Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

Benchmark computational investigations for the basic model of the salt-water complex: $NaCl(H_2O)$ and its anion $NaCl(H_2O)^-$

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S1. The principle of the IGMH method

In the IMGH analysis,[1] the interaction regions of different intensities are shown by equivalent surfaces with different δg function values, and sign(λ_2)ρ is used as the mapping function to visually distinguish the types of interactions, in which ρ is the electron density and λ_2 is the second eigenvalue of the Hessian matrix of ρ. The δg function is given by the following equation in the general three-dimensional case,

$$\delta g(\mathrm{r}) = g^{\mathrm{IGMH}}(\mathrm{r}) - g(\mathrm{r}) \tag{1}$$

with

$$g(\mathrm{r}) = \left| \sum_i \nabla \rho_i^{\mathrm{Hirsh}}(\mathrm{r}) \right| \tag{2}$$

$$g^{\mathrm{IGMH}}(\mathrm{r}) = \sum_i \left| \nabla \rho_i^{\mathrm{Hirsh}}(\mathrm{r}) \right| \tag{3}$$

where g represents gradient, which is the sum of atomic electron density gradient; r denotes Cartesian coordinate vector, and ρ_i^{Hirsh} is the electron density of the i atom, obtained from the actual electron density of the system by means of the Hirshfeld atomic space division; g^{IGMH} is the IGMH-type electron density gradient, which is equal to the sum of the absolute values of the electron density gradient of atoms. At the equilibrium structure of the molecule, the greater the density overlap between atoms, the higher the δg peak and the stronger the interaction.

In IGMH, $\delta g^{\mathrm{inter}}$ and $\delta g^{\mathrm{intra}}$ are defined to exhibit specific inter-fragment and intra-fragment interactions:

$$\delta g^{\mathrm{inter}}(\mathrm{r}) = g^{\mathrm{IGMH,inter}}(\mathrm{r}) - g^{\mathrm{inter}}(\mathrm{r}) \tag{4}$$

$$\delta g^{\mathrm{intra}}(\mathrm{r}) = \delta g(\mathrm{r}) - \delta g^{\mathrm{inter}}(\mathrm{r}) \tag{5}$$

Here g^{inter} is the amplitude obtained by superimposing the density gradients of all fragments, $g^{\mathrm{IGMH,\ inter}}$ is the sum of the amplitudes of the density gradients of all fragments, and their specific expression take the form:

$$g^{\mathrm{inter}}(\mathrm{r}) = \left| \sum_A \sum_{i \in A} \nabla \rho_i^{\mathrm{Hirsh}}(\mathrm{r}) \right| \tag{6}$$

$$g^{\mathrm{IGMH,inter}}(\mathrm{r}) = \sum_A \left| \sum_{i \in A} \nabla \rho_i^{\mathrm{Hirsh}}(\mathrm{r}) \right|, \tag{7}$$

where A stands for the sum running over all fragments with i for all atoms in the corresponding fragments.

Table S1. Geometry of the A1 isomer of neutral NaCl(H_2O) optimized at different levels.

		X	Y	Z
CCSD(T)-F12a/AVTZ	O	1.64015	-0.80427	-0.04861
	H	2.17123	-1.56144	0.19735
	H	0.70122	-1.09054	-0.02683
	Na	0.62287	1.25900	0.00894
	Cl	-1.33814	-0.27675	0.00813
B2PLYP-D3(BJ)/AVTZ	O	1.63610	-0.79350	-0.02990
	H	2.18240	-1.55344	0.17688
	H	0.69639	-1.08881	-0.01444
	Na	0.62821	1.22657	0.00546
	Cl	-1.34576	-0.26482	0.00098
B3LYP-D3(BJ)/AVTZ	O	1.64255	-0.78054	-0.02453
	H	2.20279	-1.54070	0.14477
	H	0.70382	-1.08535	-0.01225
	Na	0.62461	1.21533	0.00451
	Cl	-1.34810	-0.26461	0.00083
MP2/AVTZ	O	1.61046	-0.84142	-0.04490
	H	2.09724	-1.60645	0.26904
	H	0.65367	-1.08415	-0.02157
	Na	0.65138	1.25718	0.00813
	Cl	-1.34116	-0.25923	0.00131
DSDPBEP86-D3(BJ)/AVTZ	O	1.62937	-0.80648	-0.04142
	H	2.15068	-1.55727	0.24794
	H	0.68391	-1.08393	-0.02150
	Na	0.63075	1.23535	0.00747
	Cl	-1.34163	-0.26446	0.00134
M062X-D3/AVTZ	O	1.64699	-0.75906	-0.00002
	H	2.24698	-1.50515	0.00011
	H	0.72844	-1.10326	-0.00001
	Na	0.60951	1.20306	0.00000
	Cl	-1.34447	-0.26781	0.00000
LC-ωPBE/AVTZ	O	1.63170	-0.78157	-0.00001
	H	2.18728	-1.56053	0.00004
	H	0.69140	-1.07262	-0.00000
	Na	0.61584	1.22169	0.00000
	Cl	-1.33567	-0.26782	0.00000

Table S2. Geometry of the A2 isomer of neutral NaCl(H_2O) optimized at different levels.

