Electronic Supplementary Material (ESI) for Chemical Science.

Supplementary Information

Impact of Anion Polarizability on Ion Pairing in Microhydrated Salt Clusters

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Label	IRPD	$\nu_{Anh.}$	Assignments	Label	IRPD	$\nu_{Anh.}$	Assignments	Label	IRPD	Assignments
					XX´=I_2					
***n* = 1**		**1.0.0d**		***n* = 2**		**2.2.0**		***n* = 3**		**3.3.0a/b-321a**
a_1	3652	3660	ν_{as}(DD-H_2O)	b_1	3724	3718	ν_{free}(D-H_2O)	c_1	3679	-
a_2	3503	3505	combination	b_2	3361			c_2	3624	-
a_3	3444	3438	ν_s(DD-H_2O)	b_3	3297	3290	combination	c_3	3599	-
*	2967		D_2 stretch	b_4	3235	3194	ν_s(D-H_2O's)	c_4	3450	-
				b_5	3211	3170	combination	c_5	3394	-
				b_6	3186	3146	combination	c_6	3377	-
				*	3152	3100	ν_{as}(D-H_2O's)	c_7	3342	-
					2962		D_2 stretch	c_8	3242	-
								*	2965	D_2 stretch
					XX´=ClI					
***n* = 1**		**1.0.0c**		***n* = 2**		**2.2.0**		***n* = 3**		**3.2.1a/b**
d_1	3681	3704	ν_{as}(D-H_2O)	e_1	3720	3716	ν_{free}(D-H_2O)	f_1	3712	-
d_2	3357	3272	combination	e_2	3381			f_2	3507	-
d_3	3293	3200	ν_s(D-H_2O)	e_3	3306	3328	combination	f_3	3366	-
*	MPD			e_4	3257	3224	ν_s(D-H_2O's)	f_4	3302	-
				e_5	3216	3156	combination	f_5	3220	-
				e_6	3160	3124	ν_{as}(D-H_2O's)	f_6	3126	-
				*	2947		D_2 stretch	*	2962	D_2 stretch
					XX´=Cl_2					
***n* = 1**				***n* = 2**				***n* = 3**		
g_1	3709	1.0.0a	ν_{free}(D-H_2O)	h_1	3729	2.2.0	ν_{free}(D-H_2O)	i_1	3697 3661	3.2.1a ν_{free}(D-H_2O)
g_2	3616	1.0.0 b	ν_{as}(DD-H_2O)	h_2	*3535*	2.0.1a	ν_{as}(DD-H_2O)	i_2	3576	3.0.2 ν_{as} (DD-H_2O)

g_3	3567	1.0.0b	combination	h_3	*3394*	2.0.1a	ν_s(DD-H_2O)	i_3	3531	3.0.2	ν_{as}(DD-H_2O)
g_4	3529	1.0.0b	ν_s(DD-H_2O)	h_4	3265	2.2.0	bend overtone	i_4	3508	3.0.2	ν_{as}(ADD-H_2O)
g_5	3444	1.0.0a	ν_{HB}(D-H_2O)	h_5	3203	2.2.0	combination	i_5	3443	3.0.2	ν_s(ADD-H_2O)
g_6	3246	1.0.0a	bend overtone	h_6	3157	2.2.0	combination	i_6	3351	3.0.2	ν_s(DD-H_2O)
*	2959		D2 stretch	h_7	3045	2.2.0	combination	i_7	3312	3.2.1a	ν_s(AD-H_2O)
				h_8	3014	2.2.0	$\nu_{s,HB}$(D-H_2O's)	i_8	3227		ν_s(DD-H_2O)
				h_9	2960	2.2.0	ν_{as}(D-H_2O's)	i_9	3180		ν_s(DD-H_2O)
								i_{10}	3082	3.2.1	combination
								i_{11}	3019	3.2.1a	ν_s-D-H_2O
								i_{12}	2878	3.2.1a	ν_s-D-H_2O
								*	2957		D2 stretch

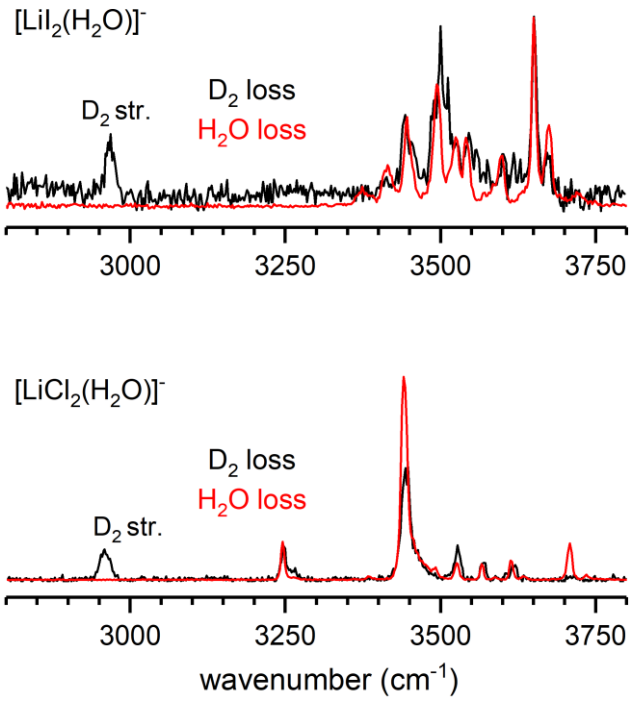

Figure S1: IRPD Spectra obtained by monitoring D_2 (black) and H_2O-loss (red) for $[LiI_2(H_2O)]^-$ and $[LiCl_2(H_2O)]^-$ as shown in top and bottom panel, respectively. Bands due to D_2 stretching mode are marked.

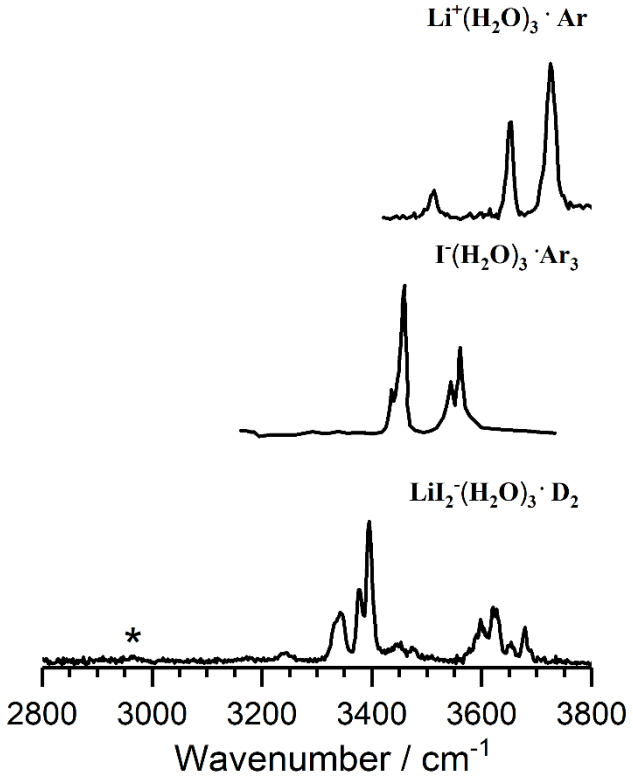

Figure S2: IRPD spectra obtained by monitoring D_2-loss (bottom panel) for $LiI_2(H_2O)_3^-$ and Ar-loss for $I^-(H_2O)_3$ (middle) and $Li^+(H_2O)_3$ (top). $Li^+(H_2O)_3$ and $I^-(H_2O)_3$ spectra are reproduced from previously published data.[2,3]

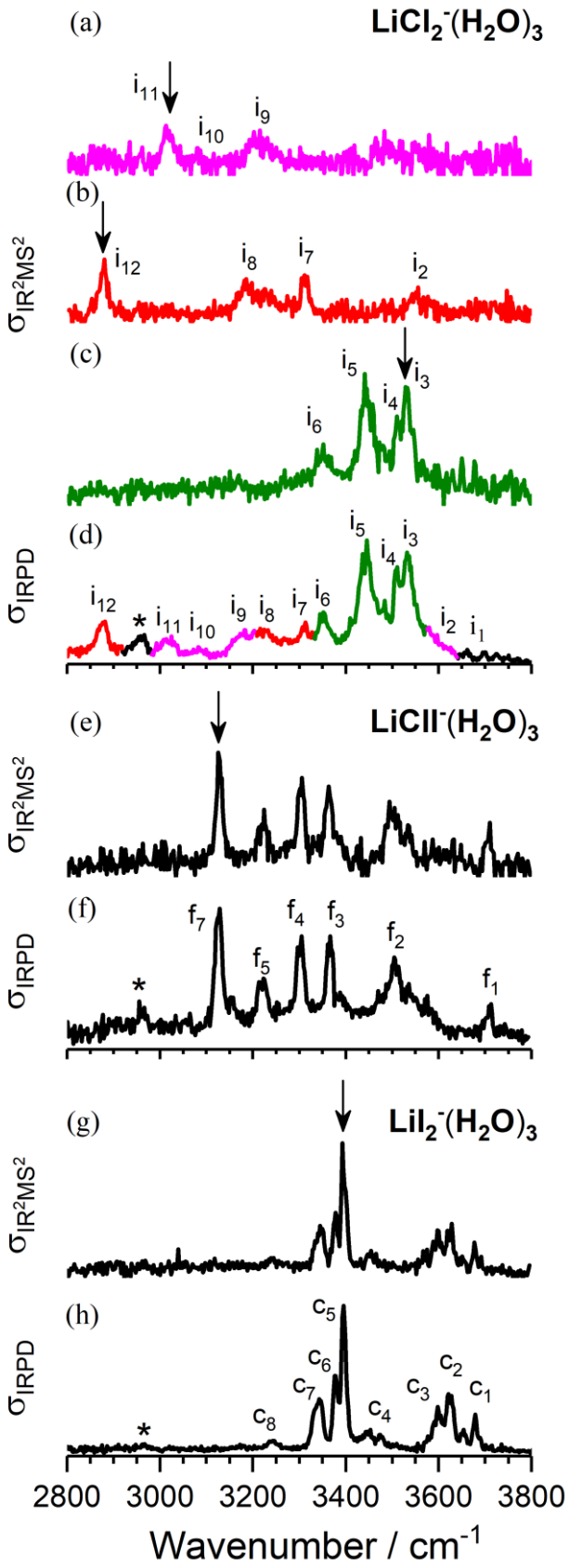

Figure S3. IRPD *vs.* IR^2MS^2 spectra for $[LiXX'(H_2O)_3]^-$ where XX'= Cl_2 (trace a-d), ClI (e-f), and I_2 (g-h). Pump wavelengths for IR^2MS^2 studies are assigned by arrows.

