diagram for $C_2F_4S_2$ is reported in Figure S1. The yellow region represents the most nucleophilic regions and correspond to the *n*-electron on F. The dark blue region along the C-S bond represents the most electrophilic regions of $C_2F_4S_2$. Four σ-holes, two on both sulfur atoms, present for $C_2F_4S_2$.

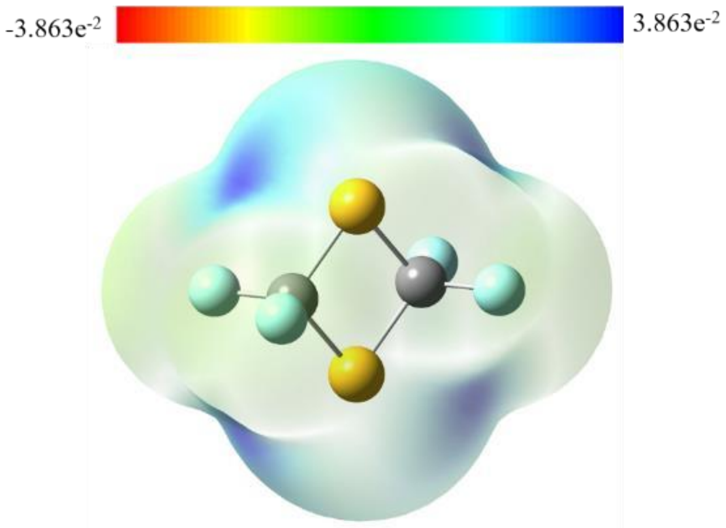


Figure S1. The MESPs of $C_2F_4S_2$ calculated at the MP2/6-311++G(d,p) level of theory.

Table S1. Theoretical spectroscopic parameters of the two most stable isomers of the $C_2F_4S_2$-H_2O complex.

	MP2/6-311++G(d,p)		**MP2/aug-cc-pVTZ**	
Isomer	I	II	I	II
A/MHz	1804	1157	1800	1197
B/MHz	859	1099	863	1096
C/MHz	732	773	733	788
P_{aa}/uÅ^2	499.30	338.42	497.15	339.97
P_{bb}/uÅ^2	191.12	315.37	192.31	301.28
P_{cc}/uÅ^2	89.04	121.43	88.45	120.92
$\|\mu_a\|$/D	2.6	0.0	2.0	0.0
$\|\mu_b\|$/D	0.4	2.6	1.0	2.5
$\|\mu_c\|$/D	0.0	0.2	0.0	0.2
$\Delta E_{0,\ \mathrm{BSSE}}$/cm^{-1}	0	642	0[a]	677[a]

[a] zero-point energies were estimated at the MP2/6-311++G(d,p) level of theory.

Structural optimizations of several possible configurations of the titled complex were carried out at the second order Møller–Plesset (MP2) level of theory employing the Pople type basis set 6-311++G(d,p). Harmonic frequency calculations at the same level of theory were also performed to verify the resulted structures to be real local minima which also provide the zero-point vibrational energies. The basis-set superposition error (BSSE) was taken into account by means of the counterpoise correction (CP) procedure.[1] The structures of the two identified isomers were re-optimized at the MP2/aug-cc-pVTZ level of theory resulting in similar geometries from the MP2/6-311++G(d,p) level of calculations. The corresponding rotational constants, electric dipole moment components and planar moments of inertia P_{gg} are given in Table S1. In additions, the most stable isomer was re-optimized by using B3LYP- GD3BJ methods, as shown in Table S2.

Table S2. The theoretical and experimental rotational constants of the most stable isomer of the $C_2F_4S_2$-H_2O complex.

	Expt.	MP2		B3LYP-GD3BJ	
	0-state	6-311++G(d,p)	aug-cc-pVTZ	6-311++G(d,p)	aug-cc-pVTZ
A/MHz	1798.48973(58)[a]	1804(0.3%)	1800(0.1%)	1768(1.7%)	1775(1.3%)
B/MHz	853.20352(18)	859(0.7%)	862(1.0%)	858(0.6%)	849(0.5%)
C/MHz	724.80366(17)	732(1.0%)	733(1.0%)	726(0.2%)	720(0.7%)

[a] Errors in parenthesis are 1σ uncertainties expressed in units of the last digit.

Bader's quantum theory of atoms in molecules (QTAIM) analysis[2] was performed to understand the intermolecular interactions by using the Multiwfn program.[3] The bond critical points (BCPs) and ring critical points (RCPs) were found, represented by orange and yellow dots, respectively. The interaction energy of each non-covalent interaction can be estimated from the electron potential density at the corresponding BCPs through $E = 0.5V(r)$.

An energy decomposition analysis of the interaction energy was carried out to provide a more quantitative understanding on the nature of the non-covalent interactions of the titled complex and compared with the σ- and π-hole type complexes of CF_3Cl-H_2O, C_2F_3Cl-H_2O and C_6F_6-H_2O. Using the Symmetry-Adapted Perturbation theory,[4] the contribution of electrostatics, induction, dispersion and exchange-repulsion to the interaction energy can be evaluated. The result of the C_6F_6-H_2O complex was obtained from the previous work reported by Evangelisti *et al.*[5] The SAPT analysis of $C_2F_4S_2$-H_2O, CF_3Cl-H_2O and C_2F_3Cl-H_2O complexes at the SAPT2+3/aug-cc-pVDZ-RI level of theory was carried out by using PSI4 package[6] based on the *ab initio* geometry optimized at the MP2/6-311++G(d,p) level of theory.