		X	Y	Z
CCSD(T)-F12a/AVTZ	O	0.00092	0.01996	0.00242
	H	-0.00193	-0.02316	0.95845
	H	0.93996	0.01360	-0.28431
	Na	-0.26057	0.79758	-2.14752
	Cl	2.20201	0.44313	-2.02932
B2PLYP-D3(BJ)/AVTZ	O	-1.63610	-0.79350	-0.02989
	H	-2.18240	-1.55345	0.17686
	H	-0.69639	-1.08881	-0.01444
	Na	-0.62821	1.22657	0.00546
	Cl	1.34576	-0.26482	0.00098
B3LYP-D3(BJ)/AVTZ	O	-1.64255	-0.78054	-0.02453
	H	-2.20279	-1.54070	0.14476
	H	-0.70382	-1.08535	-0.01225
	Na	-0.62461	1.21533	0.00451
	Cl	1.34810	-0.26461	0.00083
MP2/AVTZ	O	-1.61046	-0.84142	-0.04489
	H	-2.09725	-1.60646	0.26900
	H	-0.65367	-1.08415	-0.02157
	Na	-0.65138	1.25718	0.00813
	Cl	1.34116	-0.25923	0.00131
DSDPBEP86-D3(BJ)/AVTZ	O	-1.62937	-0.80648	-0.04142
	H	-2.15068	-1.55727	0.24794
	H	-0.68391	-1.08393	-0.02150
	Na	-0.63075	1.23535	0.00747
	Cl	1.34163	-0.26446	0.00134
M062X-D3/AVTZ	O	-1.64699	-0.75906	-0.00002
	H	-2.24698	-1.50515	0.00011
	H	-0.72844	-1.10326	-0.00001
	Na	-0.60951	1.20306	0.00000
	Cl	1.34447	-0.26781	0.00000
LC-ωPBE/AVTZ	O	-1.63170	-0.78157	-0.00001
	H	-2.18728	-1.56053	0.00004
	H	-0.69140	-1.07262	-0.00000
	Na	-0.61584	1.22169	0.00000
	Cl	1.33567	-0.26782	0.00000

Table S3. Geometry of the B isomer of neutral NaCl(H_2O) optimized at different levels.

		X	Y	Z
CCSD(T)-F12a/AVTZ	O	0.00009	-0.04063	2.96637
	H	0.00004	-0.84080	3.50007
	H	0.00066	0.68348	3.59922
	Na	-0.00019	0.07065	0.53810
	Cl	0.00006	-0.02300	-1.88945
B2PLYP-D3(BJ)/AVTZ	O	-0.00134	2.77817	0.00000
	H	-0.76795	3.36080	0.00000
	H	0.76455	3.36176	0.00000
	Na	0.00000	0.43073	0.00000
	Cl	0.00083	-1.98152	0.00000
B3LYP-D3(BJ)/AVTZ	O	-0.00025	2.73844	0.00000
	H	-0.76750	3.31982	0.00000
	H	0.76686	3.32000	0.00000
	Na	0.00000	0.43904	0.00000
	Cl	0.00016	-1.96334	0.00000
MP2/AVTZ	O	-0.00007	2.84288	0.00000
	H	-0.76387	3.43090	0.00000
	H	0.76369	3.43095	0.00000
	Na	0.00000	0.42295	0.00000
	Cl	0.00004	-2.01514	0.00000
DSDPBEP86-D3(BJ)/AVTZ	O	0.00004	2.80208	0.00000
	H	-0.76566	3.38696	0.00000
	H	0.76575	3.38694	0.00000
	Na	0.00000	0.42495	0.00000
	Cl	-0.00002	-1.99206	0.00000
M062X-D3/AVTZ	O	0.00001	2.71828	0.00000
	H	-0.76630	3.29779	0.00000
	H	0.76632	3.29778	0.00000
	Na	0.00000	0.43788	0.00000
	Cl	-0.00001	-1.9505	0.00000
LC-ωPBE/AVTZ	O	-0.00006	2.74775	0.00000
	H	-0.76663	3.32615	0.00000
	H	0.76648	3.32619	0.00000
	Na	0.00000	0.42972	0.00000
	Cl	0.00004	-1.96243	0.00000

Table S4. Geometry of the A1^{-} isomer of anion $NaCl(H_2O)^{-}$ optimized at different levels.

