Supplementary Material for: Computational Insights into the Adsorption Mechanism of Zn Ion on the Surface (110) of Sphalerite from the Perspective of Hydration

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Part 1: Cluster model calculation

1.1. Calculation method

Gaussian 09, Revision D.01 was used to calculate the cluster model hydration configuration[1]. All the cluster models were calculated at ωB97XD level[2]. For light atoms H, C, O, and Zn, the all-electron basis set of def2-SVP was utilized. In the optimization, the convergence parameters of maximum force, RMS force, maximum displacement and RMS displacement were set as 4.5×10^{-4}, 3.0×10^{-4}, 1.8×10^{-3} and 1.2×10^{-3} respectively. The stability of hydrated structures of Zn ion can be described by the adsorption energy (ΔE_{ad}, ΔG_{ad}) and successive water molecule adsorption energy (ΔE_{sad}, ΔG_{sad}), which can be calculated by the Eqs. (1), (2), (3) and (4) respectively [3]:

$$\Delta E_{ad} = E[M(H_2O)_N] - E(M) - N^*E(H_2O) \quad (1)$$

$$\Delta E_{sad} = E[M(H_2O)_{N+1}] - E[M(H_2O)_N] - E(H_2O) \quad (2)$$

$$\Delta G_{ad} = G[M(H_2O)_N] - G(M) - N^*G(H_2O) \quad (3)$$

$$\Delta G_{ad} = G[M(H_2O)_N] - G(M) - N^*G(H_2O) \quad (4)$$

where M denotes the primary component of Zn ion, and N denotes the coordinate number of H_2O. $E[M(H_2O)_{N+1}]$ and $E[M(H_2O)_N]$ denote the calculated electronic energy of $M(H_2O)_{N+1}$ and $M(H_2O)_N$, respectively; E(M) represent the calculated electronic energy of Zn^{2+}; $E(H_2O)$ represent the calculated electronic energy of H_2O. $G[M(H_2O)_{N+1}]$ and $G[M(H_2O)_N]$ denote the calculated electronic energy of $M(H_2O)_{N+1}$ and $M(H_2O)_N$ corrected by thermal free energy, respectively; G(M) represent the calculated electronic energy of Zn^{2+} corrected by thermal free energy; $G(H_2O)$ represent the calculated electronic energy of H_2O corrected by thermal free energy. The larger the negative value of ΔE_{ad} or ΔG_{ad}, the more stable the adsorption configuration. Similarly, the greater the negative value of ΔE_{sad} or ΔG_{sad}, the easier the successive adsorption of H_2O is.

1.2. Results of cluster model calculation

1.2.1. Effective hydrated components of Zn ion

According to the chemical theory of flotation solution, there are three main components of Zn ion in the solution with the change of pH, including Zn^{2+}, $[Zn(OH)]^+$ and $Zn(OH)_2$ [4, 5]. Besides, the flotation process is carried out in water environment where Zn ion will form coordinate bonds with water molecules. These hydration structure of Zn^{2+}, $[Zn(OH)]^+$ and $Zn(OH)_2$ should have the corresponding most stable configurations, so it is necessary to firstly study the most stable hydration structures of Zn^{2+}, $[Zn(OH)]^+$ and $Zn(OH)_2$.

