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

Fingerprints of Inter- and Intra-molecular Hydrogen Bonding in Saligenin-Water Clusters Revealed by Mid- and Far-Infrared Spectroscopy

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Scaling factors

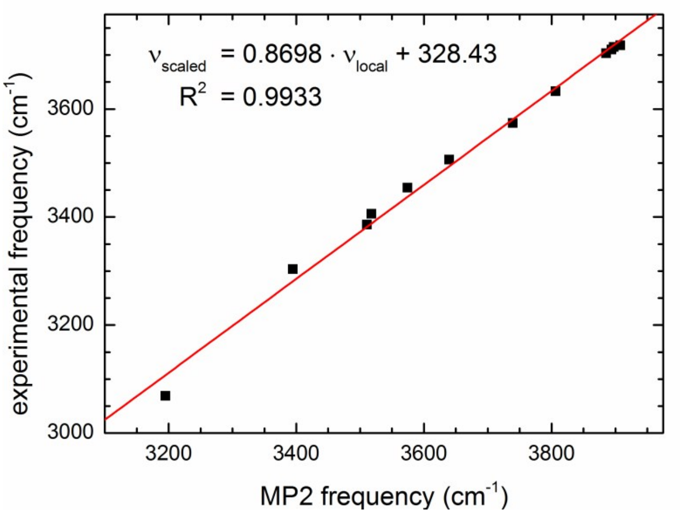

Figure SI.1. Infrared (IR) frequencies absorbed by the benzene-$(H_2O)_6$ cluster versus the calculated frequencies at the MP2/6-311++G(2d, p) level of theory based on the "book" isomer[1]. The linear fit to the data in red represents the two-parameter scaling function used for all MP2 calculations reported throughout this work. The experimental frequencies were originally measured by Pribble and Zwier[2] and later reproduced at higher resolution by Zwier and co-workers.

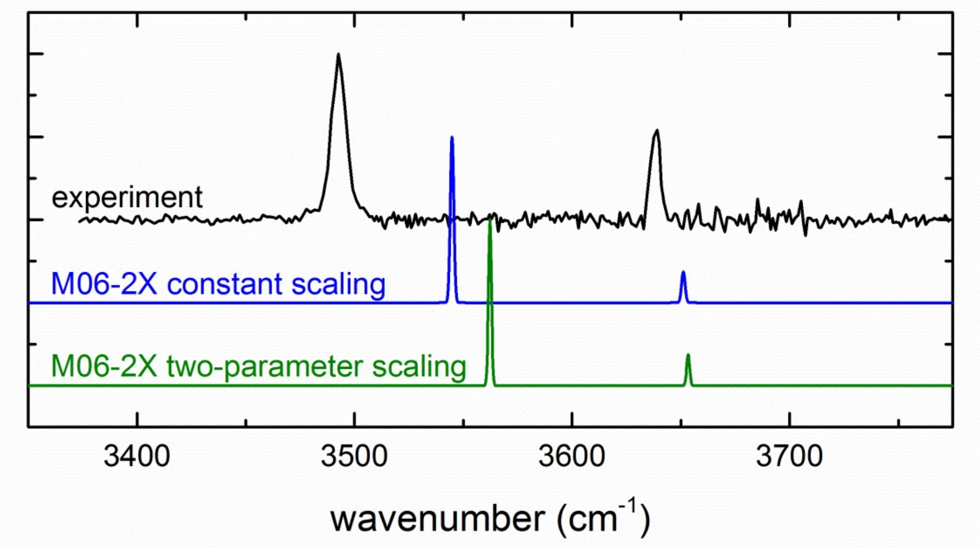

Figure SI.2. Mid-IR spectrum of bare SLG. M06-2X/6-311++G(2d, p) calculations with a constant scaling factor (0.9426) and with a two-parameter scaling function are displayed in blue and green, respectively. The two-parameter scaling function is based on the benzene-$(H_2O)_6$ cluster[1, 3]: 0.8073 ν_{local} + 526.24 in cm^{-1}. The red-shift of both OH stretch frequencies is underestimated by the constant scaled spectrum, yet more so by the two-parameter scaled spectrum, which shows that the M06-2X two-parameter scaling does not transfer from benzene to SLG, as it does for the MP2 method.

