Supporting Information

1. Quasi-Harmonic approximation

A feature of a highly hydrogen bonded system is the existence of low-frequency vibrations with frequencies as low 5-10cm^{-1}. These vibrations are poorly described by the harmonic approximation and the paper also considers the importance of describing these vibrations. A quasi-harmonic approach introduced by Grimme[69] will be used to look at the Rayleigh scattering. The uncertainty within the harmonic approximation originates from the vibrational entropy contribution given as:

$$S_V = R\left[\frac{h\omega}{k_BT\left(e^{\frac{h\omega}{k_BT}} - 1\right)} - \ln\left(1 - e^{-\frac{h\omega}{k_BT}}\right)\right] \tag{S1}$$

where R is the gas constant, h is the Planck constant, ω is the frequency, k_B is the Boltzmann constant and T is the temperature. The last term in equation S1 asymptotically goes towards minus infinity as the frequencies goes to zero, which creates inaccuracies.

To avoid this behavior the quasi-harmonic approach treats all low-frequency vibrations as rotations instead[69]. These low-frequency vibrations are often not a classical vibrational motion but rather a unison pivotal motion of the atoms. Instead of using the vibrational entropy for low-frequency vibrations the entropy contribution will be calculated as follows:

$$S_R = R\left\{\frac{1}{2} + \ln\left[\left(\frac{8\pi^3\mu' kT}{h^2}\right)^{\frac{1}{2}}\right]\right\} \tag{S2}$$

where μ' is the effective moment of inertia, which is calculated from the moment of inertia for a free rotor, μ, and is restricted to a reasonable value by introducing an average molecular moment of inertia, B_{av}, as a limiting value for very small frequencies. A limiting value of B_{av} is set to 10^{-44} kg m^2 for very small frequencies.

$$\mu' = \frac{\mu B_{av}}{\mu + B_{av}} \tag{S3}$$

To be able to interpolate between the harmonic and the quasi-harmonic approximation throughout the frequencies a weighting function (eq. S4) is used to combine S_R and S_V. The weighting function. W(ω) is calculated by introducing a Head-Gordon damping function[63]. where α=4. This damping function is shown in equation S5.

$$S = w(\omega)S_V + [1 - w(\omega)]S_R \tag{S4}$$

$$w(\omega) = \frac{1}{1 + (\omega_0/\omega)^{\alpha}} \tag{S5}$$

2. Rayleigh scattering

Plots containing non-normalized Rayleigh scattering both in the harmonic and quasi-harmonic approximation and normalized Rayleigh scattering were shown in the main article. The following tables will show the values of the normalized and non-normalized Rayleigh scattering in both the harmonic and quasi-harmonic approximation. Furthermore, the tables will show the normalization factor (Sum of Boltzmann factors) that is used to normalized the non-normalized Rayleigh scattering.

Table S2.1: $(H_2O_2)(H_2O)$

$(H_2O_2)(H_2O)_1$ – Harmonic	**PM6**	**PM7**	**ωB97X-D/ 6-31G**	**ωB97X-D/ 6-31++G(d,p) (PLUS)**
Non-normalized Rayleigh scattering (A_0^3)	59,398	35,953	27,457	37,302
Normalization factor	2.13	1.30	1.00	2.18
Normalized Rayleigh scattering (A_0^3)	27,839	27,586	27,456	27,577
Percentage of PLUS	100.95	100.03	99.56	100
$(H_2O_2)(H_2O)_1$–Quasi-harmonic				
Non-normalized Rayleigh scattering (A_0^3)	56,725	30,050	27,457	56,402
Sum of Boltzmann factors	2.06	1.09	1.00	2.05
Normalized Rayleigh scattering (A_0^3)	27529	27489	27456	27530
Percentage of Normalized PLUS Rayleigh scattering	100.00	99.85	99.73	100

Table S2.2: $(H_2O_2)(H_2O)_2$

$(H_2O_2)(H_2O)_2$ – Harmonic	**PM6**	**PM7**	**ωB97X-D/ 6-31G**	**ωB97X-D/ 6-31++G(d,p) (PLUS)**
Non-normalized Rayleigh scattering (A_0^3)	115,900	67,336	73,016	107,219
Sum of Boltzmann factors	2.14	1.25	1.35	1.98
Normalized Rayleigh scattering (A_0^3)	54204	54024	54123	54212
Percentage of PLUS	99.99	99.65	99.84	100

$(H_2O_2)(H_2O)_2$ – Quasi-harmonic				
Non-normalized Rayleigh scattering (A_0^3)	106,723	63,858	69,838	101,068
Sum of Boltzmann factors	1.97	1.18	1.29	1.86
Normalized Rayleigh scattering (A_0^3)	54187	54044	54107	54198
Percentage of Normalized PLUS Rayleigh scattering	99.98	99.72	99.83	100

Table S2.3: $(H_2O_2)(H_2O)_3$

$(H_2O_2)(H_2O)_3$ – Harmonic	**PM6**	**PM7**	**ωB97X-D/ 6-31G**	**ωB97X-D/ 6-31++G(d,p) (PLUS)**
Non-normalized Rayleigh scattering (A_0^3)	181,220	144,531	184,297	212,102
Sum of Boltzmann factors	2.01	2.22	2.06	2.95
Normalized Rayleigh scattering (A_0^3)	90085	90012	89575	90273
Percentage of PLUS	99.79	99.71	99.23	100
$(H_2O_2)(H_2O)_3$ – Quasi-harmonic				
Non-normalized Rayleigh scattering (A_0^3)	176,575	179,884	197,518	300,130
Sum of Boltzmann factors	1.96	2.00	2.20	3.32
Normalized Rayleigh scattering (A_0^3)	90069	89996	89653	90371
Percentage of PLUS	99.67	99.58	99.21	100

