

Supplemental Material for

Why Dipole Moments of HCl-Water Clusters Fail to Determine Acid Dissociation?

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Part I. Selection of basis sets in optimization calculation of $\text{HCl}(\text{H}_2\text{O})_{n=1-8}$ cluster structures

The basis set chosen for structure optimization is the 6-311+G(d, p) basis set, which includes a diffusion function for heavy atoms. This is because there will be clearly negatively charged Cl anions in $\text{HCl}(\text{H}_2\text{O})_{n=1-8}$ clusters. Adding a diffusion function to anions is a necessary step, since 6-311+G(d, p) without a diffusion function may not accurately describe the investigated cluster systems. In fact, we also consider using the 6-311++G(d, p) basis set that adds diffusion functions to both H and heavy atoms. But considering that the H atom in the mixed cluster itself has only one electron, and the electronegativity of H is very small. Also, in the H_2O molecule, the hydrogen electronic cloud will also be taken away by O atoms, resulting in a minimal effect of adding a diffusion function to the H atom. In addition, in the 6-311+G(d, p) basis set, the diffusion function added to heavy atoms can extend to the H atom, so it is not necessary to repeatedly apply a diffusion function to this atom. In order to further verify the influence of the dispersion function in the basis set on the structural optimization results, we perform the following calculations:

First, the structural optimization of $\text{HCl}(\text{H}_2\text{O})_{n=1-8}$ clusters is conducted using the B3LYP-D3(BJ) functional and the following basis sets: 6-311G(d, p), 6-311+G(d, p), and 6-311++G(d, p). The most stable structures of the optimized clusters are subsequently compared. Since the 6-311G(d, p), 6-311+G(d, p), and 6-311++G(d, p) basis sets share the same split-valence basis set theoretical framework, the configurations of the most stable structures obtained for the $\text{HCl}(\text{H}_2\text{O})_{n=1-8}$ clusters are generally similar, as depicted in Fig. S1(a-c). On the other hand, due to the differences in dispersion functions in the three basis sets, the obtained lowest energy structures of the mixed clusters are not exactly the same. These differences are evident in the detailed structural parameters of the clusters. Here, we compare the *structural parameters* in the most stable structures of $\text{HCl}(\text{H}_2\text{O})_{n=1-8}$, which are denoted as \mathbf{R}_1 , \mathbf{R}_2 , and \mathbf{R}_3 , respectively, which have been labeled in the cluster structures shown in Fig. S1(b). Specifically, \mathbf{R}_1 is the bond length of HCl in the cluster structure, \mathbf{R}_2 is the distance between the hydrogen atom of HCl and the oxygen atom of the nearest water molecule, and \mathbf{R}_3 is the hydrogen bond length between the two selected water molecules in the cluster. The values of the cluster structure parameters \mathbf{R}_1 , \mathbf{R}_2 , and \mathbf{R}_3 obtained using different basis sets are listed in Table S1. In addition, in Table S1 we also statistics the computational time required for structural optimization under different basis sets (64-core server).

To more intuitively reflect the impact of different basis sets on the cluster structure, we compare the structural parameters \mathbf{R}_1 , \mathbf{R}_2 , and \mathbf{R}_3 of the most stable cluster structures obtained under different basis sets in Fig. S2. In Fig. S2(a-c), it can be observed that the blue and green columns are nearly identical, indicating that the structural parameters obtained using the 6-311+G(d, p) basis set and

the 6-311++G(d, p) basis set with added dispersion function exhibit minimal differences. However, the calculation results obtained without adding the dispersion function using the 6-311G(d, p) basis set are notably different. As depicted in Fig. S2(a-c), the height of the red column significantly deviates from that of the blue and green columns. Besides, we present structural optimizations using the 6-311G(d, p), 6-311+G(d, p), and 6-311++G(d, p) basis sets in Fig. S2(d). It is evident that the addition of diffusion functions leads to a gradual increase in computational time.

