

The energetics of oxygen adatoms, hydroxyl species and water dissociation on Pt(111)

Eric M. Karp and Charles T. Campbell*

Departments of Chemical Engineering and Chemistry, University of Washington, Box 351700,
Seattle Washington 98195-1700, USA

and

Felix Studt, Frank Abild-Pedersen and Jens K. Nørskov

SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory,
Menlo Park California 94025, USA

Department of Chemical Engineering, Stanford University, Stanford California 94305, USA

Abstract

Calorimetric measurements of the adsorption enthalpy of $O_{2,g}$ to make $2 O_{ad}$ on Pt(111) were performed by Fiorin et al.¹ However, we show that they used a calibration value for the optical reflectivity of Pt(111) that was incorrectly reported in the literature. This error in reflectivity led to a 40% error in the adsorption energies originally reported. We use our more accurate reflectivity of 76% to recalibrate their oxygen adsorption enthalpy data and show that it gives nearly identical results below 0.15 ML to the heats of adsorption determined from the temperature programmed desorption (TPD) experiments of two separate groups (Campbell et al.² and Parker et al.³). Differences arise above 0.15 ML, but we attribute these to the very low sticking probability of $O_{2,g}$ on Pt(111) (< 0.05) above 0.15ML, which can lead to large errors in the adsorption energies measured by calorimetry. Given this, we propose that the most reliable values for the adsorption enthalpy of oxygen on Pt(111) up to $\frac{1}{4}$ ML are those derived from TPD experiments, rather than the more recent calorimetry data. The best values are well described by $(217-151\theta)$ kJ/mol O_2 below $\frac{1}{4}$ ML, where θ is the O_{ad} coverage in ML (i.e., O_{ad} per Pt surface atom). We also report calculations of coverage-dependent adsorption energies for oxygen on Pt(111) from density functional theory (DFT) and find the results to be an average of 21 kJ/mol higher than the integral heats measured by TPD. We further use these corrected adsorption enthalpies to amend the energetics of hydroxyl species on Pt(111) that we previously measured⁴. This gives revised values for the standard enthalpies of formation of the coadsorbed $(D_2O-OD)_{ad}$ complex of -511 ± 7 kJ/mol and a Pt-OD bond energy of 248 ± 7 kJ/mol for the OD species within this complex. DFT compares reasonably well, calculating an enthalpy of formation for the $(H_2O-OH)_{ad}$ complex of -456 kJ/mol and an O-Pt bond energy of 217 kJ/mol for the OH species within this complex. These revised values are used to estimate reaction enthalpies for the dissociation of adsorbed water and hydroxyl on Pt(111), and compared to DFT.

* Corresponding author: Campbell@chem.washington.edu

1. The enthalpy of dissociative O_2 adsorption on Pt(111)

Beautiful calorimetric measurements of the adsorption enthalpy of $O_{2,g}$ to make $2 O_{ad}$ on Pt(111) were performed by Fiorin et al.¹ However, Fischer-Wolfarth et al.⁵ from Schauer mann and Freund's group at the Fritz-Haber Institute, in collaboration with our group, have since uncovered a systematic error in the calorimetry measurements on Pt(111) by Fiorin et al.. The

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error originates from their use of an incorrect value for the optical reflectivity of Pt(111) at 633 nm in calibrating the heat signal. Fiorin et al. used a reflectivity of 66% for Pt(111), based on an incorrectly reported value listed in the Handbook of Chemistry and Physics (see ref.⁶). Ref.⁶ claims that its reflectivity values came from Weaver (ref.⁷) but within ref.⁷ the actual reflectivity of Pt is reported as 75%.

From integrating-sphere measurements, we found the reflectivity of Pt(111) to be 76%⁸, very close to the values reported in Weaver's original paper⁷ and by Fischer-Wolfarth et al.⁵. If we use our more accurate reflectivity of 76% to recalibrate the oxygen adsorption enthalpy data originally reported by Fiorin et al. we obtain the corrected results versus coverage shown in Fig. 1. For comparison, we show the heat of adsorption as determined from activation energies for desorption of oxygen from Pt(111) measured in TPD experiments by two separate groups (Campbell et al.² and Parker et al.³) with nearly identical results. Here we assume that the activation barrier for adsorption is negligibly small (as indeed reported³), but add the required correction of $\frac{1}{2} RT$ (where T is the desorption temperature) described elsewhere.⁹ Note the near perfect agreement between the corrected calorimetric heats of adsorption and those determined by TPD below 0.15 ML. This same correction in reflectivity applied to the calorimetric heats of adsorption for CO on Pt(111) measured by Fiorin et al. also led to near perfect agreement with our own recent calorimetric measurements for CO on Pt(111) with Fischer-Wolfarth et al.⁵ For O₂, the difference that arises above 0.15 ML in Fig. 1 is likely because the sticking probability of O₂ on Pt(111) drops rapidly to < 0.05 at ~0.15ML, making it very difficult to accurately measure adsorption energies by calorimetry. Given this, we propose that the most reliable values for the adsorption enthalpy of oxygen on Pt(111) are those presented in Fig. 1 derived from those TPD experiments^{2,3} rather than the more recent calorimetry data, except below 0.15 ML where they agree after this calibration correction (but were approximately 40% too high as originally reported)¹.

