Electronic Supplementary Material (ESI) for RSC Advances

SUPPORTING INFORMATION

Electron Detachment Dynamics of $Cu^-(H_2O)_n$ (n=1-3): A Direct Ab-initio MD study

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1. Energy diagram of the system (n=1)

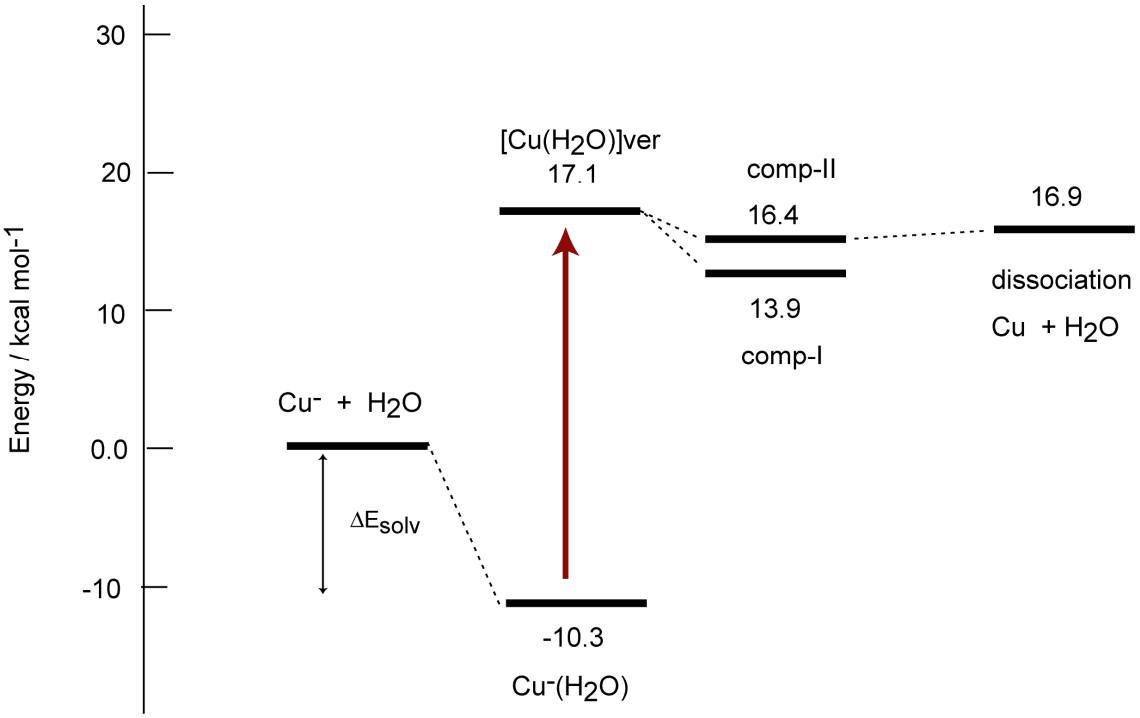

Figure S1. Energy diagram of $Cu(H_2O)$ system calculated at the MP2/6-311++G(2d,2p) level. Values indicate the relative energies in kcal/mol.

