Electronic Supplementary Information

Multi-dimensional local mode calculations for the vibrational spectra of $OH^-(H_2O)_2$ and $OH^-(H_2O)_2{\cdot}Ar$†

Masato Morita* and Kaito Takahashi*

Institute of Atomic and Molecular Sciences, Academia Sinica PO Box 23-166 Taipei 10617 Taiwan R.O.C.

E-mail: morita@gate.sinica.edu.tw kt@gate.sinica.edu.tw

Contents

1. Additional Information
  - 1-1. Energetic
  - 1-2. Inter mode coupling effect (inter water IHB OHs coupling)
  - 1-3. Inter mode coupling effect (IHB OH and O···O coupling)
  - 1-4. Temperature dependence of the simulated spectra
  - 1-5. Effect of the argon atom attachment

2. Optimized geometry (Cartesian coordinate)
  - 2-1. $OH^-(H_2O)_3$
  - 2-2. $OH^-(H_2O)_3{\cdot}Ar$

Unless otherwise stated, the electronic structure calculation is performed with MP2/6-311++G(3df,3pd).

1. Additional Information

1-1. Energetic

The binding energy of argon atom is given in Table S1. Since all the calculated binding energies are less than 1000 cm^{-1}, the vibrational modes considered in the text have enough excitation energy to dissociate the argon atom following the IR absorption in the argon predissociation spectroscopic measurements. The estimation of the rate of the dissociation between the $OH^{-}(H_2O)_2$ and argon atom and its impact on the resultant vibrational spectrum are very difficult issues at the present moment, thus we assume that the all the vibrational excitations whose excitation energies are higher than the value of 1000 cm^{-1} results in 100% dissociation as has been assumed in previous studies.

As described in the text, it is invalid to employ the counterpoise correction in the calculation of the potential energy surface and associated dipole moment function due to the occurrence of charge transfer when the IHB OH bonds are elongated. However, at around the equilibrium geometry, the counterpoise correction may give more accurate results for the energetic properties. Additionally, to show the basis set dependence, we calculated the energetic information with MP2/aug-cc-pVTZ. Significant sensitivity to the employed methods, and the isoenergetic nature between the conformers prevent us from a deterministic conclusion for existence ratio between the conformers, which is the one of the reasons that we should directly simulate the vibrational spectrum with various conformers. Subtle structural difference results in the difference of the shape of the vibrational spectra, in particular, the peaks from the IHB OH stretching vibrations are remarkable makers.

Table S1. Argon binding energy with and without the counterpoise correction.

Method	Unit	Ar- I		Ar- II	
		no CP	CP	no CP	CP
MP2/6-311++G(3df,3pd)	kcal/mol	2.20	1.55	2.17	1.61
	cm^{-1}	770	543	760	562
MP2/aug-cc-pVTZ	kcal/mol	2.12	1.78	2.12	1.79
	cm^{-1}	741	622	741	626

Table S2. Energetic with MP2/aug-cc-pVTZ.

	Conformer	Electronic Energy	Electronic Energy +ZPE	Free Energy (50K)	Free Energy (100K)
$OH^{-}(H_2O)_2$	I	0.000	0.000	0.000	0.000
	II	0.210	0.094	0.072	0.017
	I (CP)^{a}	0.000	0.000	0.000	0.000
	II (CP)^{a}	0.201	0.126	0.135	0.125

$OH^-(H_2O)_2\cdot Ar$	Ar- Ⅰ	<u>0.000</u>	<u>0.000</u>	<u>0.000</u>	<u>0.000</u>
	Ar- Ⅱ	0.202	0.081	0.067	0.020
	Ar- Ⅰ (CP)[a]	<u>0.000</u>	<u>0.000</u>	<u>0.000</u>	<u>0.000</u>
	Ar- Ⅱ (CP)[a]	0.189	0.070	0.056	0.011

[a] Geometry optimizations were performed including the counterpoise correction (a priori)

1-2. Inter mode coupling effect (inter water IHB OHs coupling)

To deeply analyze the inter mode coupling effect for the IHB OH stretching vibrations, we analyze the coupling from the view point of the harmonic and anharmonic coupling effects as was performed in our previous paper for $OH^-(H_2O)_3$.

We perform the calculation of the IHB OH peak positions by adding the harmonic coupling terms to the sum of the potential energy curves of the LM-1D (LM-2D-HC). The resultant form of the PES is given as

$$\begin{aligned} &V^{LM-2D-HC}(r^{OH(1)}, r^{OH(2)}) \\ &= V_{OH(1)}^{LM-1D}(r^{OH(1)}) + V_{OH(2)}^{LM-1D}(r^{OH(2)}) + C^{HC}(r^{OH(1)} - r_{eq}^{OH(1)})(r^{OH(2)} - r_{eq}^{OH(2)}) \end{aligned} \qquad \text{(eq S1)},$$

where $V_{OH(i)}^{LM\text{-}1D}$ is the LM-1D potential for $r^{OH(i)}$, and C^{HC} is the coupling coefficient between $r^{OH(1)}$ and $r^{OH(j)}$. C^{HC} is calculated by performing the frequency calculation using Gaussian 09 at the optimized geometry and using the keyword IOP(7/33=1) to print out the hessian matrix in internal coordinates.

In Table S3, S4 and Fig. S1, we compare the peak positions of IHB OHs with LM-2D-HC and those with LM-1D and LM-2D. Both for Conformer I and II, we can see the large anharmonic coupling effect from the difference between LM-2D-HC and LM-2D results. For example, the energy splitting of two IHB OH fundamentals of Conformer II by introducing the harmonic coupling term to LM-1D is the value of 111 cm^{-1}. Thereby, more than 140 cm^{-1} in the splitting with LM-2D originates from the anharmonic coupling. Also, for Conformer I, the large change of the energy difference between the two IHB OH peak positions of the fundamentals is observed by changing the coupling treatments from 193 cm^{-1} (LM-2D-HC) to 295 cm^{-1} (LM-2D). Although the strength of the inter mode coupling effect is small for the overtone, we see the comparative or larger anharmonic coupling effect than the harmonic coupling effect.

Table S3. Excitation energy dependence of the inter mode coupling treatment.

Conformer Ⅰ			
Mode	LM Frequency (cm^{-1})	LM-2D-HC Frequency (cm^{-1})	LM-2D Frequency (cm^{-1})
IHB OH(ν: 0→1)	1621	1645	1648
	1788	1838	1943
IHB OH(ν: 0→2)	2906	2942	2971
	3077	3120	3153

Table S4. Excitation energy dependence of the inter mode coupling treatment.

Conformer II			
Mode	LM Frequency (cm^{-1})	LM-2D-HC Frequency (cm^{-1})	LM-2D Frequency (cm^{-1})
IHB OH(ν: 0→1)	1661	1650	1631
	1661	1761	1885
IHB OH(ν: 0→2)	2933	2974	2988
	2933	2979	3015