In summary, the above comparison reveals that the performance of the 6-311+G(d, p) and 6-311++G(d, p) basis sets in optimizing the mixed cluster structures is nearly identical, consistent with our expectations. However, the computational time required with the 6-311+G(d, p) basis set is notably lower compared to the 6-311++G(d, p) basis set, suggesting that the former offers better cost performance. Additionally, optimization of clusters using the 6-311G(d, p) basis set without a dispersion function is found to introduce certain errors in the results. Consequently, we select 6-311+G(d, p) basis set for the structure optimization of mixed clusters.

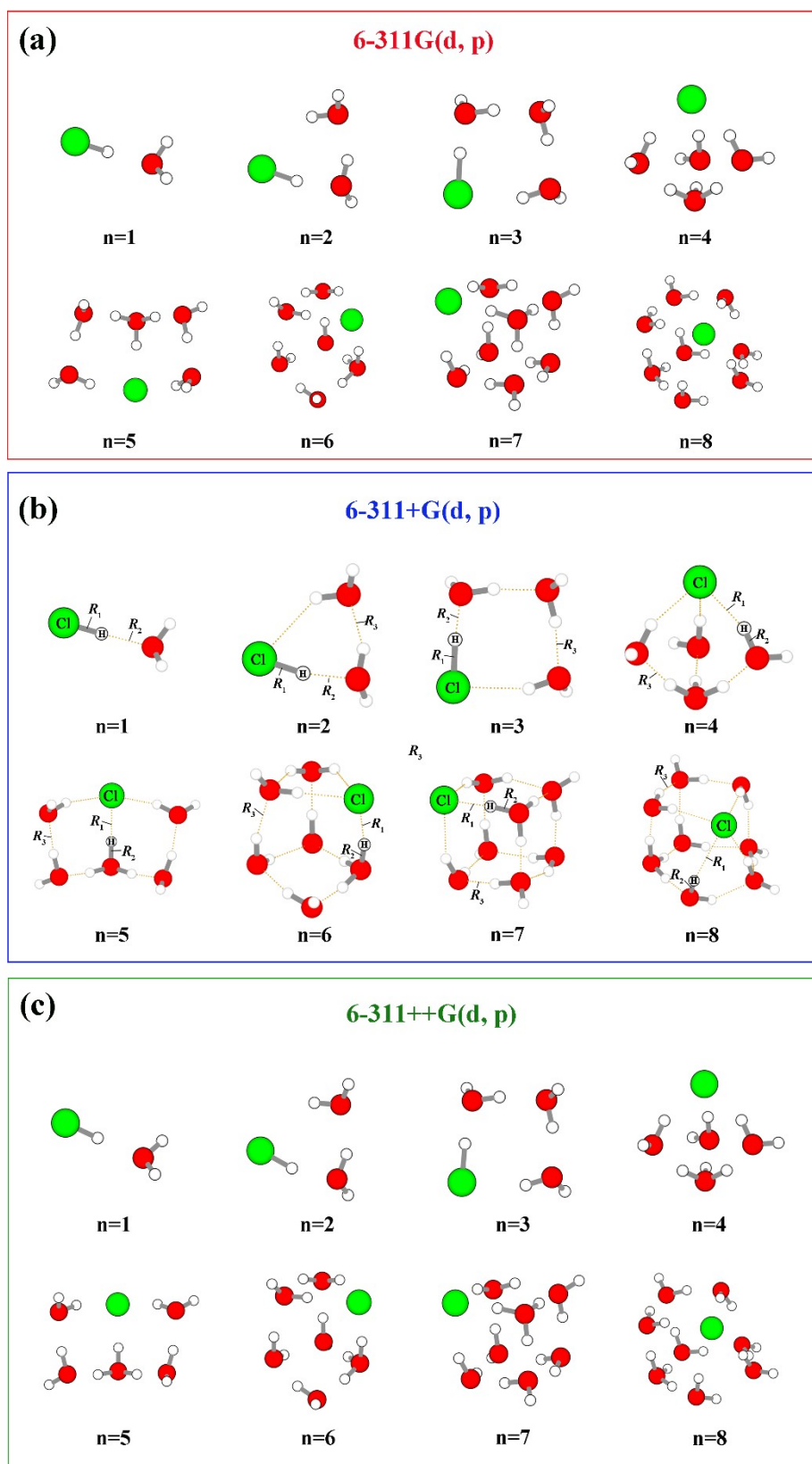


Fig. S1 compares the structural optimization results of $\text{HCl}(\text{H}_2\text{O})_{n=1-8}$ clusters using the B3LYP-D3(BJ) functional, employing three different basis sets: 6-311G(d, p), 6-311+G(d, p), and 6-311++G(d, p).

System	R_1 (Å)	R_2 (Å)	R_3 (Å)	Elapsed time (s)
6-311G (d, p)				
HCl(H ₂ O) ₁	1.30747	1.76930	-	12
HCl(H ₂ O) ₂	1.34203	1.61473	1.80287	11
HCl(H ₂ O) ₃	1.39959	1.49291	1.72228	35
HCl(H ₂ O) ₄	2.00890	0.98127	1.52630	24
HCl(H ₂ O) ₅	1.91648	1.03329	1.65074	64