REMPI spectra

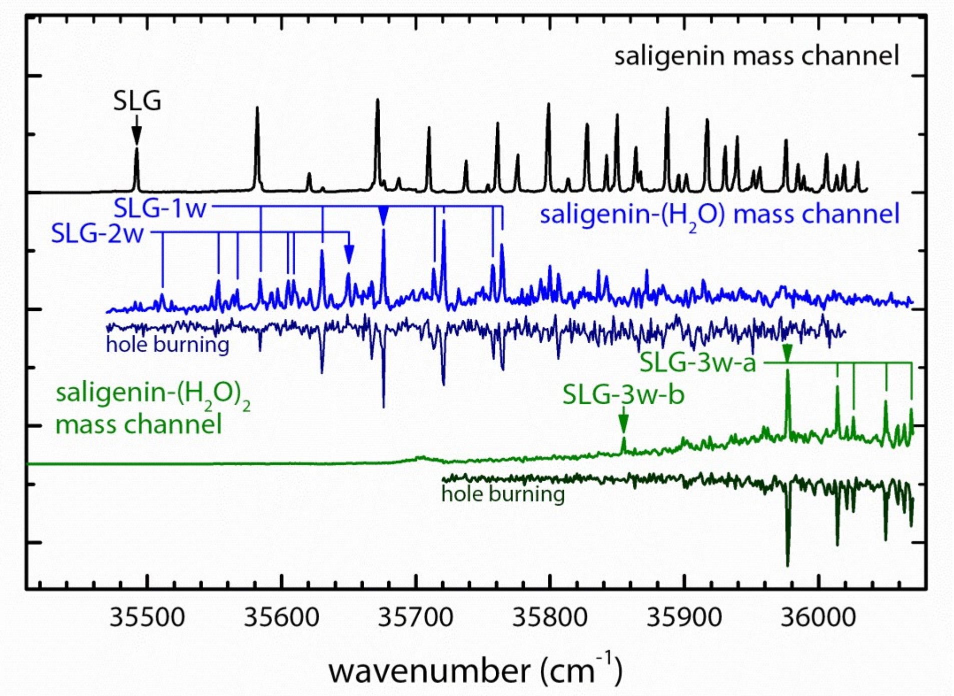

Figure SI.3. REMPI spectra for saligenin water clusters recorded in the mass channels of bare saligenin (m/z = 124 amu/e, black), saligenin-(H_2O) (m/z = 142 amu/e, blue) and saligenin-$(H_2O)_2$ (m/z = 160 amu/e, green). The features used to record the IR-UV ion-dip spectroscopy are indicated using arrows. The peaks in the saligenin-(H_2O) and saligenin-$(H_2O)_2$ mass channels were assigned to different clusters using IR-UV hole burning spectroscopy. In dark blue, the hole burning spectrum with IR frequency 3512 cm^{-1} of SLG-1w is displayed, subtracted from the REMPI spectrum of the complete ensemble to show only the reduced features. The dark green hole burning spectrum is recorded using an IR frequency of SLG-3w-a at 3501 cm^{-1}.

Assignment of saligenin water cluster structures

The structural assignments are primarily based on the comparison of the experimental mid-IR spectra with ab initio quantum chemical calculations, with support provided by the far-IR spectra. Mid-IR spectroscopy has been applied successfully to elucidate the structural preferences of similar systems such as phenol water[4-5], benzyl-alcohol water[6] and propofol water[7-8]. The isomers presented here were generated using simulated annealing molecular dynamics calculations. The level of theory applied to calculate the mid-IR spectra and optimized structures is MP2/6-311++G(2d,p)[9], using the local mode approach, which has been applied previously to successfully identify complex benzene water clusters by Tabor et al.[1].

Saligenin water 1

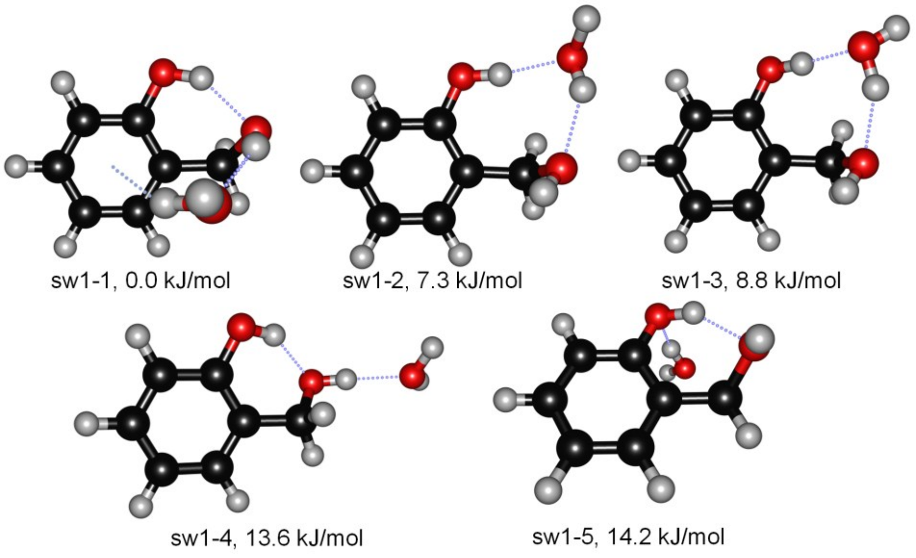

Figure SI.4. Structures and stabilization energies of the lowest energy isomers of the saligenin-(H_2O) cluster, calculated on the MP2/6-311++G(2d, p) level of theory. The assigned structure is sw1-1, the lowest energy isomer, which is similar to the structure of the benzyl alcohol-(H_2O) cluster[6].