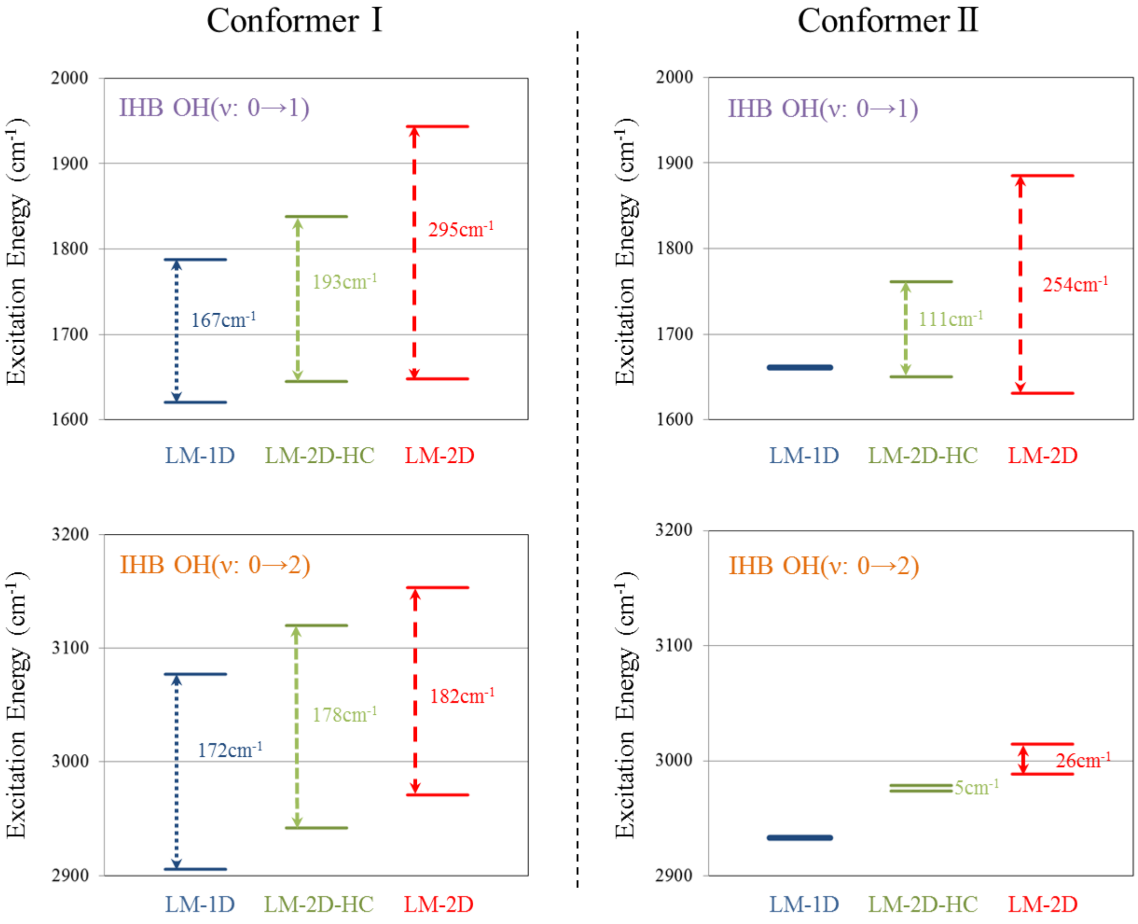


Figure S1. Excitation energies of IHB OH stretching vibrational modes with the local mode (LM-1D) model, the LM-1D plus harmonic inter mode coupling (LM-2D-HC) model and the local mode 2D (LM-2D) model for $OH^-(H_2O)_2$.

1-3. Inter mode coupling effect (IHB OH and O···O coupling)

We note that, as a zero-th order description, LM-4D(*2*IHB, *2*OO) problem can be considered as the coupling between LM-2D(*2*IHB) and LM-2D(*2*OO). We show the energy spectrum of LM-2D(*2*IHB), LM-2D(*2*OO) and LM-4D(*2*IHB, *2*OO) in Fig. S2.

We show complete listing of the peak positions with LM-2D(*2*OO) and LM-4D(*2*IHB, *2*OO) in Tables. As we can see, except for low lying states such as the fundamental, pure O···O states does not have much intensities, thus they behaves as the dark states. However, due to the large coupling with the IHB OH, near by states borrow intensity from the pure intense IHB OH intensities. As a results, the intensities of IHB OHs are decreased drastically, and, in some case, we cannot specify the state neither as IHB OH nor as O···O because of the strong mixing. Importantly, the relatively intense peaks other than the IHB OH originate from the combination band between IHB OH and the low lying , such as fundamental, the O···O modes. As a result of such large coupling, even in the energy range where is far from the peaks of IHB OH, significant changes are seen in the O···O mode compared to LM-2D(*2*OO). We note that the inter mode coupling also affect the ground state and its wave function. All in all, shifts of the peak position as well as the distribution of the intensities are an evidence of the significant coupling between IHB OH and O···O. We also show the results with LM-4D(*2*free, *2*OO) for Conformer I. We can see both the peak positions and the intensities of the free OH and O···O are essentially equal to those obtained with LM-2D(*2*free) and LM-2D(*2*OO), thus the adiabatic separation concept between the free OH and low frequency O···O is indeed valid.

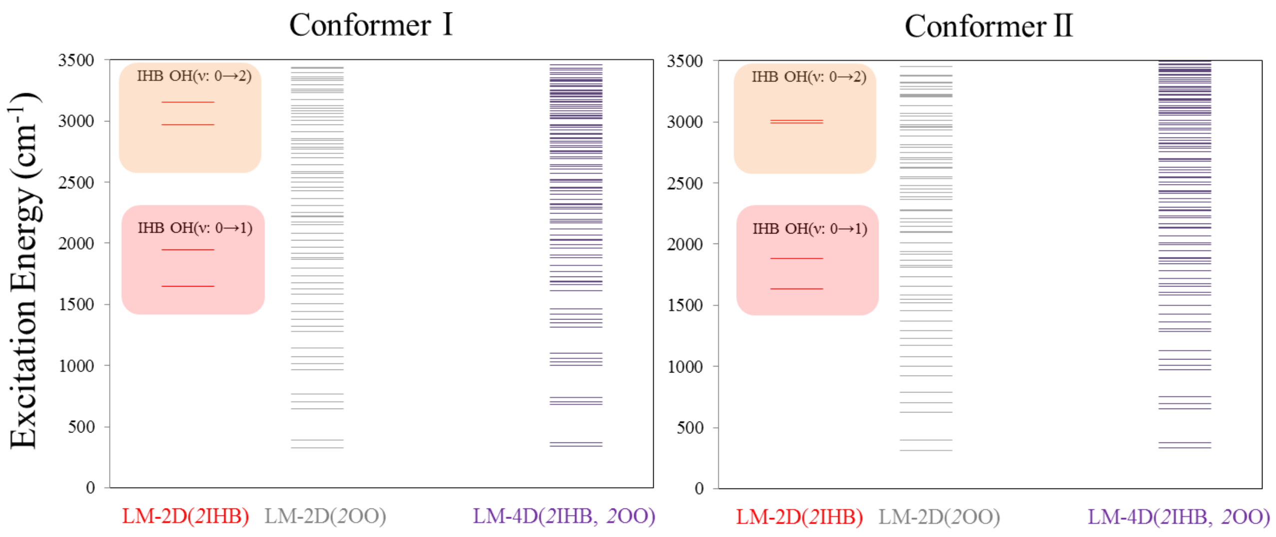


Figure S2. Excitation energies with LM-2D(*2*IHB), LM-2D(*2*OO) and LM-4D(*2*IHB, *2*OO) for $OH^{-}(H_2O)_2$.

[Conformer I]

Table S5. Peak positions and intensities with LM-2D(*2*OO) for Conformer Ⅰ.