		X	Y	Z
CCSD(T)-F12a/AVTZ	O	-0.05757	-1.23026	-1.49182
	H	0.79529	-1.60089	-1.72894
	H	-0.04886	-1.19636	-0.50899
	Na	0.00451	1.20663	-0.92674
	Cl	0.00231	-0.14821	1.33755
B2PLYP-D3(BJ) /AVTZ	O	1.53533	-1.04438	-0.10330
	H	1.82252	-1.39531	0.74466
	H	0.54962	-1.09445	-0.07908
	Na	-1.37507	-0.2001	0.00468
	Cl	0.79285	1.29511	0.00739
B3LYP-D3(BJ)/AVTZ	O	1.54389	-1.03520	-0.10369
	H	1.83480	-1.36562	0.75278
	H	0.55682	-1.09270	-0.08167
	Na	-1.38094	-0.19943	0.00489
	Cl	0.79392	1.28456	0.00684
MP2/AVTZ	O	1.49771	-1.09623	-0.10300
	H	1.75390	-1.48251	0.73980
	H	0.50866	-1.09493	-0.0788
	Na	0.82036	1.32156	0.00830
	Cl	-1.36872	-0.18764	0.00422
DSDPBEP86-D3(BJ)/AVTZ	O	1.53208	-1.04843	-0.10327
	H	1.80874	-1.39973	0.74789
	H	0.54593	-1.09104	-0.08195
	Na	0.78514	1.30299	0.00747
	Cl	-1.36752	-0.20322	0.00459
M062X-D3/AVTZ	O	1.58040	-0.99363	-0.10354
	H	1.86705	-1.23279	0.78197
	H	0.60368	-1.09749	-0.09366
	Na	0.74220	1.27451	0.00420
	Cl	-1.36930	-0.22002	0.00552
LC-ωPBE/AVTZ	O	1.52936	-1.04434	-0.10192
	H	1.80360	-1.40017	0.74511
	H	0.54362	-1.07902	-0.09345
	Na	0.77487	1.30416	0.00751
	Cl	-1.35916	-0.20658	0.00477

Table S5. Geometry of the A2^{-} isomer of anion $NaCl(H_2O)^{-}$ optimized at different levels.

		X	Y	Z
CCSD(T)-F12a/AVTZ	O	-0.05703	1.22897	-1.49291
	H	0.79604	1.59916	-1.72998
	H	-0.0486	1.19583	-0.51006
	Na	0.00406	-1.20767	-0.92547
	Cl	0.00186	0.14912	1.33744
B2PLYP-D3(BJ)/AVTZ	O	-1.53534	-1.04439	-0.10330
	H	-1.82253	-1.39531	0.74466
	H	-0.54963	-1.09445	-0.07908
	Na	-0.79284	1.295121	0.00739
	Cl	1.37507	-0.20009	0.00468
B3LYP-D3(BJ)/AVTZ	O	-1.54389	-1.03520	-0.10369
	H	-1.83479	-1.36562	0.75277
	H	-0.55682	-1.09270	-0.08167
	Na	-0.79393	1.28455	0.00684
	Cl	1.38094	-0.19942	0.00489
MP2/AVTZ	O	-1.49769	-1.09624	-0.10300
	H	-1.75391	-1.48255	0.73978
	H	-0.50864	-1.09494	-0.07881
	Na	-0.82040	1.32154	0.00830
	Cl	1.36873	-0.18762	0.00422
DSDPBEP86-D3(BJ)/AVTZ	O	-1.53209	-1.04843	-0.10327
	H	-1.80875	-1.39972	0.74790
	H	-0.54594	-1.09104	-0.08195
	Na	-0.78512	1.30300	0.00747
	Cl	1.36752	-0.20322	0.00459
M062X-D3/AVTZ	O	-1.58038	-0.99365	-0.10354
	H	-1.86700	-1.23281	0.78197
	H	-0.60365	-1.09748	-0.09367
	Na	-0.74224	1.27449	0.00420
	Cl	1.36931	-0.22000	0.00552
LC-ωPBE/AVTZ	O	-1.52936	-1.04434	-0.10192
	H	-1.80360	-1.40016	0.74511
	H	-0.54362	-1.07902	-0.09345
	Na	-0.77487	1.30416	0.00751
	Cl	1.35916	-0.20658	0.00477

Table S6. Geometry of the B^- isomer of anion $NaCl(H_2O)^-$ optimized at different levels.