The observed splittings of the rotational spectra of $C_2F_4S_2$-H_2O indicate a quantum tunneling process. Initially, two different motions were considered: (1) the internal rotation of water around its C_2 axis; and (2) the wagging of the water through the *bc* plane of the $C_2F_4S_2$ moiety. The potential energy pathways for the two motions were calculated at the MP2/6-311++G(d,p) level of theory (Figure S2). The barriers were calculated to be 169 and 1127 cm^{-1}, respectively. Therefore, the barrier to motion (2) is deemed to be too high to generate resolvable splittings. In addition, the wagging of the water inverts the μ_b dipole moment component leading to interstate transitions of the *b*-type transitions which is not in accord with the experimental evidence. Consistent with the spectral observations, the splittings can be attributed to the internal rotation of water around its C_2 axis. This motion exchanges a pair of equivalent fermions giving rise to a symmetric (v = 0) and an anti-symmetric (v = 1) tunneling state.

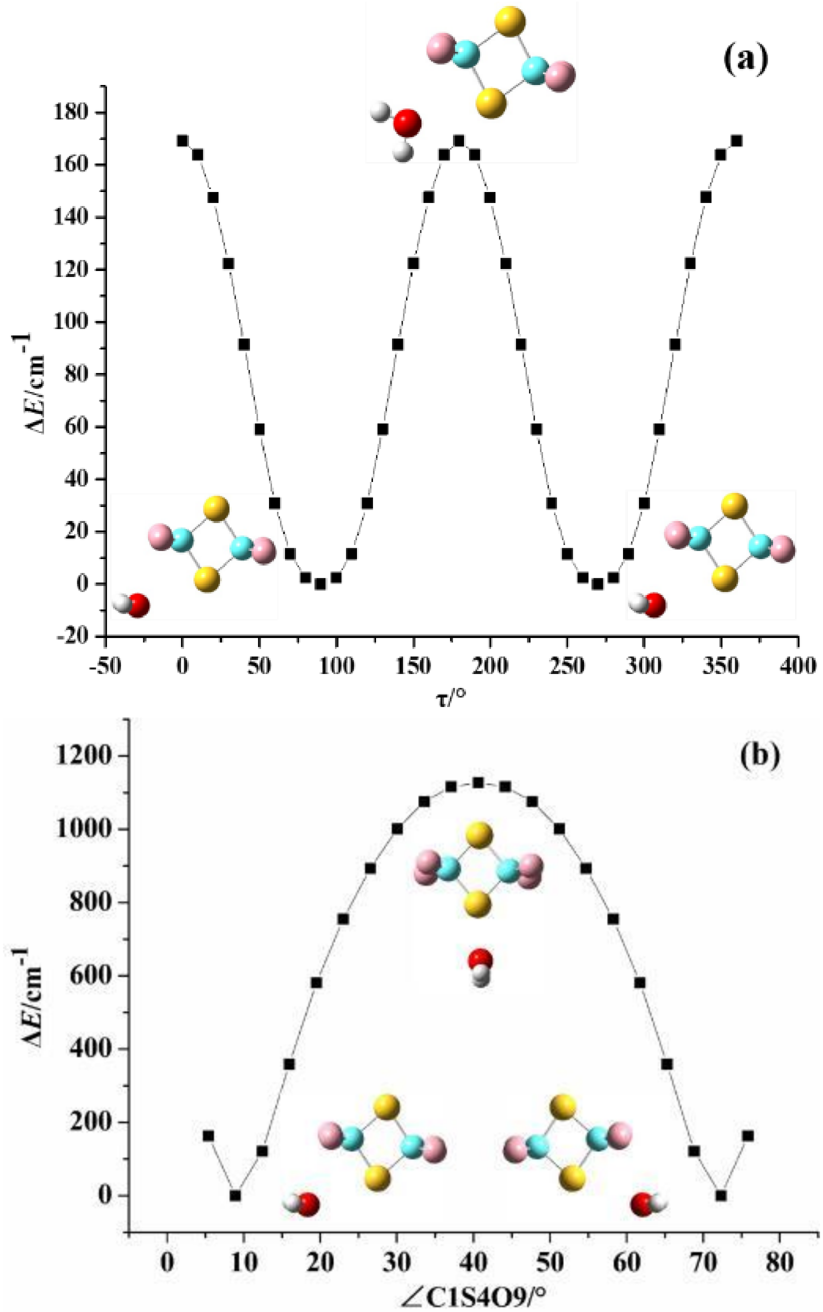
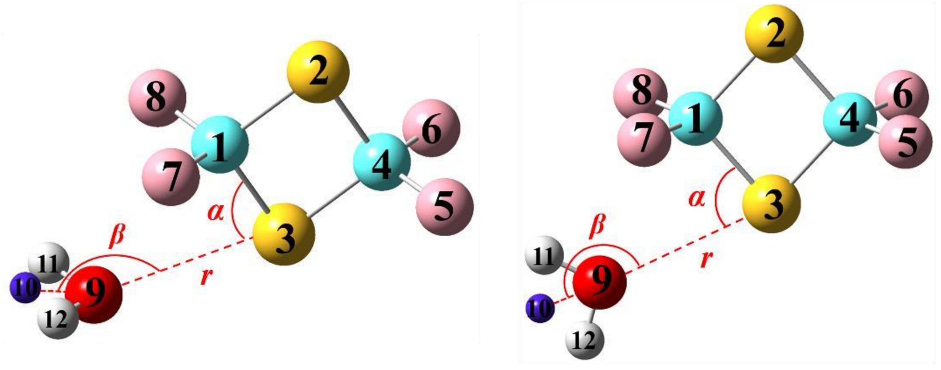


Figure S2. The potential energy surfaces for (a) the internal rotation of the water around its C_2 axis and (b) the wigging of water through the *bc* plane of $C_2F_4S_2$ moiety calculated at the MP2/6-311++G(d,p) level of theory.

The structure of the transition state for water internal rotation was assumed to that at the vertex of the potential energy curve and further confirmed by transition state optimization at the MP2/6-311++G(d,p) level of theory. The obtained geometry of the minimum and the transition state together with the structure parameters concerning the internal rotation of water *r*, *α* and *β* were shown in Figure S3. The values of *r*, *α* and *β* were calculated to 2.867 Å, 36.2°

and 152.4°for the minimum and 2.916 Å, 35.0°and 178.9° for the transition state, respectively. The r_e structure of the minimum and the TS of isomer I are reported in Table S3 where the partial r_0 structural parameter are also included for the minimum.



minimum Transition state (TS)

Figure S3. The geometries and the structure parameters concerning the internal rotation of water.