HCl(H ₂ O) ₆	1.84738	1.06434	1.82341	101
HCl(H ₂ O) ₇	1.99030	1.02455	1.59454	165
HCl(H ₂ O) ₈	1.98771	1.02335	1.61738	159
Total elapsed time: 571 s				
6-311G+ (d, p)				
HCl(H ₂ O) ₁	1.29789	1.83365	-	27
HCl(H ₂ O) ₂	1.32012	1.70198	1.85213	54
HCl(H ₂ O) ₃	1.34408	1.65112	1.76612	99
HCl(H ₂ O) ₄	1.90462	0.99394	1.53691	72
HCl(H ₂ O) ₅	1.85351	1.05040	1.67325	214
HCl(H ₂ O) ₆	1.79568	1.08609	1.83526	345
HCl(H ₂ O) ₇	1.91455	1.03816	1.63499	346
HCl(H ₂ O) ₈	1.89896	1.03795	1.64680	575
Total elapsed time: 1732 s				
6-311G++ (d, p)				
HCl(H ₂ O) ₁	1.29821	1.83434	-	24
HCl(H ₂ O) ₂	1.32051	1.70249	1.84989	59
HCl(H ₂ O) ₃	1.34443	1.65103	1.76585	106
HCl(H ₂ O) ₄	1.90534	0.99385	1.53726	178
HCl(H ₂ O) ₅	1.85511	1.04978	1.67269	252
HCl(H ₂ O) ₆	1.79758	1.08549	1.83421	483
HCl(H ₂ O) ₇	1.91667	1.03774	1.63464	441
HCl(H ₂ O) ₈	1.90077	1.03823	1.64674	813
Total elapsed time: 2456 s				

Table S1 summarizes the numerical values and calculation times of the structural parameters R_1 , R_2 , and R_3 of HCl(H₂O)_{n=1-8} clusters, obtained using the B3LYP-D3(BJ) functional with three different basis sets: 6-311G(d, p), 6-311+G(d, p), and 6-311++G(d, p).