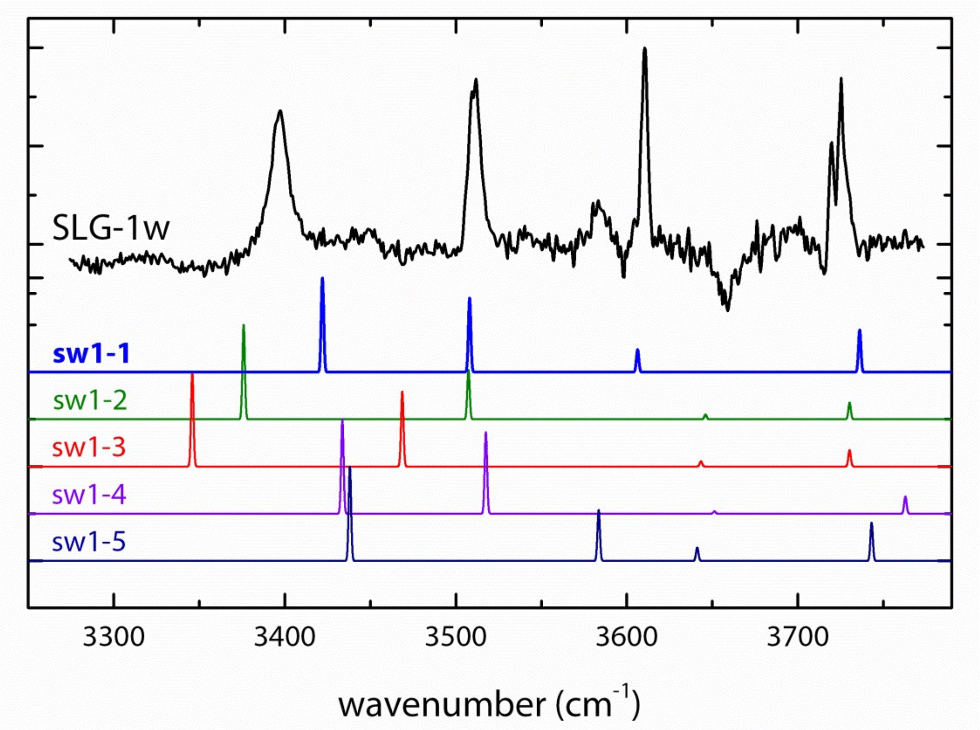

Figure SI.5. Mid-infrared spectrum of the SLG-1w cluster, alongside anharmonic calculations performed on the MP2/6-311++G(2d,p) level of theory, using the local mode approach. The assigned structure is the lowest energy isomer sw1-1, which matches best both for the positions and intensities of the experimental features.

Saligenin water 2

Seven low-energy isomers (< 12 kJ/mol) were found in the conformational search for SLG-2w (Figure SI.6). The measured SLG-2w spectrum (Figure SI.7) matches well with the IR spectra of three different isomers, namely sw2-1 (water wire), sw2-5 (water cycle) and sw2-7 (water cycle). Sw2-1 is the most stable isomer, being 6.3 and 10.2 kJ/mol more favorable than the two other conformers. On the blue side of the mid-IR spectrum (free and loosely bound OHs), sw2-1 and sw2-5 provide a significantly better match than sw2-7. As this region is the most easy to determine quantum chemically, being the least influenced by interactions and anharmonicities, it is the most reliable part of the spectrum. In the far-IR regime, displayed for these isomers at the M06-2X/6-311++G(2d, p) level of theory in Figure SI.8, the wire isomer fits better, especially in the 600-800 cm^{-1} region and around 300 cm^{-1}.

In the REMPI spectrum (Figure SI.3), it is observed that the origin transition of SLG-1w is shifted by 92 cm^{-1} with respect to the origin transition of bare SLG, while the origin of SLG-2w is positioned closer to the bare SLG origin with a shift of only 19 cm^{-1}. This behavior can be linked to the formation of a cyclic water network, e.g. in the case of propofol-water clusters[7]. This interpretation would support the assignment of a water cycle isomer. However, this pattern of UV wavelength shifts was observed for benzyl-alcohol water clusters[6], where the water-wire isomer was convincingly assigned for the benzyl alcohol-$(H_2O)_2$ cluster. Moreover, the conformation of the SLG molecule within the sw2-3 isomer is quite different from the bare SLG molecule, so that shifts of the UV transitions cannot be interpreted in terms of the assignments without further work, such as transition state calculations. Therefore, the structure sw2-1 is assigned to be present based on the energetics, UV behavior and structurally diagnostic IR spetra.