		X	Y	Z
CCSD(T)-F12a/AVTZ	O	-2.76960	0.00000	0.00000
	H	-3.37020	0.76419	-0.00001
	H	-3.37020	-0.76419	-0.00001
	Na	-0.45679	0.00000	0.00000
	Cl	2.04515	0.00000	0.00000
B2PLYP-D3(BJ)/AVTZ	O	-2.74597	0.00000	0.00000
	H	-3.34481	0.76933	0.00000
	H	-3.34481	-0.76933	0.00000
	Na	-0.48670	0.00000	0.00000
	Cl	2.00065	0.00000	0.00000
B3LYP-D3(BJ)/AVTZ	O	-2.72972	0.00000	0.00000
	H	-3.32678	0.77340	0.00000
	H	-3.32678	-0.77340	0.00000
	Na	-0.48938	0.00000	0.00000
	Cl	1.99262	0.00000	0.00000
MP2/AVTZ	O	-2.79717	0.00000	-0.09223
	H	-3.37349	0.762352	0.09550
	H	-3.37349	-0.76235	0.09550
	Na	-0.48366	0.00000	0.09155
	Cl	2.02615	0.00000	-0.02707
DSDPBEP86-D3(BJ)/AVTZ	O	-2.75759	0.00000	-0.05904
	H	-3.34606	0.765812	0.063884
	H	-3.34606	-0.76581	0.063884
	Na	-0.48252	0.00000	0.057244
	Cl	2.00356	0.00000	-0.01677
M062X-D3/AVTZ	O	-2.71137	0.00000	0.00000
	H	-3.30459	0.76982	0.00000
	H	-3.30459	-0.76982	0.00000
	Na	-0.484	0.00000	0.00000
	Cl	1.977889	0.00000	0.00000
LC-ωPBE/AVTZ	O	-2.72218	0.00000	0.00002
	H	-3.31931	0.76412	-0.00002
	H	-3.31931	-0.76412	-0.00002
	Na	-0.47694	0.00000	-0.00002
	Cl	1.98014	0.00000	0.00001

Table S7. Geometry of the Cl^- isomer of anion $NaCl(H_2O)^-$ optimized at different levels.

		X	Y	Z
CCSD(T)-F12a/AVTZ	O	-0.02887	-0.61909	-2.85438
	H	0.80742	-1.06281	-2.70562
	H	-0.15934	-0.14489	-2.01292
	Na	0.01881	-0.67647	2.14680
	Cl	-0.03072	0.75604	0.02888
B2PLYP-D3(BJ) /AVTZ	O	-2.71955	-0.55949	-0.00001
	H	-2.38221	-1.45829	0.00005
	H	-1.89967	-0.02535	-0.00001
	Na	0.15180	0.84354	0.00000
	Cl	2.13252	-0.76186	0.00000
B3LYP-D3(BJ) /AVTZ	O	-2.54905	-0.61675	0.00000
	H	-2.14997	-1.49125	0.00003
	H	-1.77049	-0.02067	-0.00001
	Na	0.21953	0.99307	0.00000
	Cl	1.87098	-0.94875	0.00000
MP2/AVTZ	O	2.77152	-0.55230	-0.09204
	H	2.69354	-0.98703	0.76105
	H	1.90343	-0.10501	-0.16830
	Na	-2.25530	-0.66865	-0.01392
	Cl	-0.11534	0.75680	0.01745
DSDPBEP86-D3(BJ)/AVTZ	O	2.73727	-0.56050	-0.07929
	H	2.56111	-1.15701	0.65220
	H	1.89335	-0.07137	-0.15312
	Na	-2.18004	-0.72039	-0.01670
	Cl	-0.13954	0.80215	0.01876
M062X-D3/AVTZ	O	…	…	…
	H	…	…	…
	H	…	…	…
	Na	…	…	…
	Cl	…	…	…
LC-ωPBE/AVTZ	O	-2.82397	-0.49617	0.08000
	H	-2.67228	-1.10266	-0.64584
	H	-1.96283	-0.04499	0.16858
	Na	2.27385	-0.63237	0.01838
	Cl	0.13027	0.71018	-0.02147

Table S8. Geometry of the $C2^-$ isomer of anion $NaCl(H_2O)^-$ optimized at different levels.

		X	Y	Z
CCSD(T)-F12a/AVTZ	O	-0.04909	0.64558	-2.83892
	H	0.82076	1.03127	-2.72468
	H	-0.17015	0.16773	-1.99810
	Na	0.00795	-0.76265	0.02633
	Cl	-0.00661	0.67424	2.14215
B2PLYP-D3(BJ)/AVTZ	O	···	···	···
	H	···	···	···
	H	···	···	···
	Na	···	···	···
	Cl	···	···	···
B3LYP-D3(BJ)/AVTZ	O	···	···	···
	H	···	···	···
	H	···	···	···
	Na	···	···	···
	Cl	···	···	···
MP2/AVTZ	O	-2.77150	-0.55229	-0.09204
	H	-2.69357	-0.98701	0.76106
	H	-1.90344	-0.10501	-0.16831
	Na	2.25532	-0.66863	-0.01392
	Cl	0.11534	0.75678	0.01745
DSDPBEP86-D3(BJ)/AVTZ	O	-2.73728	-0.56048	-0.07928
	H	-2.56106	-1.15715	0.65207
	H	-1.89337	-0.07134	-0.15309
	Na	2.18005	-0.72038	-0.01670
	Cl	0.13954	0.80215	0.01876
M062X-D3/AVTZ	O	···	···	···
	H	···	···	···
	H	···	···	···
	Na	···	···	···
	Cl	···	···	···
LC-ωPBE/AVTZ	O	-2.82394	-0.49620	-0.08001
	H	-2.67230	-1.10253	0.64598
	H	-1.96280	-0.04503	-0.16861
	Na	2.27381	-0.63240	-0.01838
	Cl	0.13028	0.71021	0.02146

Table S9. Geometry of TS1 in the anion $NaCl(H_2O)^-$ isomerization reaction pathway.