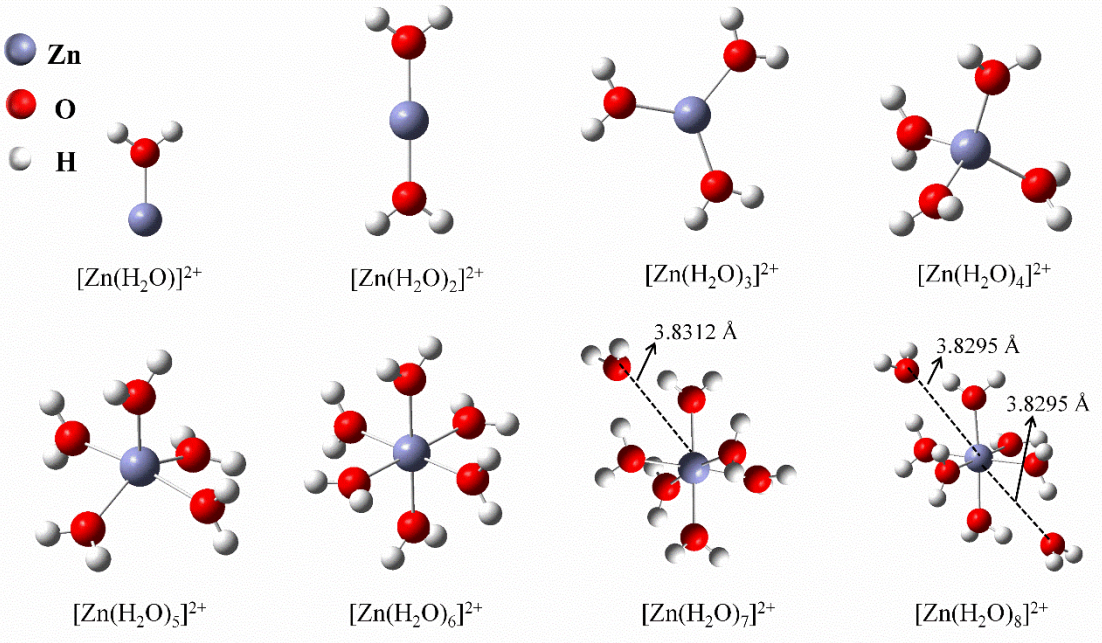


Figure S1. Optimized geometries of $[Zn(H_2O)_{1-8}]^{2+}$.

Table S1 presents the structural parameters, adsorption energies (ΔE_{ad}, ΔG_{ad}), and successive water adsorption energies (ΔE_{sad}, ΔG_{sad}) of $[Zn(H_2O)_{1-8}]^{2+}$, $[Zn(OH)(H_2O)_{1-5}]^{+}$ and $[Zn(OH)_2(H_2O)_{1-4}]$. The optimized structures of $[Zn(H_2O)_{1-8}]^{2+}$, $[Zn(OH)(H_2O)_{1-5}]^{+}$ and $[Zn(OH)_2(H_2O)_{1-4}]$ are shown in Figure S1, Figure S2 and Figure S3, respectively. For Zn^{2+}, when the number of H_2O ligands increase from 1 to 6, the ΔE_{ad} and ΔG_{ad} gradually decreases, but ΔE_{sad} and ΔG_{sad} gradually increases. When the number of H_2O ligands reached 7, ΔE_{sad} and ΔG_{sad} reached a relatively high value (−118.6 kJ/mol, −71.29 kJ/mol). According to Figure 2, the optimization results of the coordination structure of water molecules and zinc ions show that the adsorption of 1 and 5 water molecules on zinc ions is unidirectional. The adsorbed water molecules are distributed in the same hemisphere space of zinc ion, which is consistent with the previous literature conclusions [6]. When the amount of H_2O adsorbed reaches 6, the adsorption mode becomes omni-directional adsorption, and Zn^{2+} is located in the center and surrounded by 6 water molecules. In addition, when the number of adsorbed H_2O exceeds 6, the structure of hydrated Zn^{2+} complex is unstable. When the seventh water molecule is adsorbed, the bond length of Zn−O is 3.8312 Å, which is much longer than the average bond length of Zn−O (2.3491 Å). When the eighth water molecule is adsorbed, the bond length of newly formed Zn−O bond is also much longer than the average bond length of Zn−O. Therefore, the most stable hydration configuration of Zn^{2+} is the coordination structure with six water molecules [7].

