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Table S1. Optimized Geometrical Parameters (\AA and degrees) ^a and Total Binding Energies, $\Delta E(n)$ (kcal/mol), of $\text{Li}(\text{H}_2\text{O})_n$ ($n = 1\text{--}2$) Calculated at Various Levels. Imaginary Frequencies (cm^{-1}) and Symmetry of Imaginary Modes are Given if Exist.

Symbol ^b	Level ^c	$R_{\text{Li-O1}}$	θ	$R_{\text{Li-O2}}$	$\angle \text{O1LiO2}$	$R_{\text{H1-O2}}$	$\Delta E(n)$ ^d	Imag. freq. (sym)
Li(H_2O)								
Ia 1+0 (C_{2v})	A	1.909					12.5	<i>181i</i> (B_1)
	B	1.903	0.0				12.2	<i>122i</i> (B_1)
	C	1.917	0.0				<i>10.6</i> (12.2)	
Ib 1+0 (C_s)	A	1.918	29.3				<i>12.6</i>	
	B	1.910	27.1				<i>12.3</i>	
Li(H_2O) ₂								
IIa 2+0 (C_{2v})	A	1.917			142.9		25.8	<i>77i</i> (A_2), <i>66i</i> (B_1)
	B	1.871			174.3		<i>26.8</i>	
	C	1.934			123.7		20.2	<i>119i</i> (A_2), <i>62i</i> (B_2)
IIb 2+0 (C_2)	A	1.917			119.0		26.2	<i>12i</i> (B)
	C	1.935			107.7		<i>21.1</i> (25.9)	
IIg 2+0 (C_s)	A	1.909			127.4		26.1	<i>26i</i> (A'')
	C	1.924			117.6		20.5	<i>123i</i> (A'')
IIc 2+0 (C_s)	A	1.937		1.903	104.7		26.1	<i>188i</i> (A'')
	B	1.942		1.882	95.5		26.2	
	C	1.956		1.918	105.3		21.0	<i>64i</i> (A'')
IId 2+0 (C_1)	A	1.924		1.919	113.0		26.2	
IIe 1+1 (C_s)	A	1.884				1.776	22.5	<i>77i</i> (A'')
	B	1.869				1.774	22.7	
	C	1.888				1.883	<i>19.2</i> (22.4)	
IIIf 1+1 (C_1)	A	1.890				1.778	22.5	

^a Parameters are shown in Figure S1. ^b Corresponds to structures in Figure S1. ^c A: MP2/6-311++G(d,p). B: MP2/6-311++G(d,p). C: HF/6-311++G(d,p). ^d $-\Delta E(n) = E[\text{Li}(\text{H}_2\text{O})_n] - E[\text{Li}] - nE[\text{H}_2\text{O}]$ (without CPC). Values for potential minima are in italic. Values in parentheses are at MP2/6-311++G(d,p) // HF/6-311++G(d,p).

Table S2. Optimized Geometrical Parameters (\AA and degrees)^a and Total Binding Energies, ΔE (kcal/mol), of $\text{Li}(\text{H}_2\text{O})_3$ Calculated at Various Levels. Imaginary Frequencies (cm^{-1}) and Symmetry of Imaginary Modes are Presented if Exist.