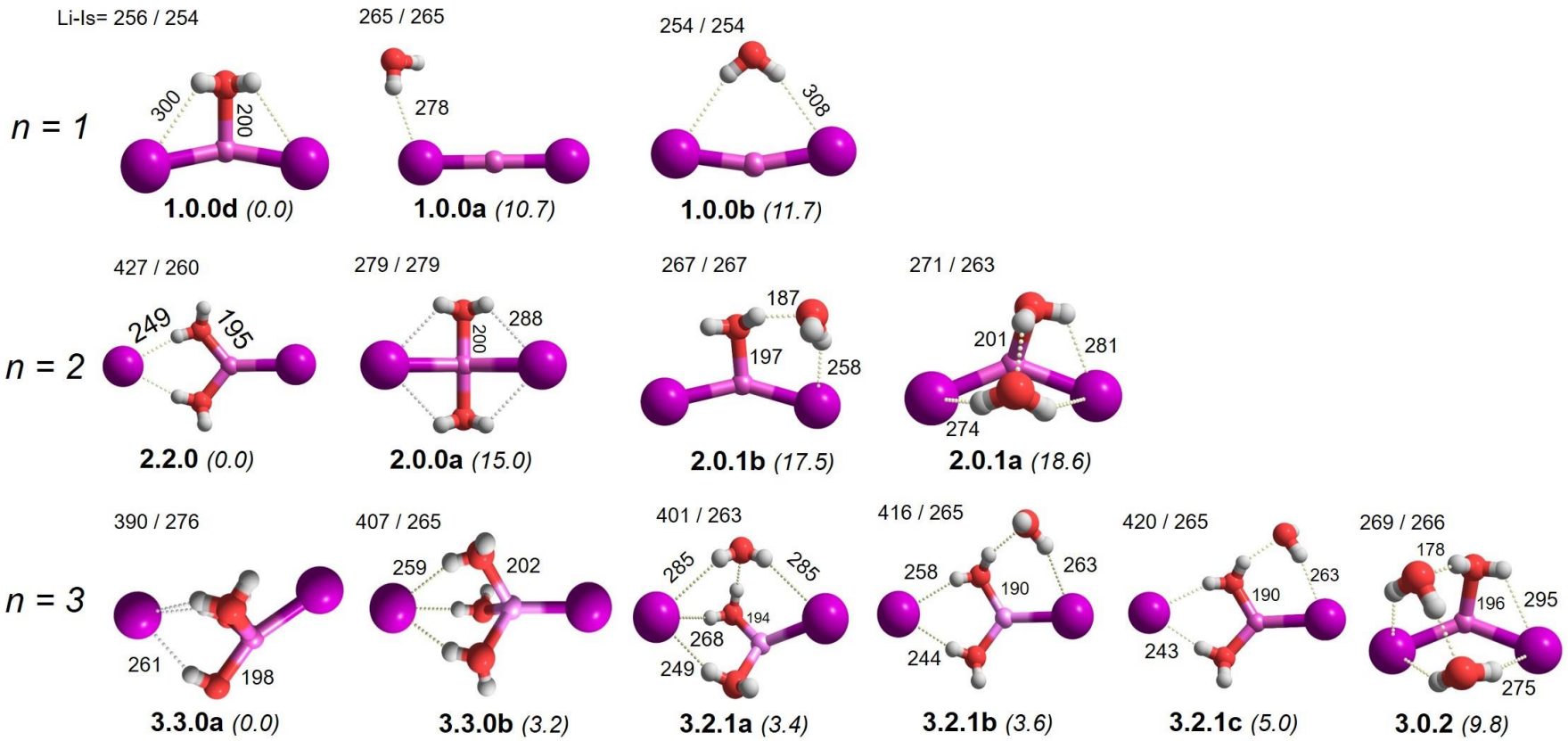

Figure S4. MP2/def2-TZVP structures of $[LiI_2(H_2O)_n]^-$ (n = 1-3) along with ZPE corrected relative energies ($\Delta E_{0,anh}$, kJ mol^{-1}) and relevant bond distances (in pm).

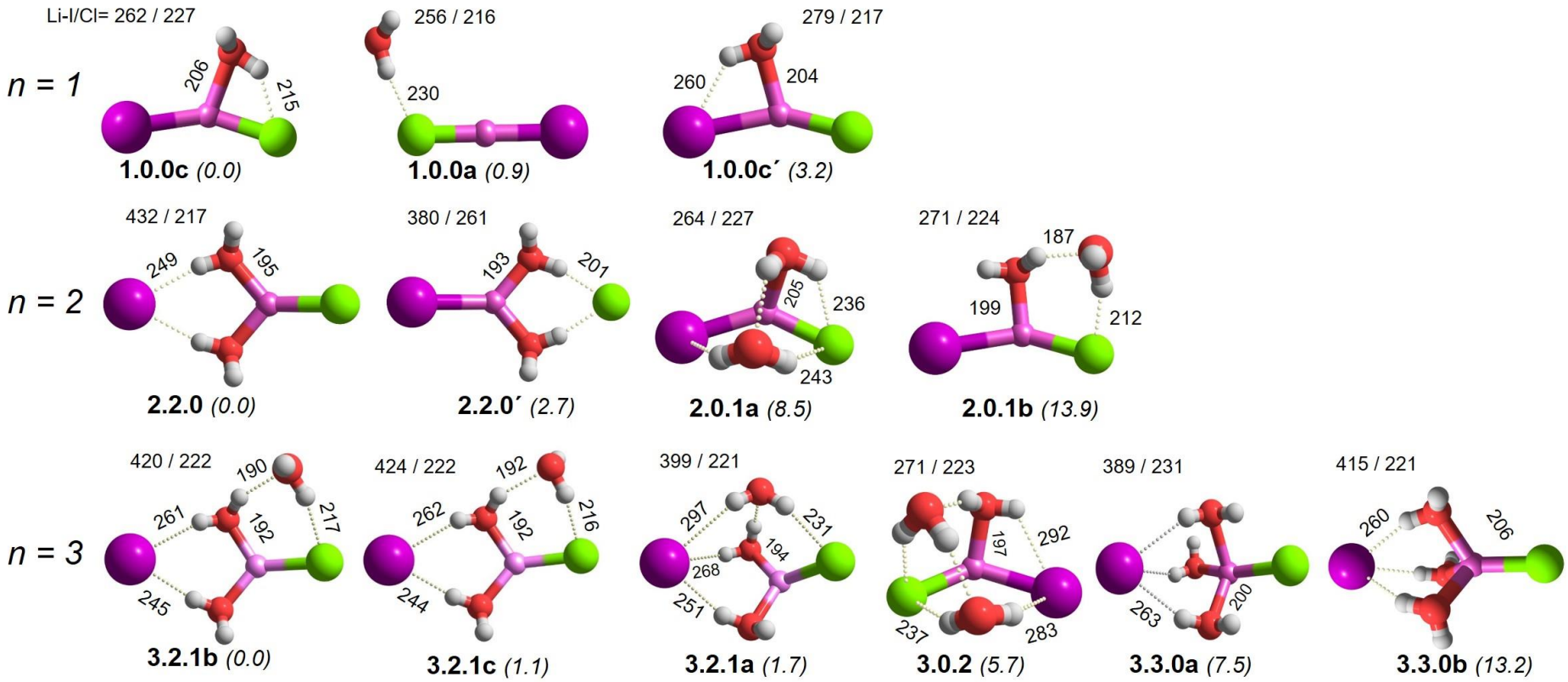

Figure S5. MP2 / def2TZVP structures of $[LiClI(H_2O)_n]^-$ (n = 1-3) along with ZPE corrected relative energies ($\Delta E_{0,anh}$, kJ mol^{-1}) and relevant bond distances (in pm).

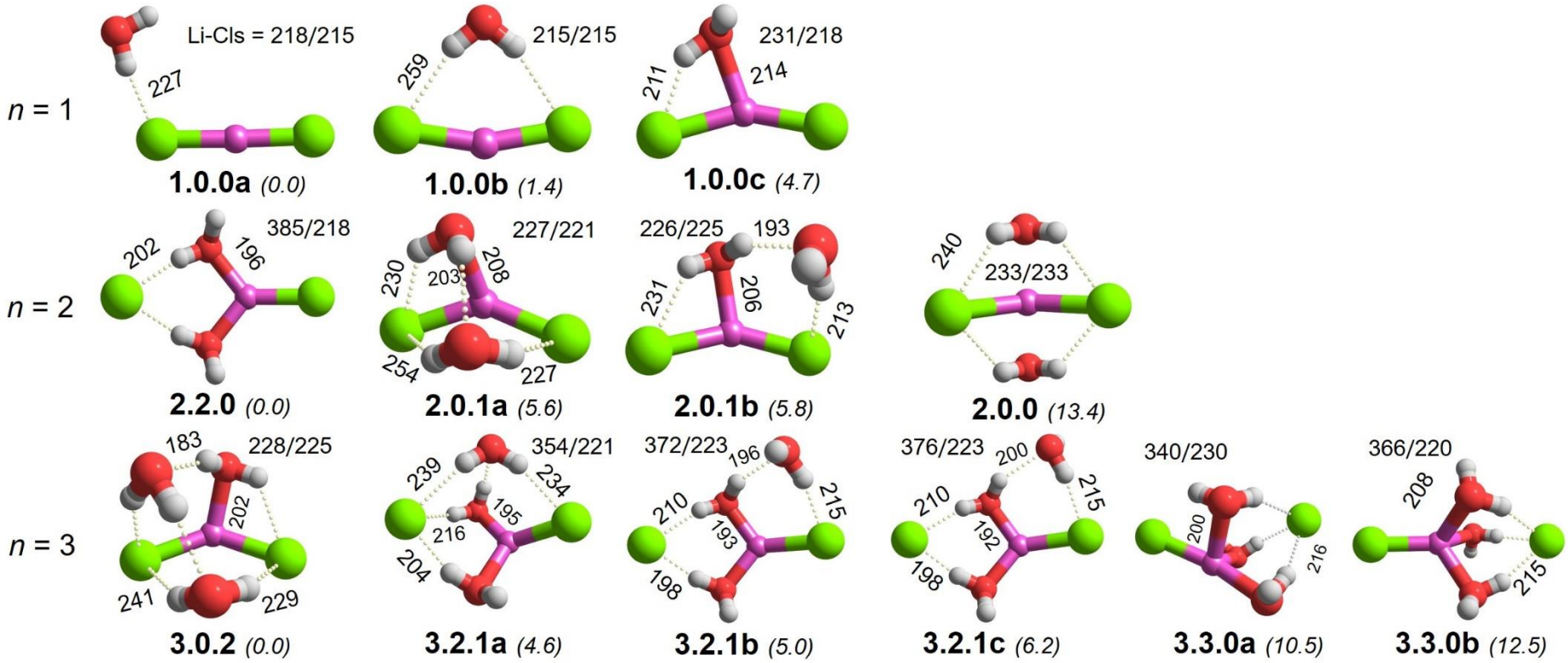

Figure S6. MP2 / def2TZVP structures of $[LiCl_2(H_2O)_n]^-$ (n = 1-3) along with ZPE corrected relative energies ($\Delta E_{0,anh}$, kJ mol^{-1}) and relevant bond distances (in pm).

