Electrical Double Layer on the Pt(111) Electrode Modeled under Ultrahigh Vacuum Conditions

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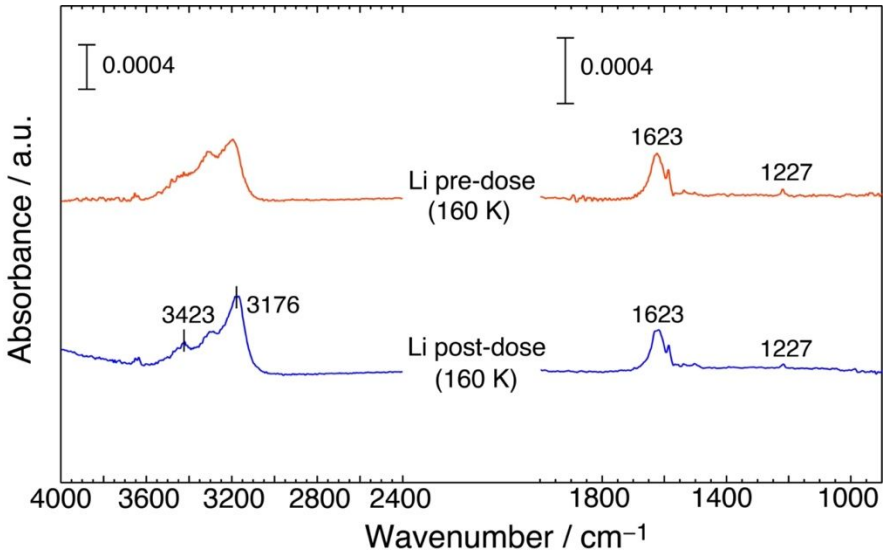

Figure S1. IR spectra of Pt(111) obtained using a different dosing sequence for Li and H_2O. H_2O (θ_{H2O} = 0.67) post-dosed onto Li (θ_{Li} = 0.16) pre-adsorbed Pt(111) (upper). Li (θ_{H2O} = 0.16) post-dosed onto H_2O (θ_{H2O} = 0.67) pre-adsorbed Pt(111) (lower).

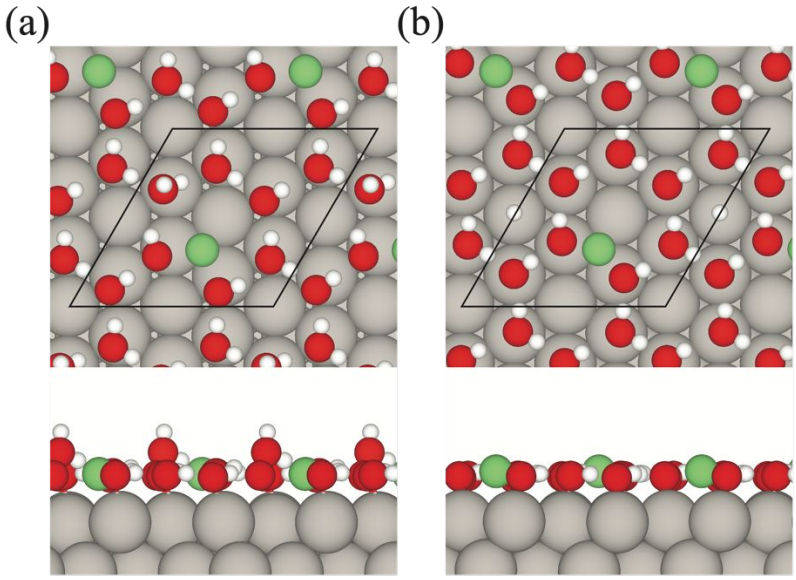

Figure S2. Possible structures for Li+OH_{ad}+H_2O/Pt(111) in which Li is coordinated by two OH groups. (a) A structure without spontaneous dissociation of a H_2O molecule. This structure is less stable by 0.31 eV than the one reported in the main text. (b) A structure with a dissociated H_2O molecule. Dissociated H atom is located at an atop Pt site. This structure is less stable by 0.57 eV than the one reported in the main text.