		X	Y	Z
CCSD(T)-F12a/AVTZ	O	-2.18039	-0.61794	-0.10938
	H	-2.94662	-0.43105	0.4492
	H	-1.75883	-1.39496	0.27895
	Na	-0.48035	1.05743	0.03113
	Cl	1.66939	-0.26646	-0.02263
B2PLYP-D3(BJ)/AVTZ	O	-2.16701	-0.59090	-0.10339
	H	-2.92951	-0.44513	0.47596
	H	-1.71354	-1.37089	0.24639
	Na	-0.50899	1.04556	0.00622
	Cl	1.62224	-0.29165	0.00214

Table S10. Geometry of TS2 in the anion $NaCl(H_2O)^-$ isomerization reaction pathway.

		X	Y	Z
CCSD(T)-F12a/AVTZ	O	0.00000	1.24368	-1.59757
	H	0.73144	1.29856	-0.96931
	H	-0.73144	1.29856	-0.96932
	Na	0.00000	-1.30349	-0.82023
	Cl	0.00000	0.21017	1.30796
B2PLYP-D3(BJ)/AVTZ	O	-1.34346	1.42571	0.00000
	H	-1.33938	0.79603	0.73497
	H	-1.33938	0.79603	-0.73497
	Na	1.22059	0.93288	0.00000
	Cl	0.00000	-1.36820	0.00000

Table S11. Geometry of TS3 in the anion $NaCl(H_2O)^-$ isomerization reaction pathway.

		X	Y	Z
CCSD(T)-F12a/AVTZ	O	0.00000	0.00000	0.00000
	H	0.00000	0.00000	0.95732
	H	0.95136	0.00000	-0.25610
	Na	0.00000	0.00016	-2.4660
	Cl	2.51042	0.00012	-1.65398
B2PLYP-D3(BJ)/AVTZ	O	1.54137	-0.98295	0.00000
	H	1.84516	-1.89285	0.00001
	H	0.55350	-1.03977	0.00000
	Na	0.77463	1.31356	0.00000
	Cl	-1.36768	-0.21488	0.00000

Table S12. Geometry of TS4 in the anion $NaCl(H_2O)^-$ isomerization reaction pathway.

		X	Y	Z
CCSD(T)-F12a/AVTZ	O	-2.27628	0.44472	-0.07509
	H	-2.28284	0.65100	0.85908
	H	-1.52330	-0.16820	-0.22176
	Na	1.26392	1.33696	0.00721
	Cl	0.48826	-1.08148	0.02742
B2PLYP-D3(BJ)/AVTZ	O	-2.26199	0.44910	-0.09595
	H	-2.32353	0.63304	0.84465
	H	-1.47390	-0.13084	-0.15479
	Na	1.25041	1.33897	-0.00461
	Cl	0.47876	-1.10727	0.00756

Table S13. Geometry of TS5 in the anion $NaCl(H_2O)^-$ isomerization reaction pathway.

		X	Y	Z
CCSD(T)-F12a/AVTZ	O	-2.76910	-0.53665	0.00037
	H	-2.45214	-1.44104	-0.00041
	H	-1.93750	-0.02853	0.00026
	Na	2.27713	-0.69664	0.00022
	Cl	0.16450	0.74140	-0.00041
B2PLYP-D3(BJ)/AVTZ	O	3.13887	0.00002	0.00012
	H	2.50993	0.73199	0.00007
	H	2.50995	-0.73197	0.00007
	Na	-2.62086	0.00002	0.00012
	Cl	-0.07655	-0.00002	-0.00015

Table S14. Geometry of TS1′ in the neutral NaCl(H_2O) isomerization reaction pathway.

		X	Y	Z
CCSD(T)-F12a/AVTZ	O	···	···	···
	H	···	···	···
	H	···	···	···
	Na	···	···	···
	Cl	···	···	···
B2PLYP-D3(BJ)/AVTZ	O	1.92731	1.90188	0.00000
	H	2.08033	2.85189	0.00000
	H	2.80251	1.49964	0.00000
	Na	0.00000	0.57396	0.00000
	Cl	-1.19420	-1.52236	0.00000

Table S15. Geometry of TS2′ in the neutral NaCl(H_2O) isomerization reaction pathway.

