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### Title

Correction to "The Surface Structure of Co<sub>3</sub>O<sub>4</sub>(111) under Reactive Gas-Phase Environments"

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## Correction to: “The Surface Structure of Co<sub>3</sub>O<sub>4</sub>(111) under Reactive Gas Phase Environments”

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A factor of two was mistakenly multiplied when calculating pressure magnitudes on the  $P_{H_2}$  and  $P_{H_2O}$  axes in **Figures 3, 4, 5, 8, 12, S9, and S10** from chemical potentials (detailed below, corrections in **bold**). This mistake does not change our conclusion, which is that the Co<sub>3</sub>O<sub>4</sub>(111) surface is hydroxylated under most water-containing reactive environments. An unrelated error in the temperature axis of **Figures S3 (bottom)** has also been corrected.

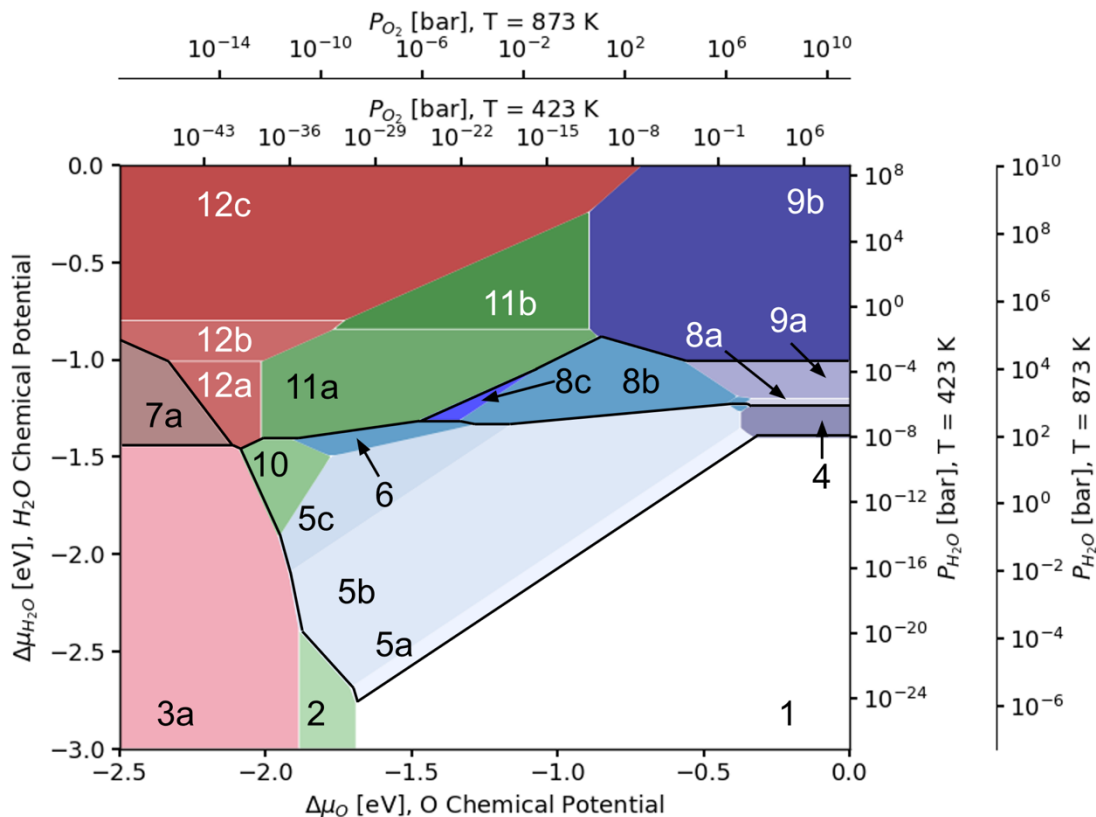
Pressures referenced in the abstract should read:

*“At 423 K, hydroxylation readily occurs on both the O-rich and Co-rich surfaces even at water pressure as low as **10<sup>-8</sup> bar**, and non-dissociated water molecules appear on the O-rich surface when water pressure is above **~10<sup>-6</sup> bar**.”*