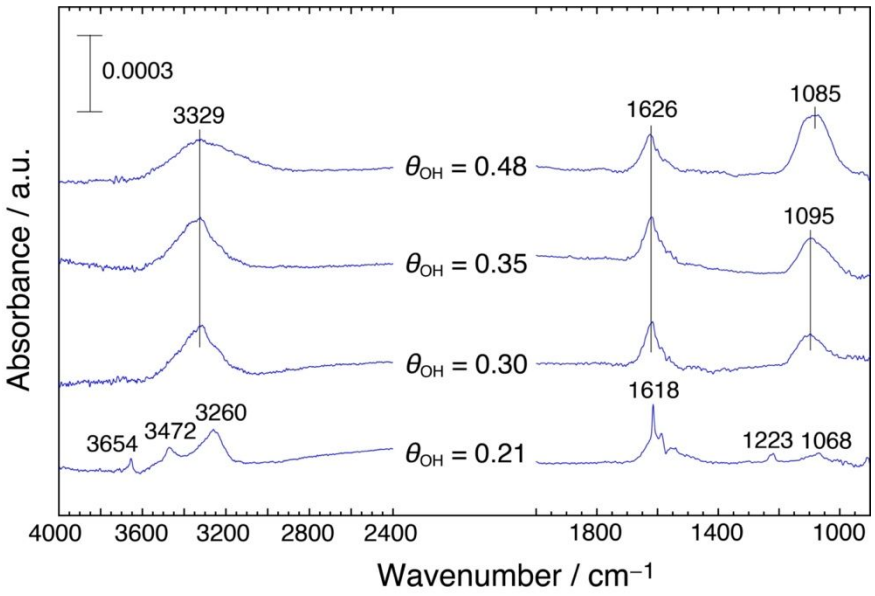

Figure S3. IR spectra as a function of the coverage of adsorbed hydroxide (θ_{OH}) for the OH_{ad} + H_2O layer onto Pt(111) with θ_{Li} = 0.15. The sample was heated at 160 K, after Li was adsorbed at 20 K. All IR spectra were measured at 20 K.

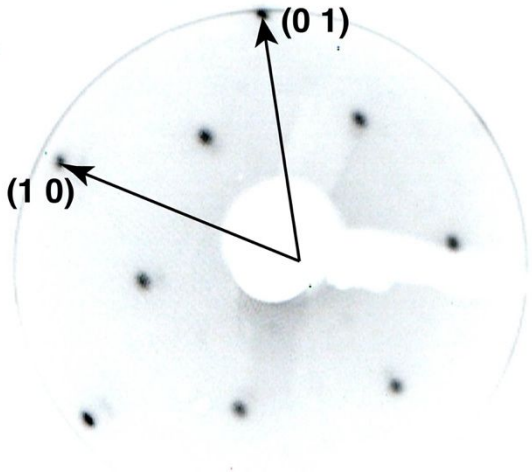

Figure S4. LEED pattern of Pt(111) at the θ_{OH} = 0.3 and θ_{Li} = 0.15.