LM-2D(2OO)								
	Frequency (cm^{-1})	Intensity (km/mol)		Frequency (cm^{-1})	Intensity (km/mol)		Frequency (cm^{-1})	Intensity (km/mol)
1	327	7.7	31	2306	0.0	61	3260	0.0
2	387	28.8	32	2365	0.0	62	3294	0.0
3	649	0.2	33	2430	0.0	63	3332	0.0
4	704	1.5	34	2462	0.0	64	3350	0.0
5	767	0.2	35	2499	0.0	65	3361	0.0
6	966	0.0	36	2503	0.0	66	3395	0.0
7	1016	0.1	37	2535	0.0	67	3431	0.0
8	1075	0.0	38	2571	0.0	68	3437	0.0
9	1141	0.0	39	2584	0.0	69	3490	0.0
10	1278	0.0	40	2640	0.0	70	3504	0.0
11	1322	0.0	41	2702	0.0	71	3510	0.0
12	1377	0.0	42	2737	0.0	72	3549	0.0
13	1440	0.0	43	2769	0.0	73	3578	0.0
14	1508	0.0	44	2787	0.0	74	3590	0.0
15	1584	0.0	45	2812	0.0	75	3610	0.0
16	1624	0.0	46	2840	0.0	76	3614	0.0
17	1675	0.0	47	2858	0.0	77	3661	0.0
18	1734	0.0	48	2910	0.0	78	3682	0.0
19	1799	0.0	49	2913	0.0	79	3695	0.0
20	1869	0.0	50	2969	0.0	80	3745	0.0
21	1884	0.0	51	3002	0.0	81	3754	0.0
22	1921	0.0	52	3034	0.0	82	3756	0.0
23	1967	0.0	53	3064	0.0	83	3801	0.0
24	2022	0.0	54	3083	0.0	84	3827	0.0
25	2085	0.0	55	3103	0.0	85	3842	0.0
26	2152	0.0	56	3127	0.0	86	3863	0.0
27	2177	0.0	57	3174	0.0	87	3866	0.0
28	2214	0.0	58	3176	0.0	88	3901	0.0
29	2223	0.0	59	3232	0.0	89	3925	0.0
30	2254	0.0	60	3248	0.0	90	3929	0.0

Table S6. Peak positions and intensities with LM-4D(*2*IHB, *2*OO) for Conformer Ⅰ.

LM-2D(2IHB)		LM-4D(2IHB, 2OO)											
Frequency (cm^{-1})	Intensity (km/mol)		Frequency (cm^{-1})	Intensity (km/mol)		Frequency (cm^{-1})	Intensity (km/mol)		Frequency (cm^{-1})	Intensity (km/mol)		Frequency (cm^{-1})	Intensity (km/mol)
		1	344	28.7	31	2182	3.5	61	2862	8.7	91	3329	8.3
1648	3692.9	2	369	178.0	32	2197	145.7	62	2892	3.7	92	3341	0.3
1943	1472.9	3	678	3.0	33	2245	1.8	63	2898	2.6	93	3356	0.8
		4	704	10.6	34	2284	5.1	64	2927	0.3	94	3380	0.6
2971	332.3	5	737	3.4	35	2294	42.2	65	2950	5.5	95	3394	0.0
3153	297.2	6	1002	0.1	36	2313	100.0	66	2960	9.7	96	3416	0.1
		7	1032	0.0	37	2324	5.2	67	2970	1.4	97	3420	0.3
		8	1061	0.1	38	2361	2.6	68	3018	0.4	98	3429	0.1
		9	1102	0.0	39	2405	13.9	69	3028	67.5	99	3432	0.1
		10	1315	0.4	40	2430	68.7	70	3040	49.8			
		11	1352	1.5	41	2451	8.7	71	3047	0.0			
		12	1377	0.6	42	2458	1.7	72	3060	22.2			
		13	1417	3.5	43	2498	1.3	73	3087	10.0			
		14	1464	1.1	44	2514	0.1	74	3102	0.2			
		15	1615	7.4	45	2521	0.4	75	3120	0.3			
		16	1661	161.7	46	2569	0.6	76	3136	2.3			
		17	1686	628.1	47	2608	1.9	77	3158	2.1			

18	1691	2314.5	48	2611	0.1	78	3160	0.1
19	1726	147.9	49	2632	13.5	79	3178	2.5
20	1769	31.6	50	2646	0.7	80	3194	0.1
21	1820	8.9	51	2691	2.5	81	3203	0.0
22	1885	1012.6	52	2706	0.2	82	3217	11.3
23	1906	77.2	53	2735	6.7	83	3227	25.2
24	1960	0.9	54	2750	28.5	84	3235	5.6
25	1990	1.4	55	2756	26.7	85	3247	6.0
26	2025	4.0	56	2787	0.6	86	3253	95.8
27	2031	112.0	57	2798	7.7	87	3285	4.0
28	2068	6.2	58	2822	41.1	88	3290	3.5
29	2118	1.5	59	2837	9.3	89	3301	18.0
30	2165	24.8	60	2854	31.6	90	3323	1.5

[Conformer Ⅱ]

Table S7. Peak positions and intensities with LM-2D(*2*OO) for Conformer Ⅱ.

LM-2D(*2*OO)								
	Frequency (cm^{-1})	Intensity (km/mol)		Frequency (cm^{-1})	Intensity (km/mol)		Frequency (cm^{-1})	Intensity (km/mol)
1	313	6.4	31	2283	0.0	61	3225	0.0
2	398	31.8	32	2362	0.0	62	3268	0.0
3	622	0.1	33	2385	0.0	63	3292	0.0
4	701	1.7	34	2424	0.0	64	3319	0.0
5	788	0.2	35	2448	0.0	65	3322	0.0
6	926	0.0	36	2482	0.0	66	3377	0.0
7	1000	0.1	37	2537	0.0	67	3385	0.0
8	1082	0.0	38	2549	0.0	68	3456	0.0
9	1171	0.0	39	2625	0.0	69	3464	0.0
10	1227	0.0	40	2630	0.0	70	3467	0.0
11	1294	0.0	41	2664	0.0	71	3473	0.0
12	1371	0.0	42	2695	0.0	72	3523	0.0
13	1456	0.0	43	2707	0.0	73	3535	0.0
14	1523	0.0	44	2748	0.0	74	3559	0.0
15	1546	0.0	45	2794	0.0	75	3572	0.0
16	1584	0.0	46	2811	0.0	76	3616	0.0
17	1656	0.0	47	2883	0.0	77	3632	0.0
18	1736	0.0	48	2885	0.0	78	3653	0.0
19	1815	0.0	49	2937	0.0	79	3699	0.0
20	1823	0.0	50	2958	0.0	80	3703	0.0
21	1869	0.0	51	2962	0.0	81	3716	0.0
22	1915	0.0	52	2978	0.0	82	3721	0.0
23	1936	0.0	53	3010	0.0	83	3772	0.0
24	2012	0.0	54	3045	0.0	84	3781	0.0
25	2095	0.0	55	3069	0.0	85	3794	0.0
26	2102	0.0	56	3133	0.0	86	3819	0.0
27	2149	0.0	57	3136	0.0	87	3853	0.0
28	2184	0.0	58	3204	0.0	88	3878	0.0
29	2211	0.0	59	3210	0.0	89	3887	0.0
30	2276	0.0	60	3220	0.0	90	3937	0.0

Table S8. Peak positions and intensities with LM-4D(*2*IHB, *2*OO) for Conformer Ⅱ.