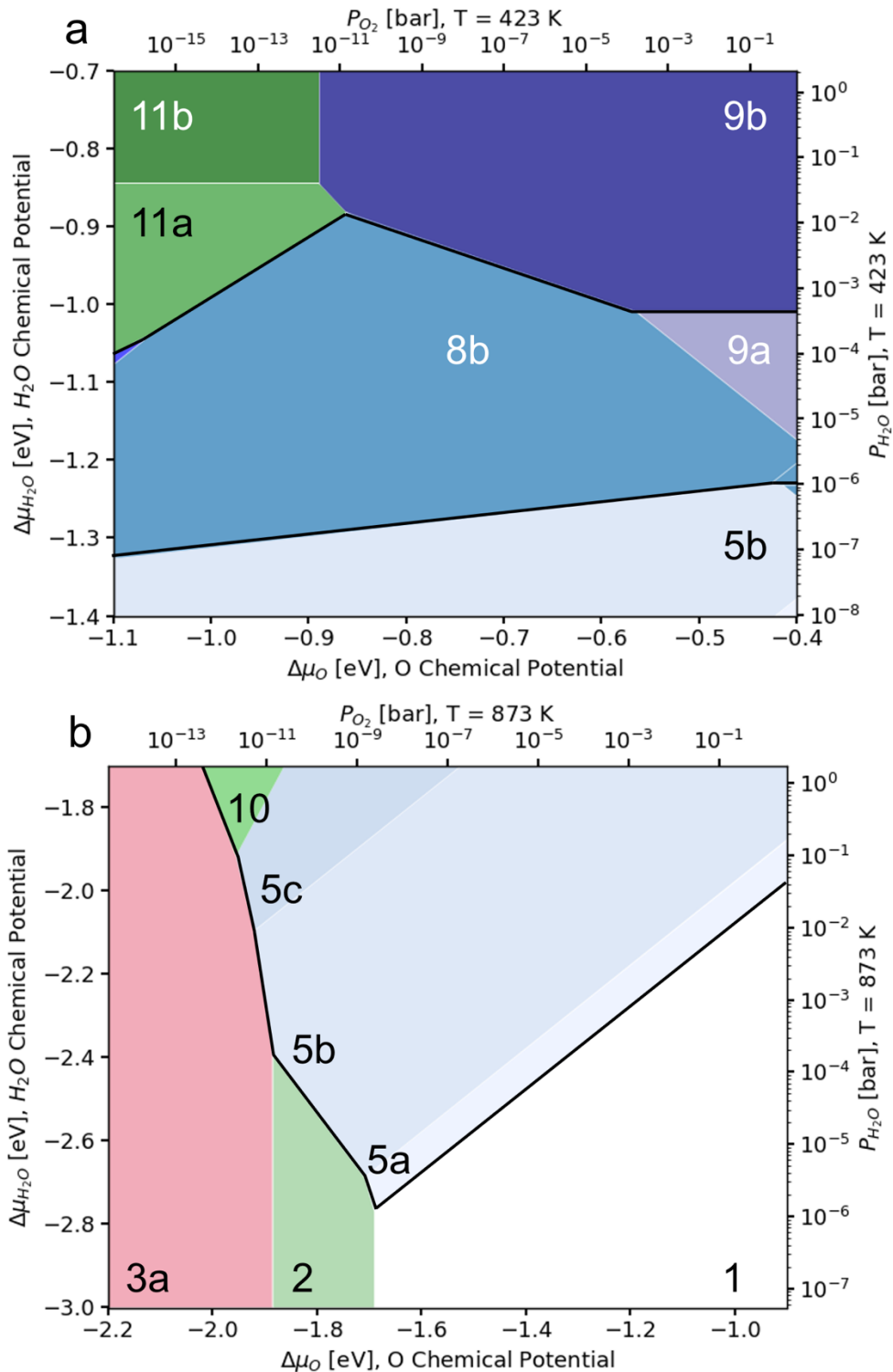
The paragraph in Section 3.1, page 6383 when interpreting the stability diagram should read:

*“Although many possible terminations of this surface exist in theory, not all terminations can be accessed under realistic pressure and temperature. At 423 K (Figure 4, top), only a fraction of the hydroxylated regions (structures 5b, 8b, 9a,b, and 11a,b) can be visited at equilibrium; however, clear separations among isolated OH, triaqua complexes, and hydroxyl networks can still be observed when  $P_{H_2O}$  is increased. When the O<sub>2</sub> pressure is between 1 bar and 10<sup>-4</sup> bar and the H<sub>2</sub>O pressure is above **10<sup>-4</sup> bar**, the surface is predicted to be heavily hydroxylated, with a triaqua complex incorporated into the OH/H<sub>2</sub>O chain (9b). Triaqua complexes are predicted to be separated from the chain below **10<sup>-4</sup> bar** (8b, 9a), and only isolated hydroxyls (5b) are stable below **10<sup>-7</sup> bar**. Overall, at 423 K, the surface stability diagram is dominated by triaqua complex regions with various amounts of additional H<sub>2</sub>O/OH groups. On the other hand, if the temperature is increased to 873 K (Figure 4, bottom), isolated hydroxyls will be exposed under **10<sup>-2</sup> bar**. We note that, for the surface Co concentration to increase to above 3.56 Co/nm<sup>2</sup>, P<sub>O<sub>2</sub></sub> needs to be reduced to below 10<sup>-11</sup> bar while P<sub>H<sub>2</sub>O</sub> is kept below **10<sup>-5</sup> bar**, i.e. in UHV conditions.”*

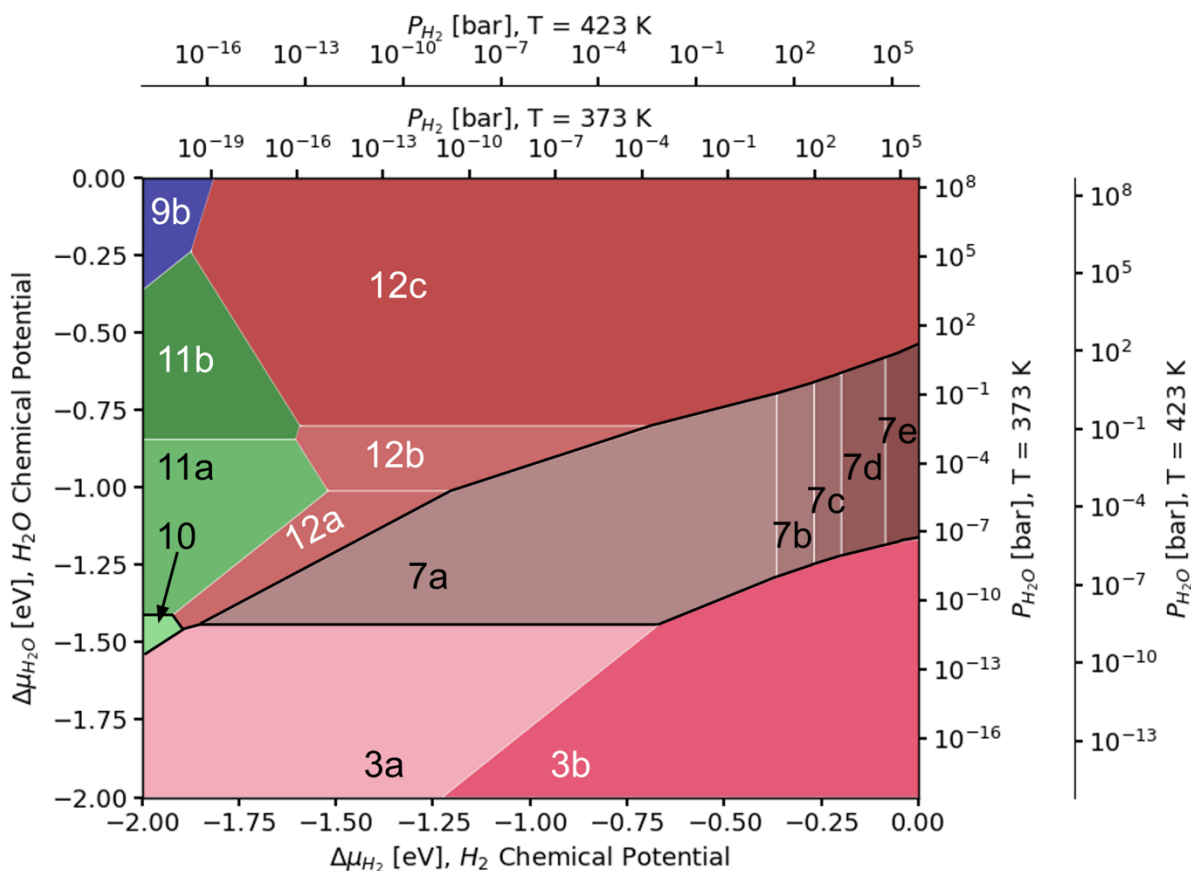
Diagrams containing correct  $P_{H_2O}$  and  $P_{H_2}$  axes are as follows:



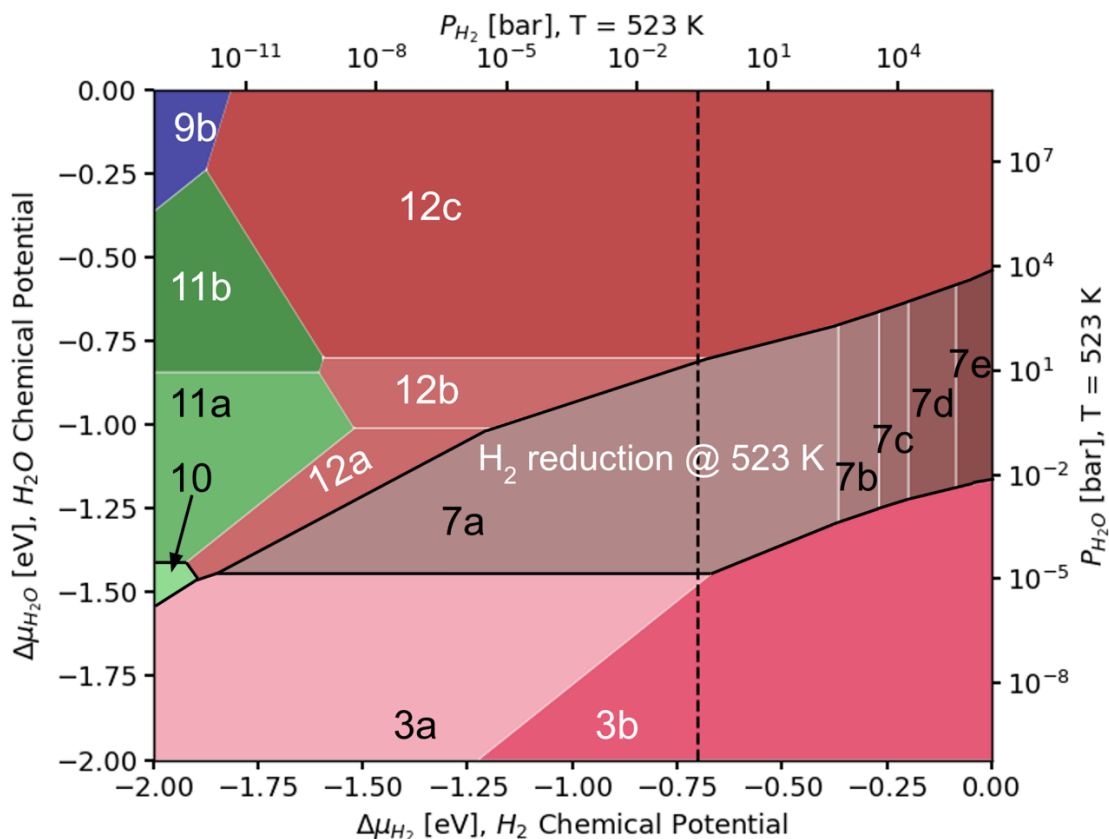
**Figure 3.** Surface stability diagram showing the most stable surface structure as a function of  $O_2$  and  $H_2O$  chemical potential and equivalent oxygen/water pressure at 423 K and 873 K. Regions are classified in three ways. (I) By surface Co concentration: blue/grey/white:  $3.56 \text{ Co/nm}^2$ ; green:  $5.33 \text{ Co/nm}^2$ , and red/brown:  $7.11 \text{ Co/nm}^2$ . (II) By general appearance of surface hydroxylation: the bottom bold line separates non-hydroxylated regions and hydroxylated regions, the middle bold line (only the segment running through the blue regions, or when  $\Delta\mu_O > -1.5$  eV) separates isolated hydroxyls and  $\text{Co}(\text{H}_2\text{O})_3$  (hereby referred to as “triaqua”) surface complexes (with eventually additional OH groups), and the top bold line separates isolated triaqua surface complexes and large OH/ $H_2O$  structures. (III) By specific numbered structure (see Table 1 for descriptions, Figure 2 and Table 2 for representative geometries, and Table S10 for all geometries).