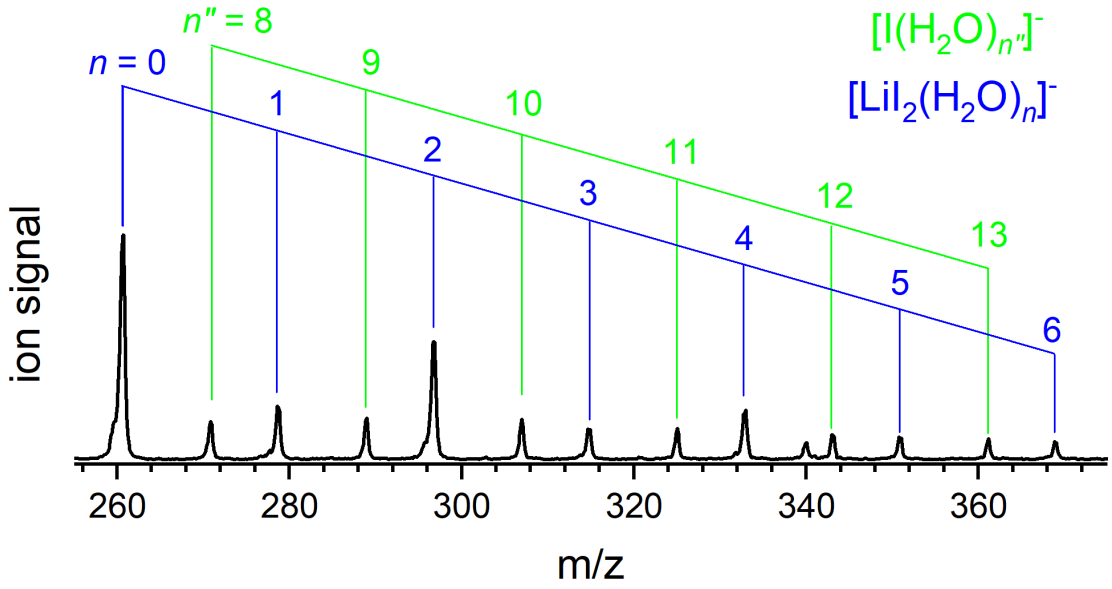

Figure S7. Quadrupole mass spectrum of microhydrated lithium diiodide [$LiI_2^-(H_2O)_n$] and iodide anion [$I^-(H_2O)_{n''}$] in the *m/z* range 255 to 375 amu obtained by ion spray of a 10 mM lithium iodide (LiI) in 1:1 water/acetonitrile solution.

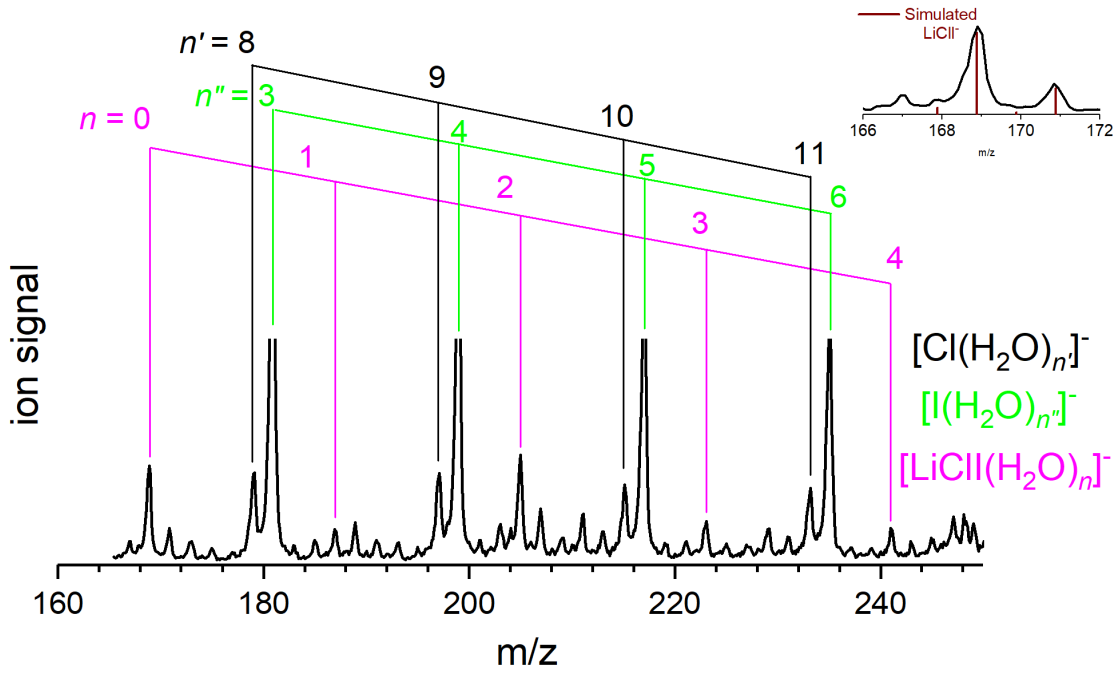

Figure S8. Quadrupole mass spectrum of microhydrated lithium chlorideiodide $[LiClI(H_2O)_n]^-$, chloride $[Cl(H_2O)_{n'}]^-$ and iodide $[I^-(H_2O)_{n''}]^-$ anions, in the *m/z* range 165 to 250 amu obtained by ion spray of a mixture of 10 mM lithium chloride (LiCl) and lithium iodide solution in 1:1 water/acetonitrile. $LiClI^-$ reflects the natural isotropic distribution of constituting ions which has been affirmed in the inset comparing with simulated mass spectrum of $LiClI^-$ (in red).

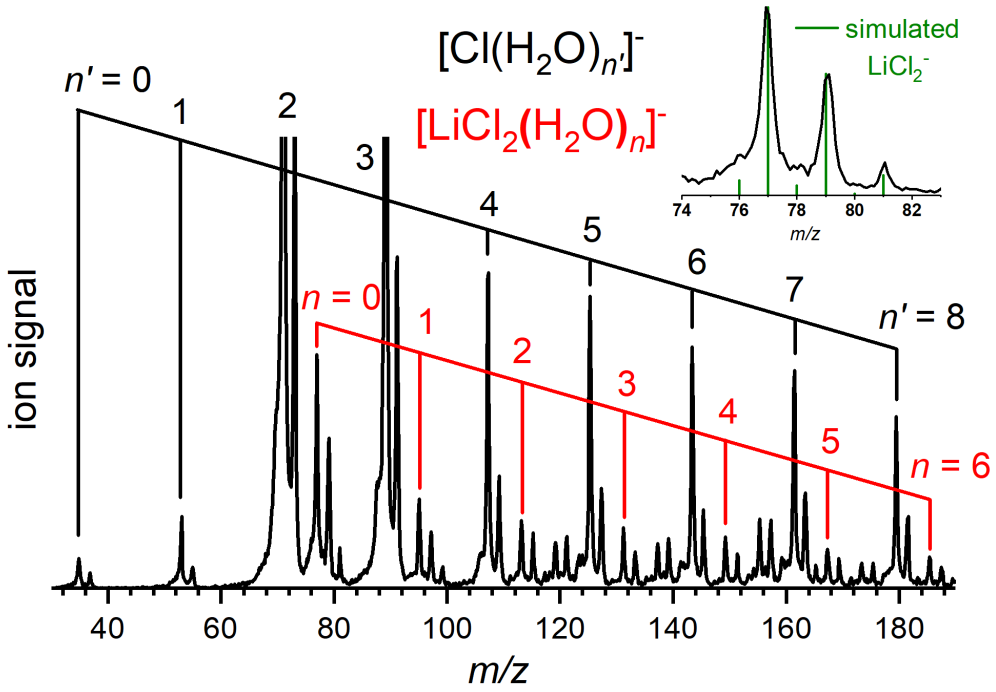

Figure S9. Quadrupole mass spectrum of microhydrated lithium dichloride $[LiCl_2(H_2O)_n]^-$ and chloride anions $[Cl(H_2O)_{n'}]^-$ in the *m/z* range up to 190 amu obtained by ion spray of a 10 mM lithium chloride (LiCl) in 1:1 water/acetonitrile solution. The observed doublets Cl^- and triplets $LiCl_2^-$ reflect the natural isotropic distribution of lithium and chlorine. It has been affirmed in the inset comparing with simulated mass spectrum of $LiCl_2^-$ (in green).

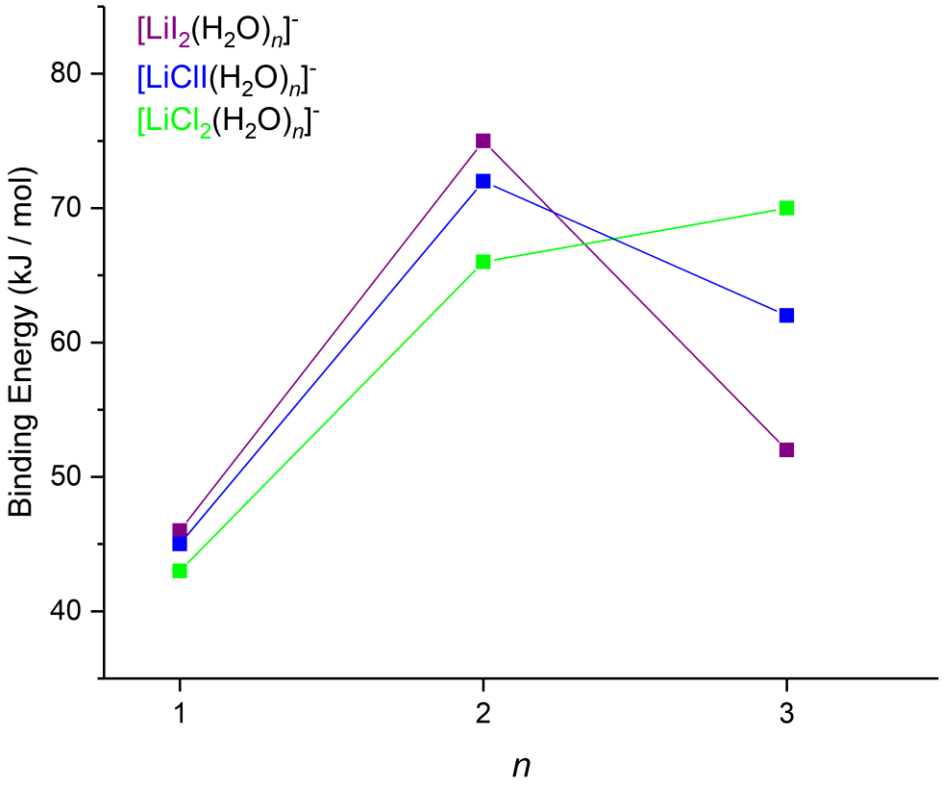

Figure S10. Calculated (MP2 / def2TZVP) sequential binding energies for each added water molecules to $[LiXX']^-$ anions where XX′=I_2, ClI, Cl_2 in the size range n = 1-3.

