Electronic Supplementary Information

Multidimensional OH local mode calculations for $OH^-(H_2O)_3$

~ Importance of intermode anharmonicity ~

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: kt@gate.sinica.edu.tw

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1. Additional Calculation Results

As described in the text, all the calculation for the electronic structure calculations including dipole moment values were performed with Gaussian 09 program with MP2/6-311++G(3df,3pd) except for Figure S2.

1-1. IHB OH and O···O coupling by LM-2D(KC) and LM-2D models

We obtained the IHB-OH and O-O stretching combination band with 2-dimensional PES and DMF. LM-2D(KC) includes the kinetic energy coupling term in Eq.(1). LM-2D does not include kinetic energy coupling term.

LM-2D(KC)

Table S1 Peak positions and intensities by LM-2D(KC) for IHB OH and O···O stretching vibrations

frequency(cm^{-1})	Intensity(km/mol)	(ν_{OH},ν_{OO})
330	34.5	(0,1)
648	2.7	(0,2)
955	0.2	(0,3)
1251	0.0	(0,4)
1534	0.0	(0,5)
1807	0.0	(0,6)
2068	0.1	(0,7)
2317	2.9	(0,8)
2358	1785.8	(1,0)
2555	0.1	(0,9)
2782	42.4	(0,10)
2787	155.9	(1,1)
3003	0.0	(0,11)
3188	13.1	(1,2)
3216	0.0	(0,12)
3422	0.0	(0,13)
3567	0.1	(1,3)
3624	0.0	(0,14)
3821	0.0	(0,15)

LM-2D (No inclusion of the kinetic energy coupling term)

Table S2 Peak positions and intensities by LM-2D for IHB OH and O···O stretching vibrations

frequency(cm^{-1})	Intensity(km/mol)	(v_{OH},v_{OO})
338	34.2	(0,1)
663	2.4	(0,2)
976	0.1	(0,3)
1277	0.0	(0,4)
1566	0.0	(0,5)
1842	0.1	(0,6)
2106	0.1	(0,7)
2344	1900.3	(1,0)
2358	11.2	(0,8)
2599	0.0	(0,9)
2785	144.6	(1,1)
2829	0.1	(0,10)
3051	0.0	(0,11)
3197	12.1	(1,2)
3267	0.0	(0,12)
3476	0.0	(0,13)
3584	0.2	(1,3)
3680	0.0	(0,14)
3879	0.0	(0,15)

1-2. Inter mode coupling effect for OH stretching vibrations

We show the dependence of the peak position on the treatment of inter mode coupling effect. As described in the text, LM is Local mode model calculation, which does not include inter mode coupling, LM-HC includes the inter mode coupling only using the harmonic term, LM-3D includes the full inter mode coupling effects.

Table S3. Peak positions by LM, LM-HC and LM-3D

Conformer Ⅰ				Conformer Ⅱ			
Stretching Mode	LM Frequency (cm^{-1})	LM-HC Frequency (cm^{-1})	LM-3D Frequency (cm^{-1})	Stretching Mode	LM Frequency (cm^{-1})	LM-HC Frequency (cm^{-1})	LM-3D Frequency (cm^{-1})
IHB OH	2423	2418	2419	IHB OH	2281	2292	2302
	2423	2418	2419		2347	2377	2450
	2423	2494	2655		2721	2740	2818
free OH	3773	3773	3773	free OH	3745	3745	3745
	3773	3773	3773		3774	3774	3774
	3773	3773	3773		3777	3777	3777

Conformer Ⅲ				Conformer Ⅳ			
Stretching Mode	LM Frequency (cm^{-1})	LM-3D Frequency (cm^{-1})	LM-3D Frequency (cm^{-1})	Stretching Mode	LM Frequency (cm^{-1})	LM-3D Frequency (cm^{-1})	LM-3D Frequency (cm^{-1})
IHB OH	2271	2290	2314	IHB OH	2682	2675	2666
	2531	2523	2533		2682	2675	2666
	2531	2587	2718		2682	2733	2876
free OH	3765	3765	3765	free OH	3731	3728	3727
	3765	3765	3765		3731	3733	3732
	3769	3769	3769		3731	3733	3732