2. Electron capture dynamics of $Cu(H_2O)_n$ (n=1).

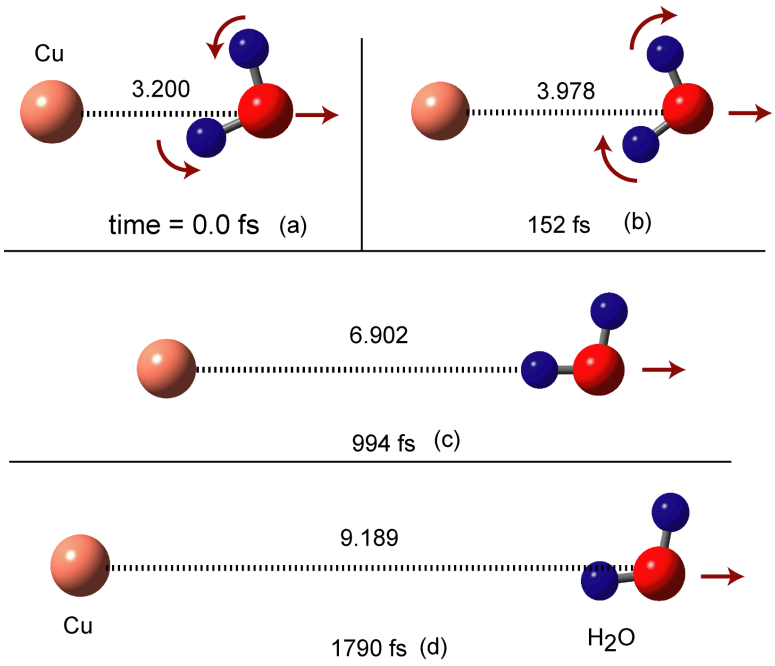

Figure S2. Snapshots of $Cu(H_2O)$ after the electron detachment obtained at the MP2/6-311++G(2d,2p) level. Values indicate bond distances in Å.

3. Electron capture dynamics of $Cu(H_2O)_n$ (n=2).

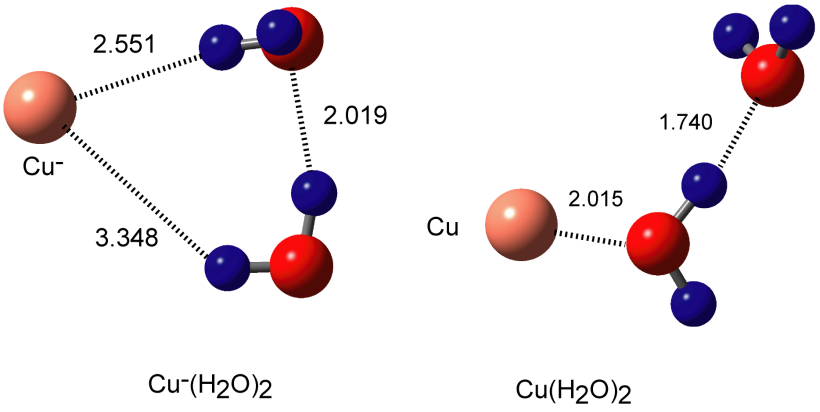

Figure S3. Optimized structures of Cu-(H2O)n and Cu(H2O)n (n=2) obtained at the MP2/6-311++G(2d,2p) level. Values indicate bond distances in Å.