Table S3. Partial $r_{0,\text{semi-exp}}$ geometry and theoretical structure (r_e) of the observed isomer together with theoretical structure (r_e) of transition state of internal rotation of water around its C_2 axis.

Bond distance/ Å			**Valence angle/°**			**Dihedral angle/°**		
	minimum	TS		minimum	TS		minimum	TS
S2C1	1.818	1.818						
S3C1	1.814	1.814	S3C1S2	98.6	98.6			
C4S3	1.814	1.813	C4S3C1	81.4	81.5	C4S3C1S2	0.0	0.0
F5C4	1.353	1.353	F5C4S3	113.5	113.5	F5C4S3C1	-119.9	-119.9
F6C4	1.353	1.353	F6C4S3	113.5	113.5	F6C4S3C1	119.9	119.9
F7C1	1.351	1.351	F7C1S3	113.8	113.8	F7C1S3C4	119.5	119.6
F8C1	1.351	1.351	F8C1S3	113.8	113.8	F8C1S3C4	-119.5	-119.6
O9C3	2.912(5)[a]	2.916	O9C3C4	158.90(6)[b]	156.9	O9C3C4S2	180.0	180.0
X10O9	1.000	1.000	X10O9S3	152.4	178.9	X10O9S3C1	0.0	0.0
H11O9	0.961	0.961	H11O9X10	52.0	52.1	H11O9X10S3	90.0	0.0
H12O9	0.961	0.961	H12O9X10	52.0	52.1	H12O9X10H11	180.0	180.0

[a] The theoretical values (re) of r_{O9C3} and ∠O9C3C4 are 2.867 Å and 158.6°, respectively.

[b] Errors in parenthesis are expressed in units of the last digit.

S1.2. Rotational Spectra

After empirical scaling to the rotational constants of the parent species, the rotational spectra of ^{34}S2 and ^{34}S3 species were measured in nature abundance. Only a small number of transitions of ^{34}S species of the excited state were measurable, such that the centrifugal distortion constants were kept at the corresponding values of the parent species. The results are listed in Table S4.

Table S4. Experimental spectroscopic parameters of ^{34}S species[a] of $C_2F_4S_2$-H_2O complex.[b]

	^{34}S2	**^{34}S3**
***A*/MHz**	1766.032(4)	1774.482(5)[c]
***B*/MHz**	851.07605(8)	853.3838(1)
***C*/MHz**	719.39207(7)	722.4479(1)
P_{cc}/uÅ^2	88.735	88.736
N^d	16	14
σ^e/kHz	1.4	1.9

[a] The transitions of ^{34}S species only for v=1 tunnelling state were measured.

[b] Centrifugal distortion constants have been fixed at the values of normal species.

[c] Errors in parenthesis are expressed in units of the last digit.

[d] Number of lines in the fit.

[e] RMS error of the fit.

From the rotational constants of the ground torsional state of the parent, ^{18}O, and those of the v = 1 state of ^{34}S, it is possible to calculate the so-called substitution coordinates, r_s, following Kraitchman's method.[7] From the rotational constants of the ground torsional state of the parent and D_2O isotopologues, the substitution coordinates of the two water hydrogens were calculated using Chujtian's equations.[8] The obtained results are given in Table S5.

Table S5. r_s, $r_{0,\text{semi-exp}}$ and r_e coordinates of the substituted atoms in the principal axes of inertia of the parent species.

	***a*/Å**			***b*/Å**			***c*/Å**		
	r_s	$r_{0,\text{semi-exp}}$	r_e	r_s	$r_{0,\text{semi-exp}}$	r_e	r_s	$r_{0,\text{semi-exp}}$	r_e
S2	±0.915(2)[a]	0.917(5)	0.902	±1.385(1)	-1.392(5)	-1.397	0.000[b]	0.000	0.000
S3	±0.182(8)	-0.220(5)	-0.216	±1.104(1)	1.116(5)	1.120	0.000[b]	0.000	0.000
O9	±3.1130(5)	-3.123(5)	-3.077	±1.333(1)	1.317(5)	1.320	0.000[b]	0.000	0.000
H10[c]	±3.505(5)	-3.668(5)	-3.620	±1.082(5)	1.080(5)	1.083	±0.794(5)	0.757(5)	0.757
H11[c]	±3.505(5)	-3.668(5)	-3.620	±1.082(5)	1.080(5)	1.083	±0.794(5)	-0.757(5)	-0.757

[a] Errors in parenthesis are expressed in units of the last digit.

[b] The *c* coordinates of S and O atoms are set to zero by symmetry.

[c] The values were calculated using Chujtian's equatuions.

Table S6. Experimental transitions frequencies of the parent species of the $C_2F_4S_2$-H_2O complex.