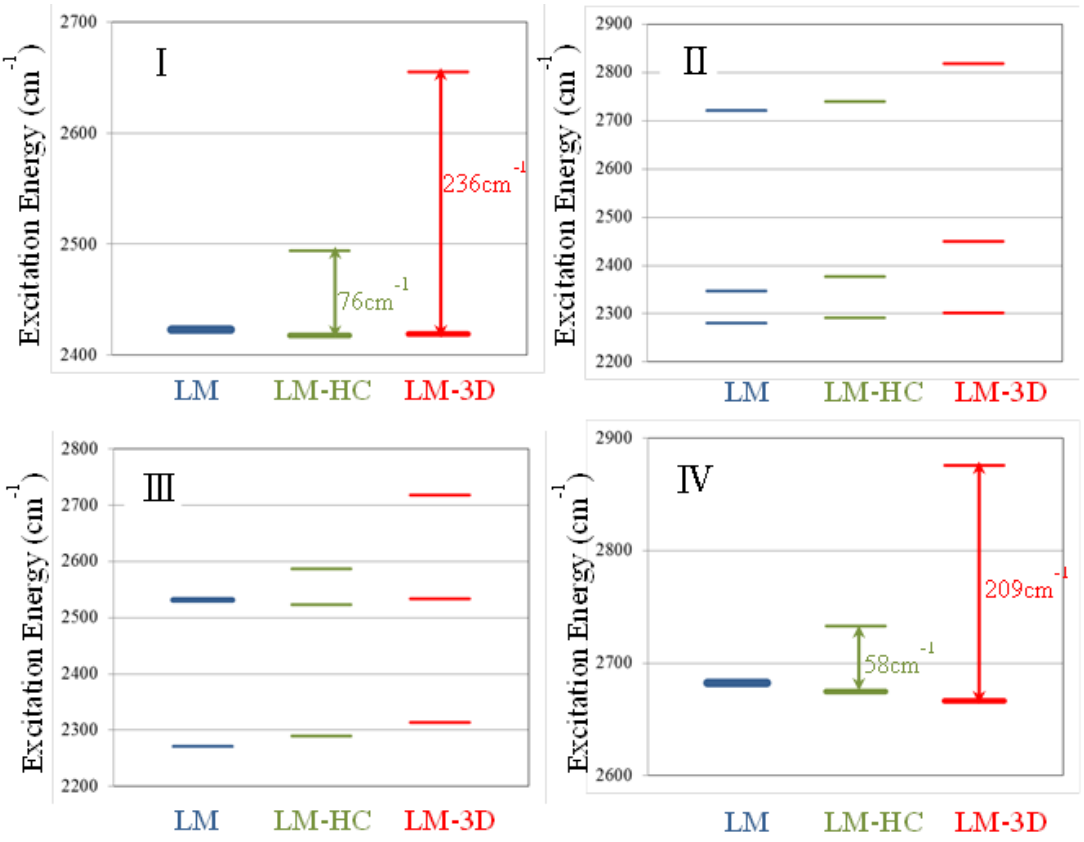

Figure S1. Dependence of inter mode coupling effect treatment for the peak positions of IHB OH stretching vibrations.