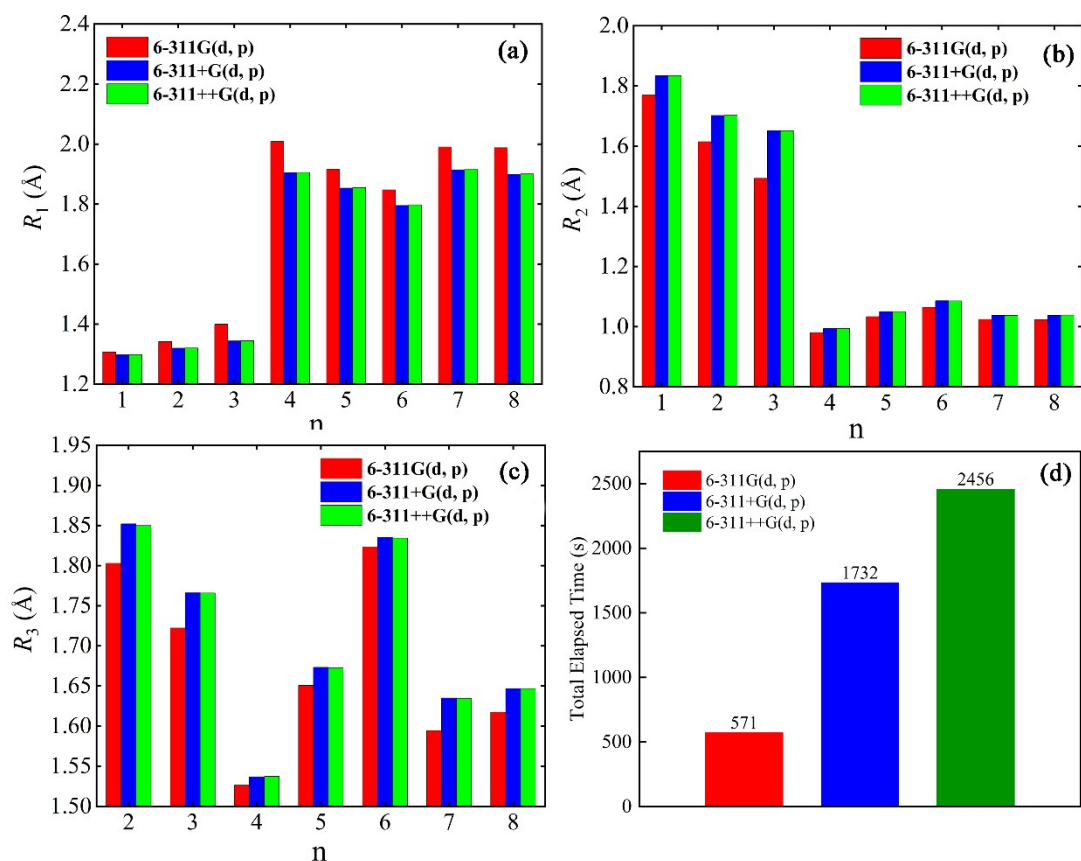


Fig. S2 illustrates the comparison of the structural parameters R_1 , R_2 , and R_3 in the most stable structures of HCl(H₂O)_{n=1-8} clusters obtained after structural optimization, based on the B3LYP-D3(BJ) functional with three different basis sets: 6-311G(d, p), 6-311+G(d, p), and 6-311++G(d, p). Additionally, the calculation times associated with each basis set are also collected and compared.

Part II. Choice criteria for HCl(H₂O)_{n=1-8} cluster structures

For structural optimization, we employ the preset convergence criteria provided by the Gaussian software:

1. Maximum Force ≤ 0.00045 (The force of the structure must be close to zero. Specifically, the maximum component of the force must be lower than the threshold value 0.00045).
2. RMS Force ≤ 0.0003 (The root mean square (RMS) of the structural force must be lower than the defined tolerance of 0.0003).
3. Maximum Displacement ≤ 0.0018 (In the subsequent calculation step, the maximum displacement must not exceed the predefined threshold of 0.0018, which refers to the greatest change among all coordinates of the molecular structure.).
4. RMS Displacement ≤ 0.0012 (The root mean square of the next step's displacement must be lower than its boundary value of 0.0012)

First, it is worth to provide a brief introduction to the concept of imaginary frequency, which occurs when the system configuration reaches a local maximum or saddle point on the potential

