Supplementary Material for PCCP

Spectral shifts of matrix isolated species as criteria for acid-base interactions with solid Xe

M. Rozenberg[a] and A. Loewenschuss[a], C.J. Nielsen[b]*
[a] Institute of Chemistry, The Hebrew University, Jerusalem 91904, Israel.
[b] Centre for Theoretical and Computational Chemistry, Department of Chemistry, University of Oslo, Blindern, N-0315 Oslo, Norway

Electronic Supplementary Information

Table S1. Calculated vibrational wavenumbers (/cm^{-1}) and infrared intensities (/km mol^{-1}) of H_2O.

	Harmonic			Anharmonic		
Calculation	ν_1 (A_1)	ν_2 (A_1)	ν_3 (B_2)	ν_1 (A_1)	ν_2 (A_1)	ν_3 (B_2)
B3LYP/DZ[a]	3752 (3)[b]	1659 (55)	3853 (20)	3571	1601	3664
B3LYP/aDZ	3795 (4)	1619 (71)	3904 (60)	3620	1568	3717
B3LYP/TZ	3800 (3)	1639 (70)	3901 (41)	3635	1588	3721
B3LYP/aTZ	3796 (5)	1627 (76)	3899 (63)	3634	1575	3722
B3LYP/QZ	3806 (4)	1635 (73)	3906 (52)	3640	1583	3726
B3LYP/aQZ	3804 (5)	1629 (76)	3906 (63)	3639	1577	3727
B3LYP/5Z	3808 (5)	1630 (75)	3909 (60)	3641	1578	3729
B3LYP/a5Z	3807 (5)	1629 (76)	3908 (63)	3640	1577	3728
MP2/DZ	3852 (7)	1678 (57)	3971 (33)	3672	1625	3786
MP2/aDZ	3803 (4)	1622 (67)	3938 (67)	3622	1573	3745
MP2/TZ	3855 (6)	1652 (65)	3976 (55)	3686	1602	3794
MP2/aTZ	3818 (6)	1628 (72)	3945 (75)	3654	1578	3768
MP2/QZ	3855 (7)	1643 (69)	3978 (68)	3683	1589	3794
MP2/aQZ	3840 (6)	1632 (73)	3966 (78)	3668	1580	3782
MP2/5Z	3849 (7)	1637 (72)	3974 (76)	3676	1583	3789
Experimental gas phase values [c]				3657	1595	3756

[a] Basis set abbreviations: a, aug-; DZ, cc-pVDZ; TZ, cc-pVTZ; QZ, cc-pVQZ; 5Z, cc-pV5Z.
[b] Infrared intensities in brackets.
[c] HITRAN database: Journal of Quantitative Spectroscopy and Radiative Transfer, 2009, 110, 533-572.

Table S2. Calculated vibrational wavenumbers (/cm^{-1}) and infrared intensities (/km mol^{-1}) of $(H_2O)_2$.

Harmonic	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9	ν_{10}	ν_{11}	ν_{12}
B3LYP/aDZ	3874 (88)[b]	3789 (11)	3672 (337)	1637 (37)	1617 (8)	360 (51)	182 (139)	154 (139)	3895 (82)	635 (93)	153 (32)	126 (135)
B3LYP/aTZ	3871 (86)	3792 (10)	3676 (334)	1647 (39)	1628 (92)	363 (52)	188 (211)	159 (68)	3891 (84)	626 (94)	158 (14)	129 (152)
B3LYP/aQZ	3879 (86)	3799 (10)	3686 (330)	1649 (39)	1630 (92)	361 (51)	183 (148)	154 (133)	3897 (85)	626 (95)	150 (39)	122 (127)
MP2/aDZ	3904 (114)	3796 (10)	3704 (280)	1643 (32)	1624 (86)	358 (54)	184 (119)	148 (161)	3925 (88)	639 (91)	150 (59)	127 (113)
MP2/aTZ	3916 (115)	3815 (11)	3720 (297)	1650 (36)	1629 (87)	359 (51)	183 (140)	153 (141)	3936 (97)	630 (91)	144 (64)	123 (195)
Anharmonic												
B3LYP/aDZ	3694	3607	3526	1585	1575	261	141	113	3701	496	191	168
B3LYP/aTZ	3687	3609	3526	1595	1576	249	-42	15	3692	503	-95	-52
MP2/aDZ	3720	3614	3554	1593	1581	329	152	123	3730	514	124	108
MP2/aTZ	3744	3647	3583	1596	1586	320	142	118	3755	503	126	97
Experimental [c]		3634	3575	1611	1594				3710			

[a] Basis set abbreviations: aDZ, aug-cc-pVDZ; aTZ, aug-cc-pVTZ; aQZ, aug-cc-pVQZ.
[b] Infrared intensities in brackets.
[c] Experimental values from Ar-matrix: G. P. Ayers, A. D. E. Pullin, *Spectrochimica Acta, Part A*, 1976, **32A**, 1695-704.