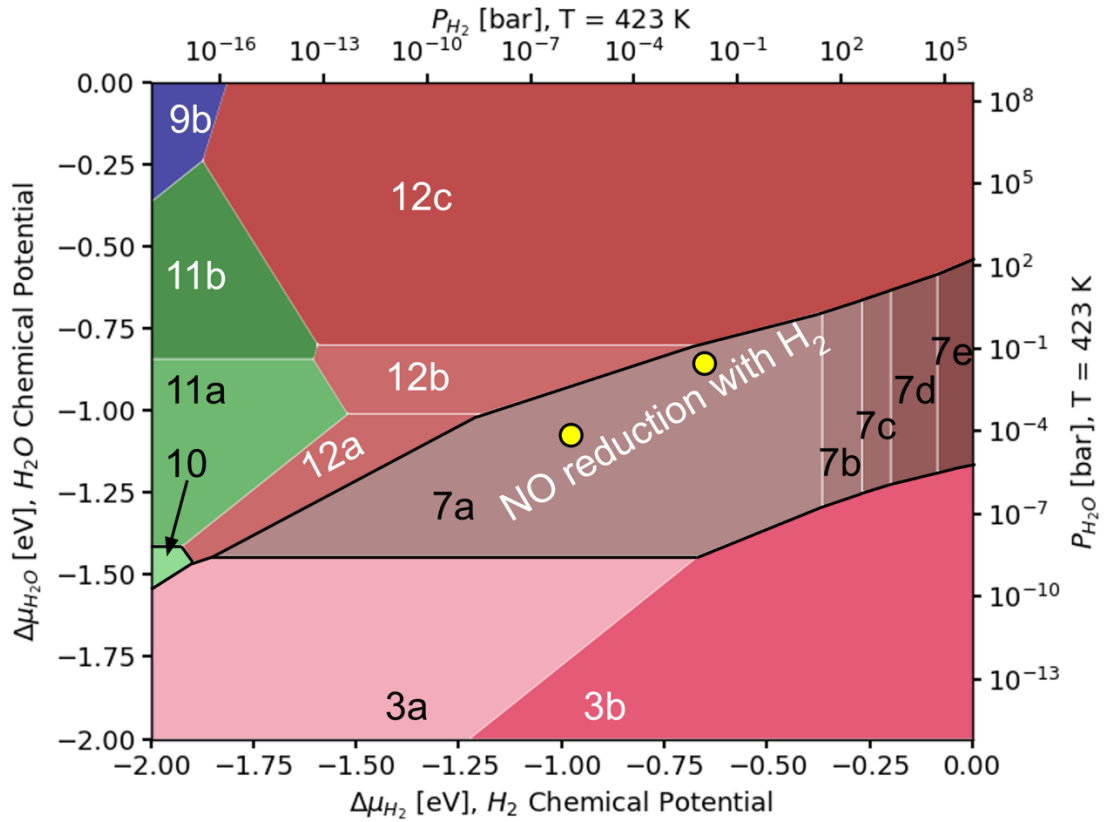
**Figure 4.** Portions of Figure 3 showing the H<sub>2</sub>O/O<sub>2</sub> surface stability diagram under realistic pressures at (top) 423 K and (bottom) 873 K. Regions are numbered and colored the same way as Figure 3. Only hydroxylated regions can be accessed at 423 K. Higher surface Co concentration can be reached under low  $P_{O_2}$ .