We calculated oxygen adsorption enthalpies on Pt(111) for different coverages ranging from 1/36 to 1/2 monolayers (ML) using density functional theory(DFT), with O_{ad} always in 3-fold hollow sites and at the greatest possible O-O separations. DFT calculations were performed using the GPAW code¹⁰, and the RPBE functional¹¹ including zero-point energy (ZPE) corrections, with a grid spacing of 0.18 Å. Surfaces were modeled by four layers, where the two bottom layers were fixed to their bulk positions while the top two layers and the adsorbates were allowed to relax. A *k*-point sampling of 4x4x1, and 2x2x1 was used for slabs consisting of 2x2 and 3x3, and 4x4 and 6x6 Pt atoms in the x and y direction, respectively. The energy of gas-phase O₂, for which the RPBE functional performs poorly, was calculated using the DFT energies for H₂ and H₂O and the literature value for the reaction energy for 2 H₂ + O₂ → 2 H₂O, as described elsewhere¹². Fig. 1 shows the integral heats of adsorption for O₂ on Pt(111) by DFT. The calculated heat of adsorption extrapolates to -237 kJ/mol in the low-coverage limit, but decreases to -217 kJ/mol at 1/4 ML and -163 kJ/mol at 1/2 ML (Note that the adsorption energies oscillate slightly with coverage in the low coverage regime. The values presented here are calculated by the best fit curve through the adsorption energies; see Figure 1). As seen, these

heats are ~ 20 kJ/mol larger than the experimental heats by TPD below $\frac{1}{4}$ ML. Getman and Schneider¹³ also calculated coverage-dependent adsorption energies for oxygen on Pt(111) using DFT. Their results were ~ 18 kJ/mol higher than our DFT results presented in Fig. 1 but otherwise produced a nearly identical trend in adsorption enthalpy vs. coverage. The small difference may be associated with differences in the details of the calculation method and/or ZPE corrections.

2. Using the corrected adsorption enthalpy for O_{ad} to revise the energetics of the $(H_2O-OH)_{ad}$ complex and related hydroxyl species on Pt(111)

In our previous study of the heat of reaction of D_2O with oxygen-dosed Pt(111), a thermodynamic cycle was constructed using measured reaction heats to calculate the standard heats of formation, ΔH_f° , of the coadsorbed (D_2O-OD) complex and adsorbed OD, and from that the Pt(111)-OD bond enthalpy (Figure 5 within ref⁴). This cycle used a value of -266 kJ/mol for the integral adsorption enthalpy of $O_{2,g}$ at 0.17 ML of O_{ad} , which was obtained from calorimetric measurements on Pt(111) from Fiorin et al.¹, but which we noted above included a calibration error. We now use these more reliable values from TPD in Fig. 1 to amend these standard enthalpies of formation of the coadsorbed (D_2O-OD) complex and adsorbed OD and the Pt(111)-OD bond enthalpy we reported in ref.⁴. Replacing the value of -266 kJ/mol for the integral adsorption enthalpy of $O_{2,g}$ at 0.17ML of O_{ad} from the uncorrected calorimetry data of Fiorin et al. with the value of -204 kJ/mol from Fig. 1 based on TPD data, we obtain the improved values listed in Table 1, along with the original values reported in ref.⁴ for comparison. The value for OD_{ad} within the (D_2O-OD) complex was estimated from ΔH_f° for this complex, assuming that the D_2O in this complex has the same ΔH_f° as the most stable structure of a pure D_2O adlayer, as originally done in ref.⁴. Table 1 also includes our calorimetric results for ΔH_f° of D_2O_{ad} in its most stable (i.e., high-coverage) structure on Pt(111) -293 ± 7 kJ/mol.¹⁴ Experimental values for isolated species were estimated from these high-coverage structures by correcting for the energy change with coverage estimated from DFT (see below).

These measurements report the energetics of deuterated hydroxyl and water, from which we can also calculate the energetics of the corresponding H isotope by correcting for the zero-point energy difference between Pt-OD and Pt-OH. Using known vibrational frequencies for H-H, D-D, O-H and O-D stretches¹⁵ the zero-point reaction energy difference between $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ and $D_2 + \frac{1}{2} O_2 \rightarrow D_2O$ is 5.2 kJ/mol in the gas phase, resulting in a difference of 2.6 kJ/mol in the heat of formation for each OH bond in the products (with OH species being less stable than the corresponding OD species). This implies that the standard heats of formation of the coadsorbed (H_2O-OH) complex and adsorbed OH should be smaller than their D analogues by 7.8 and 2.6 kJ/mol, respectively. Values for these H isotope species calculated from the D isotope results using these zero-point corrections are also listed in Table 1.