In Figures S7 to S9 it can be seen that the relative intensities of $[LiI_2(H_2O)_2]^-$ and $[LiClI(H_2O)_2]^-$ are higher in contrast to $[LiCl_2(H_2O)_2]^-$. This observation of "magic numbers" is indeed reflected in the stability of the corresponding complexes (see Figure S10). The sequential binding energy reaches a maximum at n = 2 for LiI_2 and LiClI, while the highest value is observed at n = 3 for $LiCl_2$. The latter is a consequence of the stronger Li^+-Cl^- (vs. Li^+-I^-) as well as the stronger Cl^--water (vs. I^--water) interactions.

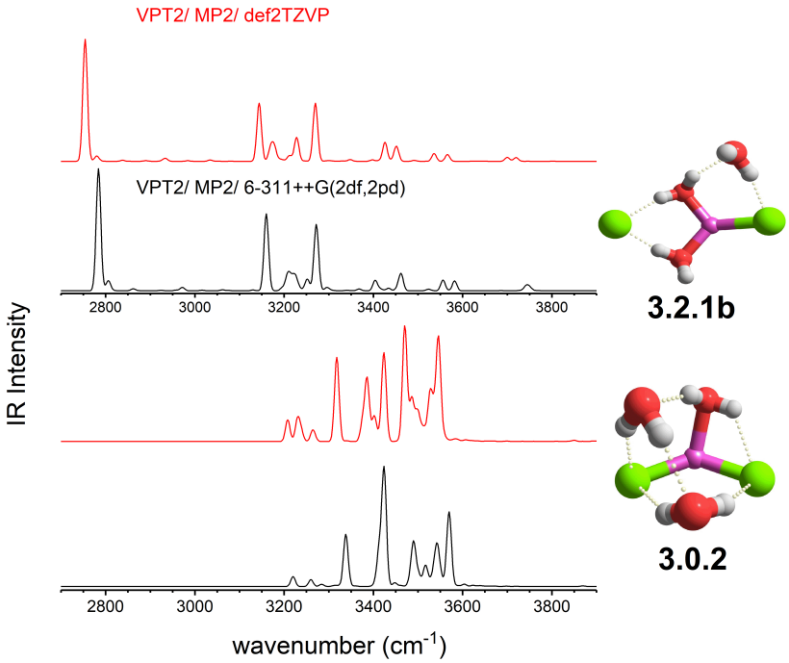

Figure S11: Comparison between anharmonic IR spectra of two individual structures of $[LiCl_2(H_2O)_3]^-$ anion, **3.0.2** and **3.2.1a**, calculated with MP2/6-311++G(2df,2pd) (in black) and MP2/ def2TZVP (in red).

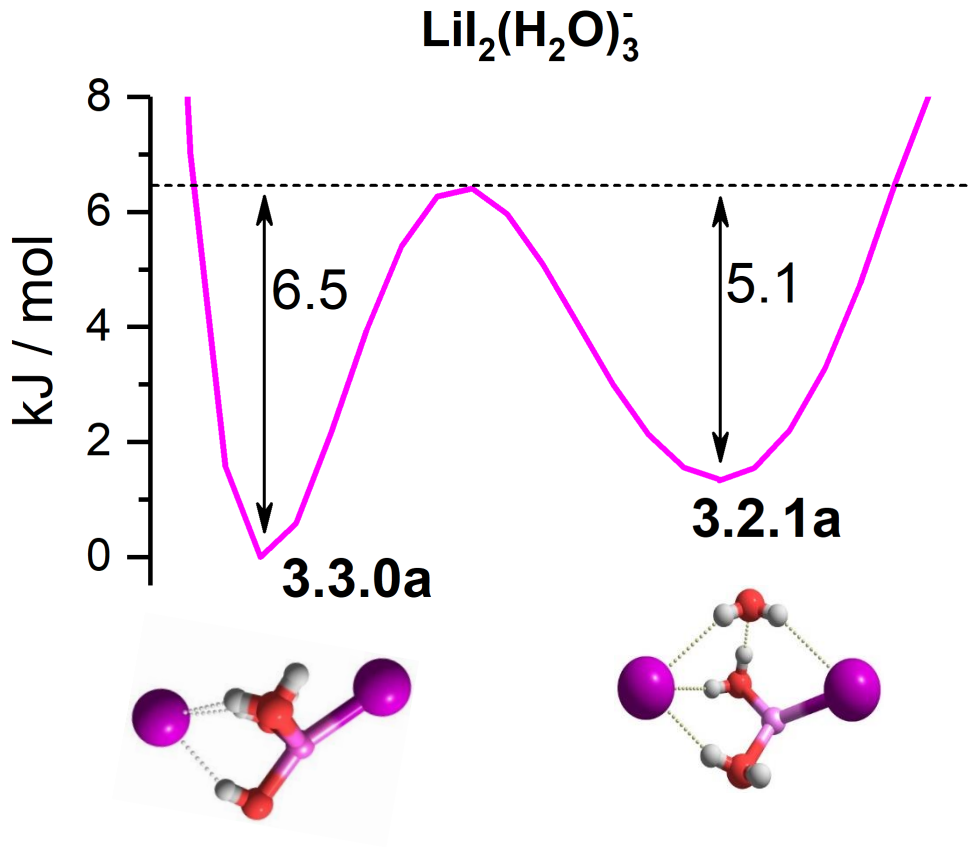

Fig S12. Potential energy surface scan at MP2 / def2TZVP exhibiting barrier height in kJ / mol for the interconversion between the structure **3.3.0a** and **3.2.1a** in case of $[LiI_2(H_2O)_3]^-$.

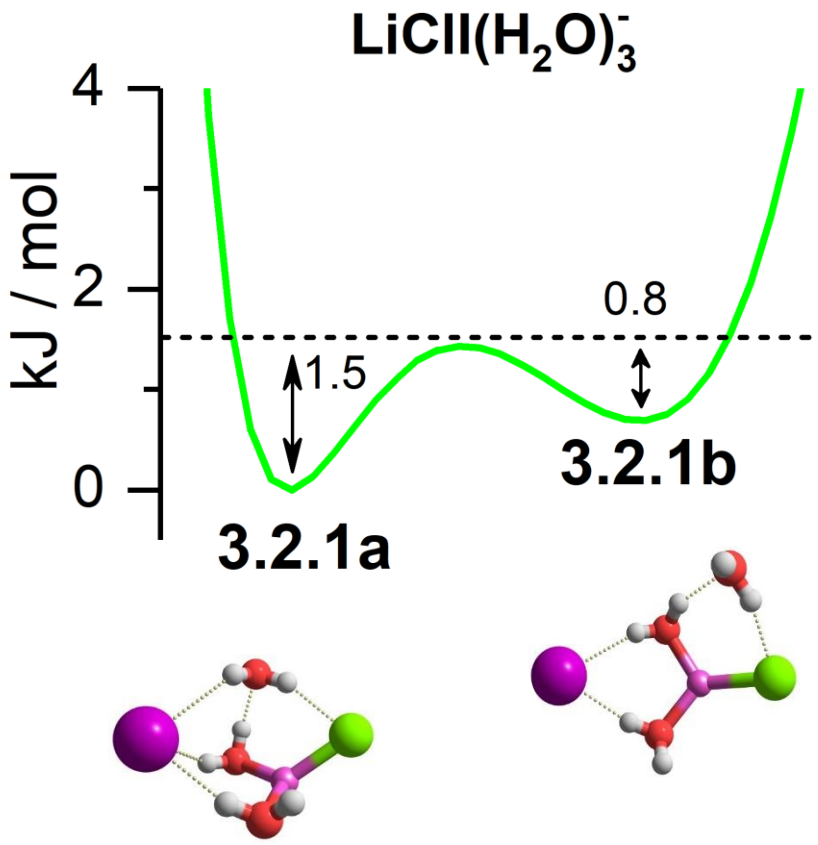

Fig S13. Potential energy surface scan at MP2 / def2TZVP exhibiting barrier height in kJ / mol for the interconversion between the structure **3.2.1a** and **3.2.1b** of $[LiClI(H_2O)_3]^-$.

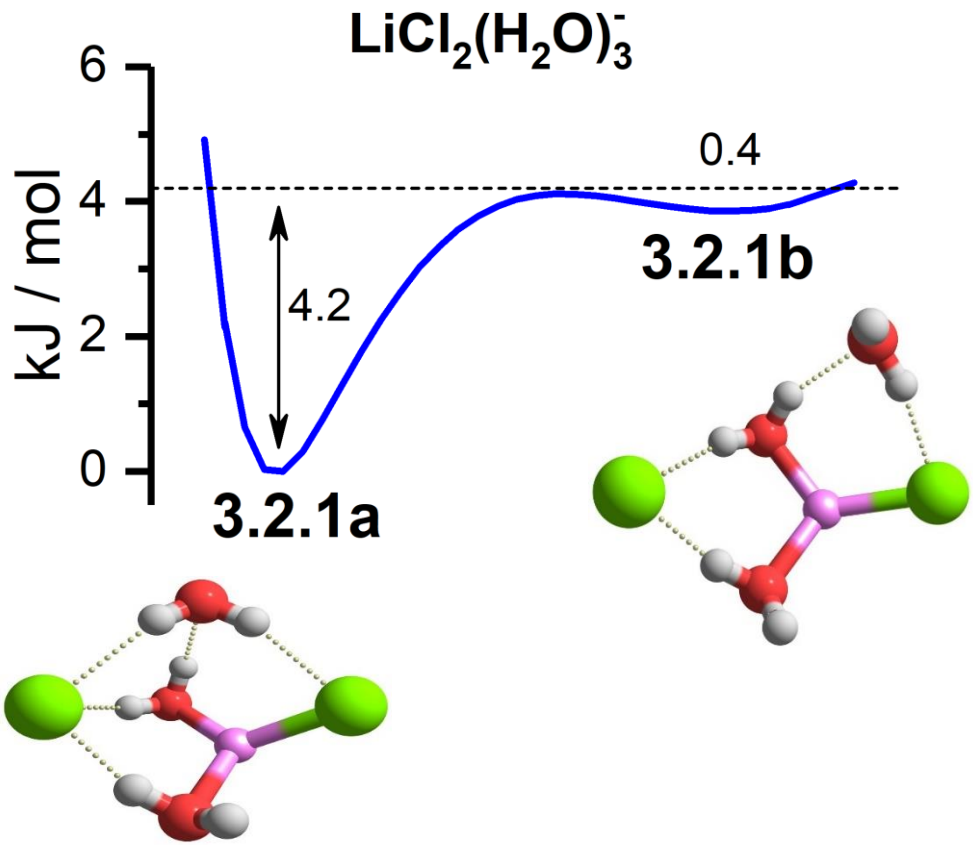

Fig S14. Potential energy surface scan at MP2/6-311++G(2df,2pd) exhibiting barrier height in kJ /mol for the interconversion between the structure **3.2.1a** and **3.2.1b** in case of $[LiCl_2(H_2O)_3]^-$.