energy surface. In this state, some vibration modes no longer correspond to real vibrational frequencies but imaginary ones. The presence of imaginary frequencies indicates that these vibrational modes correspond to directions of increasing potential energy surface, rather than oscillating around a local minimum point. Therefore, the structure obtained at this point is not really stable. In Gaussian software, determining the presence of an imaginary frequency in the system involves analyzing the calculation results of the system's vibrational frequencies. A negative value in the vibrational frequency indicates the presence of an imaginary frequency in the structure. We will closely monitor the structure throughout the calculation process to ensure that it satisfies the convergence criteria for structural optimization and does not exhibit any imaginary frequencies. This ensures that the obtained structure corresponds to a local minimum on the potential energy surface. Due to the large number of atoms in larger clusters, the vibrational modes become more complex, leading to an exceedingly large number of vibration frequencies. We are primarily concerned with the presence of imaginary frequencies, while these additional vibrational frequencies are not the main calculation focus. Besides, due to space constraints (displaying the vibrational frequencies of all structures may exceed 50 pages), we have opted to present the vibrational frequency information of the most stable structures of $\text{HCl}(\text{H}_2\text{O})_{n=1-8}$ cluster (Fig. S1(b)) in Table S2 for referring.

$\text{HCl}(\text{H}_2\text{O})_1$		$\text{HCl}(\text{H}_2\text{O})_2$		$\text{HCl}(\text{H}_2\text{O})_3$		$\text{HCl}(\text{H}_2\text{O})_4$	
Mode	Frequency (cm ⁻¹)	Mode	Frequency (cm ⁻¹)	Mode	Frequency (cm ⁻¹)	Mode	Frequency (cm ⁻¹)
1	170.9	1	86.19	1	41.73	1	74.45
2	215.78	2	170.92	2	78.03	2	74.78
3	215.96	3	204.23	3	142.89	3	114.47
4	507.93	4	225.37	4	198.5	4	186.89
5	644.41	5	258.44	5	202.7	5	186.98
6	1613.22	6	299.74	6	254.08	6	253.38
7	2662.45	7	369.78	7	260.62	7	283.23
8	3810.78	8	436.34	8	294.95	8	283.62
9	3914.54	9	600.95	9	336.1	9	315.2
		10	738.98	10	345.35	10	318.06
		11	917.25	11	439.47	11	318.2
		12	1616.53	12	477.36	12	386.86
		13	1629.18	13	561.55	13	480.93
		14	2355.99	14	764.22	14	494.47
		15	3584.15	15	845.24	15	494.55
		16	3759.35	16	908.06	16	740.66
		17	3876.65	17	1083.27	17	742.01
		18	3893.48	18	1628.06	18	793.69
				19	1636.09	19	835.89
				20	1666.17	20	1003.34
				21	1954.6	21	1004.6

				22	3324.35	22	1505.87
				23	3486.73	23	1626.97
				24	3655.95	24	1627.18
				25	3868.89	25	1642.65
				26	3882.72	26	1800.1
				27	3883.67	27	1800.53
						28	2621.73
						29	2621.92
						30	2906.14
						31	3252.9
						32	3253.22
						33	3323.05
						34	3871.99
						35	3872
						36	3872.95
HCl(H₂O)₅		HCl(H₂O)₆		HCl(H₂O)₇		HCl(H₂O)₈	
Mode	Frequency (cm⁻¹)	Mode	Frequency (cm⁻¹)	Mode	Frequency (cm⁻¹)	Mode	Frequency (cm⁻¹)
1	25.84	1	54.9	1	69.27	1	55.68
2	37.05	2	63.87	2	79.67	2	70.65
3	71.8	3	78.61	3	81.59	3	72.22
4	86.93	4	88.39	4	88.8	4	79.14
5	99.4	5	109.22	5	90.51	5	83.87
6	178.73	6	112.04	6	124.99	6	95.82
7	197.53	7	136.41	7	148.56	7	112.85
8	231.86	8	166.66	8	157.48	8	119.99
9	247.68	9	202.29	9	166.23	9	141.99
10	265.51	10	222.99	10	176.55	10	162.75
11	268.16	11	259.06	11	188.84	11	166.73
12	305.15	12	282.16	12	224.58	12	178.24
13	322.82	13	289.44	13	266.35	13	184.88
14	324.89	14	301.31	14	274.54	14	206.57
15	349.22	15	327.65	15	298.8	15	228.47
16	353.59	16	335.13	16	317.87	16	232.74
17	417.02	17	349.14	17	328.16	17	272.08
18	429.69	18	371.41	18	350.32	18	295.56
19	516.45	19	386.65	19	357.69	19	309.93
20	539.79	20	436.55	20	366.67	20	311.46
21	681.1	21	497.63	21	398.39	21	331.82
22	711.54	22	524.32	22	465.12	22	340.87
23	785.13	23	563.86	23	489.47	23	363.44
24	828.22	24	573.82	24	510.19	24	392.64