Symbol ^b	Level ^c	$R_{\text{Li-O}1}$	$R_{\text{Li-O}2}$	$R_{\text{Li-O}3}$	$\angle \text{O}1\text{LiO}2$	$\angle \text{O}2\text{LiO}3$	$\angle \text{O}1\text{LiO}3$	$R_{\text{H}1-\text{O}3}$	$R_{\text{H}2-\text{O}2}$	ΔE^d	Imag. freq. (sym.)
IIIa 3+0 (C_{2v})	A	1.902	1.913		117.3					42.3	161 <i>i</i> (B_1), 17 <i>i</i> (B_2)
	B	1.885	1.886		113.0					43.5	66 <i>i</i> (B_2), 57 <i>i</i> (B_1)
	C	1.915	1.910		115.6						33.2 (42.8)
IIIk 3+0 (C_s)	A	1.909	1.913		117.0	125.3				42.3	1 <i>i</i> (A'')
	B	1.891	1.885		112.7	133.4				43.5	51 <i>i</i> (A'')
IIIl 3+0 (C_s)	A	1.903	1.918	1.912		125.0	127.0			42.3	150 <i>i</i> (A'')
	B	1.865	1.932	1.874		126.7	140.7			44.0	41 <i>i</i> (A'')
IIIb 3+0 (C_1)	A	1.909	1.913	1.913	117.4	125.3	116.7			42.3	
IIIc 3+0 (C_1)	B	1.859	1.930	1.860	118.3	92.5	149.2			44.1	
IIId 3+0 (C_3)	A	1.907			119.6					42.4	
	B	1.880			117.5					44.0	
	C	1.912			119.9					33.3 (40.2)	
IIIf 2+1 (C_s)	A	1.880	1.971		107.7			1.798	2.030	37.8	314 <i>i</i> (A''), 114 <i>i</i> (A'')
	B	1.850	1.928		113.5			1.796	1.988	40.5	
	C	1.891	2.008		106.7			1.914	2.178	30.1	73 <i>i</i> (A'')

(Continues to next page.)

(Table S2 continued.)

Symbol ^b	Level ^c	R _{Li-O1}	R _{Li-O2}	R _{Li-O3}	∠O1LiO2	∠O2LiO3	∠O1LiO3	R _{H1-O3}	R _{H2-O2}	ΔE ^d	Imag. freq. (sym.)
III ^f 2+1 (C ₁)	A	1.884	1.975		106.6			1.773	2.014	38.3	
	C	1.890	2.010		106.0			1.912	2.174	30.1 (39.0)	
III ^g 2+1 (C _s)	A	1.921			103.2			1.994		36.4	
	B	1.888			111.2			1.994		38.2	
	C	1.931			99.7			2.126		29.1 (34.7)	
III ^h 1+2 (C _{2v})	A	1.862						1.829		31.0	15 <i>i</i> (B ₁)
	B	1.842						1.825		31.5	47 <i>i</i> (B ₂)
	C	1.863						1.929		26.4 (31.2)	
III ⁱ 1+2 (Cs)	A	1.863						1.829		31.0	
	B	1.836						1.838		31.7	63 <i>i</i> (A'')
III ^j 1+2 (C ₁)	B	1.830						1.823	1.844	31.7	

^a Parameters are shown in Figure 1. ^b Corresponds to structures in Figure 1. ^c A: MP2/6-311++G(d,p). B: MP2/6-31++G(d,p). C: HF/6-31++G(d,p). ^d $-\Delta E(n) = E[\text{Li}(\text{H}_2\text{O})_n] - E[\text{Li}] - n E[\text{H}_2\text{O}]$ (without CPC). Values for potential minima are in italic. Values in parentheses are at MP2/6-31++G(d,p)//HF/6-31++G(d,p).

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Supporting Information
(3/5)

Table S3. Mulliken Total Gross Population in Li s Basis Functions in $\text{Li}(\text{H}_2\text{O})_n$ Clusters by HF/6-31++G(d,p) Method.

<i>n</i>	structure ^a	Li s basis function			
		inner	outer	diffuse	total
0		0.32	0.60	0.03	0.96
1	Ia	0.21	0.69	0.08	0.98
2	IIb	0.17	0.59	0.14	0.90
3	IIIa	0.18	0.29	0.33	0.79
4	IVa	0.22	0.17	0.36	0.74
5	Va	0.21	0.10	0.28	0.59
6	VIa	0.21	0.10	0.21	0.52
8	VIIIa	0.20	0.17	0.15	0.52

^a Indicates the structures in Figures 1 and 2.

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Supporting Information
(4/5)