$J'_{Ka'\,Kc'}$			$J''_{Ka''Kc''}$			v	$V_{obs.}$/MHz	Δv/kHz
4	0	4	3	0	3	1	6196.8840	1
4	0	4	3	0	3	0	6196.0099	-1
4	1	4	3	1	3	1	6034.4146	0
4	1	4	3	1	3	0	6032.8246	-1
4	1	3	3	1	2	1	6543.8669	2
4	1	3	3	1	2	0	6542.0612	-3
4	2	3	3	2	2	1	6304.3361	2
4	2	3	3	2	2	0	6302.4831	0
4	2	2	3	2	1	1	6421.3696	2
4	2	2	3	2	1	0	6418.4403	-1
5	0	5	4	0	4	1	7673.9363	1
5	0	5	4	0	4	0	7673.2708	-1
5	1	5	4	1	4	1	7524.4923	0
5	1	5	4	1	4	0	7522.6518	-2
5	1	4	4	1	3	1	8151.5103	1
5	1	4	4	1	3	0	8149.5909	-2
5	2	4	4	2	3	1	7865.0309	1
5	2	4	4	2	3	0	7862.8701	-1
5	2	3	4	2	2	1	8083.2259	2
5	2	3	4	2	2	0	8079.2977	-3
5	3	3	4	3	2	1	7927.5597	0
5	3	3	4	3	2	0	7924.8296	-1
5	3	2	4	3	1	1	7942.8994	1
5	3	2	4	3	1	0	7939.8735	-1
5	4	2	4	4	1	1	7919.8005	-4
5	4	2	4	4	1	0	7917.0912	-1
5	4	1	4	4	0	1	7920.0961	-5
5	4	1	4	4	0	0	7917.3794	-1
6	0	6	5	0	5	1	9126.1695	1
6	0	6	5	0	5	0	9125.5766	-1
6	1	6	5	1	5	1	9005.5324	1
6	1	6	5	1	5	0	9003.4833	-2
6	1	5	5	1	4	1	9736.4152	3
6	1	5	5	1	4	0	9734.6679	-2
6	2	5	5	2	4	1	9415.7280	1
6	2	5	5	2	4	0	9413.3533	-2
6	2	4	5	2	3	1	9759.1218	3
6	2	4	5	2	3	0	9754.4514	-3
6	3	4	5	3	3	1	9519.8559	1
6	3	4	5	3	3	0	9516.5934	-1
6	3	3	5	3	2	1	9559.7810	2
6	3	3	5	3	2	0	9555.7647	-2
6	4	3	5	4	2	1	9512.4006	1
6	4	3	5	4	2	0	9509.0641	0
6	4	2	5	4	1	1	9513.7254	0

6	4	2	5	4	1	0	9510.3514	-1
7	0	7	6	0	6	1	10565.8743	1
7	0	7	6	0	6	0	10565.0849	-1
7	1	7	6	1	6	1	10478.3068	1
7	1	7	6	1	6	0	10476.0653	-1
7	1	6	6	1	5	1	11291.3307	2
7	1	6	6	1	5	0	11290.1188	-2
7	2	6	6	2	5	1	10954.8804	1
7	2	6	6	2	5	0	10952.3945	-3
7	2	5	6	2	4	1	11433.9759	4
7	2	5	6	2	4	0	11428.9889	-4
7	3	5	6	3	4	1	11111.1095	2
7	3	5	6	3	4	0	11107.3919	-3
7	3	4	6	3	3	1	11197.2775	3
7	3	4	6	3	3	0	11192.0081	-3
7	4	4	6	4	3	1	11109.0792	1
7	4	4	6	4	3	0	11105.0921	-1
7	4	3	6	4	2	1	11113.4470	1
7	4	3	6	4	2	0	11109.3344	-1
7	5	3	6	5	2	1	11093.2503	-1
7	5	3	6	5	2	0	11089.3946	1
7	5	2	6	5	1	1	11093.3405	-3
7	5	2	6	5	1	0	11089.4818	0
7	6	2	6	6	1	1	11083.9750	-5
7	6	2	6	6	1	0	11080.2198	4
7	6	1	6	6	0	1	11083.9840	3
7	6	1	6	6	0	0	11080.2354	18
8	0	8	7	0	7	1	12002.8056	2
8	0	8	7	0	7	0	12001.5953	-1
8	1	8	7	1	7	1	11944.1618	2
8	1	8	7	1	7	0	11941.7154	-2
8	1	7	7	1	6	1	12810.3096	2
8	1	7	7	1	6	0	12809.9648	-2
8	2	7	7	2	6	1	12481.3957	1
8	2	7	7	2	6	0	12478.8964	-2
8	2	6	7	2	5	1	13094.5647	5
8	2	6	7	2	5	0	13089.7035	-6
8	3	6	7	3	5	1	12698.4551	2
8	3	6	7	3	5	0	12694.4033	-4
8	3	5	7	3	4	1	12859.6811	4
8	3	5	7	3	4	0	12852.9422	-3
8	4	5	7	4	4	1	12709.6827	1
8	4	5	7	4	4	0	12705.0367	-2
8	4	4	7	4	3	1	12721.4754	2
8	4	4	7	4	3	0	12716.4952	-2
8	5	4	7	5	3	1	12688.2314	0
8	5	4	7	5	3	0	12683.7207	1
8	5	3	7	5	2	1	12688.5957	0

8	5	3	7	5	2	0	12684.0704	0
8	6	3	7	6	2	1	12674.4527	0
8	6	3	7	6	2	0	12670.0841	5
8	6	2	7	6	1	1	12674.4527	-6
8	6	2	7	6	1	0	12670.0841	0
8	7	2	7	7	1	1	12666.2419	0
8	7	2	7	7	1	0	12661.9557	4
8	7	1	7	7	0	1	12666.2419	0
8	7	1	7	7	0	0	12661.9557	4
9	0	9	8	0	8	1	13441.7094	3
9	0	9	8	0	8	0	13439.9708	0
9	1	9	8	1	8	1	13404.6581	3
9	1	9	8	1	8	0	13401.9781	-1
9	1	8	8	1	7	1	14292.0372	2
9	1	8	8	1	7	0	14292.6811	-1
9	2	8	8	2	7	1	13994.7929	0
9	2	8	8	2	7	0	13992.3585	-5
9	2	7	8	2	6	1	14731.7169	6
9	2	7	8	2	6	0	14727.3927	-5
9	3	7	8	3	6	1	14278.8697	3
9	3	7	8	3	6	0	14274.6345	-4
9	3	6	8	3	5	1	14546.5076	7
9	3	6	8	3	5	0	14538.3171	-4
9	4	6	8	4	5	1	14313.4349	2
9	4	6	8	4	5	0	14308.1531	-3
9	4	5	8	4	4	1	14340.9673	3
9	4	5	8	4	4	0	14334.9201	-2
9	5	5	8	5	4	1	14287.1862	1
9	5	5	8	5	4	0	14281.9843	1
9	5	4	8	5	3	1	14288.3580	1
9	5	4	8	5	3	0	14283.1114	0
9	6	4	8	6	3	1	14267.7616	0
9	6	4	8	6	3	0	14262.7520	4
9	6	3	8	6	2	1	14267.7838	-4
9	6	3	8	6	2	0	14262.7721	0
9	7	3	8	7	2	1	14256.0499	-6
9	7	3	8	7	2	0	14251.1665	5
9	7	2	8	7	1	1	14256.0499	-6
9	7	2	8	7	1	0	14251.1665	5
9	8	2	8	8	1	1	14248.5464	-11
9	8	2	8	8	1	0	14243.7481	8
9	8	1	8	8	0	1	14248.5464	-11
9	8	1	8	8	0	0	14243.7481	8
10	0	10	9	0	9	1	14883.7325	4
10	0	10	9	0	9	0	14881.4454	-1
10	1	10	9	1	9	1	14861.2823	0
10	1	10	9	1	9	0	14858.3306	0
10	1	9	9	1	8	1	15742.4882	-2