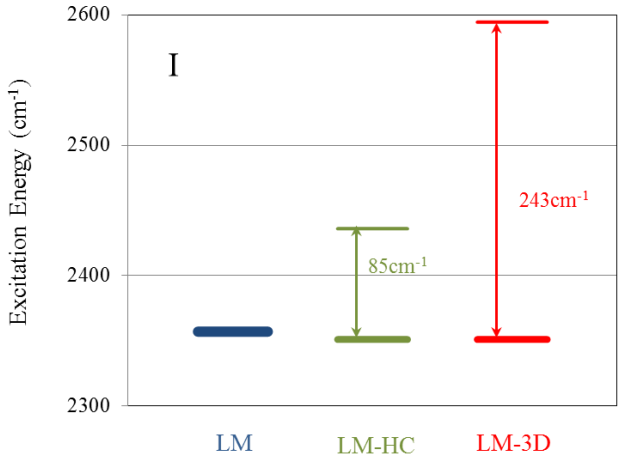

Figure S2. Dependence of inter mode coupling effect treatment for the peak positions of IHB OH stretching vibrations for Conformer I using B3LYP/6-31+G(d,p).

1-3. Temperature dependence of OH vibrational spectra

In the text, we used the temperature of 50K in the calculation of the inhomogeneous linewidths. Here we show the simulated spectra with using other temperatures (100K and 150K). As shown in Eq.(5) of the text, the value of the inhomogeneous linewidth is generally becomes large as the temperature increases.

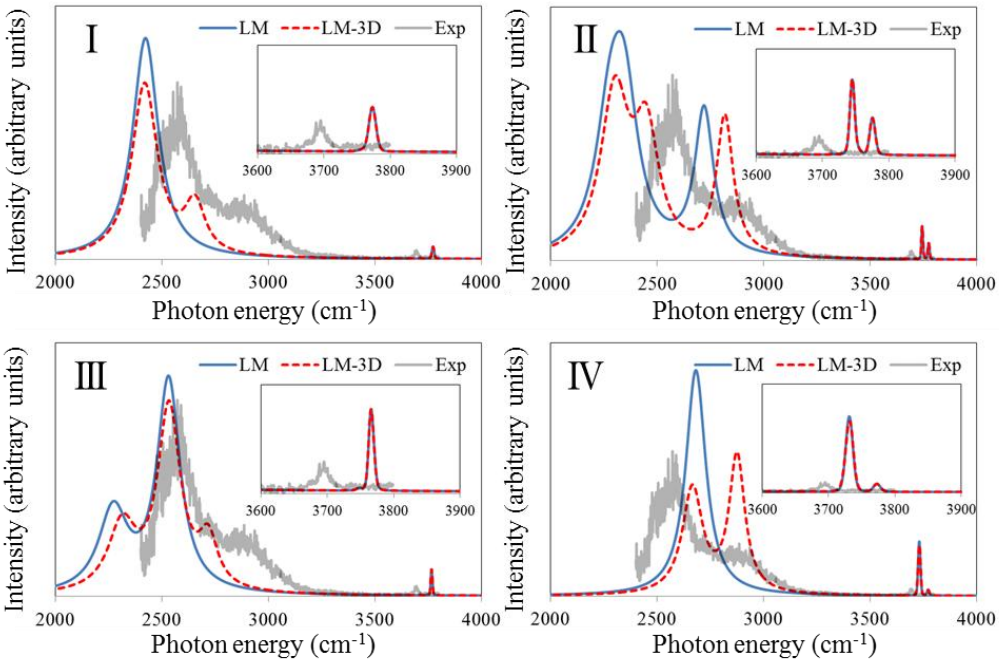

Figure S3. Vibrational spectrum for each conformer. (100K)