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Table S3. Calculated vibrational wavenumbers (/cm^{-1}) of H_2SO_4.

Harmonic	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9	ν_{10}	ν_{11}	ν_{12}	ν_{13}	ν_{14}	ν_{15}
B3LYP/DZ [a]	3713	1145	1142	761	490	399	336	222	3709	1393	1150	825	500	450	297
B3LYP/aDZ	3740	1159	1117	745	483	394	326	226	3736	1364	1158	802	494	443	308
B3LYP/TZ	3760	1196	1154	794	525	421	359	230	3756	1445	1167	851	534	480	306
B3LYP/aTZ	3751	1185	1151	786	521	418	356	229	3747	1430	1163	840	531	477	307
B3LYP/QZ	3762	1205	1150	802	533	429	365	242	3758	1452	1165	856	543	487	319
B3LYP/aQZ	3760	1202	1148	799	532	427	364	242	3756	1448	1163	851	542	486	318
B3LYP/5Z	3766	1216	1148	810	540	434	370	248	3762	1463	1164	861	550	493	323
MP2/DZ	3781	1203	1156	791	513	419	356	240	3777	1457	1170	848	519	467	314
MP2/aDZ	3731	1172	1153	762	493	405	336	234	3727	1402	1176	813	504	450	324
MP2/TZ	3793	1239	1163	833	540	437	373	241	3789	1495	1180	888	549	492	329
MP2/aTZ	3765	1219	1155	821	532	431	367	243	3761	1469	1170	874	542	486	328
MP2/QZ	3792	1242	1154	842	546	442	377	246	3788	1495	1172	895	556	498	332
Anharmonic															
B3LYP/DZ	3531	1123	1124	747	484	365	314	196	3527	1366	1123	807	491	443	242
B3LYP/aDZ	3559	1137	1099	728	477	360	306	196	3555	1331	1127	784	486	436	258
B3LYP/TZ	3597	1173	1126	780	521	409	328	344	3593	1414	1137	834	527	474	443
B3LYP/aTZ	3587	1162	1119	771	518	409	327	346	3583	1400	1132	824	524	472	445
MP2/DZ	3603	1187	1134	775	506	381	337	221	3599	1433	1142	828	512	459	274
MP2/aDZ	3542	1145	1140	745	487	373	318	220	3538	1381	1143	792	497	444	286
MP2/TZ	3617	1222	1133	817	535	397	350	219	3612	1470	1151	868	541	485	290
MP2/aTZ	3589	1202	1123	805	526	396	344	218	3585	1443	1144	853	535	479	288
Experimental [b]	3609	1220	1157	891	550					1464	1157	834			
Experimental [c]	3572	1216	1136	831	548	422	379	224	3567	1452	1157	882	558	506	288

[a] Basis set abbreviations: a, aug-; DZ, cc-pVDZ; TZ, cc-pVTZ; QZ, cc-pVQZ; 5Z, cc-pV5Z.
[b] Experimental values for gas phase: [23]
[c] Experimental values for Ar-matrix: [7, 11]

Table S4. Calculated vibrational wavenumbers (/cm^{-1}) and infrared intensities (/km mol^{-1}) of $(H_2SO_4)_2$