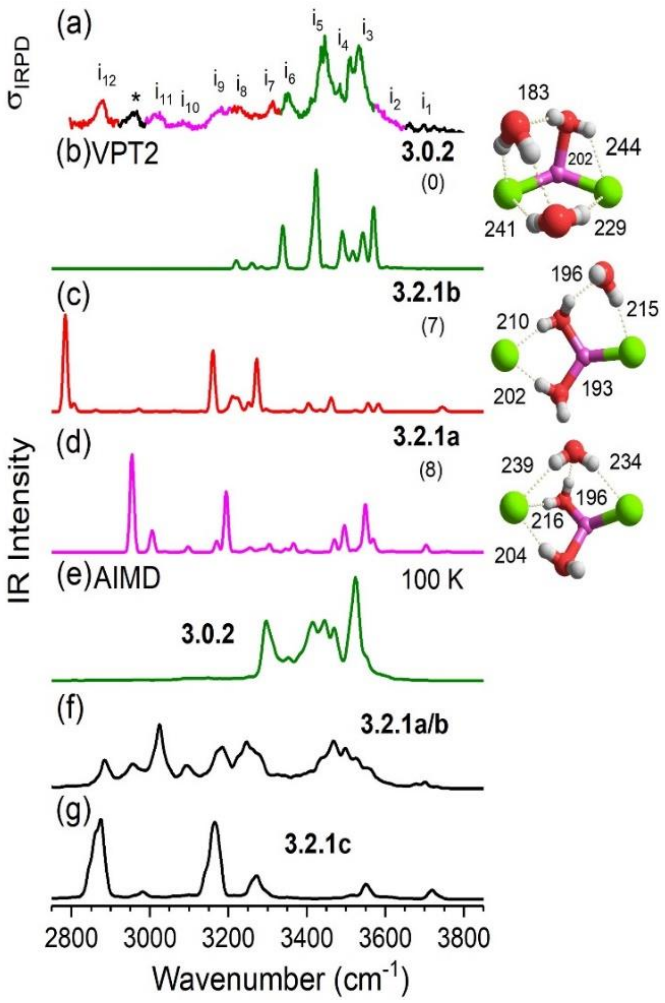

Fig S15. Comparison of the IRPD spectrum (trace a) of D_2-tagged $[LiCl_2(H_2O)_3]^-$ color coded as the contribution of multiple isomers determined with IR^2MS^2 study (see Fig S3) probing at band i_5 (green), i_{11} (pink) and i_{13} (red) to the static anharmonic VPT2/MP2/6-311+G(2df,2pd) spectra of three most stable isomers **3.0.2** (c), **3.2.1a** (b) and **3.2.1b** (a), which has already been explain in our recent publication.[1] Additionally, the AIMD simulated dynamic anharmonic spectra at 100 K are compared in trace e, f and g.

Table S2a. ZPE-corrected relative energies $\Delta E_{0,anh}$ obtained with MP2/ def2TZVP (in kJ/mol), symmetry, inter-ion ($r_{Li\text{-}X}$), $X^-\cdots HOH$ ($r_{X^-\cdots H}$) and $Li^+\cdots OH_2$ ($r_{Li^+\cdots O}$) distances (in pm) and ion-core angle $\alpha_{X\text{-}Li\text{-}X'}$ (in º) of low-energy isomers for $[LiXX'(H_2O)_{1\text{-}2}]^-$ (XX´=I_2, ClI, Cl_2). The $r_{Li\text{-}X}$ / $r_{Li\text{-}X'}$ distances of bare $(LiXX')^-$ (**0.0.0**) in footnote.[a]

n	$[LiXX'(H_2O)_n]^-$	Label	Sym.	$\Delta E_{0,anh}$[b]	Bond Distances[c]			$\alpha_{X\text{-}Li\text{-}X'}$
					$r_{Li\text{-}X}$ / $r_{Li\text{-}X'}$	$r_{X\cdots H}$	$r_{Li\cdots O}$	
1	XX' = I_2	1.0.0d	C_s	**0.0**	265/265	300	200	152
		1.0.0a	C_1	10.7	256/254	278	498	178
		1.0.0b	C_{2v}	11.7	254/254	308	352	162
	ClI	1.0.0c	C_1	**0.0**	262/227	215	208	153
		1.0.0a	C_1	0.9	256/216	230	461	178
		1.0.0c´	C_1	3.2	279/217	260	204	152
	Cl_2	1.0.0a	C_1	**0.0**	218/215	227	458	178
		1.0.0b	C_{2v}	1.4	215/215	259	316	161
		1.0.0c	C_1	4.7	231/218	211	214	153
2	I_2	2.2.0	C_s	**0.0**	427/260	247	193	158
		2.0.0	C_{2v}	15.0	279/279	288	200	132
		2.0.1b	C_1	17.5	267/267	258	197	149
		2.0.1a	C_1	18.6	271/263	274	201	136
	ClI	2.2.0	C_s	**0.0**	432/217	249	195	156
		2.2.0´	C_s	2.7	380/261	201	193	158
		2.0.1a	C_1	8.5	264/227	236	205	137
		2.0.1b	C_1	13.9	271/224	212	199	148
	Cl_2	2.2.0	C_s	**0.0**	385/218	202	196	156
		2.0.1a	C_1	5.6	227/221	230	208	138
		2.0.1b	C_1	5.8	226/225	213	206	147
		2.0.0	C_{2v}	13.4	233/233	240	210	129

[a] $r_{Li\text{-}I}$ / $r_{Li\text{-}I}$ = 255/255 in LiI_2^-; $r_{Li\text{-}I}$ / $r_{Li\text{-}Cl}$ = 258/214 in $LiClI^-$; $r_{Li\text{-}Cl}$ / $r_{Li\text{-}Cl}$ = 216/216 in $LiCl_2^-$.

[b] ZPE-corrected energies derived from anharmonic MP2/VPT2 frequencies.

[c] Inter-ion distances of solvent-shared motifs underlined.

Table S2b. ZPE-corrected relative energies $\Delta E_{0,anh}$ obtained with MP2/ def2TZVP (in kJ/mol), symmetry, inter-ion ($r_{Li\text{-}X}$), $X^-\cdots HOH$ ($r_{X^-\cdots H}$) and $Li^+\cdots OH_2$ ($r_{Li^+\cdots O}$) distances (in pm) and ion-core angle $\alpha_{X\text{-}Li\text{-}X'}$ (in °) of low-energy isomers for $[LiXX'(H_2O)_3]^-$ (XX′=I_2, ClI, Cl_2). The $r_{Li\text{-}X}$ / $r_{Li\text{-}X'}$ distances of bare $(LiXX')^-$ (**0.0.0**) in footnote.[a]

n	$[LiXX'(H_2O)_n]^-$	Label	Sym.	$\Delta E_{0,anh}$[b]	Bond Distances[c]			$\alpha_{X\text{-}Li\text{-}X'}$
					$r_{Li\text{-}X}$ / $r_{Li\text{-}X'}$	$r_{X\cdots H}$	$r_{Li\cdots O}$	
3	I_2	3.3.0a	C_1	**0.0**	390 / 276	266	198	134
		3.3.0b	C_3	3.2	407 / 265	259	202	180
		3.2.1a	C_1	3.4	401 / 263	249	194	120
		3.2.1b	C_1	3.6	416 / 265	244	190	146
		3.2.1c	C_1	5.0	420 / 265	243	190	156
		3.0.2	C_1	9.8	269 / 266	275	196	135
	ClI	3.2.1b	C_1	**0.0**	420 / 222	216	192	143
		3.2.1c	C_1	1.1	424 / 222	216	191	153
		3.2.1a	C_1	1.7	399 / 221	230	194	116
		3.0.2	C_1	5.8	271 / 223	237	197	135
		3.3.0a	C_1	6.5	389 / 231	263	200	127
		3.3.0b	C_3	13.2	415 / 221	260	206	180
	Cl_2	3.0.2	C_1	**0.0**	228 / 225	233	202	135
		3.2.1a	C_1	4.6	354 / 221	204	195	118
		3.2.1b	C_1	5.0	372 / 223	198	193	143
		3.2.1c	C_1	6.2	376 / 223	198	192	152
		3.3.0a	C_1	10.5	340 / 230	216	200	127
		3.3.0b	C_3	12.5	366 /220	215	208	180

[a] $r_{Li\text{-}I}$ / $r_{Li\text{-}I}$ = 255/255 in LiI_2^-; $r_{Li\text{-}I}$ / $r_{Li\text{-}Cl}$ = 258/214 in $LiClI^-$; $r_{Li\text{-}Cl}$ / $r_{Li\text{-}Cl}$ = 216/216 in $LiCl_2^-$.

[b] ZPE-corrected energies derived from anharmonic MP2/VPT2 frequencies.

[c] Inter-ion distances of solvent-shared motifs are underlined.

Table S3: Value for the cosine similarity (*S*) between the IRPD spectra and calculated VPT2/MP2 anharmonic spectra for $[LiI_2(H_2O)_n]^-$ (*n* = 1-3) isomers.

$[LiI_2(H_2O)_n]^-$	Structures	*S*
n = 1	**1.0.0a**	0.29
	1.0.0b	0.37
	1.0.0d	0.69
2	**2.2.0**	0.65
	2.0.0	0.04
	2.0.1a	0.06
	2.0.1b	0.09
3	**3.0.2**	0.40
	3.2.1a	0.18
	3.2.1b	0.24
	3.2.1c	0.37
	3.3.0a	0.54
	3.3.0b	0.81

[a]Cosine similarity[7] (*S*) has been employed to evaluate the agreement between anharmonic calculated and measured IR^2MS^2 spectra. This is an assessment for the similarity of two vectors, as follows: $S = \frac{\sum a_i \cdot c_i}{\sqrt{\sum a_i^2} \cdot \sqrt{\sum c_i^2}}$

The intensities of the IRPD spectrum are interpreted as vector a_i and the intensities of the calculated spectrum are interpreted as vector c_i. S-value towards 1 conveys better agreement while value towards 0 indicate poor agreement. The values for S given refer only to the region (2800 to 3750 cm^{-1}).

Table S4: Value for the cosine similarity (*S*) between the IRPD spectra and calculated VPT2/MP2 anharmonic spectra for $[LiClI(H_2O)_n]^-$ (*n* = 1-3) isomers.