LM-2D(*2*IHB)		LM-4D(*2*IHB, *2*OO)												
Frequency (cm^{-1})	Intensity (km/mol)		Frequency (cm^{-1})	Intensity (km/mol)		Frequency (cm^{-1})	Intensity (km/mol)		Frequency (cm^{-1})	Intensity (km/mol)		Frequency (cm^{-1})	Intensity (km/mol)
		1	331	16.9	31	2164	3.3	61	2830	0.1	90	3285	5.9
1631	4142.8	2	377	217.5	32	2169	0.8	62	2851	1.8	91	3291	0.5
1885	1061.0	3	655	0.3	33	2218	6.3	63	2873	0.6	92	3319	0.7
		4	696	17.5	34	2227	3.4	64	2906	0.0	93	3321	0.9
2988	223.3	5	753	2.6	35	2271	20.7	65	2936	1.2	94	3333	14.7
3015	444.9	6	972	0.0	36	2284	21.7	66	2945	11.6	95	3345	0.2
		7	1007	0.1	37	2299	111.1	67	2950	0.2	96	3359	23.0
		8	1061	0.1	38	2345	10.4	68	2952	1.7	97	3383	11.8
		9	1126	0.0	39	2370	48.0	69	2979	7.7	98	3386	0.0
		10	1282	0.0	40	2418	10.8	70	2988	2.8	99	3409	0.0
		11	1310	1.5	41	2427	1.1	71	3014	3.9			
		12	1362	0.3	42	2439	0.0	72	3054	2.0			
		13	1424	5.9	43	2439	0.5	73	3068	4.5			
		14	1495	0.4	44	2487	0.2	74	3075	94.6			
		15	1585	0.2	45	2509	0.2	75	3079	0.1			
		16	1604	30.9	46	2546	0.0	76	3093	104.3			
		17	1656	1.8	47	2548	1.4	77	3109	54.5			
		18	1676	3533.2	48	2589	0.2	78	3118	3.1			
		19	1718	216.8	49	2608	0.5	79	3131	0.1			
		20	1781	36.1	50	2628	0.3	80	3162	20.7			
		21	1838	704.1	51	2676	5.0	81	3176	0.6			
		22	1858	2.9	52	2695	1.0	82	3187	2.2			
		23	1880	2.9	53	2695	20.6	83	3192	0.5			
		24	1891	1.4	54	2698	4.6	84	3193	0.2			
		25	1944	1.5	55	2699	2.9	85	3216	2.2			
		26	1998	0.2	56	2754	1.5	86	3223	0.0			
		27	2009	12.5	57	2783	3.1	87	3249	0.0			
		28	2066	4.4	58	2797	80.7	88	3253	0.0			
		29	2132	175.7	59	2817	37.3	89	3268	0.3			
		30	2139	0.8	60	2822	50.7	90	3285	5.9			

[Conformer Ⅰ: free OH and O···O]

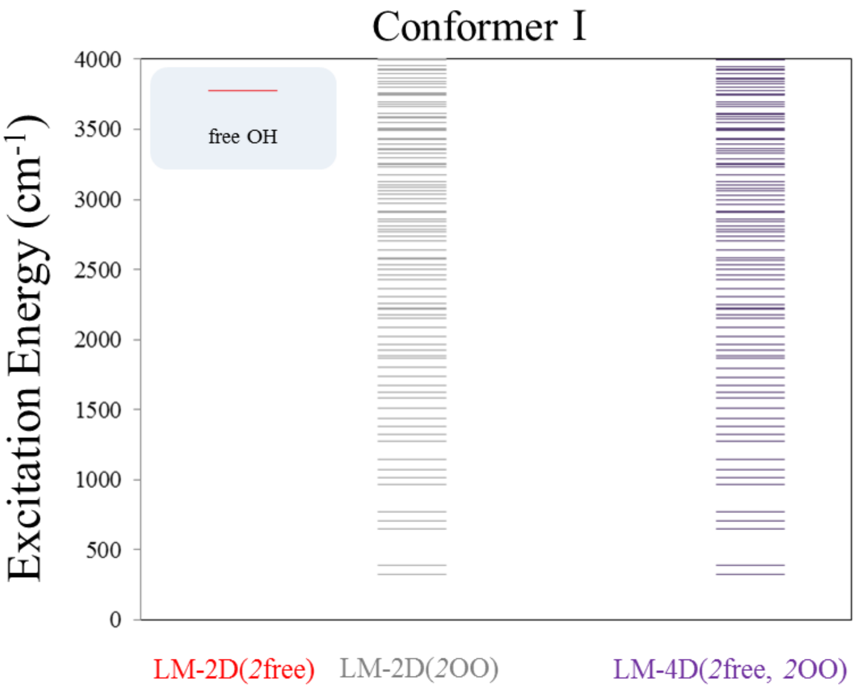


Figure. S3 Excitation energies with LM-2D(*2*IHB), LM-2D(*2*OO) and LM-4D(*2*free, *2*OO) for Conformer Ⅰ.

Table S9. Peak positions and intensities with LM-4D(*2*free, *2*OO) for Conformer Ⅰ

LM-2D(*2*free)		LM-4D(2free, 2OO)											
Frequency (cm^{-1})	Intensity (km/mol)		Frequency (cm^{-1})	Intensity (km/mol)		Frequency (cm^{-1})	Intensity (km/mol)		Frequency (cm^{-1})	Intensity (km/mol)		Frequency (cm^{-1})	Intensity (km/mol)
		1	326	7.7	31	2304	0.0	61	3257	0.0	91	3922	0.0
3774	2.3	2	387	28.9	32	2363	0.0	62	3292	0.0	92	3927	0.0
3777	1.3	3	648	0.2	33	2428	0.0	63	3330	0.0	93	3949	0.0
		4	703	1.5	34	2460	0.0	64	3347	0.0	94	3995	0.0
		5	767	0.2	35	2497	0.0	65	3359	0.0	95	3997	0.0
		6	965	0.0	36	2501	0.0	66	3393	0.0			
		7	1015	0.1	37	2534	0.0	67	3429	0.0			
		8	1074	0.0	38	2570	0.0	68	3435	0.0			
		9	1140	0.0	39	2582	0.0	69	3488	0.0			
		10	1277	0.0	40	2638	0.0	70	3502	0.0			
		11	1322	0.0	41	2700	0.0	71	3507	0.0			
		12	1377	0.0	42	2735	0.0	72	3547	0.0			
		13	1439	0.0	43	2767	0.0	73	3576	0.0			
		14	1507	0.0	44	2785	0.0	74	3588	0.0			
		15	1583	0.0	45	2810	0.0	75	3608	0.0			
		16	1623	0.0	46	2838	0.0	76	3612	0.0			
		17	1674	0.0	47	2856	0.0	77	3659	0.0			
		18	1733	0.0	48	2908	0.0	78	3680	0.0			
		19	1798	0.0	49	2911	0.0	79	3692	0.0			
		20	1868	0.0	50	2967	0.0	80	3743	0.0			
		21	1883	0.0	51	3000	0.0	81	3751	0.0			
		22	1920	0.0	52	3032	0.0	82	3753	0.0			
		23	1966	0.0	53	3062	0.0	83	3774	2.3			
		24	2021	0.0	54	3081	0.0	84	3777	1.3			
		25	2083	0.0	55	3101	0.0	85	3799	0.0			
		26	2151	0.0	56	3125	0.0	86	3825	0.0			
		27	2176	0.0	57	3172	0.0	87	3840	0.0			
		28	2213	0.0	58	3174	0.0	88	3860	0.0			
		29	2222	0.0	59	3230	0.0	89	3863	0.0			
		30	2252	0.0	60	3246	0.0	90	3899	0.0			

1-4. Temperature dependence of the simulated spectra

In the text, we used the temperature of 50K in the simulation to determine the inhomogeneous widths for IHB OH stretching vibration. Here we show the simulated spectra with using other temperatures (100K and 150K). Although the inhomogeneous linewidth generally becomes larger as the temperature increases, the impact of such increase on the overall shape of the spectra is very small due to the very large homogeneous width for IHB OHs.