Table S2.4: $(H_2O_2)(H_2O)_4$

$(H_2O_2)(H_2O)_4$ – Harmonic	**PM6**	**PM7**	**ωB97X-D/ 6-31G**	**ωB97X-D/ 6-31++G(d,p) (PLUS)**
Non-normalized Rayleigh scattering (A_0^3)	376,733	419,294	353,172	538,758
Sum of Boltzmann factors	2.79	3.10	2.63	4.01
Normalized Rayleigh scattering (A_0^3)	135011	135083	134377	134504
Percentage of PLUS	100.38	100.43	99.91	100
$(H_2O_2)(H_2O)_4$ – Quasi-harmonic				
Non-normalized Rayleigh scattering (A_0^3)	509,565	487.374	396,220	569,024
Sum of Boltzmann factors	3.79	3.61	2.97	4.25
Normalized Rayleigh scattering (A_0^3)	134545	134936	133608	133998
Percentage of PLUS	100.41	100.70	99.71	100

Table S2.5: $(H_2O_2)(H_2O)_5$

$(H_2O_2)(H_2O)_5$ – Harmonic	**PM6**	**PM7**	**ωB97X-D/ 6-31G**	**ωB97X-D/ 6-31++G(d,p) (PLUS)**
Non-normalized Rayleigh scattering (A_0^3)	699,511	1,788,745	1,909,433	1,310,511
Normalization factor	3.76	9.52	10.29	7.03
Normalized Rayleigh scattering (A_0^3)	186067	187776	185573	186524
Percentage of PLUS	99.76	99.49	100.67	100
$(H_2O_2)(H_2O)_5$ – Quasi-harmonic				
Non-normalized Rayleigh scattering (A_0^3)	1,815,811	1,418,151	1,439,901	1,750,516

Sum of Boltzmann factors	9.84	7.67	7.79	9.54
Normalized Rayleigh scattering (A_0^3)	184503	184993	184955	183462
Percentage of PLUS	100.57	100.83	100.81	100

3: Isotropic and anisotropic polarizabilities

Table S3.1: Isotropic and anisotropic polarizabilities and pure molecular Rayleigh scattering for all 48 conformers in the PLUS-pathway for $(H_2O_2)(H_2O)_5$. Sorted by Gibbs free energy with conformer 1 being the lowest Gibbs free energy conformer.

Conformer	Isotropic polarizability (a_0)	Anisotropic polarizability (a_0)	Molecular Rayleigh (A_0^3)
1	64.48	9.36	188234.1
2	64.28	10.35	187328.9
3	63.83	7.22	184019.8
4	64.54	14.14	190042.7
5	64.71	12.61	190499.4
6	64.78	14.85	191707.0
7	64.38	14.05	189081.5
8	64.64	14.31	190686.9
9	64.5	7.97	188037.0
10	63.85	6.57	184018.2
11	63.85	6.85	184067.0
12	64.67	7.53	188936.5
13	63.48	6.24	181843.2
14	64.07	11.6	186472.7
15	63.95	3.63	184203.4
16	64.77	14.56	191537.8
17	63.92	4.25	184094.3
18	64.22	10.07	186907.6
19	64.28	8.55	186886.7
20	64.65	10.01	189385.6
21	64.06	9.85	185927.1
22	63.58	8.72	182897.2
23	64.01	5.62	184788.2
24	63.31	6.33	180887.9
25	62.89	7.4	178693.7
26	63.39	3.46	180978.8
27	64.06	12.23	186610.2
28	63.89	6.4	184219.4
29	63.91	4.67	184085.5
30	64	9.9	185594.1
31	63.85	5	183782.0
32	64.1	14.07	187470.0

33	62.9	7.72	178813.2
34	64.19	14.58	188179.5
35	64.18	13.39	187689.1
36	63.94	5.42	184356.5
37	63.09	6.2	179615.4
38	64.45	10.48	188348.9
39	63.84	7.2	184073.5
40	63.86	7.38	184222.5
41	64.17	8.24	186183.2
42	64.33	10.61	187689.1
43	64.28	13.23	188211.8
44	63.39	7.19	181495.2
45	63.21	5.38	180174.0
46	63.54	6.52	182232.6
47	64.06	8.54	185613.9
48	64.01	5.07	184711.8

In table S3.1 it is clear that the isotropic polarizabilities changes very little across all 48 conformers within the PLUS pathway for $(H_2O_2)(H_2O)_5$. The anisotropic polarizability though changes significantly depending on the conformer. We see values ranging from $3.46a_0$ to $14.61a_0$. In percentage of the isotropic contribution this ranges all the way from 5% to 23%. The tendency of very small differences in the isotropic polarizability is consistent for all $(H_2O_2)(H_2O)_{1\text{-}5}$. The anisotropic polarizability varies more than the isotropic for all $(H_2O_2)(H_2O)_5$ although it is more significant for the bigger clusters $(H_2O_2)(H_2O)_{4,5}$.