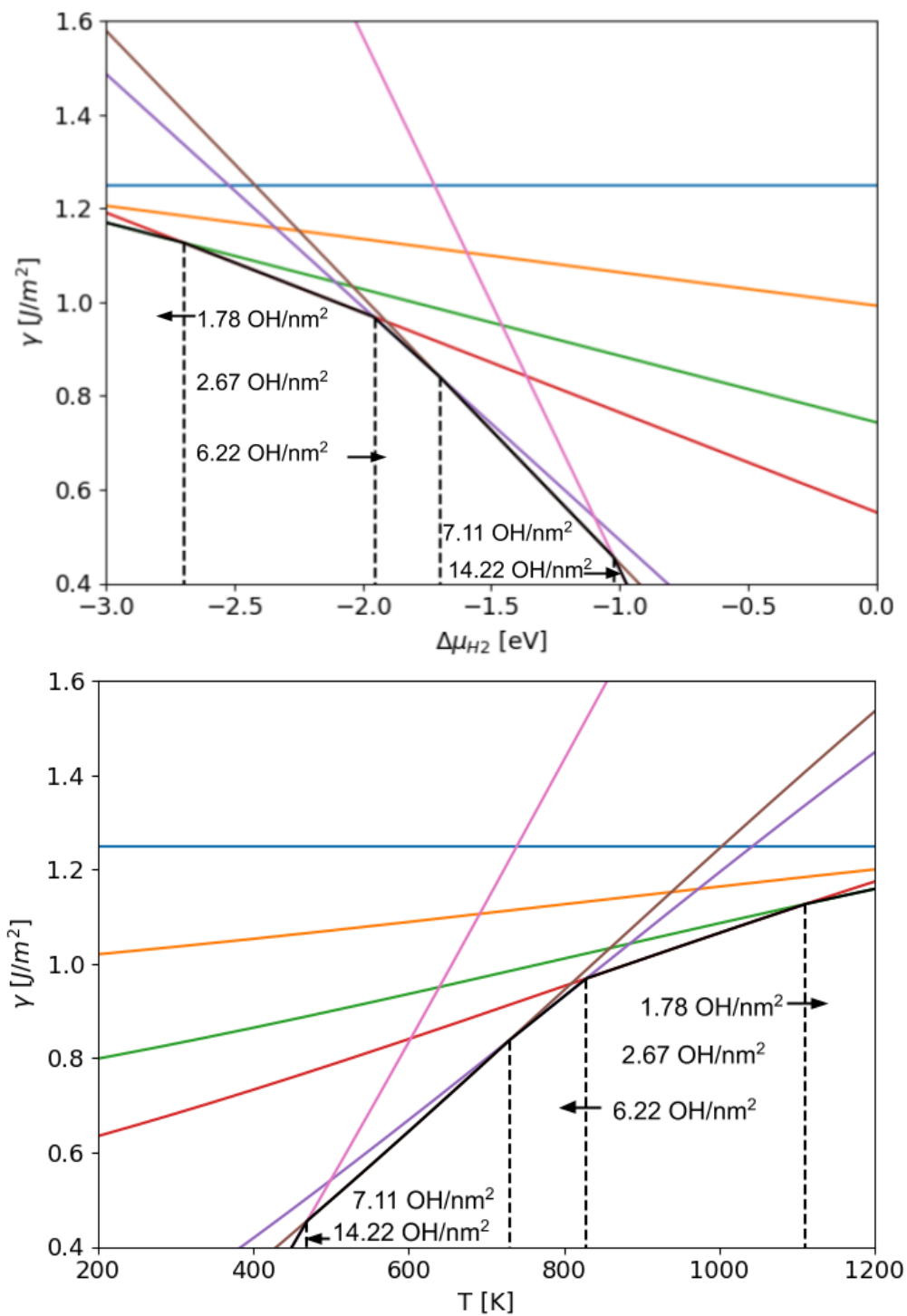
**Figure 5.** Surface stability diagram showing the most stable surface structure as a function of  $H_2$  and  $H_2O$  chemical potential and  $H_2/H_2O$  pressure at 423 K. The color scheme and numbering are the same as that in Figure 3. Regions are again classified in same three ways as those in Figure 3. (I) By surface Co concentration: blue:  $3.56 \text{ Co/nm}^2$ ; green:  $5.33 \text{ Co/nm}^2$ , and red/brown:  $7.11 \text{ Co/nm}^2$ . (II) By general appearance of surface hydroxylation: bottom bold line separates non-hydroxylated regions and hydroxylated regions and top bold line separates OH-only regions and molecular  $H_2O$ -containing structures. (III) By specific numbered structure (see Table 1 for descriptions, Table 2 for representative geometries, and Table S11 for all geometries).