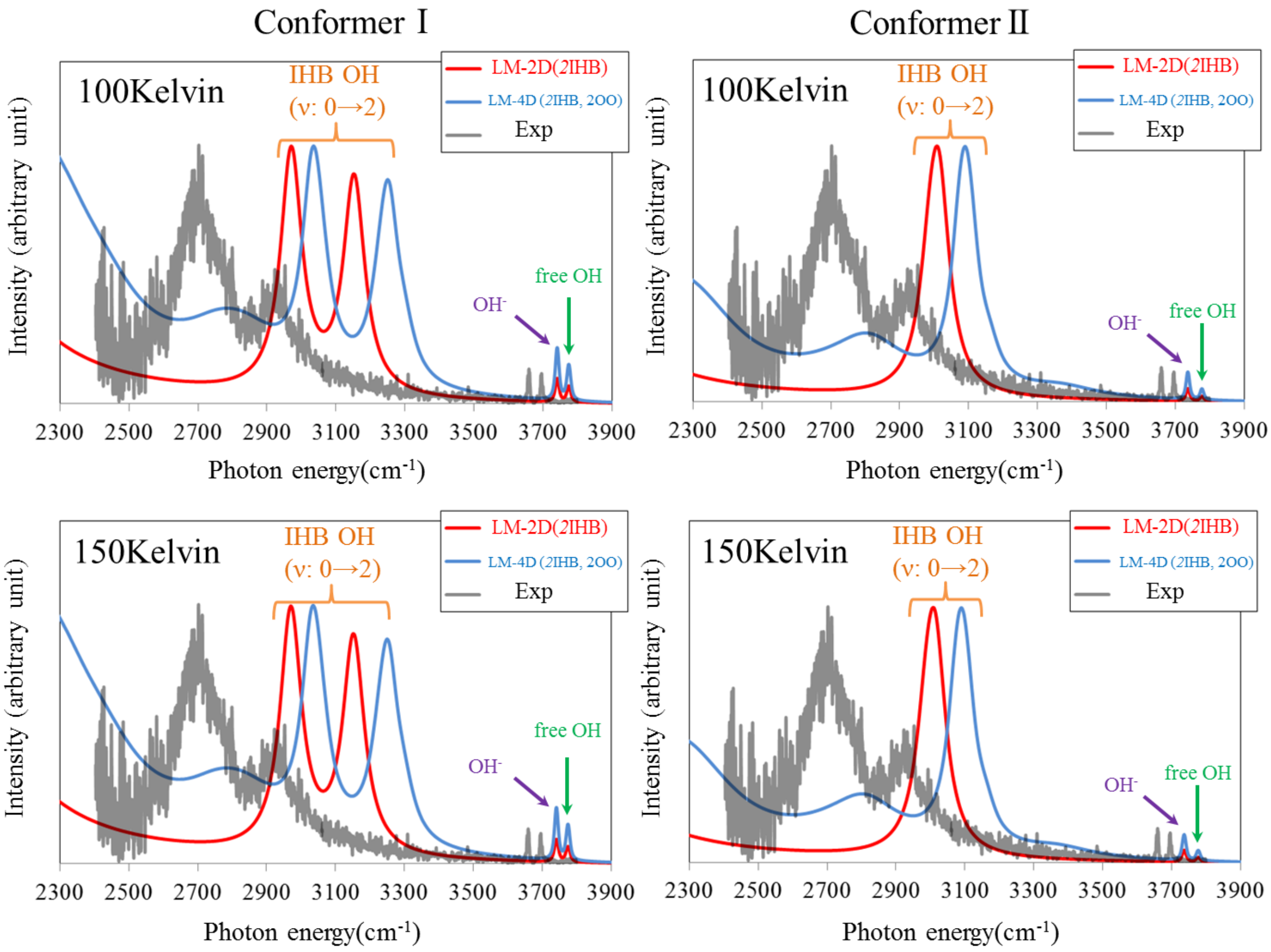


Figure S4. Simulated vibrational spectra (100K and 150K)

1-5. Effect of the argon atom attachment

As shown in Table S1, binding energy of an argon atom to $OH^{-}(H_2O)_2$ is small, which is the one of the reasons to utilize the messenger atoms (Ar, Ne, H_2 etc) in the experiment of the vibrational spectra. The attachment effect of the messenger should be small both for the structure and vibrational signature. Indeed, validity of this assumption has been confirmed for many systems. For specific systems, however, apparent messenger effects were found both for the existence ratio of the conformers/isomers and vibrational spectrum. Such messenger effects have been observed mainly for the protonated water clusters, and there is no deterministic report showing such effect for the deprotonated water clusters, $OH^{-}(H_2O)_n$. Thus, to explore the messenger effect for $OH^{-}(H_2O)_2$ is relevant. In the following, we show the lists of the peak positions and intensities for the argon atom attached structures, $OH^{-}(H_2O)_2{\cdot}Ar$. As described in the text, while the argon attachment causes the peak shift and change of the values of the intensities, overall structure of the vibrational spectrum is not changed.

[Ar-I]

Table S10. Peak positions and intensities with LM-4D(*2*IHB, *2*free) for Ar- Ⅰ.

LM-2D(*2*IHB)			LM-4D(*2*IHB, *2*OO)											
Frequency (cm^{-1})	Intensity (km/mol)		Frequency (cm^{-1})	Intensity (km/mol)		Frequency (cm^{-1})	Intensity (km/mol)		Frequency (cm^{-1})	Intensity (km/mol)		Frequency (cm^{-1})	Intensity (km/mol)
		1	341	27.3	31	2166	0.3	61	2869	36.2	91	3330	9.3
1674	3145.5	2	366	144.4	32	2221	156.5	62	2879	4.5	92	3340	0.8
1988	1567.4	3	672	2.9	33	2236	8.5	63	2907	1.9	93	3354	20.6
		4	699	8.3	34	2267	1.3	64	2910	2.7	94	3372	0.4
2986	319.4	5	730	3.6	35	2298	25.2	65	2934	0.0	95	3393	0.7
3217	250.6	6	994	0.1	36	2315	28.1	66	2949	0.6	96	3404	0.1
		7	1025	0.1	37	2328	103.4	67	2964	16.4	97	3409	0.2
		8	1052	0.1	38	2345	15.6	68	2998	1.1	98	3427	0.2
		9	1092	0.0	39	2389	3.9	69	3023	3.3	99	3433	0.0
		10	1304	0.2	40	2430	7.9	70	3042	4.2			
		11	1343	0.9	41	2438	3.6	71	3056	112.9			
		12	1367	0.6	42	2455	94.9	72	3064	0.8			
		13	1405	2.1	43	2493	0.3	73	3081	1.6			
		14	1450	0.9	44	2509	0.3	74	3100	19.8			
		15	1602	2.5	45	2524	2.0	75	3103	2.0			
		16	1652	36.9	46	2550	0.9	76	3139	0.1			
		17	1674	15.8	47	2595	0.2	77	3145	0.8			
		18	1702	1604.5	48	2621	1.4	78	3162	2.0			
		19	1717	1037.1	49	2627	0.6	79	3166	1.3			
		20	1755	59.3	50	2639	14.2	80	3175	0.2			
		21	1803	9.7	51	2671	1.0	81	3182	0.0			
		22	1889	33.0	52	2687	0.2	82	3217	1.9			
		23	1918	1054.1	53	2721	1.2	83	3221	0.3			
		24	1951	1.5	54	2757	31.3	84	3238	1.2			
		25	1975	4.9	55	2767	4.4	85	3253	0.9			
		26	2011	1.6	56	2777	1.8	86	3268	1.0			

27	2046	142.5	57	2789	34.5	87	3277	1.8
28	2052	32.4	58	2819	2.2	88	3302	99.9
29	2101	3.3	59	2824	11.8	89	3316	8.3
30	2150	1.6	60	2851	12.9	90	3321	9.8

[Ar-II]

Table S11. Peak positions and intensities with LM-4D(*2*IHB, *2*free) for Ar- II.