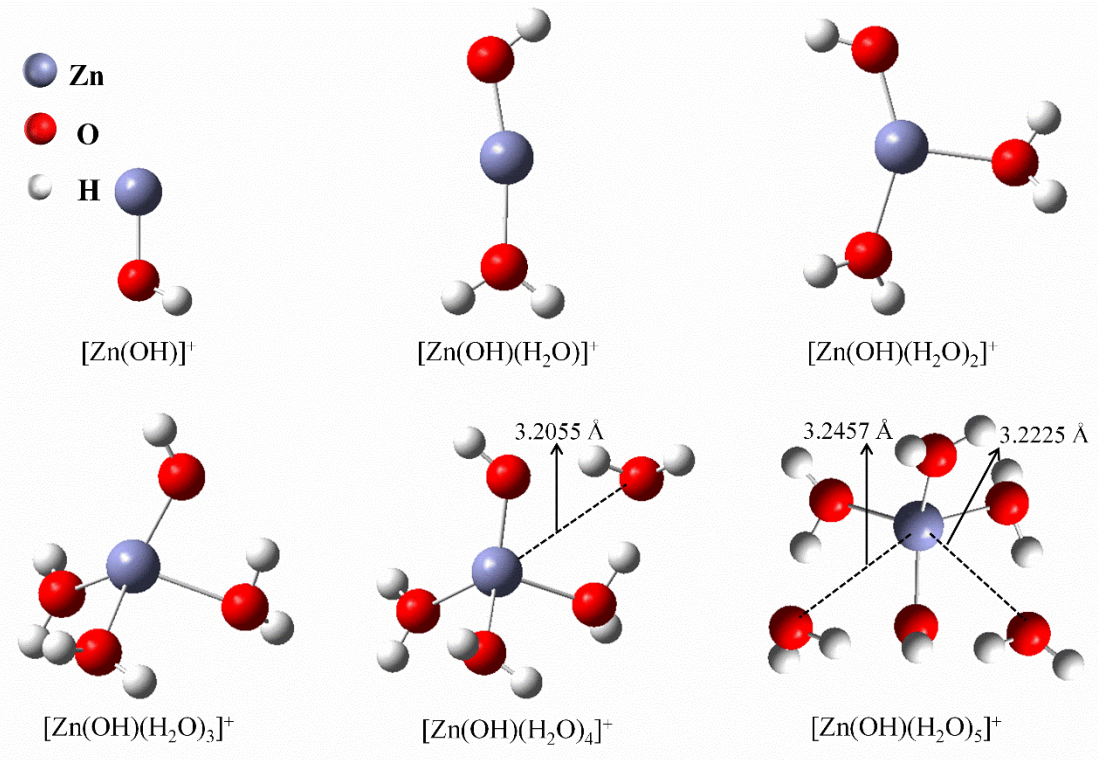


Figure S2. Optimized geometries of $[Zn(OH)(H_2O)_{1-5}]^+$.

For $[Zn(OH)]^+$, as presented in table S1, the ΔE_{ad} is gradually decreased and ΔE_{sad} is gradually increased when the number of H_2O ligands increase from 1 to 3. When the number of H_2O ligands reached 4, ΔE_{ad} and ΔG_{ad} produced an increase, but ΔE_{sad} and ΔG_{sad} reached a maximum value (−122.8 kJ/mol, −75.5 kJ/mol). As shown in Figure S2, when $[Zn(OH)]^+$ is adsorbed by three water molecules, it forms a structure similar to tetrahedron. When the fourth water molecule is adsorbed, the Zn−O bond length is 3.2055 Å, which is far greater than the average bond length of Zn−O (2.3243 Å). When the fifth water molecule is adsorbed, the bond length of newly formed Zn−O bond is also much longer than the average Zn−O bond length, indicating that the bonding between Zn and O atom in fourth and fifth H_2O is not obvious. Therefore, under the condition of the selected calculation parameters, the maximum number of water molecules in the first hydration layer of $[Zn(OH)]^+$ is 3, which is the most stable hydration configuration of $[Zn(OH)]^+$.