		X	Y	Z
CCSD(T)-F12a/AVTZ	O	0.00000	0.95081	-1.80306
	H	0.73900	1.26937	-1.27008
	H	-0.73908	1.26930	-1.27017
	Na	0.00000	-1.18232	-0.67128
	Cl	0.00000	0.26543	1.32121
B2PLYP-D3(BJ)/AVTZ	O	1.98916	-0.04787	0.00000
	H	1.69811	0.49691	0.74363
	H	1.69811	0.49691	-0.74363
	Na	0.00000	-1.33512	0.00000
	Cl	-1.13586	0.82797	0.00000

Table S16. Geometry of TS3′ in the neutral NaCl(H_2O) isomerization reaction pathway.

		X	Y	Z
CCSD(T)-F12a/AVTZ	O	-1.59952	-0.79648	-0.01972
	H	-2.16158	-1.56420	-0.02992
	H	-0.68841	-1.16514	0.07354
	Na	-0.63550	1.27146	0.00745
	Cl	1.36926	-0.21523	-0.03133
B2PLYP-D3(BJ)/AVTZ	O	-1.65599	-0.78700	-0.00001
	H	-2.09606	-1.63945	0.00001
	H	-0.69117	-1.00556	-0.00005
	Na	-0.61133	1.23663	0.00000
	Cl	1.33881	-0.27424	0.00000

Table S17. The harmonic frequencies of the isomers of $NaCl(H_2O)^-$ and $NaCl(H_2O)$ at different levels. The values to the right of the forward slash indicate that the harmonic frequencies were scaled by a frequency correction factor.

species	note	frequency								
		v1	v2	v3	v4	v5	v6	v7	v8	v9
$NaCl^-$+	CCSD(T)-F12a/AVTZ	3941	3831	1646	266					
H2O	b2plyp-D3(BJ)/AVTZ	3924	3812	1635	263					
	b3lyp-D3(BJ)/AVTZ	3899/3774	3796/3675	1627/1575	260/252					
	mp2/AVTZ	3948/3789	3822/3668	1628/1563	262/251					
	dsdpbep86-D3(BJ)/AVTZ	3939/3928	3824/3814	1640/1636	269/268					
NaCl+	CCSD(T)-F12a/AVTZ	3941	3831	1646	350					
H2O	b2plyp-D3(BJ)/AVTZ[a]	3924	3812	1635	355					
	b3lyp-D3(BJ)/AVTZ[b]	3899/3774	3796/3675	1627/1575	355/344					
	mp2/AVTZ[c]	3948/3789	3822/3668	1628/1563	347/333					
	dsdpbep86-D3(BJ)/AVTZ[d]	3939/3928	3824/3814	1640/1636	355/354					
A^-	CCSD(T)-F12a/AVTZ	3877	3430	1654	783	379	290	246	182	150
	b2plyp-D3(BJ)/AVTZ[a]	3848	3358	1637	785	375	296	245	176	153
	b3lyp-D3(BJ)/AVTZ[b]	3811/3689	3324/3217	1625/1573	778/753	370/358	299/289	242/234	171/165	152/147
	mp2/AVTZ[c]	3880/3724	3348/3214	1638/1572	808/775	388/372	292/280	248/238	184/177	145/139
	dsdpbep86-D3(BJ)/AVTZ[d]	3871/3860	3377/3367	1644/1640	794/792	376/375	297/296	250/250	183/183	155/155
B^-	CCSD(T)-F12a/AVTZ	3658	3623	1594	360	348	227	172	78	62
	b2plyp-D3(BJ)/AVTZ[a]	3580	3536	1569	350	293	207	130	51	38
	b3lyp-D3(BJ)/AVTZ[b]	3512/3399	3486/3375	1548/1498	350/339	284/275	204/198	125/121	49/47	39/38
	mp2/AVTZ[c]	3662/3515	3601/3457	1582/1518	340/326	309/296	209/201	158/152	55/53	42/40
	dsdpbep86-D3(BJ)/AVTZ[d]	3639/3629	3593/3583	1585/1581	352/351	301/300	211/211	138/138	51/51	31/31
C^-	CCSD(T)-F12a/AVTZ	3894	3600	1682	624	300	252	166	20	11
	b2plyp-D3(BJ)/AVTZ[a]	3877	3530	1670	629	325	249	168	17	8
	b3lyp-D3(BJ)/AVTZ[b]	3848/3725	3490/3378	1661/1608	626/606	338/327	245/237	169/136	33/32	17/17
	mp2/AVTZ[c]	3899/3742	3540/3398	1663/1596	646/620	322/309	250/240	170/163	37/35	15/14
	dsdpbep86-D3(BJ)/AVTZ[d]	3892/3881	3554/3545	1674/1669	633/631	315/314	255/255	169/169	29/29	16/16
A	CCSD(T)-F12a/AVTZ	3923	3474	1648	661	503	319	248	182	82
	b2plyp-D3(BJ)/AVTZ[a]	3905	3411	1633	653	511	322	256	177	71
	b3lyp-D3(BJ)/AVTZ[b]	3883/3759	3372/3264	1621/1569	642/621	513/497	321/311	258/250	174/169	58/56
	mp2/AVTZ[c]	3917/3759	3399/3263	1635/1569	694/667	505/485	317/305	245/235	186/179	114/109
	dsdpbep86-D3(BJ)/AVTZ[d]	3917/3907	3423/3414	1641/1637	673/672	503/502	324/323	256/255	183/182	101/101
B	CCSD(T)-F12a/AVTZ	3918	3900	1664	358	342	227	204	32	16
	b2plyp-D3(BJ)/AVTZ[a]	3902	3862	1656	368	345	229	209	28	7
	b3lyp-D3(BJ)/AVTZ[b]	3884/3760	3796/3675	1650/1597	372/360	348/337	236/229	200/193	32/31	13/13
	mp2/AVTZ[c]	3920/3763	3875/3719	1649/1582	357/342	337/324	212/204	202/194	25/24	9/9
	dsdpbep86-D3(BJ)/AVTZ[d]	3914/3904	3898/3887	1659/1654	367/366	341/340	219/219	210/210	25/25	4/4