10	1	9	9	1	8	0	15743.8832	-5
10	2	9	9	2	8	1	15495.3124	1
10	2	9	9	2	8	0	15492.9883	-6
10	2	8	9	2	7	1	16338.7726	6
10	2	8	9	2	7	0	16335.4027	-5
10	3	8	9	3	7	1	15849.5351	2
10	3	8	9	3	7	0	15845.2796	-6
10	3	7	9	3	6	1	16249.7264	9
10	3	7	9	3	6	0	16240.4956	-5
10	4	7	9	4	6	1	15918.8357	3
10	4	7	9	4	6	0	15912.9854	-4
10	4	6	9	4	5	1	15976.1340	5
10	4	6	9	4	5	0	15968.7397	-3
10	5	6	9	5	5	1	15890.3964	1
10	5	6	9	5	5	0	15884.4715	-1
10	5	5	9	5	4	1	15893.6265	1
10	5	5	9	5	4	0	15887.5798	-1
10	6	5	9	6	4	1	15864.2736	0
10	6	5	9	6	4	0	15858.5901	3
10	6	4	9	6	3	1	15864.3673	-2
10	6	4	9	6	3	0	15858.6800	2
10	7	4	9	7	3	1	15848.1861	-4
10	7	4	9	7	3	0	15842.6744	7
10	7	3	9	7	2	1	15848.1861	-5
10	7	3	9	7	2	0	15842.6744	5
10	8	3	9	8	2	1	15837.8838	-9
10	8	3	9	8	2	0	15832.4849	9
10	8	2	9	8	1	1	15837.8838	-9
10	8	2	9	8	1	0	15832.4849	9
10	9	2	9	9	1	1	15830.8788	-15
10	9	2	9	9	1	0	15825.5609	12
10	9	1	9	9	0	1	15830.8788	-15
10	9	1	9	9	0	0	15825.5609	12
4	4	1	3	3	0	1	13317.9643	-4
4	4	1	3	3	0	0	13379.7952	-4
4	4	0	3	3	1	1	13318.7498	0
4	4	0	3	3	1	0	13380.5633	-2
5	4	2	4	3	1	1	14896.7929	1
5	4	2	4	3	1	0	14958.1537	-2
5	4	1	4	3	2	1	14902.3095	-1
5	4	1	4	3	2	0	14963.5616	-2
5	5	1	4	4	0	1	16897.5374	-1
5	5	0	4	4	1	1	16897.5838	6
7	1	7	6	0	6	1	10714.2785	0
7	1	7	6	0	6	0	10717.5026	4
8	1	8	7	0	7	1	12092.5646	0
8	1	8	7	0	7	0	12094.1319	2
6	0	6	5	1	5	1	8769.5617	4

6	0	6	5	1	5	0	8762.0486	-5
7	0	7	6	1	6	1	10329.9028	2
7	0	7	6	1	6	0	10323.6495	-4
8	0	8	7	1	7	1	11854.4013	2
8	0	8	7	1	7	0	11849.1784	-5
5	3	3	4	2	2	1	12790.9901	-2
5	3	3	4	2	2	0	12835.1408	14
5	3	2	4	2	3	1	12989.4936	0

Table S7. Experimental transitions frequencies of the D_2O species.

$J'_{Ka'\ Kc'}$			$J''_{Ka''Kc''}$			v	$V_{obs.}$/MHz	Δv/kHz
4	0	4	3	0	3	1	5961.5849	3
4	0	4	3	0	3	0	5961.7707	-3
4	1	4	3	1	3	1	5803.5595	2
4	1	4	3	1	3	0	5803.9710	3
4	1	3	3	1	2	1	6278.0286	5
4	1	3	3	1	2	0	6278.3424	0
5	0	5	4	0	4	1	7388.3356	2
5	0	5	4	0	4	0	7388.4770	-3
5	1	5	4	1	4	1	7238.3947	-3
5	1	5	4	1	4	0	7238.8791	0
5	1	4	4	1	3	1	7823.8535	2
5	1	4	4	1	3	0	7824.1794	-1
6	0	6	5	0	5	1	8790.8734	2
6	0	6	5	0	5	0	8791.0001	-2
6	1	6	5	1	5	1	8665.1645	-2
6	1	6	5	1	5	0	8665.7108	0
6	1	5	5	1	4	1	9350.8328	3
6	1	5	5	1	4	0	9351.1092	-1
6	2	5	5	2	4	1	9045.8253	1
6	2	5	5	2	4	0	9046.3335	-2
6	2	4	5	2	3	1	9346.7404	-3
6	2	4	5	2	3	0	9347.7435	1
7	0	7	6	0	6	1	10179.4235	1
7	0	7	6	0	6	0	10179.6036	-1
7	1	7	6	1	6	1	10084.3592	-3
7	1	7	6	1	6	0	10084.9666	0
7	1	6	6	1	5	1	10852.8336	2
7	1	6	6	1	5	0	10852.9838	-2
7	2	6	6	2	5	1	10527.7123	1
7	2	6	6	2	5	0	10528.2465	-1
7	2	5	6	2	4	1	10953.3379	-1
7	2	5	6	2	4	0	10954.4007	2
7	3	5	6	3	4	1	10663.1703	0
7	3	5	6	3	4	0	10663.9642	0
7	3	4	6	3	3	1	10730.9600	0
7	3	4	6	3	3	0	10732.0762	0
8	0	8	7	0	7	1	11563.3381	0
8	0	8	7	0	7	0	11563.6340	-1
8	1	8	7	1	7	1	11497.0132	-2
8	1	8	7	1	7	0	11497.6830	0
8	1	7	7	1	6	1	12324.2158	3
8	1	7	7	1	6	0	12324.1565	-6
8	2	7	7	2	6	1	11998.6299	1
8	2	7	7	2	6	0	11999.1716	1
8	2	6	7	2	5	1	12550.4449	0