$[LiClI(H_2O)_n]^-$	Structures	*S*
n = 1	**1.0.0a**	0.20
	1.0.0c	0.67
	1.0.0c´	0.42
2	**2.2.0**	0.49
	2.2.0´	0.11
	2.0.1a	0.11
	2.0.1b	0.24
3	**3.0.2**	0.46
	3.2.1a	0.38
	3.2.1b	0.38
	3.2.1c	0.36
	3.3.0a	0.57
	3.3.0b	0.26

Table S5: Cartesian coordinates (in Ångstrom) for the MP2 / def2TZVP optimized structure of $[LiCl_2(H_2O)_n]^-$ where n = 1-3.

***n* = 1**

1.0.0a

	X	Y	Z
Li	0.866375000000	-0.380629000000	0.000216000000
Cl	-1.186398000000	-1.112384000000	-0.000045000000
O	-3.240640000000	1.330957000000	0.000115000000
H	-2.695807000000	0.523152000000	0.000246000000
H	-2.576799000000	2.021676000000	-0.000952000000
Cl	2.868668000000	0.403526000000	-0.000006000000

1.0.0b

Li	0.000918000000	-0.871667000000	0.002658000000
Cl	2.128062000000	-0.524296000000	-0.000228000000
Cl	-2.126649000000	-0.526191000000	-0.000223000000
O	-0.002936000000	2.166606000000	0.000710000000
H	-0.762754000000	1.568526000000	-0.003102000000
H	0.759451000000	1.571895000000	-0.002871000000

1.0.0c

Li	0.196331000000	-0.090057000000	-0.222285000000
Cl	2.351988000000	-0.328698000000	0.016290000000
Cl	-1.987937000000	-0.747514000000	0.019729000000
O	-0.629827000000	1.890227000000	-0.097043000000
H	-1.389228000000	1.286553000000	0.049860000000
H	-0.350001000000	2.157402000000	0.781032000000

1.1.0

Li	1.117938000000	0.111460000000	-0.020401000000
Cl	-3.051992000000	-0.363985000000	0.003741000000

O	-0.511577000000	0.954797000000	-0.021045000000
H	-0.739833000000	1.873393000000	0.116715000000
H	-1.416900000000	0.469181000000	-0.022432000000
Cl	3.222318000000	-0.242799000000	0.004216000000

***n* = 2**

2.2.0

Li	0.958663000000	0.000005000000	0.354263000000
O	-0.299484000000	1.493174000000	0.454428000000
H	-0.138033000000	2.191554000000	-0.181772000000
H	-1.193549000000	1.130275000000	0.219776000000
O	-0.299479000000	-1.493172000000	0.454430000000
H	-1.193532000000	-1.130292000000	0.219699000000
H	-0.137978000000	-2.191570000000	-0.181738000000
Cl	3.058765000000	0.000002000000	-0.219525000000
Cl	-2.789423000000	-0.000002000000	-0.275158000000

2.0.1a

Cl	-2.203407000000	-0.614562000000	-0.153972000000
Cl	1.967741000000	-0.874499000000	0.170011000000
H	0.263413000000	1.794544000000	-0.495874000000
H	1.464932000000	1.049405000000	-1.014413000000
H	-1.021279000000	0.799408000000	1.175808000000
H	0.464400000000	0.691887000000	1.489135000000
Li	-0.076729000000	-0.435278000000	-0.725355000000
O	0.631417000000	1.442394000000	-1.322850000000
O	-0.248286000000	1.343184000000	1.416443000000

2.0.1b

Li	0.308426000000	-0.575778000000	0.471016000000
Cl	-1.806796000000	-1.221619000000	0.134470000000
Cl	2.400813000000	-0.444484000000	-0.348027000000
O	0.454920000000	1.368233000000	1.172917000000
H	1.294298000000	1.292311000000	0.689175000000
H	-0.178728000000	1.734063000000	0.533591000000
O	-1.593148000000	1.713828000000	-0.781133000000
H	-1.837558000000	0.804228000000	-0.497638000000
H	-1.195767000000	1.563986000000	-1.641975000000

2.0.0

Li	-0.000026000000	-0.000120000000	0.605917000000
Cl	-2.085365000000	0.000073000000	-0.390973000000
Cl	2.085203000000	-0.000064000000	-0.391048000000
O	0.000298000000	2.095316000000	0.687676000000
H	0.769622000000	1.933423000000	0.118526000000
H	-0.769249000000	1.934569000000	0.118584000000
O	0.000020000000	-2.095470000000	0.687587000000
H	0.769435000000	-1.933160000000	0.118630000000
H	-0.769516000000	-1.933398000000	0.118756000000

2.0.1c

Li	-1.525821000000	-0.318034000000	0.203816000000
Cl	-3.521695000000	0.205790000000	-0.364651000000
Cl	0.541503000000	-0.746783000000	0.798720000000
O	2.429873000000	1.720689000000	0.298908000000
H	1.824341000000	1.009976000000	0.584732000000
H	1.871639000000	2.262508000000	-0.261582000000
O	3.290350000000	-0.744271000000	-1.146056000000
H	3.293749000000	0.157742000000	-0.803293000000

H	2.489218000000	-1.090589000000	-0.733288000000

***n* = 3**

3.0.2

Cl	-1.725824000000	-1.114666000000	-0.764348000000
Cl	2.334841000000	-0.452350000000	-0.083749000000
H	-0.230406000000	1.954359000000	-0.418438000000
H	1.263589000000	1.666175000000	-0.665634000000
H	-1.928244000000	0.948957000000	0.307600000000
H	-1.003180000000	1.093142000000	1.469009000000
H	-0.647380000000	-1.009327000000	1.385223000000
H	0.778784000000	-0.551594000000	1.588689000000
Li	0.305152000000	-0.227770000000	-1.066704000000
O	0.422648000000	1.790317000000	-1.128568000000
O	-1.517369000000	1.642681000000	0.851272000000
O	-0.093018000000	-0.530389000000	2.021208000000

3.2.1a

Li	0.751344000000	0.661063000000	0.897245000000
O	-0.244720000000	2.131173000000	0.073340000000
H	0.273216000000	2.194031000000	-0.735096000000
H	-1.040519000000	1.603449000000	-0.191024000000
O	-0.406516000000	-0.637201000000	1.789443000000
H	-1.233092000000	-0.414213000000	1.309415000000
H	-0.115422000000	-1.408396000000	1.270471000000
Cl	2.534439000000	0.158261000000	-0.292902000000
Cl	-2.340020000000	0.059499000000	-0.485296000000
O	0.174489000000	-2.073418000000	-0.561314000000
H	-0.579549000000	-1.517825000000	-0.819684000000
H	0.950190000000	-1.506595000000	-0.708188000000

3.2.1b

Li	-0.486916000000	-0.791592000000	0.595774000000
O	0.992101000000	-1.936133000000	0.092023000000
H	0.879198000000	-2.371951000000	-0.754503000000
H	1.722654000000	-1.273041000000	-0.065809000000
O	0.292751000000	0.869764000000	1.196698000000
H	1.176066000000	0.884617000000	0.762619000000
H	-0.242084000000	1.539412000000	0.741890000000
Cl	-2.579096000000	-0.823849000000	-0.149002000000
Cl	2.873588000000	0.314672000000	-0.339232000000
O	-1.729609000000	2.165285000000	-0.364494000000
H	-2.147712000000	1.279837000000	-0.309126000000
H	-1.375669000000	2.180590000000	-1.256243000000

3.2.1c

Li	0.751344000000	0.661063000000	0.897245000000
O	-0.244720000000	2.131173000000	0.073340000000
H	0.273216000000	2.194031000000	-0.735096000000
H	-1.040519000000	1.603449000000	-0.191024000000
O	-0.406516000000	-0.637201000000	1.789443000000
H	-1.233092000000	-0.414213000000	1.309415000000
H	-0.115422000000	-1.408396000000	1.270471000000
Cl	2.534439000000	0.158261000000	-0.292902000000
Cl	-2.340020000000	0.059499000000	-0.485296000000
O	0.174489000000	-2.073418000000	-0.561314000000
H	-0.579549000000	-1.517825000000	-0.819684000000
H	0.950190000000	-1.506595000000	-0.708188000000

3.3.0

Li	0.908418000000	0.001214000000	0.000696000000

O	-0.216157000000	-1.173404000000	-1.276274000000
H	-0.092034000000	-0.856915000000	-2.173152000000
H	-1.125459000000	-0.894473000000	-1.033812000000
O	-0.217528000000	-0.520140000000	1.655230000000
H	-0.093892000000	-1.456085000000	1.824696000000
H	-1.126292000000	-0.447849000000	1.291450000000
O	-0.217603000000	1.693664000000	-0.376515000000
H	-1.126490000000	1.342437000000	-0.258091000000
H	-0.095674000000	2.310676000000	0.347637000000
Cl	3.113261000000	0.000109000000	-0.000351000000
Cl	-2.751797000000	-0.000249000000	-0.000846000000

Table S4: Cartesian coordinates (in Ångstrom) for the MP2/def2TZVP optimized structure of $[LiClI(H_2O)_n]^-$ where n = 1-3.

***n* = 1**

1.0.0a

	X	Y	Z
Li	0.660152000000	-0.507717000000	-0.032246000000
Cl	2.743244000000	-1.073508000000	0.016236000000
O	4.879018000000	1.358646000000	-0.080833000000
H	4.318056000000	0.576996000000	-0.239009000000
H	4.528472000000	1.686242000000	0.752858000000
I	-1.820647000000	0.125290000000	-0.000876000000

1.0.0c

Li	-1.121794000000	0.011276000000	-0.255756000000
Cl	-3.217294000000	-0.821414000000	0.023716000000
O	-2.015825000000	1.881900000000	-0.095741000000
H	-2.776561000000	1.282632000000	0.077728000000
H	-1.776172000000	2.269181000000	0.752676000000

I 1.485636000000 -0.088242000000 0.005653000000

1.0.0c´

Li 1.389778000000 0.060160000000 -0.285109000000

O 1.082767000000 2.070607000000 -0.094189000000

H 0.144557000000 1.908549000000 0.123671000000

H 1.514418000000 2.329662000000 0.727688000000

Cl 3.425843000000 -0.622618000000 0.023589000000

I -1.372260000000 -0.196208000000 0.006726000000

***n* = 2**

2.2.0

Li 2.357714000000 0.000000000000 0.365194000000

O 1.108574000000 1.494051000000 0.526658000000

H 1.243864000000 2.251585000000 -0.051313000000

H 0.171422000000 1.225173000000 0.389431000000

O 1.108574000000 -1.494051000000 0.526658000000

H 0.171422000000 -1.225173000000 0.389431000000

H 1.243864000000 -2.251585000000 -0.051313000000

I -1.941588000000 0.000000000000 -0.098416000000

Cl 4.427253000000 0.000000000000 -0.293075000000

2.2.0´

Li 0.496664000000 0.000000000000 0.424783000000

O 1.737389000000 -1.472267000000 0.449940000000

H 1.595259000000 -2.253253000000 -0.092217000000

H 2.643784000000 -1.128631000000 0.207939000000

O 1.737389000000 1.472267000000 0.449940000000

H 2.643783000000 1.128632000000 0.207936000000

H 1.595258000000 2.253254000000 -0.092216000000

I -2.069660000000 0.000000000000 -0.068528000000

Cl 4.230921000000 0.000000000000 -0.298402000000

2.0.1a

Li	-0.835469000000	-0.440683000000	0.576686000000
Cl	-2.783851000000	-1.432041000000	0.103807000000
O	-3.288918000000	1.494825000000	-0.719340000000
H	-3.321476000000	0.547653000000	-0.437320000000
H	-3.044167000000	1.431193000000	-1.648973000000
I	1.765436000000	-0.068684000000	-0.094450000000
O	-1.119269000000	1.478456000000	1.033442000000
H	-0.277248000000	1.785828000000	0.665866000000
H	-1.827832000000	1.756081000000	0.418680000000