25	920.92	25	697.94	25	536.64	25	401.55
26	989.18	26	709.33	26	560.61	26	413.98
27	1021.89	27	758.91	27	583.8	27	471.06
28	1366.59	28	774.46	28	616.23	28	499.55
29	1630.24	29	800.67	29	657.12	29	550.89
30	1635.03	30	830.86	30	663.85	30	577.18
31	1655.97	31	884.98	31	703.56	31	594.12
32	1669.09	32	981.28	32	754.29	32	618.76
33	1748.85	33	1101.09	33	779.58	33	646.33
34	1772.55	34	1368.97	34	839.07	34	683.52
35	2478.48	35	1622.84	35	863.58	35	719.2
36	2716.45	36	1646.41	36	899.11	36	728.19
37	2902.16	37	1662.36	37	1041.22	37	747.76
38	3256.58	38	1696.68	38	1132.92	38	763.08
39	3274.77	39	1703.93	39	1170.47	39	819.92
40	3429.83	40	1718.72	40	1343.21	40	861.7
41	3459.51	41	1788.58	41	1626.38	41	896.36
42	3875.59	42	2312.41	42	1631.49	42	939.55
43	3876.42	43	2695.93	43	1645.73	43	969.31
44	3880.69	44	3030.12	44	1654.93	44	1054.28
45	3881.31	45	3148.85	45	1693.37	45	1081.54
		46	3245.3	46	1698.93	46	1408.54
		47	3355.5	47	1714.55	47	1622.62
		48	3573.49	48	1754.26	48	1635.88
		49	3625.51	49	1862.4	49	1663.97
		50	3721.47	50	2844.01	50	1686.49
		51	3746.82	51	2995.04	51	1698
		52	3871.11	52	3090.07	52	1703.79
		53	3872.28	53	3141.75	53	1728.84
		54	3881.94	54	3178.08	54	1805.01
				55	3546.19	55	1857.76
				56	3557.83	56	2299.5
				57	3568.41	57	2676.36
				58	3619.89	58	2891.79
				59	3701.94	59	3132.44
				60	3739.78	60	3232.1
				61	3869.81	61	3406.13
				62	3872.88	62	3502.6
				63	3877.19	63	3547.59
						64	3553.58
						65	3570.98
						66	3581
						67	3608.05

						68	3700.13
						69	3746.33
						70	3862.91
						71	3876.37
						72	3877.21

Table S2 provides vibrational frequencies of the most stable structures of $\text{HCl}(\text{H}_2\text{O})_{n=1-8}$ clusters calculated at the B3LYP-D3(BJ)/6-311+G(d, p) level.

Part III. Calculation of dipole moments of $\text{HCl}(\text{H}_2\text{O})_{n=1-8}$ clusters

To ensure the accuracy of the calculation results of dipole moments of $\text{HCl}(\text{H}_2\text{O})_{n=1-8}$ clusters, we should choose a sufficiently appropriate theoretical method to acquire the dipole moments. In this article, the selected computing approach is based on B3LYP/def2-TZVPD, and this part will offer a detailed support confirming the rationality of the B3LYP/def2-TZVPD technique for getting dipole moments of investigated water clusters.