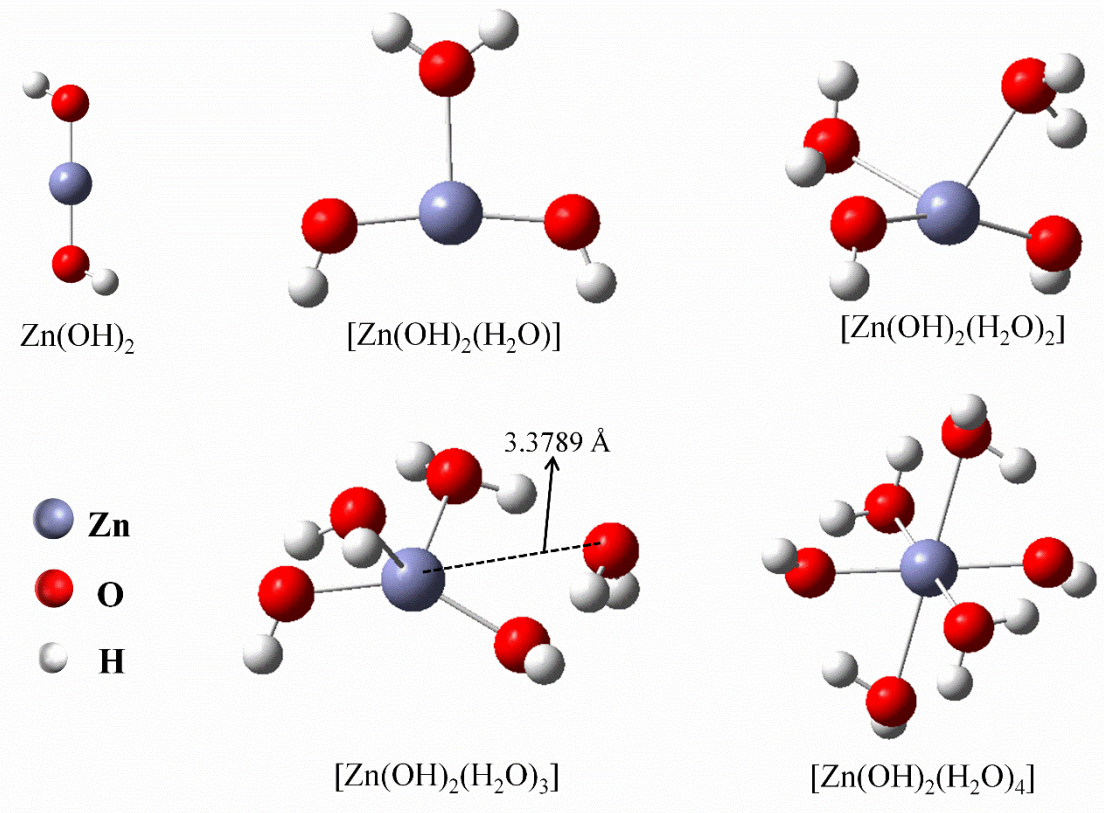


Figure S3. Equilibrium geometries of $[Zn(OH)_2(H_2O)_{1-5}]$.

In high alkalinity, zinc ion mainly exists as $Zn(OH)_2$. It can be seen from table S1 that the ΔE_{ad} is also gradually decreased when the number of H_2O ligands increase from 1 to 4. As shown in Figure S3, $Zn(OH)_2$ can adsorb two water molecules at most. When water molecules continue to adsorb on $[Zn(OH)_2(H_2O)_2]$, the distance between the Zn atom and the O atom in the third water is much greater than the distance between the initial two water molecules and the zinc atom. When the fourth water molecule continues to adsorb on $[Zn(OH)_2(H_2O)_3]$, the ΔE_{sad} and ΔG_{sad} reached a maximum value (−67.4 kJ/mol, −13.2 kJ/mol), indicating that the most stable hydration configuration of $Zn(OH)_2$ is $[Zn(OH)_2(H_2O)_2]$.

According to cluster model calculations, the most stable hydration configurations of Zn^{2+}, $[Zn(OH)]^+$ and $Zn(OH)_2$ were obtained through the above bond length and energy analysis, which is corresponding to the results of periodic model calculations. Therefore, adsorption behaviors and bonding mechanisms of $[Zn(H_2O)_6]^{2+}$, $[Zn(OH)(H_2O)_3]^+$ and $[Zn(OH)_2(H_2O)_2]$ on sphalerite (110) surface were further investigated.

Table S1. Structural parameters, adsorption energies (ΔE_{ad}, ΔG_{ad}), and successive water adsorption energies (ΔE_{sad}, ΔE_{sad}) of $[Zn(H_2O)_{1-8}]^{2+}$, $[Zn(OH)(H_2O)_{1-5}]^{+}$ and $[Zn(OH)_2(H_2O)_{1-4}]$.