2.0.1b

Li	-0.929359000000	-0.389018000000	0.738623000000
O	-1.909375000000	1.264635000000	1.467816000000
H	-1.690674000000	1.789102000000	0.675304000000
H	-2.708474000000	0.787593000000	1.179642000000
Cl	-2.860286000000	-1.126698000000	-0.195737000000
O	-1.387177000000	1.599590000000	-1.325271000000
H	-1.913887000000	0.781307000000	-1.375999000000
H	-0.467288000000	1.286149000000	-1.342167000000
I	1.595579000000	-0.136548000000	0.015746000000

***n* = 3**

3.0.2

Cl	-2.534944000000	-1.338122000000	-0.772419000000
H	-1.618194000000	1.926473000000	-0.493032000000
H	-0.082207000000	2.036878000000	-0.740511000000
H	-3.178478000000	0.730297000000	0.208883000000
H	-2.340863000000	1.062239000000	1.410672000000
H	-1.649365000000	-0.994315000000	1.403632000000
H	-0.339668000000	-0.348198000000	1.836090000000
Li	-0.678684000000	-0.148679000000	-1.135344000000

O	-0.916961000000	1.811367000000	-1.176205000000
O	-2.874584000000	1.503296000000	0.720281000000
O	-1.275896000000	-0.410735000000	2.089787000000
I	1.790159000000	-0.083975000000	-0.003009000000

3.2.1a

Li	1.962922000000	0.662419000000	0.967204000000
O	0.868605000000	2.135798000000	0.293906000000
H	1.265654000000	2.199133000000	-0.585348000000
H	-0.020579000000	1.745891000000	0.134251000000
O	0.954883000000	-0.713200000000	1.897978000000
H	0.013960000000	-0.528397000000	1.714170000000
H	1.136036000000	-1.447199000000	1.269119000000
Cl	3.526323000000	0.236746000000	-0.538093000000
O	1.334230000000	-2.134414000000	-0.443844000000
H	2.057901000000	-1.535304000000	-0.714880000000
H	0.525319000000	-1.711970000000	-0.776258000000
I	-1.812760000000	0.018121000000	-0.165649000000

3.2.1b

Li	-1.860794000000	-0.834708000000	0.599458000000
O	-0.433042000000	-2.094566000000	0.236667000000
H	-0.475094000000	-2.583593000000	-0.591732000000
H	0.412603000000	-1.585281000000	0.179443000000
O	-1.036587000000	0.784669000000	1.232243000000
H	-0.099286000000	0.847186000000	0.962757000000
H	-1.510212000000	1.515457000000	0.789763000000
Cl	-3.899705000000	-0.717392000000	-0.278462000000
O	-2.900044000000	2.242095000000	-0.285297000000
H	-3.391355000000	1.388614000000	-0.286321000000
H	-2.583973000000	2.316139000000	-1.192313000000

I 2.160039000000 0.100824000000 -0.120661000000

3.2.1c

Li -1.842031000000 -0.823468000000 0.436568000000
O -0.353414000000 -2.048238000000 0.271867000000
H -0.291655000000 -2.658527000000 -0.469737000000
H 0.483182000000 -1.521125000000 0.228311000000
O -1.068388000000 0.885577000000 0.822188000000
H -0.132572000000 0.986894000000 0.562370000000
H -1.593758000000 1.583786000000 0.390151000000
Cl -3.971960000000 -0.847445000000 -0.205857000000
O -3.282781000000 2.196760000000 -0.299797000000
H -3.591752000000 1.269225000000 -0.421494000000
H -3.833717000000 2.515141000000 0.422815000000
I 2.257478000000 0.121298000000 -0.092012000000

3.3.0a

Li 0.542550000000 0.472073000000 0.640249000000
O 1.161803000000 -1.378010000000 0.991628000000
O 2.172407000000 1.448860000000 1.409243000000
I -2.073931000000 -0.044597000000 -0.047208000000
H 0.519156000000 -1.919983000000 0.517806000000
H 2.008851000000 -1.416728000000 0.492356000000
H 2.824841000000 0.838647000000 0.990272000000
H 2.243780000000 2.236639000000 0.857034000000
O 1.121788000000 1.027738000000 -1.229689000000
H 1.942776000000 0.496028000000 -1.330340000000
H 0.427890000000 0.613836000000 -1.759148000000
Cl 3.686791000000 -0.511159000000 -0.503303000000

3.3.0b

Li 2.115283000000 0.000008000000 0.000003000000

O	1.023455000000	-1.201428000000	-1.272306000000
H	1.189295000000	-0.958768000000	-2.189459000000
H	0.079005000000	-1.000288000000	-1.118798000000
O	1.023451000000	-0.501171000000	1.676628000000
H	1.189298000000	-1.416797000000	1.924982000000
H	0.079002000000	-0.468789000000	1.425680000000
O	1.023454000000	1.702582000000	-0.404281000000
H	0.079004000000	1.469068000000	-0.306847000000
H	1.189298000000	2.375506000000	0.264468000000
Cl	4.323443000000	0.000005000000	-0.000010000000
I	-2.041739000000	0.000002000000	-0.000004000000

Table S4: Cartesian coordinates (in Ångstrom) for the MP2/def2TZVP optimized structure of $[LiI_2(H_2O)_n]^-$ where n = 1-3.

***n* = 1**

1.0.0a

	X	Y	Z
Li	-0.318675000000	-0.301781000000	-0.002335000000
O	3.370878000000	2.891871000000	-0.002591000000
H	3.310332000000	1.923136000000	-0.008836000000
H	2.444985000000	3.153175000000	0.026261000000
I	2.221781000000	-0.633742000000	0.000231000000
I	-2.821146000000	0.118535000000	-0.000037000000

1.0.0b

Li	-0.000348000000	-0.631848000000	-0.002508000000
O	0.002962000000	2.886645000000	-0.000523000000
H	-0.760314000000	2.292732000000	0.002176000000
H	0.765141000000	2.291284000000	0.001838000000
I	-2.506811000000	-0.242900000000	0.000072000000

I 2.506292000000 -0.243545000000 0.000074000000

1.0.0d

Li 0.002050000000 0.195848000000 0.479359000000
O -0.007384000000 2.160306000000 0.089502000000
H 0.771016000000 2.168298000000 -0.486511000000
H -0.794926000000 2.157192000000 -0.474415000000
I -2.571497000000 -0.210072000000 -0.011261000000
I 2.572947000000 -0.208711000000 -0.011252000000

***n* = 2**

2.2.0

Li -0.901359000000 0.000814000000 0.495059000000
O 0.315437000000 1.493040000000 0.575945000000
H 1.251582000000 1.234450000000 0.404871000000
H 0.163059000000 2.285711000000 0.052103000000
I -3.426182000000 -0.000091000000 -0.100763000000
I 3.328629000000 -0.000119000000 -0.118440000000
O 0.315307000000 -1.492004000000 0.576184000000
H 0.162468000000 -2.286033000000 0.054616000000
H 1.251306000000 -1.233764000000 0.403964000000

2.0.0

Li 0.001641000000 0.000010000000 0.918247000000
O -0.000358000000 1.985542000000 1.179346000000
H 0.776975000000 2.113900000000 0.611397000000
H -0.778949000000 2.111420000000 0.612473000000
I -2.550114000000 0.000270000000 -0.227072000000
I 2.550457000000 0.000076000000 -0.226888000000
O -0.001651000000 -1.987542000000 1.178170000000

H -0.780440000000 -2.112037000000 0.611309000000

H 0.775379000000 -2.115660000000 0.609836000000

2.0.1a

Li 0.053186000000 0.074438000000 0.874554000000

O -0.404161000000 1.960617000000 1.397282000000

H -0.128952000000 2.327485000000 0.532196000000

H -1.360167000000 1.834544000000 1.284283000000

I -2.445851000000 -0.398779000000 -0.050692000000

O 0.166889000000 2.064402000000 -1.353386000000

H -0.558059000000 1.441779000000 -1.524490000000

H 0.959071000000 1.497586000000 -1.317152000000

I 2.499185000000 -0.346973000000 0.013906000000

2.0.1b

Li 0.123784000000 0.007472000000 0.530854000000

I -2.424032000000 -0.623545000000 0.017713000000

O -1.826765000000 2.772331000000 -0.629550000000

H -2.237000000000 1.917716000000 -0.377948000000

H -1.618883000000 2.636063000000 -1.561266000000

I 2.711509000000 -0.253876000000 -0.092116000000

O 0.256690000000 1.907878000000 1.020900000000

H 1.158148000000 2.052475000000 0.697638000000

H -0.349268000000 2.432998000000 0.461595000000

***n* = 3**

3.0.2

H -0.210637000000 2.212773000000 -1.231196000000

H 1.236978000000 1.736404000000 -1.556183000000

H -1.963288000000 2.189653000000 -0.023622000000

H -0.765519000000 2.476570000000 0.854935000000

H -0.655395000000 0.537200000000 1.886654000000

H 0.825200000000 0.874352000000 1.746261000000

Li	0.057754000000	-0.150881000000	-0.971629000000
O	0.310914000000	1.601028000000	-1.803379000000
O	-1.243453000000	2.834309000000	0.076946000000
O	-0.017325000000	1.249982000000	2.058928000000
I	-2.381699000000	-0.646436000000	-0.043611000000
I	2.550724000000	-0.392373000000	0.016783000000

3.2.1a

Li	-0.812728000000	-0.531035000000	1.292762000000
O	0.155575000000	-2.034998000000	0.552779000000
H	-0.307007000000	-2.224392000000	-0.274060000000
H	1.035489000000	-1.688376000000	0.276423000000
O	0.337842000000	0.829245000000	2.029113000000
H	1.250741000000	0.586237000000	1.781183000000
H	0.157995000000	1.564801000000	1.402099000000
O	-0.030050000000	2.265089000000	-0.303795000000
H	0.715172000000	1.753395000000	-0.664639000000
H	-0.826909000000	1.794474000000	-0.602117000000
I	2.863983000000	-0.083118000000	-0.248396000000
I	-2.926139000000	-0.080424000000	-0.204848000000