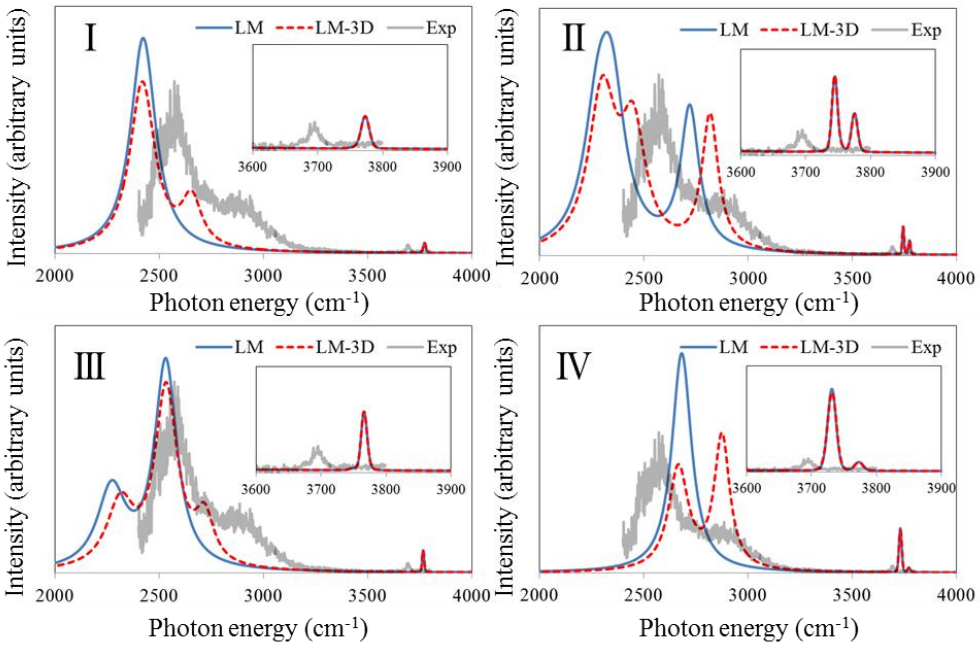

Figure S4. Vibrational spectrum for each conformer. (150K)

In the text, we considered the simple Boltzmann distribution using the argon attached structures to calculate the existence ratio of 4 conformers at the temperature of 50K. Here we calculate the existence ratio of conformers using other temperatures (100K and 150K), and obtain the vibrational spectra using this ratio.

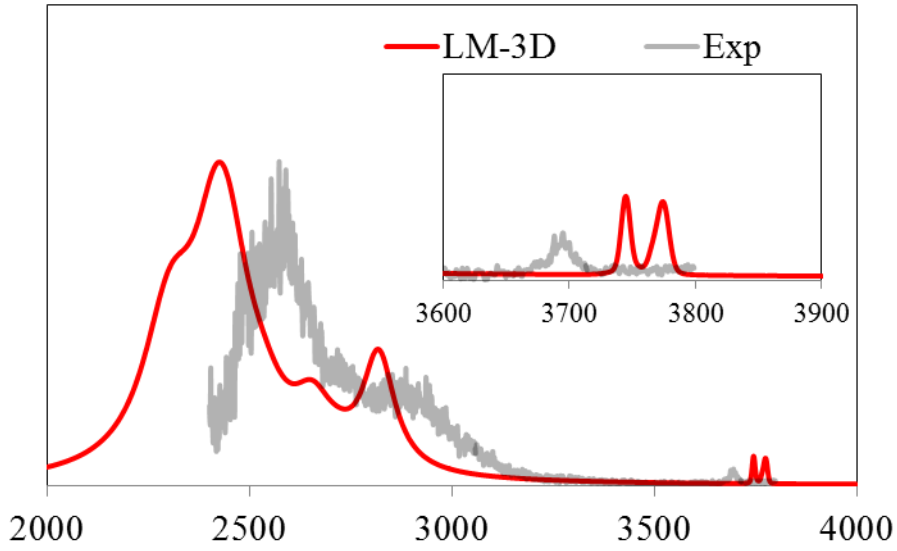

Figure S5. Vibrational spectrum (100K)