	B3LYP/aDZ [a]	B3LYP/aTZ	MP2/aDZ
$\nu_1(A_g)$	3734	3746	3722
$\nu_2(A_g)$	3154	3155	3202
$\nu_3(A_g)$	1391	1425	1413
$\nu_4(A_g)$	1268	1295	1293
$\nu_5(A_g)$	1159	1168	1175
$\nu_6(A_g)$	1069	1128	1103
$\nu_7(A_g)$	854	901	868
$\nu_8(A_g)$	768	811	784
$\nu_9(A_g)$	729	741	744
$\nu_{10}(A_g)$	501	539	514
$\nu_{11}(A_g)$	493	532	501
$\nu_{12}(A_g)$	456	491	459
$\nu_{13}(A_g)$	386	416	391
$\nu_{14}(A_g)$	340	370	351
$\nu_{15}(A_g)$	239	256	250
$\nu_{16}(A_g)$	150	152	163
$\nu_{17}(A_g)$	123	126	110
$\nu_{18}(A_g)$	51	53	49
$\nu_{19}(A_u)$	3733 (255)[c]	3746 (268)	3721 (263)
$\nu_{20}(A_u)$	3235 (3037)	3236 (3050)	3277 (2752)
$\nu_{21}(A_u)$	1353 (550)	1398 (830)	1378 (693)
$\nu_{22}(A_u)$	1273 (279)	1287 (110)	1298 (181)
$\nu_{23}(A_u)$	1159 (112)	1192 (242)	1179 (116)
$\nu_{24}(A_u)$	1109 (388)	1147 (279)	1139 (378)
$\nu_{25}(A_u)$	858 (515)	905 (552)	875 (494)
$\nu_{26}(A_u)$	773 (275)	812 (303)	795 (297)
$\nu_{27}(A_u)$	748 (6)	765 (48)	752 (7)
$\nu_{28}(A_u)$	509 (87)	549 (92)	514 (81)
$\nu_{29}(A_u)$	494 (35)	533 (41)	504 (33)
$\nu_{30}(A_u)$	476 (32)	512 (27)	478 (41)
$\nu_{31}(A_u)$	381 (62)	410 (58)	386 (67)
$\nu_{32}(A_u)$	355 (17)	379 (13)	377 (25)
$\nu_{33}(A_u)$	234 (123)	252 (139)	245 (113)
$\nu_{34}(A_u)$	177 (55)	184 (61)	179 (48)
$\nu_{35}(A_u)$	42 (5)	42 (5)	40 (5)
$\nu_{36}(A_u)$	26 (2)	31 (3)	21 (2)

[a] Basis set abbreviations: aDZ, aug-cc-pVDZ; aTZ, aug-cc-pVTZ.
[c] Infrared intensities in brackets.

Table S5. Calculated vibrational wavenumbers (/cm^{-1}) and intensities (/km mol^{-1}) of the H_2SO_4*H_2O complex.

Harmonic	a H_2O	Free OH	s H_2O	Bonded OH								
B3LYP/aDZ	3863 (118)[b]	3743 (111)	3712 (97)	3123 (1243)	1618 (53)	1419 (187)	1290 (168)	1154 (67)	1102 (178)	859 (195)	832 (142)	752 (96)
B3LYP/aTZ	3859 (117)	3755 (117)	3720 (90)	3131 (1257)	1633 (53)	1440 (289)	1332 (113)	1172 (126)	1155 (126)	885 (300)	855 (73)	793 (103)
B3LYP/aQZ												
MP2/aDZ	3887 (129)	3733 (112)	3725 (75)	3173 (1142)	1622 (49)	1440 (221)	1325 (148)	1172 (59)	1140 (191)	870 (199)	847 (140)	766 (111)
MP2/aTZ	3897 (138)	3767 (130)	3733 (96)	3151 (1261)	1630 (46)	1468 (316)	1357 (90)	1206 (160)	1162 (94)	919 (283)	877 (94)	826 (97)
Anharmonic												
B3LYP/aDZ	3680	3558	3534	2881	1563	1372	1260	1136	1087	791	792	736
Experimental[c]	3696		3582	2658[d]					929	839		

Harmonic												
B3LYP/aDZ	518 (252)	501 (16)	490 (27)	467 (16)	391 (55)	339 (41)	327 (30)	248 (24)	230 (66)	216 (64)	126 (22)	46 (2)
B3LYP/aTZ	540 (74)	529 (28)	522 (131)	495 (71)	418 (58)	361 (3)	329 (74)	252 (29)	225 (65)	220 (62)	125 (21)	46 (2)
B3LYP/aQZ												
MP2/aDZ	527 (238)	509 (15)	501 (30)	473 (7)	399 (59)	347 (3)	328 (78)	260 (22)	229 (125)	222 (6)	137 (18)	45 (2)
MP2/aTZ	553 (137)	542 (44)	537 (90)	509 (22)	429 (56)	373 (5)	331 (78)	263 (19)	236 (134)	227 (11)	146 (20)	46 (2)
Anharmonic												
B3LYP/aDZ	436	489	485	457	370	269	283	229	170	208	100	40

[a] Basis set abbreviations: a, aug-; DZ, cc-pVDZ; TZ, cc-pVTZ; QZ, cc-pVQZ
[b] Infrared intensities in brackets.
[c] Experimental values from Ar-matrix: [7,11]
[d] center of doublet 2722 and 2593 cm^{-1}.