**Figure 8.** Gas phase environmental conditions during vibrational characterization by Busca et al. represented as a dashed line on the  $H_2O/H_2$  surface stability diagram (Figure 5), as  $H_2O$  chemical potential is not well-defined. The corresponding termination should contain 7.11  $Co/nm^2$  and 7.11  $OH/nm^2$  (structure 7a, brown) because an unrealistic high pressure of  $H_2O$  must be applied to generate a mixed  $OH/H_2O$  layer (structure 12c, red).

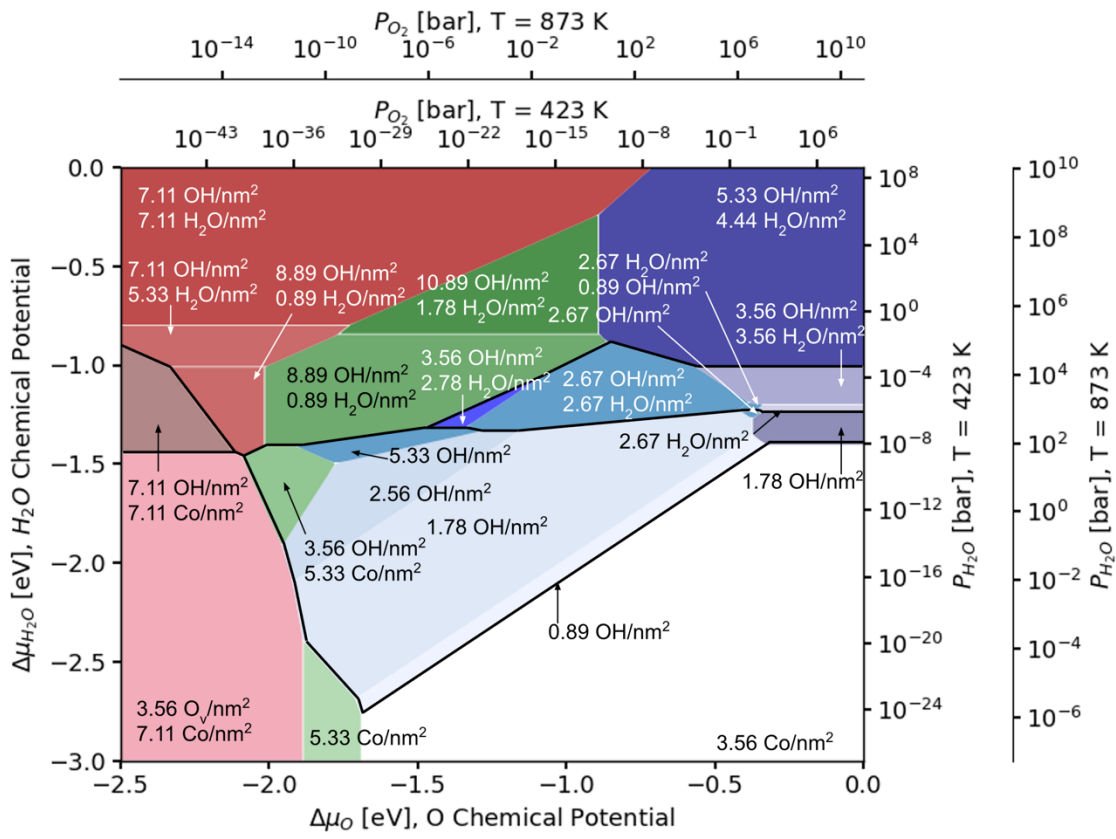


**Figure 12.** Surface stability diagram as a function of  $\text{H}_2$  and  $\text{H}_2\text{O}$  chemical potential and hydrogen/water pressure at 423 K. Conditions in NO reduction with  $\text{H}_2$  found in the literature are marked on the diagram as yellow circles.