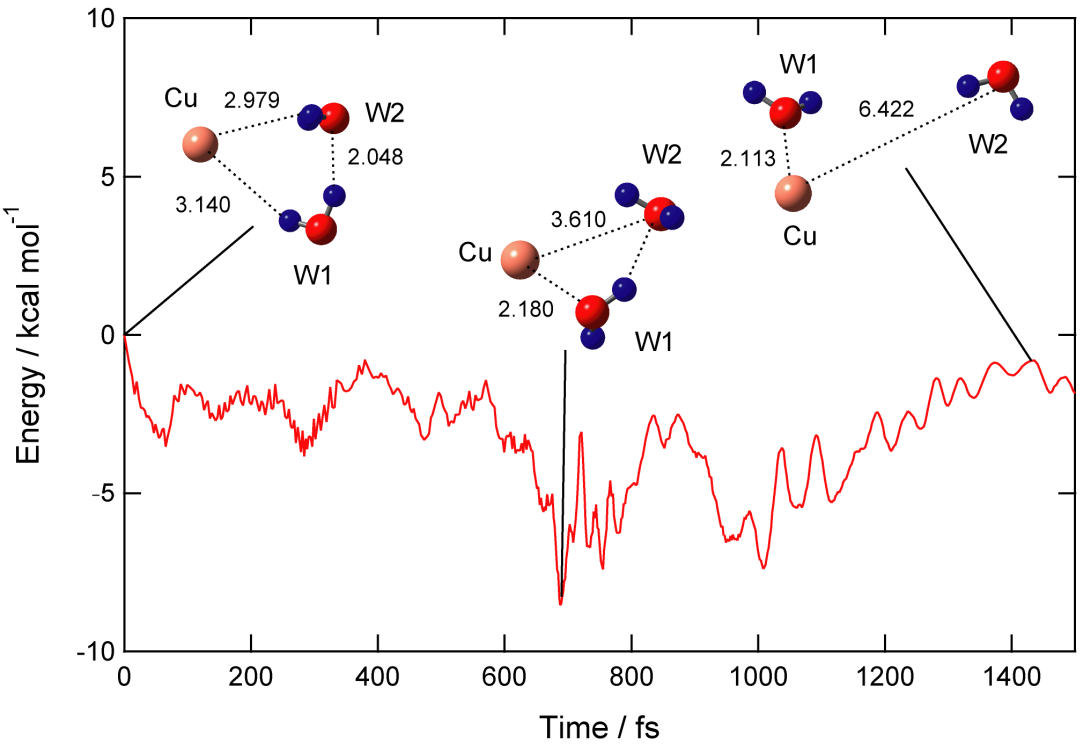

Figure S4. Time evolution of potential energy of the $Cu(H_2O)_n$ (n=2) system and snapshots for electron detachment of $Cu^-(H_2O)_2$ obtained by direct ab-initio MD calculation at the MP2/6-311++G(2d,2p) level. Values indicate bond distances between molecules in Å. Partial complex channel (products are $CuH_2O + H_2O$) was obtained as product channel.

4. Optimized structure of $Cu(H_2O)_n$ (n=3).

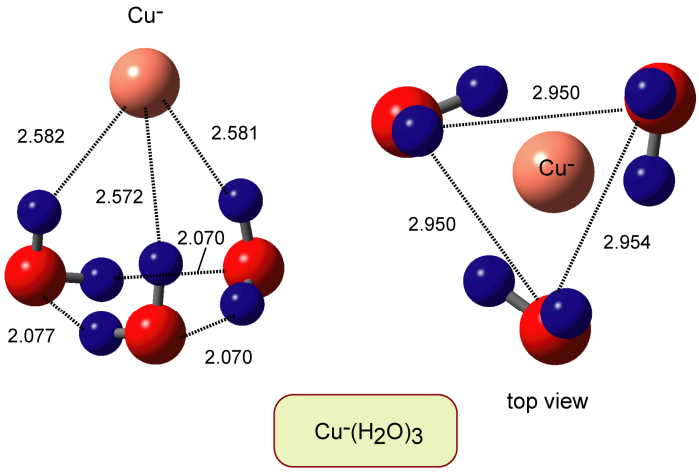

Figure S5. Optimized structures of $Cu^-(H_2O)_n$ (n=3) obtained at the MP2/6-311++ G(2d,2p) level. Values indicate bond distances in Å.

4. Optimized structure of $Cu(H_2O)_n$ (n=6).

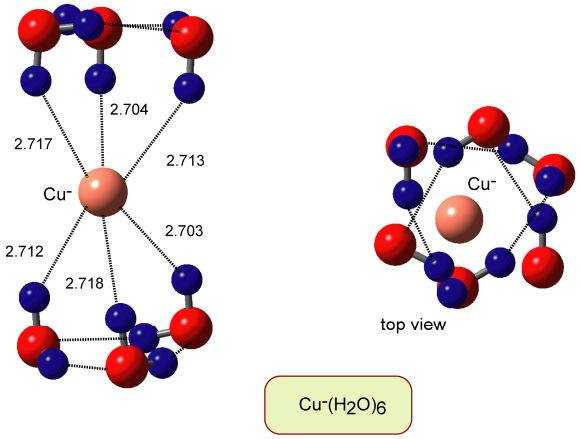

Figure S6. Optimized structures of $Cu^-(H_2O)_n$ (n=6) obtained at the MP2/6-311++ G(2d,2p) level. Values indicate bond distances in Å.