Table S6. Calculated vibrational wavenumbers (/cm^{-1}) and infrared intensities (/km mol^{-1}) in various $H_2O{\cdot}Xe$ aggregates.

Species	Calculation	ν_1 (H_2O)	ν_2 (H_2O)	ν_3 (H_2O)
$H_2O{\cdot}Xe$	MP2/aDZ	3798 (20)[b]	1622 (42)	3932 (129)
	MP2/aTZ	3810 (36)	1623 (40)	3936 (158)
	MP2/aQZ	3827 (42)	1628 (40)	3953 (167)
$H_2O{\cdot}Xe_2$	MP2/aDZ	3795 (10)	1619 (23)	3928 (222)
	MP2/aTZ	3804 (19)	1617 (20)	3926 (311)
	MP2/aQZ	3819 (58)	1631 (30)	3934 (285)
$H_2O{\cdot}Xe_3$	MP2/aDZ	3795 (10)	1616 (61)	3923 (185)
	MP2/aTZ	3802 (14)	1611 (60)	3920 (249)
$H_2O{\cdot}Xe_4$	MP2/aDZ	3791 (22)	1623 (76)	3916 (78)
	MP2/aTZ	3802 (36)	1629 (78)	3914 (98)
$H_2O{\cdot}Xe_5$	MP2/aDZ	3791 (20)	1622 (40)	3916 (142)

[a] Basis set abbreviations: a, aug-; DZ, cc-pVDZ; TZ, cc-pVTZ; QZ, cc-pVQZ; 5Z, cc-pV5Z.
[b] Infrared intensities in brackets.

Table S7. Calculated vibrational wavenumbers (/cm^{-1}) and infrared intensities (/km mol^{-1}) in the $(H_2O)_2 \cdot Xe_3$ aggregate.

Calculation	ν_1 $(H_2O)_2$	ν_2 $(H_2O)_2$	ν_3 $(H_2O)_2$	ν_4 $(H_2O)_2$	ν_5 $(H_2O)_2$	ν_9 $(H_2O)_2$
MP2/aDZ	3895 (192)[b]	3782 (27)	3681 (209)	1635 (24)	1628 (70)	3904 (103)

[a] Basis set abbreviations: a, aug-; DZ, cc-pVDZ; TZ, cc-pVTZ; QZ, cc-pVQZ; 5Z, cc-pV5Z.
[b] Infrared intensities in brackets.

Table S8. Calculated vibrational wavenumbers (/cm^{-1}) and infrared intensities (/km mol^{-1}) in the $H_2SO_4 \cdot Xe_2$ aggregate.

Calculation	MP2/aDZ [a]	MP2/aTZ
ν_1	3687 (166)[b]	3678 (204)
ν_2	1152 (177)	1221 (139)
ν_3	1185 (0)	1182 (42)
ν_4	762 (107)	823 (101)
ν_5	492 (28)	533 (25)
ν_6	432 (33)	479 (26)
ν_7	353 (1)	389 (1)
ν_8	264 (38)	311 (28)
ν_9	3680 (426)	3670 (726)
ν_{10}	1398 (297)	1463 (316)
ν_{11}	1186 (67)	1193 (62)
ν_{12}	808 (234)	870 (259)
ν_{13}	502 (19)	541 (25)
ν_{14}	452 (48)	494 (53)
ν_{15}	354 (39)	415 (25)

[a] Basis set abbreviations: a, aug-; DZ, cc-pVDZ; TZ, cc-pVTZ; QZ, cc-pVQZ; 5Z, cc-pV5Z.
[b] Infrared intensities in brackets.

Table S9. Calculated vibrational wavenumbers (/cm^{-1}) and infrared intensities (/km mol^{-1}) in the $(H_2SO_4)_2 \cdot Xe_2$ aggregate. Results from MP2/aug-cc-pVDZ calculation.