LM-2D(*2*IHB)		LM-4D(*2*IHB, *2*OO)											
Frequency (cm^{-1})	Intensity (km/mol)		Frequency (cm^{-1})	Intensity (km/mol)		Frequency (cm^{-1})	Intensity (km/mol)		Frequency (cm^{-1})	Intensity (km/mol)		Frequency (cm^{-1})	Intensity (km/mol)
		1	329	17.7	31	2157	9.5	61	2823	77.3	91	3293	0.2
1651	3652.4	2	375	183.6	32	2163	0.7	62	2861	1.3	92	3312	0.5
1900	1141.3	3	652	0.3	33	2209	8.8	63	2864	1.6	93	3314	0.1
		4	693	15.0	34	2220	3.4	64	2897	0.0	94	3336	0.0
3007	232.7	5	749	2.8	35	2266	5.7	65	2927	1.2	95	3360	15.4
3033	388.0	6	968	0.0	36	2292	38.7	66	2941	0.9	96	3377	0.1
		7	1003	0.1	37	2308	109.1	67	2944	1.3	97	3378	8.7
		8	1057	0.1	38	2339	29.8	68	2954	9.0	98	3399	23.8
		9	1121	0.0	39	2376	37.4	69	2988	4.9	99	3400	0.0
		10	1278	0.0	40	2412	18.4	70	2994	2.0			
		11	1305	1.1	41	2427	0.9	71	3005	4.0			
		12	1357	0.3	42	2432	0.6	72	3045	0.6			
		13	1418	4.1	43	2440	0.2	73	3059	0.9			
		14	1488	0.4	44	2478	0.2	74	3072	0.9			
		15	1580	0.1	45	2501	0.2	75	3097	100.9			
		16	1599	16.2	46	2539	0.5	76	3105	23.6			
		17	1650	1.6	47	2546	0.5	77	3120	0.8			
		18	1689	2698.7	48	2591	0.4	78	3123	116.4			
		19	1713	619.3	49	2599	0.5	79	3125	5.2			
		20	1775	20.7	50	2637	0.4	80	3167	16.3			
		21	1848	768.6	51	2667	2.6	81	3168	0.8			
		22	1850	2.9	52	2690	0.3	82	3180	10.5			
		23	1874	8.5	53	2691	0.8	83	3185	0.6			
		24	1886	1.7	54	2704	21.9	84	3186	0.4			
		25	1938	2.5	55	2705	3.9	85	3224	2.8			
		26	1992	1.3	56	2745	0.8	86	3227	0.0			
		27	2022	9.6	57	2775	1.7	87	3246	0.1			
		28	2058	4.6	58	2796	34.0	88	3246	0.0			
		29	2131	0.6	59	2820	3.0	89	3270	0.3			
		30	2141	174.8	60	2823	40.3	90	3291	2.0			

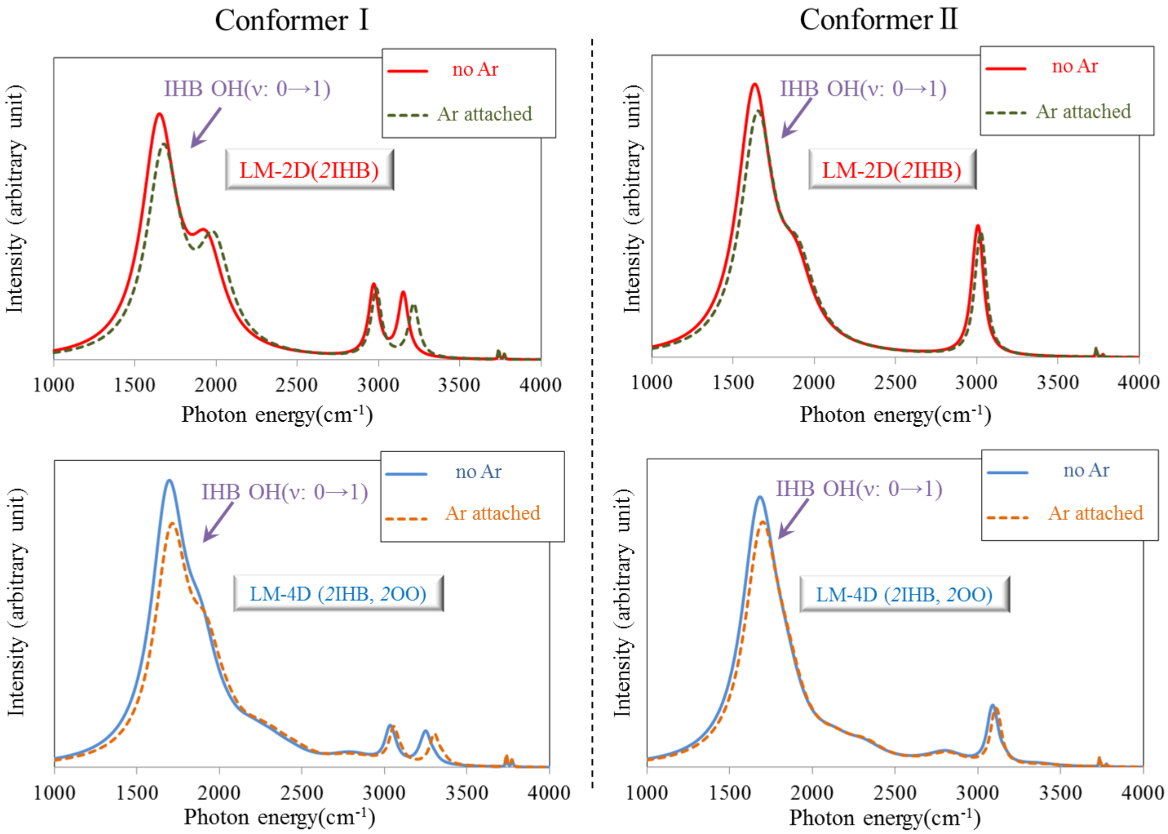


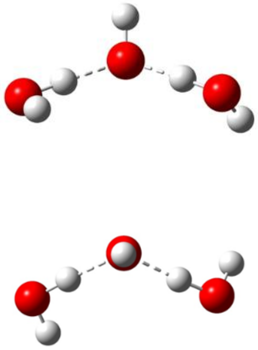
Figure S5. Argon attachment effect on the shape of the IHB OH fundamental intense peaks

2. Optimized geometry (Cartesian coordinate)

2-1. $OH^-(H_2O)_2$

[Conformer I]

MP2/6-311++G(3df,3pd)



O	1.238899	2.251199	-0.372819
O	-2.672016	0.393650	-0.177450
O	-0.188739	0.266806	0.405310
H	0.697494	1.438635	-0.045017
H	0.542208	2.875471	-0.578798
H	-1.671742	0.365488	0.088672
H	-2.737228	-0.349743	-0.777559
H	-0.089275	0.147379	1.352442

MP2/6-311++G(3df,3pd): Counterpoise optimization

O	1.337307	2.258655	-0.398799
O	-2.775622	0.273811	-0.138115
O	-0.250744	0.372719	0.404078
H	0.747684	1.491548	-0.063052
H	0.689400	2.948928	-0.543097
H	-1.781901	0.339618	0.114710
H	-2.763548	-0.421558	-0.796158
H	-0.082975	0.125164	1.315214

MP2/aug-cc-pVTZ

O	1.361083	2.242557	-0.380846
O	-2.778459	0.259658	-0.137579
O	-0.266160	0.393177	0.349830
H	0.732447	1.479359	-0.078046

H	0.746141	2.972668	-0.486644
H	-1.769090	0.340380	0.086620
H	-2.789059	-0.490063	-0.737545
H	-0.117302	0.191150	1.278990

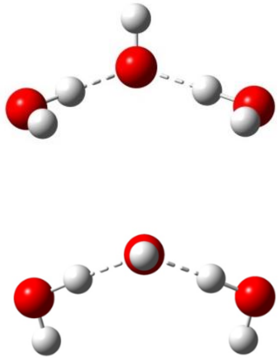
MP2/aug-cc-pVTZ: Counterpoise optimization