8	2	6	7	2	5	0	12551.4614	0
8	3	6	7	3	5	1	12188.1067	0
8	3	6	7	3	5	0	12188.9732	1
8	3	5	7	3	4	1	12316.4539	1
8	3	5	7	3	4	0	12317.8883	-1
9	0	9	8	0	8	1	12948.0117	-1
9	0	9	8	0	8	0	12948.4589	1
9	1	9	8	1	8	1	12904.4183	-3
9	1	9	8	1	8	0	12905.1619	3
9	1	8	8	1	7	1	13762.1972	2
9	1	8	8	1	7	0	13761.8973	-2
9	2	8	8	2	7	1	13457.9854	-2
9	2	8	8	2	7	0	13458.5146	-1
9	2	7	8	2	6	1	14129.1960	-1
9	2	7	8	2	6	0	14130.0725	1
9	3	7	8	3	6	1	13707.8212	-1
9	3	7	8	3	6	0	13708.7271	1
9	3	6	8	3	5	1	13924.5240	-2
9	3	6	8	3	5	0	13926.2934	2
10	0	10	9	0	9	1	14335.3191	-2
10	0	10	9	0	9	0	14335.9282	2
10	1	10	9	1	9	1	14307.8834	-4
10	1	10	9	1	9	0	14308.7104	5
10	1	9	9	1	8	1	15169.4553	4
10	1	9	9	1	8	0	15168.9424	-1
10	2	9	9	2	8	1	14905.7547	-1
10	2	9	9	2	8	0	14906.2610	0
10	2	8	9	2	7	1	15683.3688	0
10	2	8	9	2	7	0	15684.0117	1
4	4	1	3	3	0	1	13196.5820	0
4	4	1	3	3	0	0	13177.1181	-2
4	4	0	3	3	1	1	13197.1830	-2
4	4	0	3	3	1	0	13177.7291	2
5	4	2	4	3	1	1	14712.5079	-1
5	4	2	4	3	1	0	14693.1490	2
5	4	1	4	3	2	1	14716.7688	1
5	4	1	4	3	2	0	14697.4273	-1
7	1	7	6	0	6	1	10356.9239	4
7	1	7	6	0	6	0	10355.8145	-2
8	1	8	7	0	7	1	11674.5152	3
8	1	8	7	0	7	0	11673.8945	0

Table S8. Experimental transitions frequencies of the HDO species.

$J'_{K_a' K_c'}$			$J''_{K_a'' K_c''}$			v	$V_{obs.}$/MHz	Δv/kHz
4	0	4	3	0	3	1	6076.8598	2
4	0	4	3	0	3	1	5916.5924	2
4	1	4	3	1	3	1	6407.9416	1
4	1	3	3	1	2	1	6176.2569	-6
4	2	3	3	2	2	1	6284.4582	-3
4	2	2	3	2	1	1	7528.3294	-1
5	0	5	4	0	4	1	7378.5185	3
5	1	5	4	1	4	1	7984.0777	1
5	1	4	4	1	3	1	7706.1580	-8
5	2	4	4	2	3	1	7908.9339	16
5	2	3	4	2	2	1	7764.0196	-6
5	3	3	4	3	2	1	7777.5190	2
5	3	2	4	3	1	1	8955.2298	1
6	0	6	5	0	5	1	8831.9105	2
6	1	6	5	1	5	1	9539.5460	1
6	1	5	5	1	4	1	9226.8485	-10
6	2	5	5	2	4	1	9548.1007	6
6	2	4	5	2	3	1	9323.4408	-11
6	3	4	5	3	3	1	9358.6591	0
6	3	3	5	3	2	1	9315.9502	1
6	4	3	5	4	2	1	9317.0640	5
6	4	2	5	4	1	1	10368.8110	6
7	0	7	6	0	6	1	10277.3954	3
7	1	7	6	1	6	1	11067.6826	2
7	1	6	6	1	5	1	10736.8444	-13
7	2	6	6	2	5	1	11188.2003	4
7	2	5	6	2	4	1	10882.2201	-18
7	3	5	6	3	4	1	10958.5268	1
7	3	4	6	3	3	1	10879.0996	2
7	4	4	6	4	3	1	10882.7706	0
7	4	3	6	4	2	1	11778.6687	1
8	0	8	7	0	7	1	11716.1535	3
8	1	8	7	1	7	1	12562.6555	2
8	1	7	7	1	6	1	12235.0966	-13
8	2	7	7	2	6	1	12816.5520	12
8	2	6	7	2	5	1	12437.7716	-29
8	3	6	7	3	5	1	12581.4390	5
8	3	5	7	3	4	1	12446.0069	5
8	4	5	7	4	4	1	12455.9326	-2
8	4	4	7	4	3	1	13189.9087	-1
9	0	9	8	0	8	1	13149.6092	0
9	1	9	8	1	8	1	14022.3016	-2
9	1	8	8	1	7	1	13721.0454	-4
9	2	8	8	2	7	1	13987.3176	13
9	3	7	8	3	6	1	14227.9398	12