[a] Since the B2PLYP-D3(BJ)/AVTZ frequency correction factor is 0.9999, which is close to 1,[2] and the result is rounded, the non-resonant and resonant frequencies are almost identical.

[b] Frequency correction factor 0.9680 for B3LYP-D3(BJ)/AVTZ.[3]

[c] Frequency correction factor of 0.9598 for MP2/AVTZ.[4]

[d] Frequency correction factor of 0.9973 for DSDPBEP86-D3BJ/AVTZ.[3]

Table S18. ADCH charge analysis for different isomers of the $NaCl(H_2O)^-$ and $NaCl(H_2O)$ complex.

	ADCH charges						
Atoms	NaCl +H_2O	$NaCl^-$+H_2O	A	A^-	B	B^-	C^-
O	-0.6790	-0.6790	-0.4591	-0.3394	-0.4299	-0.0064	-0.6933
1H	0.3395	0.3395	0.3642	0.1092	0.3211	-0.1915	0.3116
H	0.3395	0.3395	0.0184	0.3318	0.3211	-0.1915	0.2584
Na	0.7973	-0.5921	0.7090	-0.6448	0.4626	0.1314	-0.5632
Cl	-0.7973	-0.4079	-0.6325	-0.4568	-0.6749	-0.7420	-0.3135

Note: Structure based on B2PLYP-D3(BJ)/AVTZ level optimization, 1H in the isomer indicates the H atom away from the Cl atom. ADCH charges[5] were calculated using Multiwfn and the results were retained to four decimal places.

Table S19. Comparison between theoretical and experimental energies, adiabatic detachment energy (ADE), for different isomers (in cm^{-1}).

	Isomer	$NaCl(H_2O)^-$			$NaCl(H_2O)$		
		A^-	B^-	C^-	A1	A2	B
ΔE	Expt_1[a]	0	186(22)	481(48)	0	123(10)	1821(24)
	B3LYP-D3(BJ)/def2-QZVPP[a]	0	51	330	0	88	1604
	LC-ω PBE/6-311++G(d,p)[b]	0	234	274		0	1839
	B2PLYP-D3(BJ)/AVTZ	0	-44	186	0	0	1736
	B3LYP-D3(BJ)/AVTZ	0	-42	240	0	0	1880
	B3LYP-D3(BJ)/AVTZ[c]	0	798	18	0	0	869
	MP2/AVTZ	0	-10	192	0	0	1620
	DSDPBEP86-D3(BJ)/AVTZ	0	-25	179	0	0	1669
	CCSD(T)-F12a/AVTZ	0	49	155	0	3	1623
	CCSD(T) /CBS	0	37	133	0	0	1601
	FPA	0	-12	282	0	0	1547
ADE	Expt_1[a]	3643(22)	5278(17)				
	Expt_2[b]	3710(81)	5081(65)				
	B3LYP-D3(BJ)/def2-QZVPP[a]	3726	5279				
	LC-ω PBE/6-311++G(d,p)[b]						
	B2PLYP-D3(BJ)/AVTZ	3672	5453				
	B3LYP-D3(BJ)/AVTZ	3692	5612				
	B3LYP-D3(BJ)/AVTZ[c]	4912	6186				
	MP2/AVTZ	3661	5290				
	DSDPBEP86-D3(BJ)/AVTZ	3665	5359				
	CCSD(T)-F12a/AVTZ	3637	5210				
	CCSD(T) /CBS	3603	5162				
	FPA	3670	5231				
VDE	Expt_1[a]			7680(200)			
	Expt_2[b]	4355(81)	5162(65)	7743(65)			
	B3LYP-D3(BJ)/def2-QZVPP[a]			7857			
	LC-ω PBE/6-311++G(d,p)[b]	4275	5323	7501			
	B2PLYP-D3(BJ)/AVTZ	4408	5396	7748			
	B3LYP-D3(BJ)/AVTZ	4391	5455	7812			
	B3LYP-D3(BJ)/AVTZ[c]	5947	6599	9518			
	MP2/AVTZ	4617	5387	7550			
	DSDPBEP86-D3(BJ)/AVTZ	4415	5376	7631			
	CCSD(T)-F12a/AVTZ	4503	5254	7563			
	CCSD(T) /CBS	4487	5233	7541			
	FPA	4822	5168	7954			