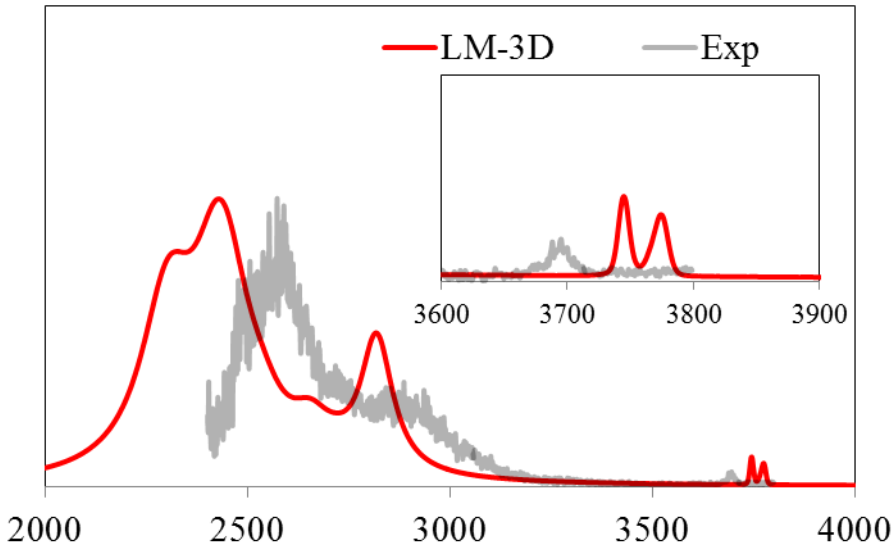

Figure S6. Vibrational spectrum (150K)

1-4. Comparison of the vibrational spectra with and without counterpoise correction

As described in the text, we obtained the counterpoise corrected potential energy surface/curve for the calculation of the vibrational spectrum (Argon attached/CP). The cartesian coordinate of the optimized structure with counterpoise correction is given in the end of ESI. We defined the 4 fragments as one OH^- and three water monomers and one argon atom for the counterpoise correction.

Table S4. LM-3D calculation for Conformer Ⅰ-1

Stretching Mode	Argon attached		Argon attached/CP	
	Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)
IHB OH	2381	2644	2480	2467
	2381	2644	2480	2468
	2619	583	2693	636
free OH	3775	3.3	3779	6.9
	3775	5.9	3779	6.9
	3775	5.8	3779	3.9
OH^- [a]	3740	0.18	3745	0.52

[a] OH^- is calculated with LM.

1-5. Energetics with counterpoise correction for $OH^-(H_2O)_3 \cdot Ar$ (Table S5)

Table S5. Relative energies (kcal/mol) for $OH^-(H_2O)_3 \cdot Ar$ with MP2/6-311++G(3df,3pd)

Conformer		Electronic Energy a posteriori	Electronic Energy a priori	Electronic Energy +ZPE [b]	Free Energy (50K) [b]
I	1	0.204	0.211	0.000	0.000
II	1	0.171	0.176	0.233	0.372
	2	0.203	[a]	[a]	[a]
	3	0.175	[a]	[a]	[a]
	4	0.183	0.190	0.248	0.237
III	1	0.347	0.344	0.475	0.579
	2	0.656	0.663	0.789	0.916
IV	1	0.308	0.292	1.236	1.559
	2	0.000	0.000	0.941	1.170

[a] We could not find the optimized structure.

[b] "Electronic Energy +ZPE" and "Free Energy" are calculated with a priori treatment (counterpoise optimization).

2. Optimized geometry (Cartesian coordinate)

2-1. $OH^-(H_2O)_3$

[Conformer I (C3)]

O	-2.343748	-0.176497	-0.284685
O	1.324725	-1.941497	-0.284685
O	1.019024	2.117994	-0.284685

O	0.000000	0.000000	0.854585
H	-1.468286	-0.081040	0.208469
H	-2.181309	-0.956538	-0.816924
H	0.804325	-1.231053	0.208469
H	1.919040	-1.410800	-0.816924
H	0.663960	1.312093	0.208469
H	0.262268	2.367337	-0.816924
H	0.000000	0.000000	1.813478