9	3	6	8	3	5	1	14016.0616	10
9	4	6	8	4	5	1	14039.2944	-3
9	4	5	8	4	4	1	14604.0587	0
10	0	10	9	0	9	1	14579.1630	-8
10	1	10	9	1	9	1	15450.7774	-22
10	1	9	9	1	8	1	15194.7866	-9
10	2	9	9	2	8	1	15892.0180	14
10	3	7	9	3	6	1	15588.0134	20
10	4	7	9	4	6	1	15636.5516	-1
10	4	6	9	4	5	1	14800.1773	4
5	4	2	4	3	1	1	10531.5073	1
7	1	7	6	0	6	1	11878.8546	3
8	1	8	7	0	7	1	8577.7933	7
6	0	6	5	1	5	1	10114.6984	-5
7	0	7	6	1	6	1	11615.9668	1
8	0	8	7	1	7	1	6076.4140	-3
4	0	4	3	0	3	0	5915.7692	0
4	1	4	3	1	3	0	6407.0394	-2
4	1	3	3	1	2	0	6175.2955	-1
4	2	3	3	2	2	0	6282.9775	4
4	2	2	3	2	1	0	7527.9798	5
5	0	5	4	0	4	0	7377.5500	-1
5	1	5	4	1	4	0	7983.0967	-4
5	1	4	4	1	3	0	7705.0140	-1
5	2	4	4	2	3	0	7906.9330	4
5	2	3	4	2	2	0	7762.5617	5
5	3	3	4	3	2	0	7775.9300	6
5	3	2	4	3	1	0	8954.9093	7
6	0	6	5	0	5	0	8830.8140	-3
6	1	6	5	1	5	0	9538.6139	-3
6	1	5	5	1	4	0	9225.5433	1
6	2	5	5	2	4	0	9545.6832	2
6	2	4	5	2	3	0	9321.6679	-1
6	3	4	5	3	3	0	9356.5519	4
6	3	3	5	3	2	0	9314.0836	8
6	4	3	5	4	2	0	9315.1801	9
6	4	2	5	4	1	0	10368.3760	8
7	0	7	6	0	6	0	10276.1706	-2
7	1	7	6	1	6	0	11066.9621	-2
7	1	6	6	1	5	0	10735.4248	8
7	2	6	6	2	5	0	11185.5762	1
7	2	5	6	2	4	0	10880.1511	1
7	3	5	6	3	4	0	10955.7642	3
7	3	4	6	3	3	0	10876.8371	7
7	4	4	6	4	3	0	10880.4554	7
7	4	3	6	4	2	0	10862.1324	6
7	5	3	6	5	2	0	10862.2034	-19

7	5	2	6	5	1	0	10853.5680	6
7	6	2	6	6	1	0	10853.5680	0
7	6	1	6	6	0	0	11777.9864	-1
8	0	8	7	0	7	0	11714.7863	-3
8	1	8	7	1	7	0	12562.2743	-1
8	1	7	7	1	6	0	12233.5792	0
8	2	7	7	2	6	0	12813.9265	0
8	2	6	7	2	5	0	12435.4402	-3
8	3	6	7	3	5	0	12577.9042	-1
8	3	5	7	3	4	0	12443.3258	6
8	4	5	7	4	4	0	12453.1164	7
8	4	4	7	4	3	0	12423.2101	7
8	5	4	7	5	3	0	12423.4947	-33
8	5	3	7	5	2	0	12410.4945	3
8	6	3	7	6	2	0	12410.4945	-3
8	6	2	7	6	1	0	13188.9118	-6
9	0	9	8	0	8	0	13148.0767	3
9	1	9	8	1	8	0	14022.3016	3
9	1	8	8	1	7	0	13719.4530	-8
9	2	8	8	2	7	0	14421.6957	1
9	2	7	8	2	6	0	13984.7700	-11
9	3	7	8	3	6	0	14223.6120	-6
9	3	6	8	3	5	0	14012.9506	1
9	4	6	8	4	5	0	14035.8728	12
9	4	5	8	4	4	0	13987.9350	5
9	5	5	8	5	4	0	13988.8545	-53
9	5	4	8	5	3	0	13970.0200	-2
9	6	4	8	6	3	0	13970.0377	4
9	6	3	8	6	2	0	14602.7121	5
10	0	10	9	0	9	0	14577.4323	7
10	1	10	9	1	9	0	15451.0615	9
10	1	9	9	1	8	0	15193.1191	-5
10	2	9	9	2	8	0	16002.4653	4
10	2	8	9	2	7	0	15525.4945	-20
10	3	8	9	3	7	0	15887.0587	-12
10	3	7	9	3	6	0	15584.4799	-4
10	4	7	9	4	6	0	15632.3940	46
10	4	6	9	4	5	0	13287.8059	5
4	4	1	3	3	0	0	13288.4877	-2
4	4	0	3	3	1	0	14834.2122	1
5	4	2	4	3	1	0	14839.0026	-2
5	4	1	4	3	2	0	10533.3810	1
7	1	7	6	0	6	0	11879.7972	-5
8	1	8	7	0	7	0	8573.5978	2
6	0	6	5	1	5	0	10111.1633	-6
7	0	7	6	1	6	0	11612.9802	-2
8	0	8	7	1	7	0	11228.8935	-1

4	3	2	3	2	1	0	12708.4779	1
5	3	3	4	2	2	0	12889.9055	3
5	3	2	4	2	3	0	6076.8598	2

Table S9. Experimental transitions frequencies of the ^{18}O species.

