Supplementary material: Ab initio study of water dissociation on a charged Pd(111) surface

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I. EFFECT OF THE FIELD ON THE ADSORPTION ENERGY

In the main text, we report the adsorption energy E_{ads} calculated as

$$E_{\text{ads}} = E_{\text{isol}} + E_{\text{clean}} - E_{\text{full}}, \tag{1}$$

where E_{isol}, E_{clean} and E_{full} denote the energies of an isolated water molecule, clean Pd surface and the surface with a water molecule adsorbed, respectively, all three relaxed in the electric fields of the same strength. In addition to that, we report here the values of E^0_{ads} calculated against the zero-field gas-phase reference as follows:

$$E^0_{\text{ads}} = E^0_{\text{isol}} + E_{\text{clean}} - E_{\text{full}}, \tag{2}$$

where E_{clean} and E_{full} are as defined before, while E^0_{isol} is the energy of an isolated molecule with no external field applied. This data is given in Table S1 and Fig. S1.

TABLE S1. Adsorption energies E^0_{ads} at different electric field strengths relative to the zero-field reference.

El. field (V/Å)	-0.74	-0.44	-0.29	-0.15	-0.07	No field	0.07	0.15	0.44	0.74
E^0_{ads} (eV)	0.612	0.478	0.450	0.460	0.469	0.481	0.497	0.515	0.618	0.762

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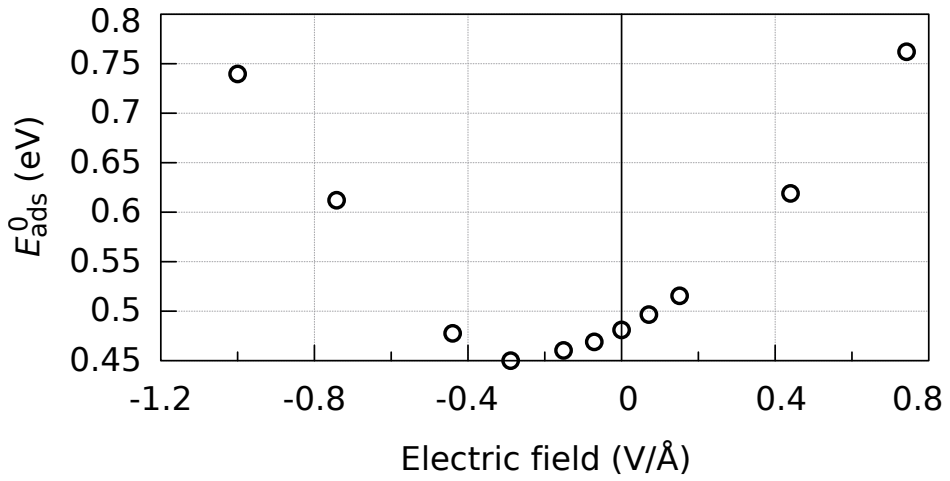

FIG. S1. Adsorption energies $E^0_{\rm ads}$ calculated by the Expression 2 at different electric field strengths.

II. MODE-RESOLVED ZPE EFFECT ON THE DISSOCIATION BARRIER

We show the contributions to the ZPE from individual vibrational modes of the adsorbed water molecule in table S2.

In order to see more clearly how the shifts of the vibrational modes contribute to the total zero point energy (ZPE) effect on the reaction barrier, we calculate a cumulative ZPE difference between the reactant and the transition state as follows:

$$\Delta^{\rm ZPE}_{\rm cumul}(\omega) = \sum_{\omega_i \leq \omega} \frac{\hbar\omega_i^{\rm TS}}{2} - \sum_{\omega_i \leq \omega} \frac{\hbar\omega_i^{\rm ini}}{2}, \tag{3}$$

where $\omega_i^{\rm TS}$ and $\omega_i^{\rm ini}$ are the normal modes of the transition state and the reactant, respectively. We show $\Delta^{\rm ZPE}_{\rm cumul}(\omega)$ in figure S2.

One can see that despite multiple shifts of the individual modes, all the ZPE differences between the most distant electric field values of + and –0.74 V/Å below 1000 cm^{-1} cancel out, ending up with almost equal ZPE contribution to the barrier.