3.2.1b

Li	-0.702909000000	-0.526526000000	0.766749000000
O	0.548307000000	-1.930687000000	0.382580000000
H	0.413295000000	-2.486611000000	-0.391838000000
H	1.441280000000	-1.524073000000	0.251866000000
O	0.277409000000	1.036265000000	1.243136000000
H	1.209755000000	0.982667000000	0.949800000000
H	-0.111670000000	1.822366000000	0.814724000000
O	-1.389051000000	2.780869000000	-0.212618000000
H	-2.080373000000	2.092353000000	-0.149659000000
H	-1.117342000000	2.734824000000	-1.136519000000

I 3.318899000000 -0.026201000000 -0.152185000000

I -3.189456000000 -0.297072000000 -0.110898000000

3.2.1c

Li -0.680015000000 -0.486813000000 0.528110000000

O 0.638777000000 -1.869367000000 0.388039000000

H 0.613083000000 -2.561186000000 -0.280278000000

H 1.531696000000 -1.451637000000 0.289067000000

O 0.255215000000 1.142570000000 0.777011000000

H 1.197227000000 1.125290000000 0.514913000000

H -0.171897000000 1.922177000000 0.378912000000

O -1.741318000000 2.862499000000 -0.208831000000

H -2.238417000000 2.044633000000 -0.409057000000

H -2.197039000000 3.201850000000 0.569589000000

I -3.254423000000 -0.363502000000 -0.082722000000

I 3.444687000000 -0.012089000000 -0.111565000000

3.3.0a

Li -0.649710000000 0.920947000000 0.423203000000

O -0.008253000000 -0.510797000000 1.625143000000

O 0.772298000000 2.340382000000 0.726130000000

I -3.136871000000 -0.181030000000 -0.058592000000

H -0.642865000000 -1.214046000000 1.429845000000

H 0.865609000000 -0.806703000000 1.304188000000

H 1.549355000000 1.746919000000 0.782173000000

H 0.871860000000 2.723874000000 -0.154512000000

O -0.056177000000 0.669318000000 -1.498678000000

H 0.789278000000 0.182549000000 -1.455546000000

H -0.743594000000 0.045889000000 -1.775979000000

I 3.016051000000 -0.298830000000 -0.096512000000

3.3.0b

Li -0.777197000000 0.004342000000 -0.004261000000

O	0.242058000000	-1.250620000000	1.214468000000
H	0.067688000000	-1.119571000000	2.152481000000
H	1.192741000000	-1.054279000000	1.091441000000
O	0.246043000000	-0.431684000000	-1.696173000000
H	0.075037000000	-1.316294000000	-2.036448000000
H	1.195863000000	-0.418273000000	-1.461222000000
I	-3.431111000000	-0.000091000000	0.000961000000
I	3.292348000000	-0.000498000000	0.001443000000
O	0.246648000000	1.685276000000	0.468489000000
H	1.196717000000	1.474489000000	0.365870000000
H	0.079974000000	2.428363000000	-0.121004000000

Benchmark of the Dispersion Corrected XC-Functionals for the AIMD simulations

DFT-based calculations have bee have been done using FHI-Aims.[4–8] The WFT-based MP2 and CC calculations have been carried out using ORCA 4.0.1.2.[9,10] In the calculations scalar relativistic effects have been included using the ZORA.

The first task was the generation of a structure set representing the PES surface well enough, to determine the global minimum of the system. Therefore, an *ab initio* random structure search was done. Structures were generated and subsequently optimized using PBE[10] and the van-der-Waals Tkatschenko-Scheffler (vdW-TS) dispersion correction.[12] The Y-Li-X angle, the total energy, and the Li-X distances have been used to determine different minima on the PES. Using empirical cutoffs (changes in the internal coordinates or energy from one structure to another), a subset of structures was chosen to be compared in the benchmark. The geometries have been refined using MP2[13,14] with the ma-def2-TZVPP basis set.[15,16] The energies of the refined structures have then been calculated using the DLPNO-CCSD(T) method[17–22] at the ma-def2-SVP, ma-def2-TZVPP, and ma-def2-QZVPP levels to extrapolate the energy at the CBS-limit using Truhlar's extrapolation scheme.[23] This consists of a separate extrapolation of the Hartree-Fock energy

$$E_{HF}^{n} = E_{HF}^{CBS} + Ae^{-\alpha\sqrt{n}} \quad (1)$$

with the fitted parameters E_{HF}^{CBS}, A and α and the correlation energy, according to

$$E_{corr}^{n} = E_{corr}^{CBS} + Bn^{-\beta}. \quad (2)$$

Here, B, β and E_{corr}^{n} are parameters resulting from the least-squares fitting algorithm in a two-point extrapolation (using only the correlation energy at ma-def2-TZVPP and ma-def2-QZVPP), with β=3.

Since the gas phase cluster are expected to be weakly bound, a dispersion correction needs to be included and carefully chosen for these systems. The considered dispersion corrections are the vdw-TS dispersion correction and the many-body dispersion correction (MBD).[24,25] In order to choose the ideal pair of XC-functional and dispersion correction, the investigated clusters have been benchmarked and their relative energies, *i.e.*, their ordering, have been compared to the ordering in the reference method – DLPNO-CCSD(T) at CBS. The results are shown in boxplots in Figs. S11 – S13. In general, PBE0 performs better than PBE as expected. However, in the case of ClI and Cl_2, the performance of PBE is only slightly worse than PBE0, the influence of the dispersion correction is higher. For the ClI and I_2 clusters, the many-body dispersion correction proves to give better results concerning the relative energies. This can be expected, since the interaction of iodine should be stronger influenced by dispersion effects, due to the larger polarizability and the weaker Li-I bond. For both clusters, the boxplot of PBE0-MBD is showing relatively small boxes close to ≈10 meV, which proves it to be the best method for these clusters. For Cl_2 the benchmark shows that the many-body dispersion (MBD) gives worse results than the vdW-TS correction. One might expect a certain overestimation of the dispersion interaction, since Li-Cl should have a bonding interaction, which is dominated by electrostatics, compared to iodine.

The most accurate results are seen for B3LYP-TS, with a small advantage over PBE0-TS. Interestingly, the performance of PBE and PBE0, both with the vdW-TS dispersion correction, is extremely similarly, so PBE-TS is probably the best choice for the AIMD simulation since it has a large cost advantage over B3LYP-TS and PBE0-TS.

In summary, the best combination of XC-functional and vdW correction, which gives overall good agreement in all clusters, is PBE0-TS. The MBD correction might be slightly better but had convergence problems in some of the AIMD simulations.

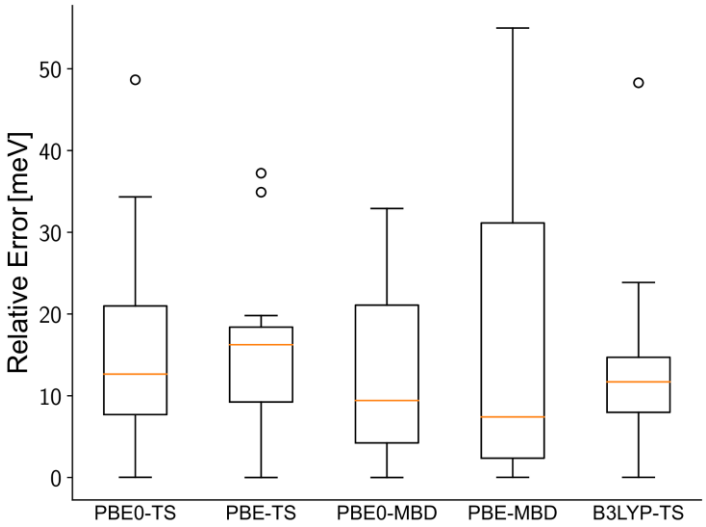

Figure S16. $[LiCl_2(H_2O)_3]^-$ Benchmark of the different combinations of XC-functional with the dispersion corrections: vdW and MBD.

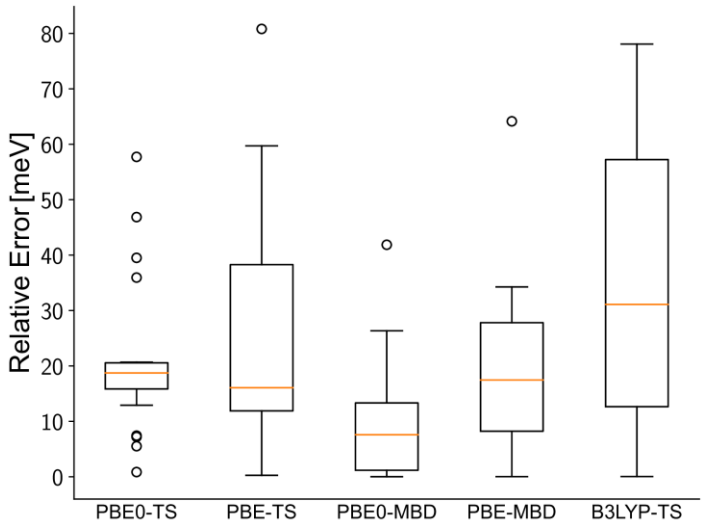

Figure S17. $[LiI_2(H_2O)_3]^-$ Benchmark of the different combinations of XC-functional with the dispersion corrections: vdW and MBD.

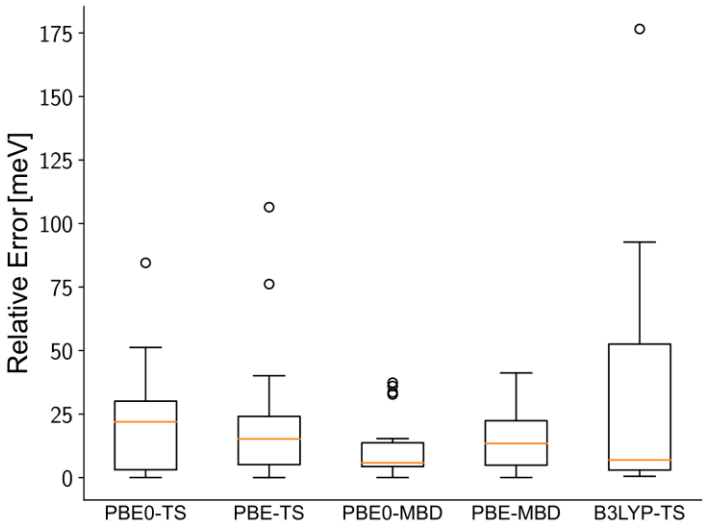

Figure S18. $[LiClI(H_2O)_3]^-$ Benchmark of the different combinations of XC-functional with the dispersion corrections: vdW and MBD.

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