O	1.398300	2.241080	-0.408247
O	-2.822440	0.198252	-0.116138
O	-0.297520	0.445707	0.361342
H	0.752521	1.501938	-0.093576
H	0.813765	3.001159	-0.460809
H	-1.822023	0.324528	0.107337
H	-2.791339	-0.509591	-0.764164
H	-0.111661	0.185813	1.269035

[Conformer II]

MP2/6-311++G(3df,3pd)

O	2.266862	-0.434728	0.182226
O	-2.266847	-0.435076	0.182104
O	0.000091	-1.294215	-0.637817
H	1.363802	-0.792092	-0.172141
H	2.020150	-0.082958	1.037943
H	-1.363704	-0.792288	-0.172221
H	-2.020298	-0.083556	1.037970
H	0.000124	-2.250431	-0.552683



MP2/6-311++G(3df,3pd): Counterpoise optimization

O	2.408799	-0.415262	0.071267
O	-2.408872	-0.415919	0.071249

O	0.000077	-1.244292	-0.393710
H	1.466479	-0.753977	-0.151464
H	2.322970	-0.194414	0.998857
H	-1.466460	-0.754388	-0.151472
H	-2.323025	-0.194758	0.998762
H	0.000213	-2.192334	-0.538108

MP2/aug-cc-pVTZ

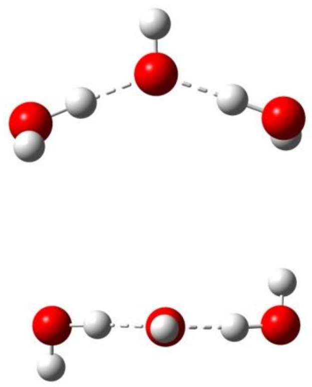
O	2.354628	-0.438408	0.114516
O	-2.354652	-0.438889	0.114419
O	0.000083	-1.241265	-0.518513
H	1.415246	-0.770876	-0.168267
H	2.201310	-0.150325	1.017579
H	-1.415191	-0.771164	-0.168326
H	-2.201422	-0.150732	1.017472
H	0.000178	-2.203684	-0.503498

MP2/aug-cc-pVTZ: Counterpoise optimization

O	2.401310	-0.428959	0.081852
O	-2.401336	-0.429453	0.081746
O	0.000080	-1.229750	-0.443795
H	1.454327	-0.757503	-0.163148
H	2.293477	-0.185366	1.004275
H	-1.454275	-0.757803	-0.163211
H	-2.293584	-0.185800	1.004163
H	0.000180	-2.190708	-0.496499

[Other (C_2 symmetry)]

MP2/6-311++G(3df,3pd), NOTE: Saddle point (imaginary frequency 49.8 cm^{-1})



O	0.094101	2.395431	-0.309846
O	-0.094101	-2.395431	-0.309846
O	0.000000	0.000000	0.582045
H	0.089020	1.434663	0.065475
H	-0.784522	2.462094	-0.684744
H	-0.089020	-1.434663	0.065475
H	0.784522	-2.462094	-0.684744
H	0.000000	0.000000	1.541665

MP2/6-311++G(3df,3pd): Counterpoise optimization, NOTE: Saddle point (imaginary frequency 27.6 cm^{-1})

O	-0.006425	2.398109	-0.322613
O	0.006417	-2.398102	-0.322629
O	0.000009	0.000000	0.649231
H	0.030714	1.459356	0.088042
H	-0.857239	2.383814	-0.761541
H	-0.030713	-1.459351	0.088031
H	0.857244	-2.383823	-0.761532
H	-0.000006	-0.000004	1.607953

MP2/aug-cc-pVTZ, NOTE: Saddle point (imaginary frequency 25.2 cm^{-1})

O	0.094197	2.415244	-0.305306
O	-0.094197	-2.415244	-0.305306
O	0.000000	0.000000	0.558036
H	0.088506	1.446426	0.056747
H	-0.795083	2.498961	-0.657864
H	-0.088506	-1.446426	0.056747
H	0.795083	-2.498961	-0.657864
H	0.000000	0.000000	1.520289

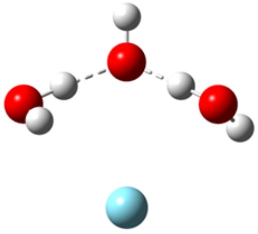
MP2/aug-cc-pVTZ: Counterpoise optimization, NOTE: Saddle point (imaginary frequency 22.1 cm^{-1})

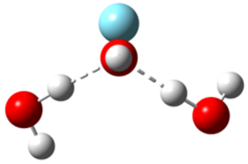
O	-0.002558	2.424698	-0.307187
O	0.002572	-2.424706	-0.307175
O	-0.000016	-0.000002	0.586232
H	0.034101	1.464875	0.067698
H	-0.886495	2.455069	-0.680947
H	-0.034105	-1.464881	0.067706
H	0.886499	-2.455053	-0.680960
H	0.000003	0.000000	1.548403

2-2. $OH^{-}(H_2O)_3\cdot Ar$

[Ar-I]

MP2/6-311++G(3df,3pd)





O	2.127837	0.307094	-2.266212
O	-2.031084	0.443472	-2.062735
O	0.034682	-0.918134	-1.417366
H	1.316886	-0.209753	-1.903034
H	1.730189	1.146127	-2.502563
H	-1.193322	-0.088480	-1.771034
H	-2.481505	-0.185359	-2.627425
H	0.071824	-0.994632	-0.461172
Ar	-0.062520	-1.408618	-4.596927

MP2/6-311++G(3df,3pd): Counterpoise optimization

O	2.313712	0.161955	-2.284141
O	-2.303973	0.305712	-2.033080
O	0.014979	-0.670988	-1.424435

H	1.424466	-0.198747	-1.925537
H	2.102631	1.084079	-2.433260
H	-1.379970	-0.049554	-1.763281
H	-2.646050	-0.414832	-2.562806
H	0.055516	-0.842657	-0.481585
Ar	-0.068325	-1.283250	-4.700343

MP2/aug-cc-pVTZ

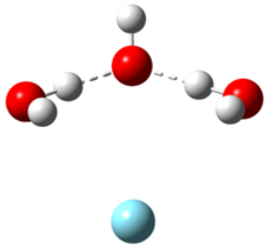
O	1.096178	2.181821	-0.704752
O	-2.746344	0.036012	0.069171
O	-0.398858	0.763477	0.824255
H	0.500690	1.579862	-0.107618
H	1.174677	2.978152	-0.173691
H	-1.807309	0.311449	0.401184
H	-2.657428	0.139218	-0.881686
H	0.093930	-0.023170	1.079745
Ar	-2.029256	3.526256	0.766604

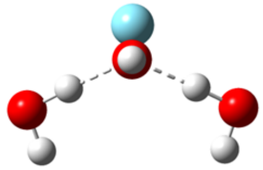
MP2/aug-cc-pVTZ: Counterpoise optimization

O	1.152500	2.207434	-0.694246
O	-2.780925	0.023199	0.094272
O	-0.394039	0.753291	0.780692
H	0.543330	1.594935	-0.129204
H	1.221032	2.988498	-0.139871
H	-1.835962	0.296231	0.400532
H	-2.706579	0.096072	-0.860492
H	0.097881	-0.023620	1.065414
Ar	-2.070958	3.557037	0.756116

[Ar-II]

MP2/6-311++G(3df,3pd), NOTE: Saddle point (imaginary frequency 31.8 cm^{-1})





O	-0.488411	-0.997220	2.210260
O	-0.488363	-0.997282	-2.210268
O	0.718159	-1.464568	0.000016
H	0.020098	-1.192634	1.332639
H	-1.398571	-0.966248	1.914166
H	0.020128	-1.192655	-1.332628
H	-1.398533	-0.966340	-1.914203
H	0.969357	-2.391303	0.000026
Ar	0.570844	1.753612	-0.000007