As an illustration, we apply B3LYP/6-311+G(d, p), MP2/aug-cc-pVTZ, M06-2X/def2-TZVPD, and B3LYP/def2-TZVPD calculation means to obtain the dipole moments of the HCl molecule, the H_2O molecule, and the HCl- H_2O dimer, respectively. In our paper, B3LYP/6-311+G(d, p) is the calculation level selected for structural optimization of clusters. The MP2/aug-cc-pVTZ and M06-2X/def2-TZVPD methods are chosen for comparison since they have been widely used in the calculation of HCl-water clusters before.¹⁻⁵ The experimental data of the dipole moments of the HCl molecules, the H_2O molecule and the HCl- H_2O dimer come from the work of Z. Kisiel and B. A. Pietrewicz et al.⁶ Correspondingly, the theoretical and experimental data are collected in Table S3. To exhibit the comparison outcomes more clearly, we also plot the data in Table S3 into histograms, as shown in Figs. S3 and S4.

Specifically, as depicted in Fig. S3(a), the experimentally measured dipole moment for HCl was 1.1085 D.⁶ However, using different calculation methods, including B3LYP/6-311+G(d,p), MP2/aug-cc-pVTZ, M06-2X/def2-TZVPD, and B3LYP/def2-TZVPD, the dipole moments of HCl are calculated here to be 1.4061 D, 1.2498 D, 1.1252 D, and 1.0971 D, respectively. The differences to the experimental values are corresponding to 0.2976 D, 0.1413 D, 0.0167D, and 0.0114D. In conclusion, the dipole moment value of HCl calculated by the B3LYP/def2-TZVPD method has the smallest deviation from the experimental value, with an error of only 0.0114 D. The calculated dipole moment of the H_2O molecule in Fig. S3(b) is similar to Fig. S3(a). Through the above analysis, it suggests that the B3LYP/def2-TZVPD method performs best in calculating the dipole moments of both HCl and H_2O molecules, exhibiting the smallest errors from the experimental values.

Next, Fig. 4 illustrates the comparison between the dipole moment values of the HCl- H_2O dimer obtained by various theoretical calculation methods and the experimental value, which was 3.4337 D.⁶ The dipole moments of the HCl- H_2O dimer obtained using the B3LYP/6-311+G(d, p), MP2/aug-cc-pVTZ, M06-2X/def2-TZVPD, and B3LYP/def2-TZVPD calculation methods are 4.2219 D, 3.7502 D, 3.6628 D, and 3.6324 D, respectively. It can be observed that the theoretical calculated dipole moment values are all slightly larger than the experimental value of 3.4337 D. This may be because theoretical calculations often struggle to fully simulate the complexity of experimental conditions, *i.e.*, experimental measurements may have systematic errors or not account

for all sources of uncertainty, leading to discrepancies between experimental results and theoretical calculations. However, it is worth noting that the dipole moment value of the HCl-H₂O dimer obtained using the B3LYP/def2-TZVPD method is the closest to the experimental value among the theoretical calculations.

In short, through comparison, we can find that the B3LYP/def2-TZVPD method performs best in the calculation of cluster dipole moments, and the results are closer to the experimental values. For the M06-2X/def2-TZVPD method, it yields satisfactory results and the error is still within a reasonable range, but the dipole moment values obtained with the MP2/aug-cc-pVTZ method are slightly higher than the experimental values. As for the low-accuracy B3LYP/6-311+G(d, p) approach employed for cluster structure optimization calculations, it is entirely unsuitable for dipole moment calculations. This also indicates that after using relatively low-precision calculation methods to optimize the cluster structure, higher-precision calculation methods should be used to calculate cluster-correlated properties to ensure the accuracy of the results.

Table S3 Theoretical and experimental dipole moment values of HCl molecule, H₂O molecule, and HCl-H₂O dimer.