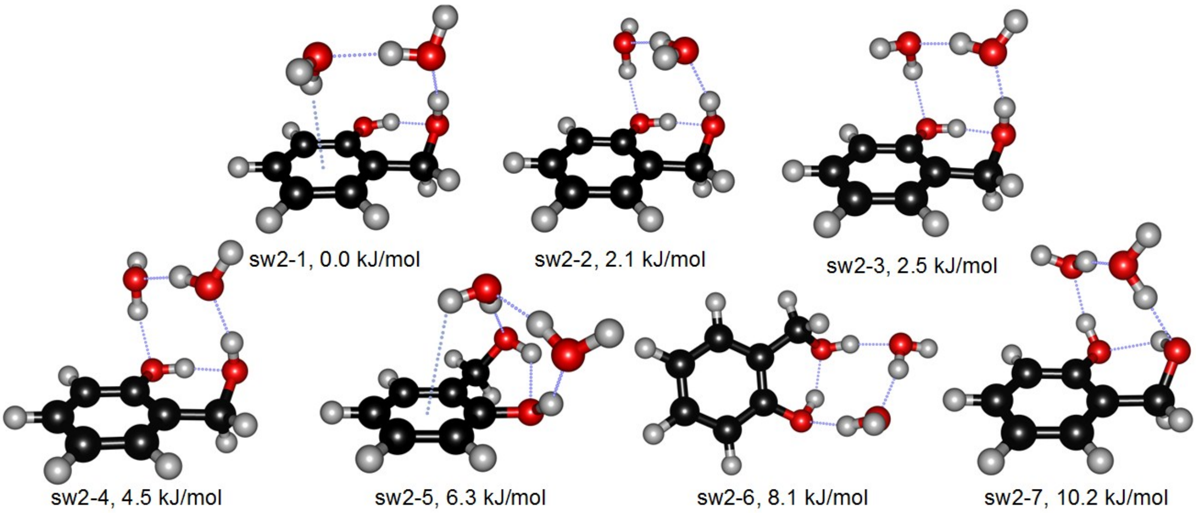
sw2-1, 0.0 kJ/mol
sw2-2, 2.1 kJ/mol
sw2-3, 2.5 kJ/mol
sw2-4, 4.5 kJ/mol
sw2-5, 6.3 kJ/mol
sw2-6, 8.1 kJ/mol
sw2-7, 10.2 kJ/mol

Figure SI.6. Structures and stabilization energies of the lowest energy isomers of the saligenin-$(H_2O)_2$ cluster, calculated on the MP2/6-311++G(2d, p) level of theory. The assigned structure is sw2-1, the lowest energy isomer, which is similar to the structure of the benzyl alcohol-$(H_2O)_2$ cluster[6].

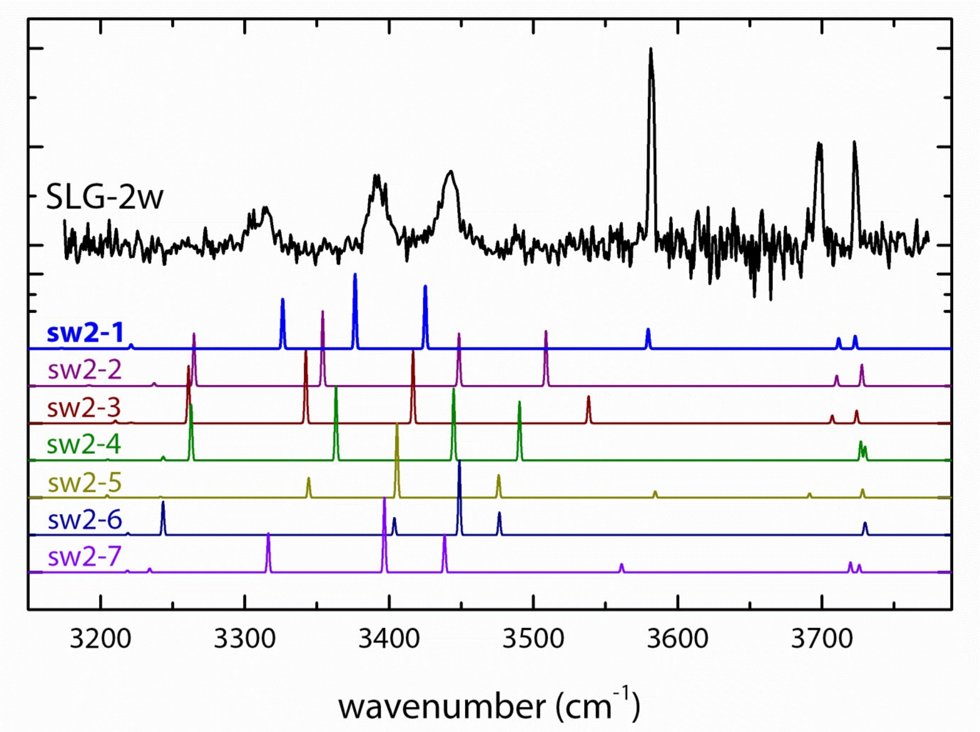

Figure SI.7. Experimental mid-IR spectrum of the SLG-2w cluster and anharmonic calculations performed on the MP2/6-311++G(2d,p) level of theory using the local mode approach. The assignment cannot be performed based on the mid-IR, with isomers sw2-1, sw2-5 and sw2-7 all matching well to the experimental spectrum.