[Conformer II]

O	-2.354953	-1.130973	-0.442096
O	1.997697	-0.619204	-0.968042
O	0.385413	2.114717	0.052857
O	-0.103607	-0.370555	0.625925
H	-1.505096	-0.833711	0.019744
H	-2.012177	-1.617940	-1.192291
H	1.223936	-0.651954	-0.336766
H	2.059296	0.329079	-1.105484
H	0.192754	1.164179	0.347662
H	-0.398175	2.328797	-0.455145
H	0.005130	-0.621490	1.545103

[Conformer III]

O	-1.897084	-1.576048	-0.741185
O	1.551365	-0.766516	-0.939550
O	0.711787	2.435949	0.334950
O	-0.353839	0.049706	0.635521
H	-1.383992	-0.921861	-0.175203

H	-1.181309	-2.082057	-1.129512
H	0.846283	-0.488663	-0.266422
H	1.236853	-0.346956	-1.741791
H	0.233326	1.565326	0.491939
H	1.553437	2.123552	-0.001520
H	-0.292030	-0.235678	1.549581

[Conformer IV (C3)]

O	-0.123210	1.896870	-0.450405
O	-1.581133	-1.055139	-0.450405
O	1.704343	-0.841732	-0.450405
O	0.000000	0.000000	1.352249
H	-0.036682	1.309832	0.355026
H	-0.803449	1.416020	-0.929485
H	-1.116007	-0.686684	0.355026
H	-0.824585	-1.403817	-0.929485
H	1.152689	-0.623149	0.355026
H	1.628034	-0.012203	-0.929485
H	0.000000	0.000000	2.309567

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

[Conformer I-1]

O	-1.531756	1.947508	0.986191
O	-0.920714	-2.300294	0.986191
O	2.452470	0.352786	0.986191
O	0.000000	0.000000	1.824963
H	-0.925780	1.218006	1.335355

H	-2.212781	1.443959	0.538663
H	-0.591934	-1.410752	1.335355
H	-0.144115	-2.638304	0.538663
H	1.517714	0.192746	1.335355
H	2.356896	1.194345	0.538663
H	0.000000	0.000000	2.785083
Ar	0.000000	0.000000	-1.636893

[Conformer II-1]

O	-2.741797	-0.024503	0.685975
O	1.586048	-1.674780	0.909837
O	1.490482	1.682427	1.037591
O	-0.340946	-0.036432	1.709496
H	-1.816436	-0.002078	1.096256
H	-2.742851	-0.870056	0.236313
H	0.802548	-1.150952	1.244340
H	2.186418	-0.959729	0.686667
H	0.762560	1.043141	1.339314
H	1.049563	2.191506	0.356529
H	-0.440988	-0.060811	2.664068
Ar	-0.115845	0.021632	-1.759873

[Conformer II-2]

O	-0.283956	-2.458720	-0.455562
O	-0.640602	1.958873	-0.465979
O	-3.520488	0.364612	0.072584
O	-1.115041	-0.320514	0.782671
H	-0.617735	-1.656661	0.062613

H	0.323284	-2.056821	-1.077728
H	-0.708036	1.103445	0.048280
H	-1.568137	2.107206	-0.665204
H	-2.608767	0.083810	0.413615
H	-3.717652	-0.323605	-0.564042
H	-0.959964	-0.341876	1.728991
Ar	2.290344	0.335605	-0.172858

[Conformer II-3]

O	0.293420	-2.541122	-1.795750
O	1.252410	1.717342	-2.310228
O	-1.965354	1.011042	-2.435591
O	-0.137704	-0.103623	-0.977366
H	0.101141	-1.615806	-1.435931
H	1.096172	-2.395583	-2.297600
H	0.842412	1.017323	-1.728444
H	0.476602	1.997610	-2.802107
H	-1.297581	0.579104	-1.805038
H	-2.187988	0.284685	-3.019574
H	-0.223223	-0.013505	-0.026459
Ar	-1.222413	3.237192	-0.046424