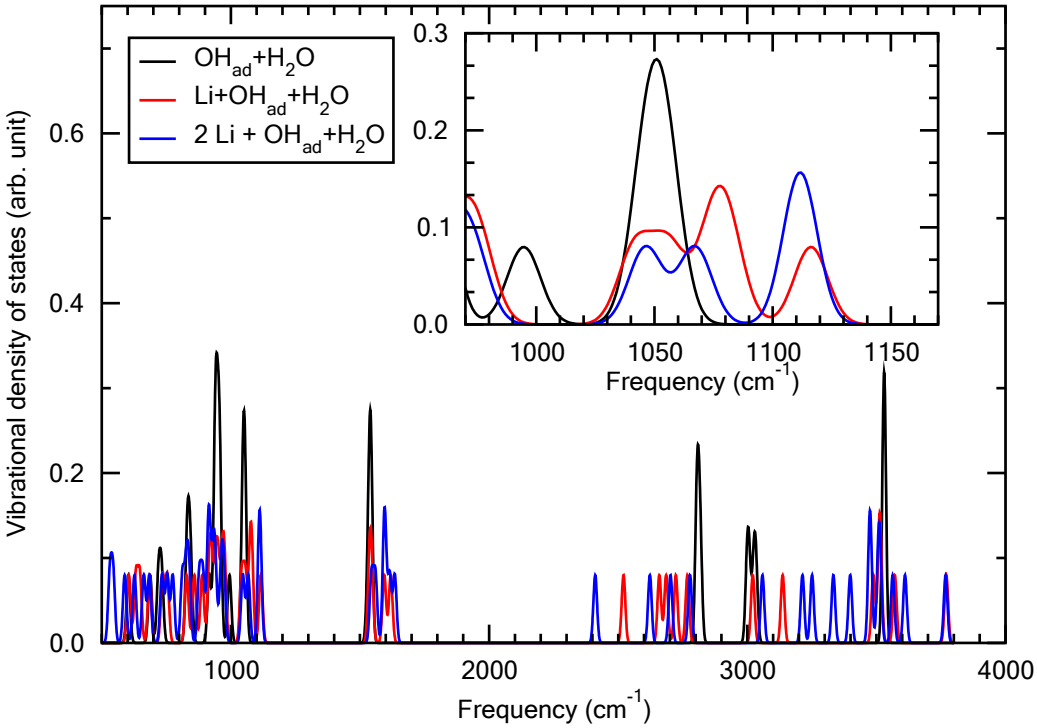

Figure S5. Vibrational densities of states (VDOSs) for OH_{ad}+H_2O layer on Pt(111) ($\sqrt{3} \times \sqrt{3}$)*R*30°, one-Li co-adsorbed OH_{ad}+H_2O layer on Pt(111) ($2\sqrt{3} \times 2\sqrt{3}$)*R*30°, and two-Li co-adsorbed OH_{ad}+H_2O layer on Pt(111) ($2\sqrt{3} \times 2\sqrt{3}$)*R*30°. Inset shows VDOS at around 950-1150 cm^{-1}. Only the Γ-point were considered in the calculation of the vibrational frequencies. A gaussian with the broadening width of 5 cm^{-1} was used to calculate VDOSs.

Table S1. Comparison of the calculated and experimental frequencies for OH_{ad}+H_2O/Pt(111)($\sqrt{3}\times\sqrt{3}$). *ν* and *δ* are stretching and bending modes, respectively, and ∥ *and* ⊥ indicate the modes relative to OH or H_2O molecular planes, respectively.

Expt.[a]		DFT (GGA-PW91)[b]		DFT(GGA-PBE)[c]	
Frequency (cm^{-1})	Mode	Frequency (cm^{-1})	Mode	Frequency (cm^{-1})	Mode
3476	*ν*(OH)	3329	*ν*(OH)	3530	*ν*(OH)
1024	$\delta_{\parallel}$(OH)	1036	$\delta_{\parallel}$(OH)+$\delta_{\perp}$(H_2O)	1046	$\delta_{\perp}$(OH)+$\delta_{\perp}$(H_2O)
911	$\delta_{\parallel}$(OH)	986	$\delta_{\perp}$ (H_2O)	916	$\delta_{\parallel}$(OH)+$\delta_{\parallel}$(H_2O)
823	$\delta_{\parallel}$(OH)	831	$\delta_{\parallel}$(OH)+$\delta_{\perp}$(H_2O)	830	$\delta_{\parallel}$(OH)+$\delta_{\parallel}$(H_2O)
436	*ν*(Pt-OH)	436	*ν*(Pt-OH)	423	*ν*(Pt-OH)

[a]Ref. 1

[b]Ref. 2

[c]This work

Table S2. Calculated frequencies for $OH+H_2O/Pt(111)(\sqrt{3}\times\sqrt{3})$, $Li+OH+H_2O/Pt(111)$ $(2\sqrt{3}\times2\sqrt{3})$, and $2Li+OH+H_2O/Pt(111)$ $(2\sqrt{3}\times2\sqrt{3})$. ν and δ are stretching and bending modes, respectively, and $\parallel$ *and* $\perp$ indicate the modes relative to OH or H_2O molecular planes, respectively.