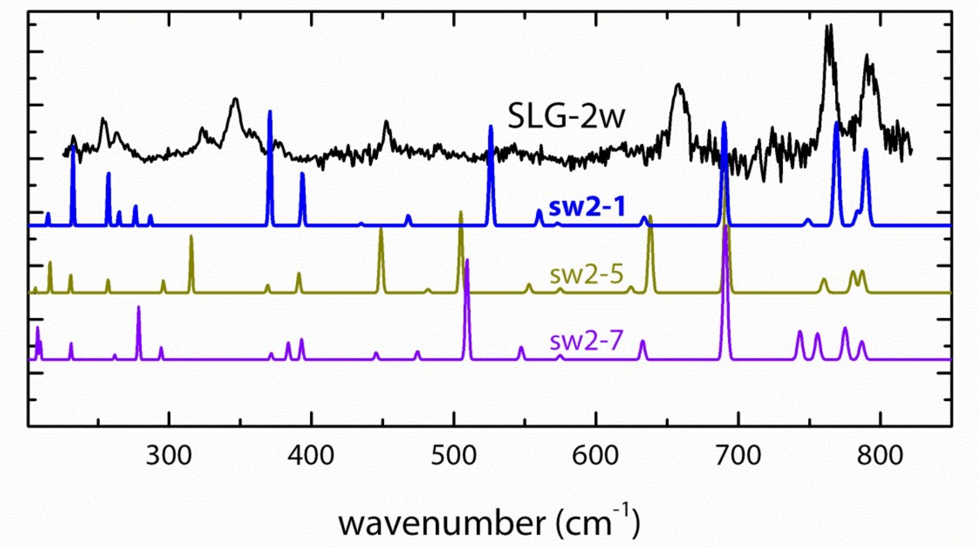

Figure SI.8. Experimental far-infrared spectrum of the SLG-2w cluster, with the calculated spectra of isomers sw2-1, sw2-5 and sw2-7 on the harmonic M06-2X/6-311++G(2d,p) level of theory. The spectrum of the sw2-1 isomer reproduces the experimental spectrum especially well in the region from 600 to 800 cm^{-1}, as well as below 300 cm^{-1}. Based on these characteristics, structure sw2-1 is assigned.

Saligenin water 3

For the SLG-3w-a spectrum, the isomer sw3-1 clearly provides the best match, which is also the most stable structure (see Figures SI.9 and SI.10). Therefore, we have assigned the structure sw3-1 to SLG-3w-a. For SLG-3w-b, the isomers sw3-2 and sw3-3 both provide a good match to the spectrum. At the blue side of the spectrum above 3500 cm^{-1}, where the quantum chemical calculations perform optimally, the sw3-2 spectrum matches significantly better to the measured spectrum. Below 3500 cm^{-1}, where the H-bonded OH stretching vibrations are present, the sw3-3 structure fits slightly better, although the spectrum of the sw3-2 geometry also matches well. The sw3-2 spectrum displays a blue-shift below 3500 cm^{-1} with respect to the measurements, consistent with the match of the sw3-1 spectrum to SLG-3w-a. Lastly, the sw3-2 structure is slightly more stable (0.5 kJ/mol difference). Based on this argumentation structure sw3-2 is assigned to the SLG-3w-b spectrum.

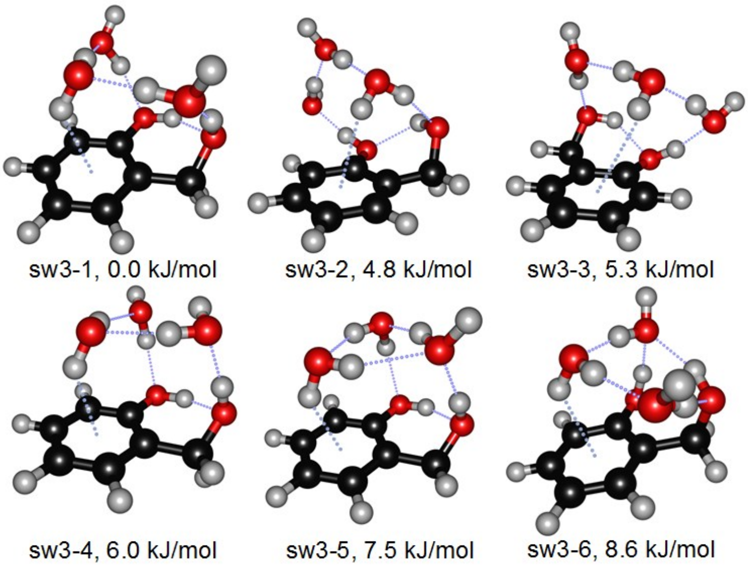

Figure SI.9. Structures and stabilization energies of the lowest energy isomers of the saligenin-(H_2O)$_3$ cluster, calculated on the MP2/6-311++G(2d, p) level of theory. The assigned structures are sw3-1 and sw3-2, for the SLG-3w-a and SLG-3w-b spectra, respectively. The water molecules in both isomers form a 10-membered cycle, similar to the structure of the isolated five water cluster[10].