$\nu_1(A_g)$	$\nu_2(A_g)$	$\nu_3(A_g)$	$\nu_4(A_g)$	$\nu_5(A_g)$	$\nu_6(A_g)$	$\nu_7(A_g)$	$\nu_8(A_g)$	$\nu_9(A_g)$	$\nu_{10}(A_g)$	$\nu_{11}(A_g)$	$\nu_{12}(A_g)$
3670	3183	1411	1294	1190	1100	863	786	760	516	500	460

$\nu_{13}(A_g)$	$\nu_{14}(A_g)$	$\nu_{15}(A_g)$	$\nu_{16}(A_g)$	$\nu_{17}(A_g)$	$\nu_{18}(A_g)$	$\nu_{19}(A_g)$	$\nu_{20}(A_g)$	$\nu_{21}(A_g)$
403	365	284	167	114	74	45	26	11

$\nu_{22}(A_u)$	$\nu_{23}(A_u)$	$\nu_{24}(A_u)$	$\nu_{25}(A_u)$	$\nu_{26}(A_u)$	$\nu_{27}(A_u)$	$\nu_{28}(A_u)$	$\nu_{29}(A_u)$
3670 (673)	3259 (2933)	1375 (708)	1300 (192)	1194 (119)	1137 (369)	871 (442)	801 (282)

$\nu_{30}(A_u)$	$\nu_{31}(A_u)$	$\nu_{32}(A_u)$	$\nu_{33}(A_u)$	$\nu_{34}(A_u)$	$\nu_{35}(A_u)$	$\nu_{36}(A_u)$	$\nu_{37}(A_u)$
761 (7)	513 (79)	503 (31)	480 (33)	409 (59)	383 (38)	282 (60)	182 (51)

$\nu_{38}(A_u)$	$\nu_{39}(A_u)$	$\nu_{40}(A_u)$	$\nu_{41}(A_u)$	$\nu_{42}(A_u)$
72 (6)	46 (2)	31 (1)	8 (0)	6 (0)

Table S10. Calculated vibrational wavenumbers (/cm^{-1}) and infrared intensities (/km mol^{-1}) in the $H_2SO_4 \cdot H_2O \cdot Xe_2$ aggregate.

MP2/aDZ	MP2/aTZ
3878 (117)	3883 (124)
3721 (67)	3733 (77)
3694 (211)	3685 (332)
3148 (1070)	3123 (1146)
1621 (44)	1630 (42)
1441 (202)	1468 (294)
1325 (146)	1358 (75)
1182 (35)	1212 (160)
1139 (208)	1182 (94)
878 (193)	917 (242)
842 (139)	896 (110)
767 (110)	826 (102)
527 (247)	550 (122)
508 (15)	541 (37)
500 (35)	533 (143)
472 (8)	509 (23)
406 (53)	446 (49)
358 (14)	397 (20)
333 (114)	341 (95)
270 (41)	301 (55)
234 (82)	242 (72)
229 (2)	237 (3)
133 (14)	133 (15)
64 (2)	87 (5)
59 (5)	62 (3)
46 (1)	51 (1)
36 (3)	41 (4)
28 (1)	32 (0)
20 (0)	22 (0)
15 (1)	17 (1)