$J'_{Ka'\,Kc'}$			$J''_{Ka''Kc''}$			v	$V_{obs.}$/MHz	Δv/kHz
6	0	6	5	0	5	1	8845.5173	0
6	0	6	5	0	5	0	8844.9822	1
6	1	6	5	1	5	1	8723.0684	1
6	1	6	5	1	5	0	8721.1523	-1
6	1	5	5	1	4	1	9432.8225	1
6	1	5	5	1	4	0	9431.0375	2
6	2	5	5	2	4	1	9119.5744	0
6	2	5	5	2	4	0	9117.2797	0
6	2	4	5	2	3	1	9443.9255	1
6	2	4	5	2	3	0	9439.3882	0
6	3	4	5	3	3	1	9217.2319	1
6	3	4	5	3	3	0	9214.0928	0
6	3	3	5	3	2	1	9253.1901	0
6	3	3	5	3	2	0	9249.3761	1
6	4	3	5	4	2	1	9209.7338	-2
6	4	3	5	4	2	0	9206.5402	2
6	4	2	5	4	1	1	9210.8823	-1
6	4	2	5	4	1	0	9207.6542	2
7	0	7	6	0	6	1	10240.5933	0
7	0	7	6	0	6	0	10239.9186	0
7	1	7	6	1	6	1	10150.1782	0
7	1	7	6	1	6	0	10148.0922	0
7	1	6	6	1	5	1	10942.2488	1
7	1	6	6	1	5	0	10940.9310	0
7	2	6	6	2	5	1	10611.3398	0
7	2	6	6	2	5	0	10608.9315	0
7	2	5	6	2	4	1	11066.4475	1
7	2	5	6	2	4	0	11061.5396	-2
7	3	5	6	3	4	1	10758.2303	0
7	3	5	6	3	4	0	10754.6437	0
7	3	4	6	3	3	1	10836.0884	1
7	3	4	6	3	3	0	10831.0957	0
7	4	4	6	4	3	1	10755.2760	0
7	4	4	6	4	3	0	10751.4578	2
7	4	3	6	4	2	1	10759.0588	-1
7	4	3	6	4	2	0	10755.1320	0
7	5	3	6	5	2	1	10740.4027	-2
7	5	3	6	5	2	0	10736.7094	2
7	5	2	6	5	1	1	10740.4787	-3
7	5	2	6	5	1	0	10736.7832	2
7	6	2	6	6	1	1	10731.7552	-6
7	6	2	6	6	1	0	10728.1557	4
8	0	8	7	0	7	1	11632.1291	1
8	0	8	7	0	7	0	11631.0955	1
8	1	8	7	1	7	1	11570.5406	1

8	1	8	7	1	7	0	11568.2759	0
8	1	7	7	1	6	1	12418.0887	1
8	1	7	7	1	6	0	12417.5686	0
8	2	7	7	2	6	1	12091.2156	0
8	2	7	7	2	6	0	12088.7862	-2
8	2	6	7	2	5	1	12676.7915	2
8	2	6	7	2	5	0	12671.9353	-1
8	3	6	7	3	5	1	12295.8788	0
8	3	6	7	3	5	0	12291.9537	0
8	3	5	7	3	4	1	12442.3045	1
8	3	5	7	3	4	0	12435.9123	-1
8	4	5	7	4	4	1	12304.5863	0
8	4	5	7	4	4	0	12300.1329	0
8	4	4	7	4	3	1	12314.8149	0
8	4	4	7	4	3	0	12310.0733	1
9	0	9	8	0	8	1	13025.1518	1
9	0	9	8	0	8	0	13023.6412	0
9	1	9	8	1	8	1	12985.5978	1
9	1	9	8	1	8	0	12983.1294	-1
9	1	8	8	1	7	1	13858.3178	1
9	1	8	8	1	7	0	13858.7550	-1
9	2	8	8	2	7	1	13558.6675	-1
9	2	8	8	2	7	0	13556.2980	-2
9	2	7	8	2	6	1	14265.9378	2
9	2	7	8	2	6	0	14261.5224	-2
4	4	1	3	3	0	1	13148.1522	0
4	4	0	3	3	1	1	13148.8524	-1
5	4	2	4	3	1	1	14677.0581	0
5	4	2	4	3	1	0	14736.8051	-1
5	4	1	4	3	2	1	14682.0066	3
5	4	1	4	3	2	0	14741.6528	0
7	1	7	6	0	6	1	10400.0217	-2
7	1	7	6	0	6	0	10403.4865	1
8	1	8	7	0	7	1	11729.9701	0
8	1	8	7	0	7	0	11731.8450	2
6	0	6	5	1	5	1	8473.2219	0
6	0	6	5	1	5	0	8465.7565	-4
7	0	7	6	1	6	1	9990.7473	0
7	0	7	6	1	6	0	9984.5192	-6
8	0	8	7	1	7	1	11472.6980	0
5	3	3	4	2	2	1	12569.5319	-1
5	3	2	4	2	3	1	12754.3169	-1

Table S10. Experimental transitions frequencies of the ^{34}S species.

$J'_{Ka'\,Kc'}$			$J''_{Ka''Kc''}$			ν	$V_{obs.}$/MHz (S3)	Δv/kHz	$V_{obs.}$/MHz (S2)	Δv/kHz
6	0	6	5	0	5	1	9096.1946	0	9059.3520	0
6	1	6	5	1	5	1	8978.5114	1	8942.8437	-1
6	1	5	5	1	4	1	9720.7636	2	9688.3697	2
6	2	5	5	2	4	1	9396.8550	-3	9363.6766	-3
7	0	7	6	0	6	1	10529.9153	1	10486.6841	0
7	1	7	6	1	6	1	10445.7902	1	10403.8543	0
7	1	6	6	1	5	1	11268.9860	1	11229.7733	0
7	2	6	6	2	5	1	10931.3416	-3	10892.1132	-3
7	2	5	6	2	4	1	11427.2192	-1	11393.4776	1
8	0	8	7	0	7	1	11961.5658	0	11912.1978	0
8	1	8	7	1	7	1	11906.0763	1	11857.8562	2
8	1	7	7	1	6	1	12779.5197	-5	12732.9086	0
8	2	7	7	2	6	1	12452.6367	-3	12407.1729	-2
8	2	6	7	2	5	1	13084.3110	3	13044.7715	1
9	0	9	8	0	8	1		-	13340.1883	1
-9	1	9	8	1	8	1		-	13306.5252	1

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