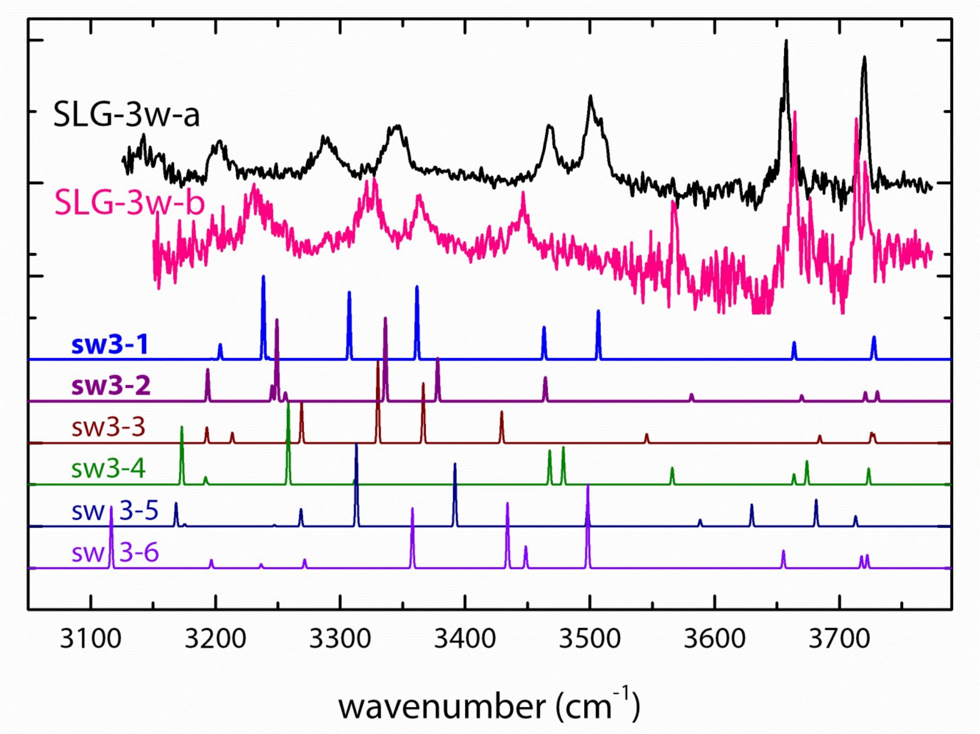

Figure SI.10. Experimental mid-infrared spectra of the two SLG-3w clusters, alongside anharmonic calculations performed on the MP2/6-311++G(2d,p) level of theory using the local mode approach. The SLG-3w-a IR spectrum (black) is assigned to isomer sw3-1, where the water molecules form a 10-membered H-bonded ring together with the two OH groups of SLG. The SLG-3w-b IR spectrum (pink) is assigned to the sw3-2 isomer, a 10-membered ring including five H-bonds as well, for which the H-bond direction around the ring is inverted with respect to sw3-1.

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Atomic coordinates and local mode model Hamiltonian matrices

Table SI.1: Atomic coordinates of the optimized geometry (MP2/6-311++G(2d,p) level of theory) of the saligenin molecule.

Saligenin	N_{atoms} = 17		
C	-0.81452	-1.21900	0.25471
C	0.56629	-1.35408	0.11203
C	1.36043	-0.23390	-0.18608
C	0.74202	1.00732	-0.36237
C	-0.63774	1.14907	-0.22157
C	-1.41153	0.03017	0.09468
H	-1.40181	-2.10119	0.48845
H	1.35728	1.87154	-0.60147
H	-1.10377	2.11917	-0.35709
H	-2.48695	0.12594	0.20638
C	2.85186	-0.38668	-0.25894
O	3.25017	-1.49151	-1.09849
H	3.31710	0.54341	-0.59845
H	3.26288	-0.63396	0.72280
H	2.91958	-1.31106	-1.98962
O	1.11433	-2.59320	0.29413
H	1.99195	-2.58992	-0.13178

Table SI.2: Local mode hamiltonian matrix of saligenin: local mode frequencies are on the diagonal, couplings off-diagonal.