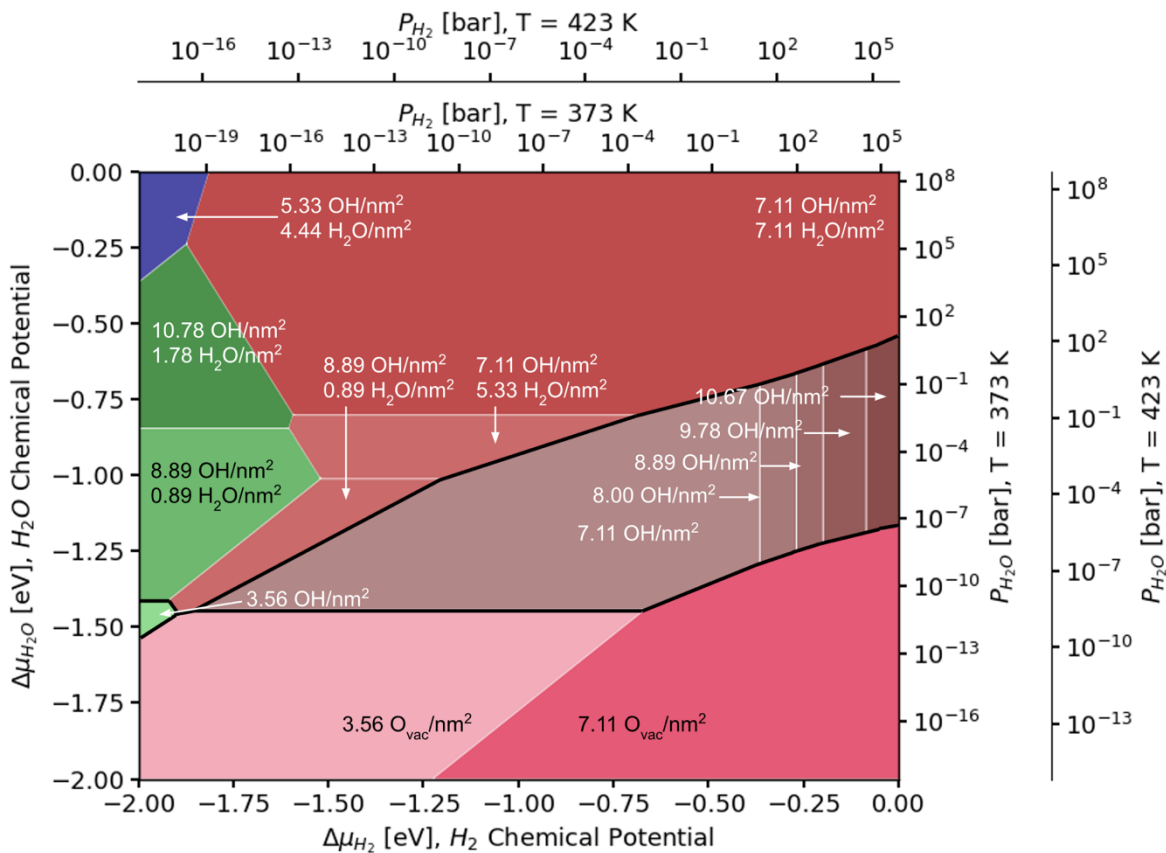


**Figure S3** Reduction of  $(Co^{Td})_x$  through  $H_2$  chemisorption at oxygen rich conditions,  $\Delta\mu_O = 0$  eV. Surface energy of is plotted as (top)  $\gamma(\Delta\mu_{H_2})$  and (bottom)  $\gamma(T, P_{H_2}=10^{-5}$  bar).





**Figure S9.** O<sub>2</sub>/H<sub>2</sub>O surface stability diagram with all regions labeled



**Figure S10.** Fully labeled H<sub>2</sub>/H<sub>2</sub>O surface stability diagram