Zn ion	N	D(Zn−O)$_{min}$ (Å)	D(Zn−O)$_{max}$ (Å)	D(Zn−O)$_{avg}$ (Å)	ΔE_{ad} (kJ/mol)	ΔE_{sad} (kJ/mol)	ΔG_{ad} (kJ/mol)	ΔG_{sad} (kJ/mol)
Zn^{2+}	1	1.8830	1.8830	1.8830	−424.2		−403.2	
	2	1.8803	1.8803	1.8803	−804.4	−380.2	−749.7	−346.6
	3	1.9376	1.9376	1.9376	−1078.9	−274.4	−987.0	−237.3
	4	1.9836	1.9836	1.9836	−1299.88	−221.0	−1166.6	−179.6
	5	2.0208	2.0968	2.0536	−1445.8	−145.9	−1265.6	−99.0
	6	2.1017	2.1018	2.1017	−1580.1	−134.3	−1355.8	−90.1
	7	2.0762	3.8312	2.3491	−1698.7	−118.6	−1427.1	−71.3
	8	2.0979	3.8295	2.5350	−1815.6	−116.9	−1498.7	−71.6
$[Zn(OH)]^{+}$	1	1.9118	1.9118	1.9118	−265.9		−229.1	
	2	1.9864	2.0153	2.0009	−429.9	−164.0	−352.8	−123.8
	3	2.0185	2.0469	2.0469	−565.3	−135.4	−442.7	−89.9
	4	1.9905	3.2055	2.3242	−688.1	−122.8	−518.2	−75.5
	5	1.9726	3.2457	2.4941	−799.5	−111.5	−578.2	−60.1
$Zn(OH)_2$	1	2.1683	2.1683	2.1683	−74.8		−37.6	
	2	2.1907	2.2129	2.2018	−172.9	−98.1	−79.0	−41.3
	3	2.0492	3.3789	2.5386	−267.6	−94.7	−127.6	−48.6
	4	2.2411	2.3115	2.2727	−335.0	−67.4	−140.8	−13.2

Part 2: The data of periodic calculation model

Table S2. Structural parameters, adsorption energies (ΔE_{ad}), and successive water adsorption energies (ΔE_{sad}) of $[Zn(H_2O)_{1-8}]^{2+}$, $[Zn(OH)(H_2O)_{1-5}]^{+}$ and $[Zn(OH)_2(H_2O)_{1-4}]$.

Zn ion	N	D(Zn−O)$_{min}$ (Å)	D(Zn−O)$_{max}$ (Å)	D(Zn−O)$_{avg}$ (Å)	ΔE_{ad} (kJ/mol)	ΔE_{sad} (kJ/mol)
Zn^{2+}	1	1.8568	1.8568	1.8568	−472.3	
	2	1.8466	1.8471	1.8469	−868.8	−396.5
	3	1.9202	1.9251	1.9219	−1105.9	−237.1
	4	1.9791	1.9856	1.9833	−1292.2	−186.2
	5	2.0261	2.1237	2.0636	−1405.4	−113.3
	6	2.1079	2.1234	2.1146	−1512.0	−105.6
	7	2.0963	3.8293	2.3633	−1611.8	−100.8
	8	2.1072	3.8331	2.5479	−1712.6	−100.8
$[Zn(OH)]^{+}$	1	1.8905	1.8905	1.8905	−248.6	
	2	1.9746	2.0616	2.0181	−372.5	−123.8
	3	2.0435	2.1115	2.0888	−470.4	−97.9
	4	2.0002	3.3084	2.3294	−399.6	71.2
	5	1.9813	3.2386	2.5000	−661.4	−1095.4
$Zn(OH)_2$	1	2.2061	2.2061	2.2061	−44.2	
	2	2.4084	2.4446	2.4265	−87.4	−43.2
	3	2.0955	3.3945	2.5898	−166.1	−77.8
	4	2.1325	3.3666	2.6654	−202.6	−36.5

Note: The Zn−O bond length are not including the O atom in hydroxyl.