Saligenin - Model Hamiltonian matrix	
3640.8	-5.6000
-5.6000	3503.9

Table SI.3: Atomic coordinates of the optimized geometry (MP2/6-311++G(2d,p) level of theory) of the sw1-1 cluster.

Saligenin-(H_2O)	N_{atoms} = 20		
C	-1.67879	0.95109	0.70364
C	-0.41481	1.00991	0.11380
C	0.04287	-0.05158	-0.68733
C	-0.77735	-1.17149	-0.85871
C	-2.04107	-1.23725	-0.26949
C	-2.48980	-0.16577	0.50669
C	1.39341	0.05061	-1.34467
O	2.40435	0.49936	-0.42795
O	0.34789	2.11943	0.32789
H	-2.00607	1.78706	1.31371
H	-0.41662	-1.99629	-1.46906
H	-2.66740	-2.11075	-0.41660
H	-3.47034	-0.20256	0.97091
H	1.67092	-0.91065	-1.78861
H	1.37288	0.80036	-2.13991
H	2.43130	-0.16420	0.28728
H	1.27378	1.87003	0.12458
O	1.69797	-1.57612	1.38857
H	1.79899	-1.69005	2.34080
H	0.74598	-1.47727	1.23844

Table SI.4: Local mode Hamiltonian matrix of structure sw1-1: local mode frequencies are on the diagonal, couplings off-diagonal.

Saligenin-(H_2O) - Model Hamiltonian matrix				
3506.5	-16.360	-6.9300	-11.610	0
-16.360	3425.4	-0.3700	-3.3500	0
-6.9300	-0.3700	3699.4	-61.240	45.250
-11.610	-3.3500	-61.240	3632.4	45.250
0	0	45.250	45.250	3146.7

Table SI.5: Atomic coordinates of the optimized geometry (MP2/6-311++G(2d,p) level of theory) of the sw2-1 cluster.

Saligenin-$(H_2O)_2$	N_{atoms} = 23		
C	1.72377	-0.66083	0.99905
C	0.41335	-0.98096	0.62874
C	-0.04267	-0.69765	-0.67251
C	0.82943	-0.08440	-1.57391
C	2.14158	0.23095	-1.21443
C	2.58728	-0.06684	0.07587
C	-1.43688	-1.10745	-1.07457
O	-2.39928	-0.83605	-0.04956
O	-0.38850	-1.57665	1.55124
H	2.05062	-0.89969	2.00658
H	0.47125	0.14260	-2.57534
H	2.81013	0.69232	-1.93404
H	3.60610	0.16587	0.37026
H	-1.71646	-0.61408	-2.01095
H	-1.47415	-2.18857	-1.23556
H	-2.44925	0.14284	0.03071
H	-1.31182	-1.47173	1.22605
O	0.39465	2.40966	0.85298
H	0.79075	1.54133	1.03448
H	0.92043	2.74327	0.11532
O	-2.19867	1.89486	0.01447
H	-1.30421	2.13180	0.34143
H	-2.80968	2.47871	0.47696

Table SI.6: Local mode Hamiltonian matrix of structure sw2-1: local mode frequencies are on the diagonal, couplings off-diagonal.

Saligenin-$(H_2O)_2$ - Model Hamiltonian matrix

3368.9	-25.130	-6.3200	-1.4500	-30.760	-11.350	0	0
-25.100	3351.5	-3.8200	-0.1400	-6.9800	-0.9600	0	0
-6.3200	-3.8200	3588.0	-49.660	-21.050	-0.0700	45.2500	0
-1.4500	-0.1400	-49.660	3690.2	-12.060	-0.2600	45.2500	0
-30.800	-6.9800	-21.050	-12.060	3405.4	-60.730	0	45.250
-11.400	-0.9600	-0.0700	-0.2600	-60.730	3708.4	0	45.250
0	0	45.250	45.250	0	0	3183.1	0
0	0	0	0	45.250	45.250	0	3241.2

Table SI.7: Atomic coordinates of the optimized geometry (MP2/6-311++G(2d,p) level of theory) of the sw3-1 cluster.

Saligenin-$(H_2O)_3$-a	N_{atoms} = 26		
C	1.12144	-1.63045	-0.24068
C	0.67533	-0.44277	-0.81929
C	0.96544	0.79833	-0.23183
C	1.66991	0.81745	0.97341
C	2.10838	-0.36477	1.57285
C	1.84281	-1.58893	0.95285
C	0.53857	2.06933	-0.92087
O	-0.78665	1.97053	-1.46297
O	-0.07556	-0.51955	-1.96971
H	0.88544	-2.57368	-0.72295
H	1.87187	1.77489	1.44688
H	2.65569	-0.33145	2.50909
H	2.18606	-2.51531	1.40265
H	0.60767	2.91214	-0.22719
H	1.19339	2.27124	-1.77308
H	-1.38800	1.94092	-0.68241
H	-0.49954	0.37099	-2.06722
O	-1.99919	-2.18641	-0.74107
H	-2.84968	-2.32643	-1.17115
H	-1.45709	-1.67998	-1.37512
O	-1.55761	-0.80184	1.68161
H	-0.60960	-0.93032	1.82718
H	-1.75938	-1.35697	0.90160
O	-1.99196	1.77162	0.94314
H	-1.86768	0.84735	1.27015
H	-2.84326	2.06442	1.28467

Table SI.8: Local mode Hamiltonian matrix of structure sw3-1: local mode frequencies are on the diagonal, couplings off-diagonal.