	$P(\text{HCl/D})$	$P(\text{H}_2\text{O/D})$	$P(\text{HCl-H}_2\text{O/D})$
B3LYP/6-311+G(d, p)	1.4061	2.1616	4.2219
MP2/aug-cc-pVTZ	1.2498	1.9635	3.7502
M06-2X/def2-TZVPD	1.1252	1.8868	3.6628
B3LYP/def2-TZVPD	1.0971	1.8508	3.6324
Experimental Data	1.1085	1.8550	3.4337

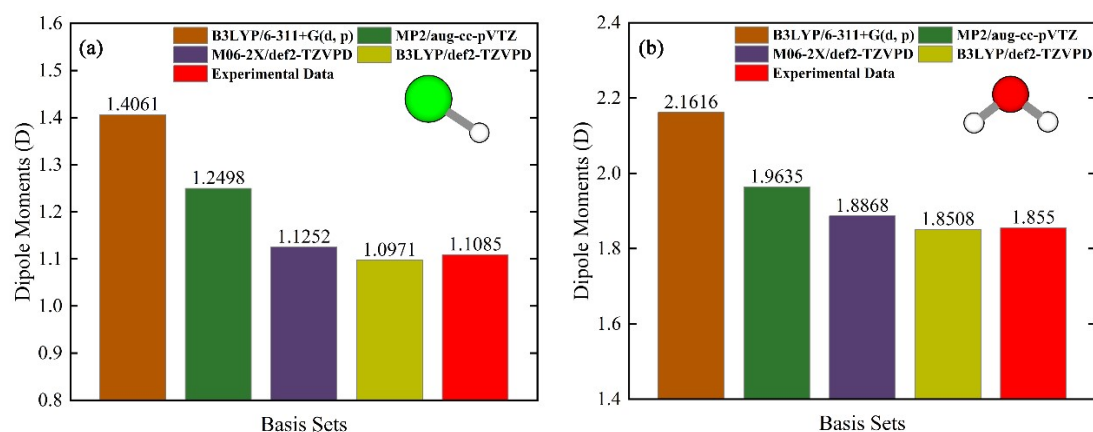


Fig. S3 Comparison of dipole moment values of HCl molecule (a) and H₂O molecule (b) obtained by different theoretical calculation methods with the experimental value.

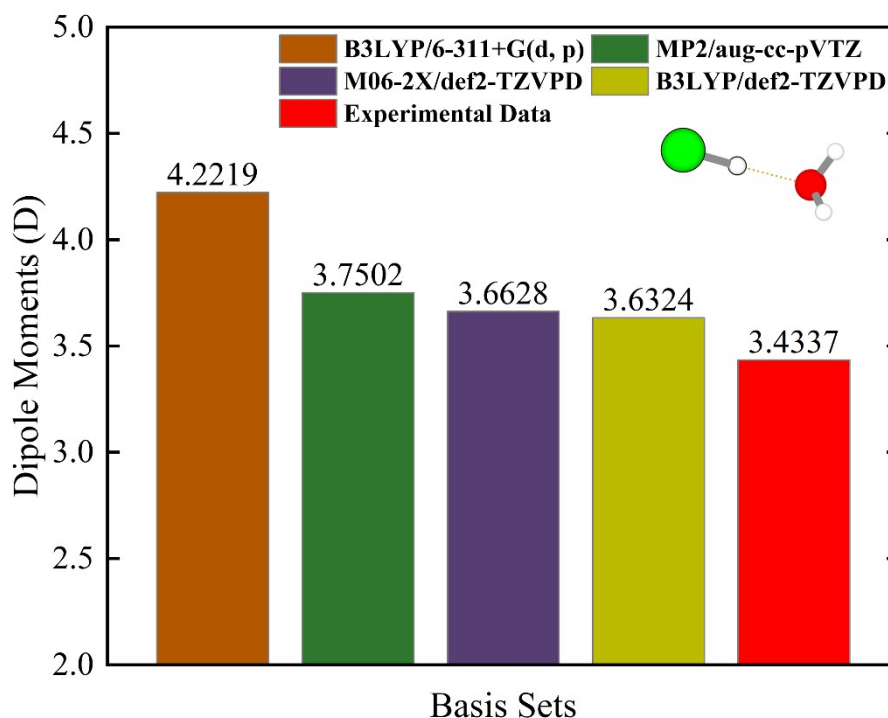


Fig. S4 The dipole moment values of the HCl-H₂O dimer are obtained by different theoretical calculation methods and compared with the experimental value.

References:

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