[Conformer II-4]

O	0.846635	-0.950528	-0.977793
O	1.223630	3.401261	-0.044454
O	-1.851327	2.075666	-0.062384
O	0.391346	0.992127	0.683723
H	0.663035	-0.224468	-0.294731

H	1.569493	-0.573117	-1.480396
H	1.028360	2.477223	0.280287
H	0.339109	3.682157	-0.290445
H	-1.010919	1.638614	0.294306
H	-2.030682	1.553671	-0.845681
H	0.471124	0.758299	1.610385
Ar	-2.036120	-1.641421	0.623956

[Conformer III-1]

O	-1.731528	0.910106	-2.505859
O	-0.423740	-1.217370	0.015297
O	-1.781693	0.898720	2.519902
O	-2.415439	0.464584	-0.000537
H	-2.044984	0.809484	-1.556004
H	-1.176313	0.133926	-2.599046
H	-1.242317	-0.620222	0.008578
H	0.292190	-0.580439	0.024088
H	-2.076097	0.802383	1.563520
H	-1.228560	0.122013	2.620750
H	-3.282543	0.052426	-0.010114
Ar	0.273245	2.471664	0.030842

[Conformer III-2]

O	2.419824	-0.934817	-2.162717
O	-0.025458	1.687884	-1.251546
O	-2.406012	-0.627160	-1.309280
O	0.189774	-0.857369	-0.797481
H	1.555691	-0.976121	-1.640892

H	2.733832	-0.054970	-1.950069
H	0.080777	0.710257	-0.998562
H	0.202189	1.678328	-2.182666
H	-1.450766	-0.842286	-1.110847
H	-2.351101	0.328415	-1.382766
H	0.356617	-1.120869	0.110013
Ar	-1.337679	1.198604	1.784338

[Conformer IV-1]

O	0.586622	1.797695	0.914023
O	-1.850161	-0.390818	0.914023
O	1.263539	-1.406878	0.914023
O	0.000000	0.000000	2.725386
H	0.451789	1.226825	1.724496
H	-0.231958	1.610441	0.446687
H	-1.288356	-0.222151	1.724496
H	-1.278704	-1.006102	0.446687
H	0.836567	-1.004673	1.724496
H	1.510662	-0.604339	0.446687
H	0.000000	0.000000	3.682727
Ar	0.000000	0.000000	-2.236878

[Conformer IV-2]

O	0.498055	1.768967	0.935540
O	-1.803272	-0.608243	1.166481
O	1.349479	-1.399385	1.107935
O	0.081595	0.051361	2.869447
H	0.416619	1.232236	1.776894

H	-0.313728	1.507246	0.493347
H	-1.235299	-0.332180	1.939524
H	-1.178668	-1.171761	0.701216
H	0.935692	-0.953764	1.904209
H	1.546305	-0.626232	0.572089
H	0.144450	0.139375	3.820693
Ar	-0.441228	-3.499048	3.065111

[Conformer I-1] Counterpoise optimization

O(Fragment=1)	-2.154113	1.242107	-0.678238
O(Fragment=2)	2.152759	1.244467	-0.678249
O(Fragment=3)	0.001357	-2.486573	-0.678243
O(Fragment=4)	0.000002	0.000000	-1.574268
H(Fragment=1)	-1.360148	0.746800	-1.050964
H(Fragment=1)	-1.736220	1.984172	-0.239852
H(Fragment=2)	1.326829	0.804524	-1.050975
H(Fragment=2)	2.586451	0.511535	-0.239843
H(Fragment=3)	0.033325	-1.551326	-1.050969
H(Fragment=3)	-0.850231	-2.495695	-0.239846
H(Fragment=4)	-0.000003	-0.000003	-2.533283
Ar(Fragment=5)	-0.000008	-0.000009	2.084392