MP2/6-311++G(3df,3pd): Counterpoise optimization

O	-0.368767	-0.956772	2.374775
O	-0.368754	-0.956942	-2.374774
O	0.499694	-1.520462	0.000026
H	0.008626	-1.184980	1.449037
H	-1.312460	-1.010393	2.222330
H	0.008631	-1.185086	-1.449019
H	-1.312449	-1.010473	-2.222312
H	0.865057	-2.407356	0.000057
Ar	0.505130	1.817825	-0.000120

MP2/aug-cc-pVTZ

O	-0.413157	-0.975991	2.304494
O	-0.413101	-0.976256	-2.304553
O	0.609350	-1.466105	0.000013
H	0.022513	-1.177501	1.387139

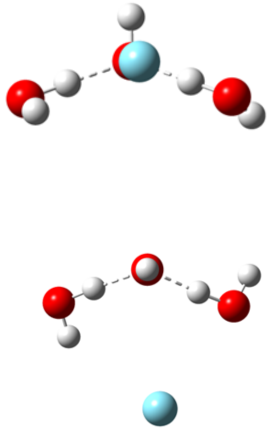
H	-1.349635	-0.995316	2.092848
H	0.022548	-1.177673	-1.387169
H	-1.349568	-0.994983	-2.092805
H	0.877740	-2.390817	0.000080
Ar	0.518018	1.740006	-0.000047

MP2/aug-cc-pVTZ: Counterpoise optimization

O	-0.374773	-0.965193	2.361428
O	-0.374726	-0.965280	-2.361454
O	0.540756	-1.491923	0.000007
H	0.020154	-1.178546	1.432807
H	-1.318979	-1.004759	2.191604
H	0.020185	-1.178599	-1.432820
H	-1.318934	-1.004829	-2.191634
H	0.841550	-2.406431	0.000036
Ar	0.489475	1.780925	0.000026

[Other-1 (Conformer I type**)]**

MP2/6-311++G(3df,3pd)



O	2.369956	0.073189	-2.066752
O	-2.073444	0.675482	-1.996000
O	0.037952	-0.461484	-1.137528
H	1.447297	-0.167409	-1.679601
H	2.209919	0.945170	-2.429072
H	-1.206987	0.237992	-1.630473
H	-2.563497	-0.086601	-2.306241
H	0.060923	-0.408108	-0.179406
Ar	0.117244	3.108236	-1.544741

MP2/6-311++G(3df,3pd): Counterpoise optimization, NOTE: We could not find the corresponding structure.

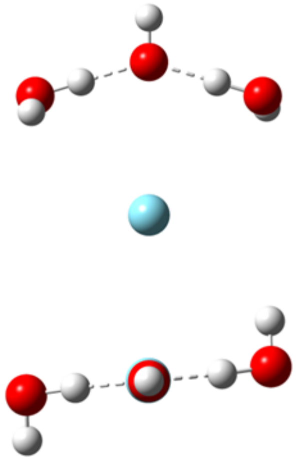
MP2/aug-cc-pVTZ, NOTE: We could not find the corresponding structure.

MP2/aug-cc-pVTZ: Counterpoise optimization, NOTE: We could not find the corresponding structure.

[Other-2 (C_2 symmetry)]

MP2/6-311++G(3df,3pd), NOTE: Saddle point (imaginary frequency 22.6 cm^{-1})

O	0.090728	2.452438	1.248133
O	-0.090728	-2.452438	1.248133
O	0.000000	0.000000	1.981760
H	0.084240	1.466508	1.548995
H	-0.809662	2.571656	0.944575
H	-0.084240	-1.466508	1.548995
H	0.809662	-2.571656	0.944575
H	0.000000	0.000000	2.942004
Ar	0.000000	0.000000	-1.332172



MP2/6-311++G(3df,3pd): Counterpoise optimization, NOTE: Saddle point (imaginary frequency 21.6 cm^{-1})

O	0.004063	2.476414	-0.830735
O	-0.004032	-2.476408	-0.830737
O	-0.000014	0.000002	-1.593760
H	-0.029465	1.500250	-1.142232
H	0.903289	2.550302	-0.510259
H	0.029467	-1.500244	-1.142237
H	-0.903252	-2.550321	-0.510252
H	-0.000026	0.000000	-2.553181
Ar	-0.000030	0.000006	1.824955

MP2/aug-cc-pVTZ, NOTE: Saddle point (imaginary frequency 20.9 cm^{-1})

O	0.091648	2.469848	1.050067
O	-0.091648	-2.469848	1.050067
O	0.000000	0.000000	1.758010
H	0.084749	1.477586	1.338536
H	-0.818348	2.603894	0.774119
H	-0.084749	-1.477586	1.338536
H	0.818348	-2.603894	0.774119
H	0.000000	0.000000	2.720950
Ar	0.000000	0.000000	-1.518856

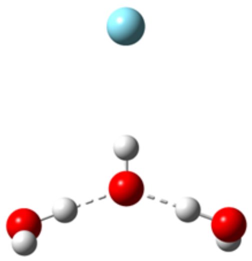
MP2/aug-cc-pVTZ: Counterpoise optimization, NOTE: Saddle point (imaginary frequency 20.9 cm^{-1})

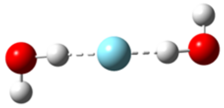
O	0.001554	2.485512	-0.827858
O	-0.001543	-2.485504	-0.827843
O	-0.000008	0.000002	-1.549748
H	-0.032665	1.498334	-1.121332
H	0.917110	2.579786	-0.554207
H	0.032664	-1.498326	-1.121320
H	-0.917111	-2.579799	-0.554236
H	-0.000005	-0.000010	-2.512612
Ar	0.000004	0.000004	1.788885

[Other-3 (C_2 symmetry)]

MP2/6-311++G(3df,3pd), NOTE: Triple saddle point (imaginary frequency 78.3, 24.2, 12.4 cm^{-1})

O	0.092512	2.406924	-2.304144
O	-0.092512	-2.406924	-2.304144
O	0.000000	0.000000	-1.440630
H	0.088042	1.441152	-1.943147
H	-0.788198	2.481014	-2.672721





H	-0.088042	-1.441152	-1.943147
H	0.788198	-2.481014	-2.672721
H	0.000000	0.000000	-0.481745
Ar	0.000000	0.000000	2.369311

MP2/6-311++G(3df,3pd): Counterpoise optimization, NOTE: Double saddle point (imaginary frequency 18.5, 11.8 cm^{-1})

O	-0.006000	2.409575	-2.024537
O	0.005936	-2.409545	-2.024412
O	0.000090	0.000040	-1.078239
H	0.030765	1.465793	-1.626562
H	-0.860761	2.405046	-2.455947
H	-0.030729	-1.465741	-1.626480
H	0.860661	-2.405098	-2.455897
H	0.000077	0.000069	-0.119718
Ar	-0.000039	-0.000139	2.978599

MP2/aug-cc-pVTZ, NOTE: Triple saddle point (imaginary frequency 44.2, 15.0, 13.1 cm^{-1})

O	0.094670	2.426363	-1.890877
O	-0.094670	-2.426363	-1.890877
O	0.000000	0.000000	-1.055867
H	0.088775	1.452753	-1.543321
H	-0.796882	2.518219	-2.235607
H	-0.088775	-1.452753	-1.543321
H	0.796882	-2.518219	-2.235607
H	0.000000	0.000000	-0.094219
Ar	0.000000	0.000000	2.742192

MP2/aug-cc-pVTZ: Counterpoise optimization, NOTE: We could not find the corresponding structure.