III. ESTIMATE OF TUNNELING CROSSOVER TEMPERATURES

We estimate tunneling crossover temperature as $T_c = \hbar\omega^{\rm TS}/(2\pi k_B)$, where $\omega^{\rm TS}$ is the imaginary frequency of the unstable mode at the transition state. The results are given in Table II of the main text. For comparison, in Ref. [1], a value of T_c=142 K for the dissociation

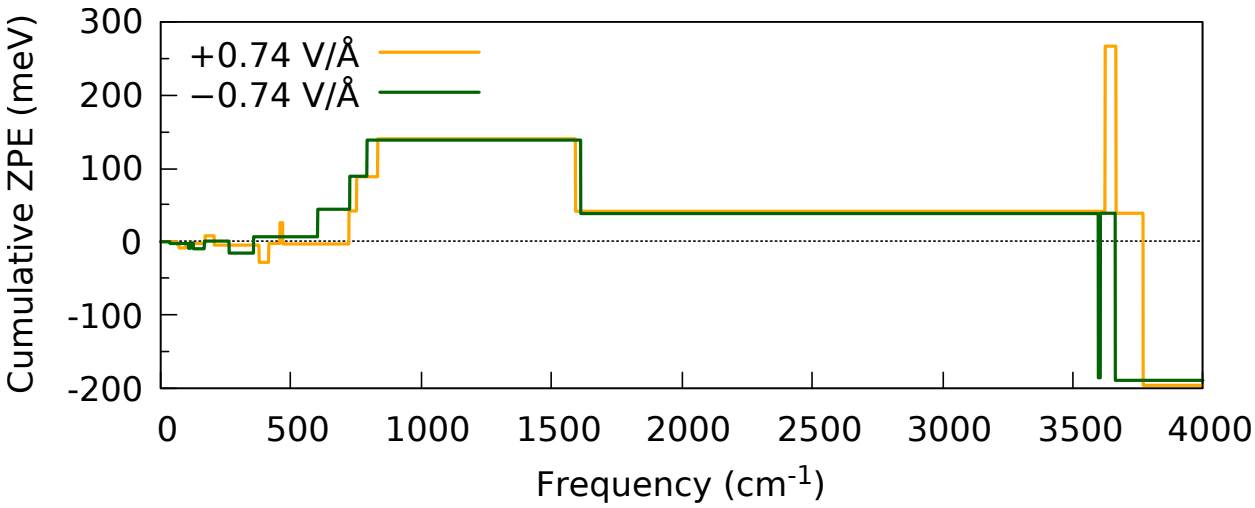

FIG. S2. Cumulative contribution of the vibrational modes to the total ZPE effect on the barrier of water dissociation, calculated by Eq. 3.

of water on Pd(111) was reported, with a different exchange-correlation functional.

[1] Y. Cao and Z.-X. Chen, Theoretical studies on the adsorption and decomposition of H2O on Pd(111) surface, Surface Science **600**, 4572 (2006).

TABLE S2. The frequencies of the individual vibrational modes of the water molecule adsorbed at Pd(111) surface ("ini") and of the transition state of its dissociation ("TS"). The values are calculated with PBE + vdW^{surf}.

-0.74		-0.44		-0.29		-0.15		0		+0.15		+0.44		+0.74	
ini	TS	ini	TS	ini	TS	ini	TS	ini	TS	ini	TS	ini	TS	ini	TS
30.0	-800.5	27.0	-729.5	29.9	-640.5	24.7	-673.1	13.9	-645.4	-23.4	-621.7	-41.9	-564.4	-42.6	-451.7
35.5	115.2	31.6	121.0	71.1	118.8	76.0	119.3	75.3	117.7	70.5	114.4	59.4	107.4	63.8	96.8
106.2	167.5	103.2	180.4	115.9	183.8	107.7	180.5	97.9	183.4	78.5	186.2	60.5	183.4	70.8	170.1
125.2	309.2	131.4	369.1	129.9	386.8	158.8	389.4	172.9	393.5	189.9	402.6	202.2	413.5	205.6	414.1
262.6	356.7	196.9	396.4	416.1	413.6	437.9	417.0	449.2	429.3	457.8	434.5	409.4	449.3	378.0	457.4
309.4	602.6	219.3	645.5	470.6	643.6	478.8	642.9	473.6	646.7	463.4	653.7	462.2	673.3	468.0	722.8
1611.5	725.5	1593.7	736.9	1569.2	727.2	1569.1	732.9	1573.1	737.0	1576.4	761.1	1582.1	747.4	1592.0	751.1
3597.5	791.1	3604.3	774.4	3561.5	773.8	3579.4	774.6	3600.5	773.9	3618.5	783.0	3652.5	768.1	3665.8	832.4
3662.4	3605.4	3683.3	3620.3	3655.4	3624.1	3676.2	3626.5	3700.3	3628.5	3721.5	3634.5	3760.0	3632.9	3769.8	3623.6