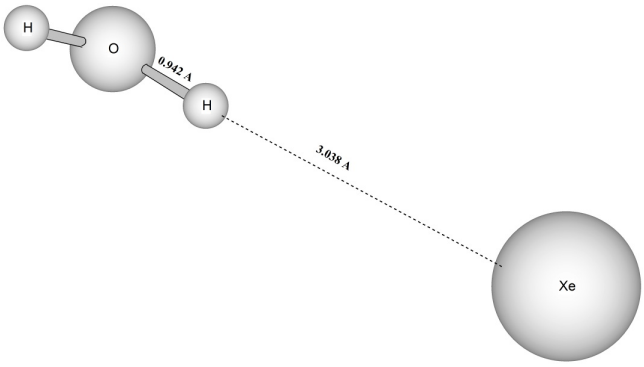

Figure S1

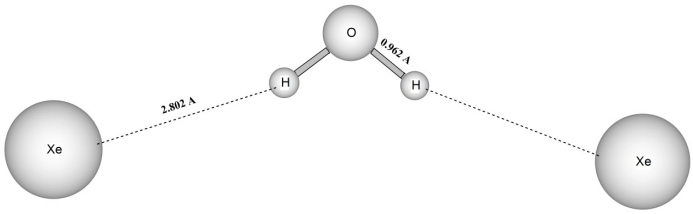

Figure S2

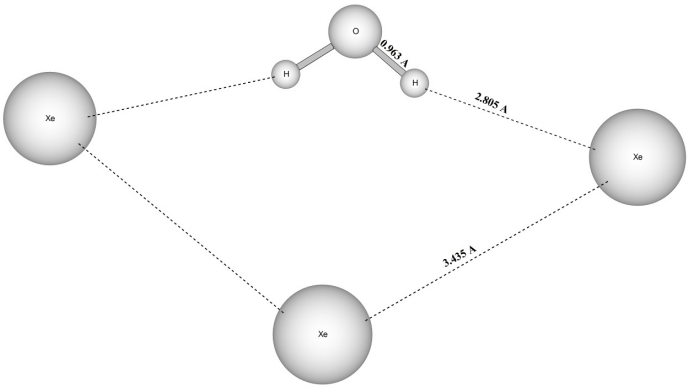

Figure S3

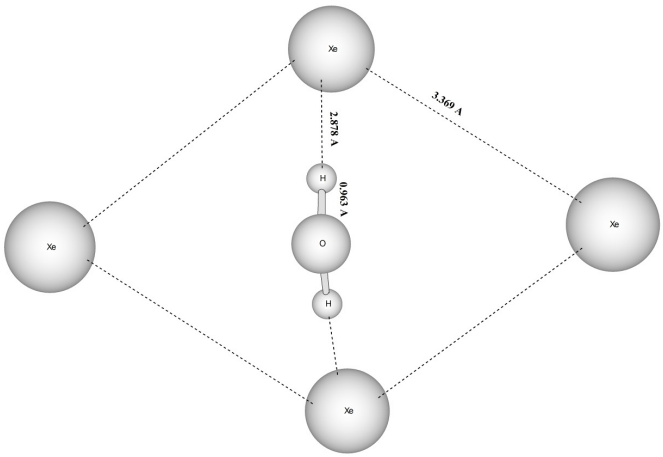

Figure S4

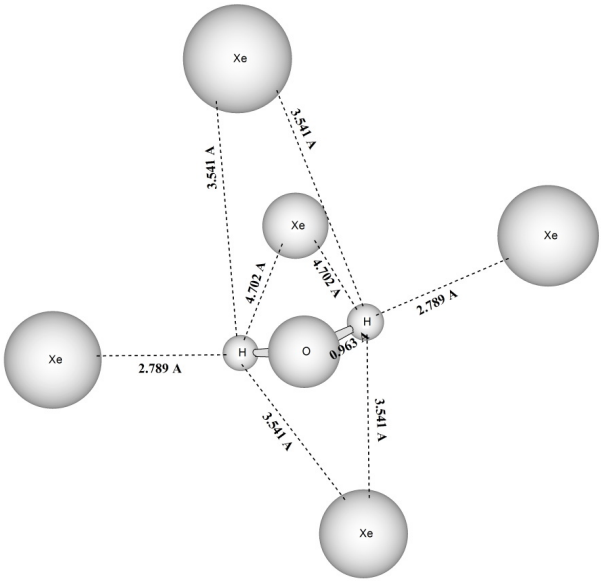

Figure S5

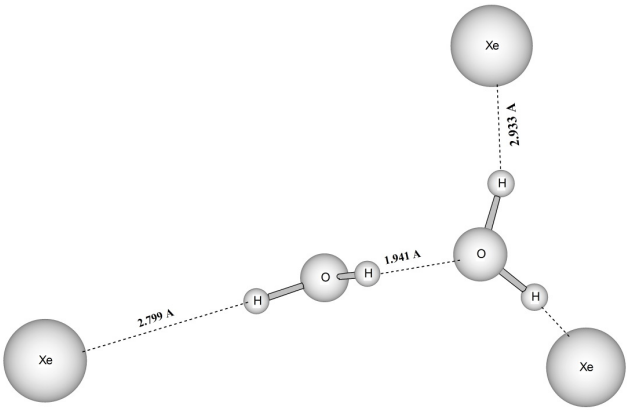

Figure S6

Figure Captions (ESI):

Figure S1:
Configuration of the $H_2O\cdots Xe$ aggregate

Figure S2:
Configuration of the $H_2O\cdots Xe_2$ aggregate

Figure S3:
Configuration of the $H_2O\cdots Xe_3$ aggregate

Figure S4:
Configuration of the $H_2O\cdots Xe_4$ aggregate

Figure S5:
Configuration of the $(H_2O)_2\cdots Xe_3$ aggregate