Table S3. The adsorption energies of Zn^{2+}, $[Zn(OH)]^{+}$ and $Zn(OH)_2$ on the sphalerite (110) surface (kJ/mol).

Adsorbates	Adsorption sites	Adsorption energies
Zn^{2+}	T sites	−17.4
$[Zn(OH)]^{+}$	T sites	−158.6
$Zn(OH)_2$	T sites	−231.0

Table S4. The adsorption energies of $[Zn(H_2O)_5]^{2+}$, $[Zn(OH)(H_2O)_3]^{+}$ and $[Zn(OH)_2(H_2O)_2]$ on the sphalerite (110) surface (kJ/mol).

Adsorbates	Adsorption sites	Adsorption energies
$[Zn(H2O)_5]^{2+}$	T sites	−144.5
$[Zn(OH)(H2O)_3]^{+}$	T sites	−177.1
$[Zn(OH)_2(H2O)_2]$	T sites	−237.5

Table S5. Hirshfeld charge populations of bonding atoms before and after $[Zn(H_2O)_5]^{2+}$, $[Zn(OH)(H_2O)_3]^{+}$ and $[Zn(OH)_2(H_2O)_2]$ adsorption.

Adsorbates	Bond	Atoms	State	Charge/e
$[Zn(H_2O)_5]^{2+}$	H_{b-1}–S_6	H_{b-1}	Before	0.11
			After	0.10
		S_6	Before	−0.30
			After	−0.27
	H_{b-2}–S_8	H_{b-2}	Before	0.12
			After	0.10
		S_8	Before	−0.27
			After	−0.26
	H_{b-3}–S_3	H_{b-3}	Before	0.14
			After	0.09
		S_3	Before	−0.27
			After	−0.26
	Zn_{b-1}–S_7	Zn_{b-1}	Before	0.40
			After	0.39
		S_7	Before	−0.27
			After	−0.24
$[Zn(OH)(H_2O)_3]^{+}$	O_{c-1}–Zn_6	O_{c-1}	Before	−0.42
			After	−0.32
		Zn_6	Before	0.31
			After	0.26
	H_{c-1}–S_2	H_{c-1}	Before	0.18
			After	0.07
		S_2	Before	−0.31
			After	−0.24
	H_{c-2}–S_6	H_{c-2}	Before	0.18
			After	0.09
		S_6	Before	−0.30
			After	−0.26
$[Zn(OH)_2(H_2O)_2]$	O_{d-1}–Zn_6	O_{d-1}	Before	−0.44
			After	−0.32
		Zn_6	Before	0.31
			After	0.24
	O_{d-2}–Zn_7	O_{d-2}	Before	−0.43
			After	−0.31
		Zn_7	Before	0.31
			After	0.24
	H_{d-1}–S_2	H_{d-1}	Before	0.18
			After	0.10
		S_2	Before	−0.30
			After	−0.24
	H_{d-2}–S_6	H_{d-2}	Before	0.18
			After	0.11
		S_6	Before	−0.29
			After	−0.28

Table S6. Mulliken bond populations after the sphalerite adsorbed by $[Zn(H_2O)_5]^{2+}$, $[Zn(OH)(H_2O)_3]^{+}$ and $[Zn(OH)_2(H_2O)_2]$.

Adsorbates	Bond	Bond population
$[Zn(H_2O)_5]^{2+}$	$H_{b\text{-}1}$–S_6	0.06
	$H_{b\text{-}2}$–S_8	0.07
	$H_{b\text{-}3}$–S_3	0.07
	$Zn_{b\text{-}1}$–S_7	0.30
$[Zn(OH)(H_2O)_3]^{+}$	$O_{c\text{-}1}$–Zn_6	0.29
	$H_{c\text{-}1}$–S_2	0.17
	$H_{c\text{-}2}$–S_6	0.15
$[Zn(OH)_2(H_2O)_2]$	$O_{d\text{-}1}$–Zn_6	0.31
	$O_{d\text{-}2}$–Zn_7	0.31
	$H_{d\text{-}1}$–S_2	0.11
	$H_{d\text{-}2}$–S_6	0.09

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