Saligenin-$(H_2O)_3$-a - Model Hamiltonian matrix

3333.6	-31.930	-0.0500	-6.4200	-4.3900	-5.8300	-35.910	-12.180	0	0	0
-31.930	3245.2	1.0100	-22.040	-1.8700	-3.5600	-9.2600	-1.1700	0	0	0
-0.0500	1.0100	3709.7	-60.440	-0.0700	-7.7800	-1.1900	0.1800	45.250	0	0
-6.4200	-22.040	-60.440	3498.2	2.7300	-21.660	-5.1000	-0.0900	45.250	0	0
-4.3900	-1.8700	-0.0700	2.7300	3648.8	-46.680	-19.850	-0.5900	0	45.250	0
-5.8300	-3.5600	-7.7800	-21.660	-46.680	3466.9	-31.480	-0.4900	0	45.250	0
-35.910	-9.2600	-1.1900	-5.1000	-19.850	-31.480	3288.9	-68.720	0	0	45.250
-12.180	-1.1700	0.1800	-0.0900	-0.5900	-0.4900	-68.720	3712.6	0	0	45.250
0	0	45.250	45.250	0	0	0	0	3211.7	0	0
0	0	0	0	45.250	45.250	0	0	0	3258.1	0
0	0	0	0	0	0	45.250	45.250	0	0	3265.1

Table SI.9: Atomic coordinates of the optimized geometry (MP2/6-311++G(2d,p) level of theory) of the sw3-2 cluster.

Saligenin-$(H_2O)_3$-b N_{atoms} = 26

C	-1.3971233	-0.2001388	-0.2423528
C	-0.3204962	-0.6108885	0.54728445
C	-0.0136851	0.06173585	1.74012412
C	-0.8056616	1.14392203	2.12962349
C	-1.8864202	1.56197639	1.34982456
C	-2.173836	0.88708975	0.16172142
C	1.20654688	-0.3605371	2.50914449
O	2.39424643	-0.2664806	1.69781553
O	0.48993615	-1.6571928	0.20363515
H	-1.6124239	-0.726465	-1.1670686
H	-0.5616067	1.6698363	3.04951817
H	-2.4931195	2.40496352	1.663453
H	-3.0073	1.20459735	-0.4571673
H	1.36656505	0.29993524	3.36212415
H	1.09981725	-1.3853043	2.8780372
H	2.28386502	-0.9570114	1.02291416
H	0.3947894	-1.8383354	-0.7660548
O	1.85154281	0.50588322	-2.587643
H	1.86451959	1.17743165	-3.2771628
H	1.8537355	0.9996184	-1.7341561
O	1.82801282	1.81592474	-0.1816023
H	2.15925519	1.214919	0.51685927
H	0.91740576	1.99431658	0.09206978
O	0.38697542	-1.7693952	-2.4710647
H	0.83192126	-2.46754	-2.9639153
H	0.91053806	-0.948861	-2.6319612

Table SI.10: Local mode Hamiltonian matrix of structure sw3-2: local mode frequencies are on the diagonal, couplings off-diagonal.

Saligenin-$(H_2O)_3$-b - Model Hamiltonian matrix

3580.0	-7.2800	-0.1700	-4.2400	-14.280	0.6500	-0.6400	-2.5200	0	0	0
-7.2800	3235.6	-1.3200	-13.100	-4.4000	-1.9800	-16.720	-42.550	0	0	0
-0.1700	-1.3200	3716.8	-63.540	0.0100	-0.3700	-0.4800	-10.500	45.250	0	0
-4.2400	-13.100	-63.540	3325.6	-29.060	-16.070	0.4100	-34.590	45.250	0	0
-14.280	-4.4000	0.0100	-29.060	3453.7	-45.020	-0.0100	-6.6500	0	45.250	0
0.6500	-1.9800	-0.3700	-16.070	-45.020	3656.6	-0.0300	-3.2000	0	45.250	0
-0.6400	-16.720	-0.4800	0.4100	-0.0100	-0.0300	3706.7	-64.330	0	0	45.250
-2.5200	-42.550	-10.500	-34.590	-6.6500	-3.2000	-64.330	3327.5	0	0	45.250
0	0	45.250	45.250	0	0	0	0	3288.5	0	0
0	0	0	0	45.250	45.250	0	0	0	3271.5	0
0	0	0	0	0	0	45.250	45.250	0	0	3262.5