$OH+H_2O/Pt(111)(\sqrt{3}\times\sqrt{3})$		$Li+OH+H_2O/Pt(111)$ $(2\sqrt{3}\times2\sqrt{3})$		$2Li+OH+H_2O/Pt(111)$ $(2\sqrt{3}\times2\sqrt{3})$	
Frequency (cm^{-1})	Mode	Frequency (cm^{-1})	Mode	Frequency (cm^{-1})	Mode
1055	$\delta_\perp(OH)+\delta_\parallel(H_2O)$	1116	$\delta_\perp(H_2O)$	1138	$\delta_\perp(OH)+\delta_\perp(H_2O)$
1048	$\delta_\perp(OH)+\delta_\perp(H_2O)$	1081	$\delta_\perp(OH)+\delta_\perp(H_2O)$	1135	$\delta_\perp(OH)+\delta_\perp(H_2O)$
1046	$\delta_\perp(OH)+\delta_\perp(H_2O)$	1074	$\delta_\perp(OH)+\delta_\perp(H_2O)$	1041	$\delta_\perp(OH)+\delta_\perp(H_2O)$
995	$\delta_\perp(OH)+\delta_\parallel(H_2O)$	1056	$\delta_\perp(OH)+\delta_\perp(H_2O)$	1038	$\delta_\perp(OH)+\delta_\perp(H_2O)$
958	$\delta_\perp(OH)+\delta_\parallel(H_2O)$	1042	$\delta_\perp(OH)+\delta_\perp(H_2O)$	942	$\delta_\perp(OH)+\delta_\perp(H_2O)$
956	$\delta_\perp(OH)+\delta_\parallel(H_2O)$	976	$\delta_\perp(OH)+\delta_\perp(H_2O)$	937	$\delta_\perp(OH)+\delta_\perp(H_2O)$
953	$\delta_\perp(OH)+\delta_\parallel(H_2O)$	967	$\delta_\perp(OH)+\delta_\perp(H_2O)+\delta_\parallel(H_2O)$	927	$\delta_\perp(OH)+\delta_\perp(H_2O)$
946	$\delta_\perp(OH)+\delta_\parallel(H_2O)$	951	$\delta_\perp(OH)+\delta_\perp(H_2O)+\delta_\parallel(H_2O)$	902	$\delta_\perp(H_2O)$
943	$\delta_\perp(OH)+\delta_\parallel(H_2O)$	941	$\delta_\perp(OH)+\delta_\perp(H_2O)+\delta_\perp(H_2O)$	887	$\delta_\parallel(OH)+\delta_\parallel(H_2O)+\delta_\perp(H_2O)$
939	$\delta_\perp(OH)+\delta_\parallel(H_2O)$	926	$\delta_\perp(OH)+\delta_\perp(H_2O)+\delta_\parallel(H_2O)$	885	$\delta_\parallel(OH)+\delta_\parallel(H_2O)+\delta_\perp(H_2O)$
938	$\delta_\perp(OH)+\delta_\parallel(H_2O)$	916	$\delta_\perp(OH)+\delta_\perp(H_2O)+\delta_\parallel(H_2O)$	860	$\delta_\perp(OH)+\delta_\parallel(H_2O)$
916	$\delta_\parallel(OH)+\delta_\parallel(H_2O)$	889	$\delta_\perp(OH)+\delta_\perp(H_2O)+\delta_\perp(H_2O)$	841	$\delta_\perp(OH)+\delta_\parallel(OH)+\delta_\parallel(H_2O)$
844	$\delta_\parallel(OH)+\delta_\parallel(H_2O)$	859	$\delta_\perp(OH)+\delta_\parallel(H_2O)$	766	$\delta_\parallel(OH)+\delta_\parallel(H_2O)$
836	$\delta_\parallel(OH)+\delta_\parallel(H_2O)$	829	$\delta_\parallel(OH)+\delta_\parallel(H_2O)+\delta_\perp(H_2O)$	745	$\delta_\parallel(OH)+\delta_\parallel(H_2O)$
830	$\delta_\parallel(OH)+\delta_\parallel(H_2O)$	754	$\delta_\parallel(OH)+\delta_\parallel(H_2O)$	679	$\delta_\parallel(OH)+\delta_\parallel(H_2O)$

References

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