[a] denotes density generalization calculations and experimental data by Lu and Ning.[6]

[b] denotes theoretical calculations and experimental data by Hou et al.,[7] and the numbers in the parentheses

indicate the experimental uncertainty.

[c] the single point energies were calculated using the Beijing Density Function (BDF) software at the B3LYP-D3(BJ)/AVTZ level based on the structure obtained at the B3LYP-D3(BJ)/AVTZ level (Gaussian 16).

Noted that since the isomer C^- cannot be obtained at the M062X-D3/aVTZ level and the A obtained by optimization at the LC-ωPBE/AVTZ level, with a structure like TS3, is a five-atom coplanar structure, which is inconsistent with the results of many previous studies, we do not consider the A and B calculation levels in the energy calculations and frequency analysis work.

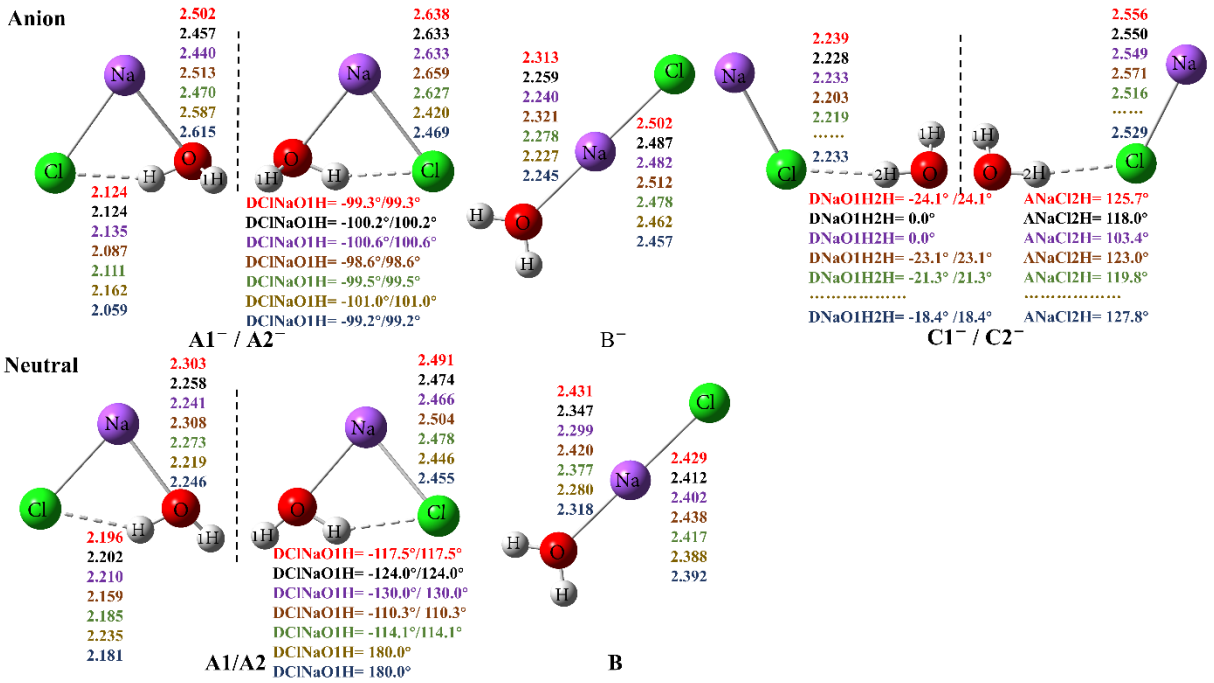

Fig. S1 Optimized geometries for isomers of $NaCl(H_2O)^-$ and $NaCl(H_2O)$ (lengths in Å and angles in °). The seven entries are determined by CCSD(T)-F12a/aVTZ (red), B2PLYP-D3(BJ)/aVTZ (black), B3LYP-D3(BJ)/aVTZ (purple), MP2/ aVTZ (brown), DSD-PBEP86-D3(BJ)/aVTZ (green), M062X-D3/aVTZ (olive green) and LC-ωPBE/aVTZ (navy blue).

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