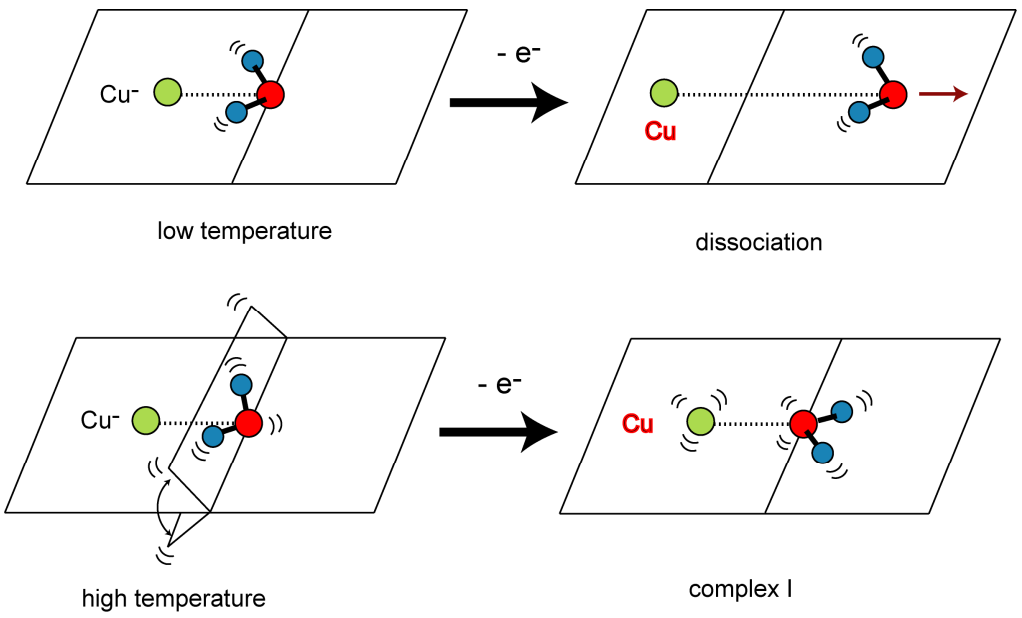

Figure S7. Model of temperature effect on the reaction channels.

Table S1. Optimized geometrical parameters of $Cu^{-}(H_2O)$ and CuH_2O calculated at the MP2, MP4SDQ, CCSD and QCISD/6-311++G(2d,2p) and QCISD/6-311++G(3df,3pd) levels of theory. Bond lengths and angles are in Å and in degrees, respectively.

		MP2	MP4SDQ	CCSD	QCISD	QCISD [a]
$Cu^{-}(H_2O)$	R_1	3.404	3.485	3.603	3.603	3.508
C_s	R_2	0.961	0.958	0.958	0.958	0.959
	R_3	0.974	0.969	0.966	0.966	0.968
	θ_1	99.4	100.2	100.8	100.8	100.1
	θ_2	75.2	75.6	75.3	75.3	74.4
$Cu(H_2O)(I)$	R_1	2.200	2.179	2.260	2.164	2.158
Cs	R_2	0.962	0.960	0.959	0.960	0.961
	θ_1	105.2	105.5	105.4	105.6	105.3
	ϕ	54.5	54.0	53.6	55.4	43.2
$Cu(H_2O)(II)$	R_1	3.965	3.956	4.137	4.019	3.908
	R_2	0.960	0.958	0.957	0.958	0.959
	R_3	0.958	105.5	0.956	0.957	0.957
	θ_1	104.0	54.0	104.5	104.4	104.2

[a] Optimized geometry calculated at the QCISD/6-311++G(3df,3pd) level.

Table S1 (continue).

		QCISD [a]	Ref.10
$Cu^{-}(H_2O)$	R_1	3.508	3.257
C_s	R_2	0.959	0.964
	R_3	0.968	0.986
	θ_1	100.1	99.0
	θ_2	74.4	
$Cu(H_2O)(I)$	R_1	2.158	2.068
Cs	R_2	0.961	0.966
	θ_1	105.3	105.3
	ϕ	43.2	
$Cu(H_2O)(II)$	R_1	3.908	3.520
	R_2	0.959	0.965
	R_3	0.957	0.962
	θ_1	104.2	103.9

[a] Optimized geometry calculated at the QCISD/6-311++G(3df,3pd) level.

Table 2. Harmonic vibrational frequencies of $Cu^-(H_2O)$ and CuH_2O calculated at the MP2/6-311++G(2d,2p) level of theory. Zero point energies (ZPEs) are given in kcal/mol.

mode	$Cu^-(H_2O)$	$Cu(H_2O)(I)$	$Cu(H_2O)(II)$
O-H asym	3874 (a')	3917 (a'')	3964 (a')
O-H sym	3601 (a')	3794 (a')	3841 (a')
H-O-H sci	1670 (a')	1649 (a')	1660 (a')
H_2O bend	538 (a'')	392 (a'')	102 (a'')
Cu-OH_2 str	169 (a')	337 (a')	61 (a')
H_2Orot	96 (a')	157 (a')	33 (a')
ZPE	14.22	14.65	13.81

Vibratrional frequencies of H_2O are calculated to be 3986, 3865, and 1660 cm^{-1}, and ZPE of H_2O is 13.60 kcal/mol at the MP2/6-311++G(2d,2p) level.