3. DFT values for the formation enthalpies of the $(H_2O-OH)_{ad}$ complex and hydroxyl species on Pt(111)

Table 1 also includes our DFT results for the heats of formation of the coadsorbed (H₂O–OH) complex, adsorbed H₂O and adsorbed OH on Pt(111). The results in Table 1 show that the (H₂O–OH)_{ad} complex is ~47 kJ/mol less stable by DFT than in the experiment, but this error drops to only 20 kJ/mol after subtracting the enthalpy of adsorbed water to estimate the heat of formation of the OH_{ad} within this (H₂O–OH)_{ad} complex. Note that our calculations of OH_{ad} in a water environment on Pt(111), using this same DFT method, were also found to be in good agreement with electrochemical measurements of the oxygen reduction reaction on Pt(111).^{16,17} Our calculated DFT adsorption energy for high-coverage H₂O is for a $\sqrt{3}$ structure at 2/3 ML, which is known to give a DFT adsorption energy very close to that in the more complex, slightly higher-coverage ($\sqrt{39} \times \sqrt{39}$)R16.1° structure¹⁸. This DFT value in Table 1 gives high-coverage H₂O_{ad} to be ~19 kJ/mol less stable than the experimental value.

Experimental values for “isolated” adsorbates could not be measured but are available with DFT. To provide our best estimate of experimental values in the low-coverage limit, the measured values for the high-coverage case were corrected by adding the energy difference between this and the low-coverage limit as estimated by DFT, shown in parentheses in Table 1.

4. Estimates of O–Pt(111) bond enthalpies for surface O, OH and H₂O, and comparison to DFT

Table 1 also lists the experimental and DFT values for the O–Pt(111) bond enthalpies for adsorbed O_{ad}, OH_{ad} and H₂O_{ad}, calculated from the difference between their heats of formation listed here and that for the corresponding gas-phase species. Bond enthalpies to Pt(111) are thus defined here to include all metal-adsorbate and adsorbate-adsorbate interaction energies. As seen, the O–Pt(111) bond enthalpy for OH_{ad} within (H₂O–OH)_{ad} complex is ~31 kJ/mol weaker according to DFT than the experimental value of 248 kJ/mol; and that for H₂O_{ad} is ~16 kJ/mol weaker according to DFT than the experimental value of 46 kJ/mol. The difference is most likely due to small errors in calculating the binding of H₂O to the Pt(111) surface. Most of this interaction is due to van der Waals forces that are not described well by the functional used in this study. (When we instead used BEEF, a functional that is known to describe van der Waals interactions better¹⁹ the binding energy of H₂O to the Pt(111) surface in the low coverage regime increases by 24 kJ/mol, much closer to experiment.)

5. Enthalpies for reactions involving surface hydroxyls on Pt(111)

The enthalpies of formation in Table 1 allow us to estimate reaction enthalpies ($\Delta H^{\circ}_{\text{rxn}}$) for the following reactions involving surface hydroxyls on Pt(111):



and



The values listed above were calculated using the experimental values of ΔH_f^0 each adsorbate in its most stable structures, which for O_{ad} and H_{ad} are the low-coverage limits, but for H_2O_{ad} is its high-coverage structure and for OH_{ad} is in the $(H_2O-OH)_{ad}$ complex. These elementary steps have been proposed to take place in many important catalytic reactions over Pt. Note that Reactions (1) and (2) are rather endothermic, and therefore probably rather slow steps in these catalytic mechanisms.

Table 2 summarizes these reaction energies, and compares them to values based on DFT energies and values for the adsorbates in their low-coverage limit, estimated as described. The energy for Reaction (1) is accurately estimated with DFT, but Reaction (2) is less uphill by 27 kJ/mol, and Reaction (3) is estimated to be 14 kJ/mol exothermic by DFT, but 17 kJ/mol endothermic experimentally.

The reaction energies in Table 1 can also be compared to earlier DFT calculations by Mavrikakis's group, who found the following energies for Reactions (1) through (3) at 1/4ML coverage of 50 kJ/mol, 15 kJ/mol, and -36 kJ/mol, respectively.²⁰

In summary, we corrected the enthalpy of O_2 adsorption using our more accurate reflectivity of 76% and show that it gives nearly identical results below 0.15 ML to the heats of adsorption determined from TPD experiments.^{2,3} We further use these corrected adsorption enthalpies to amend the energetics of hydroxyl species on Pt(111) that we previously measured²¹, giving revised values for the standard enthalpies of formation of the coadsorbed (H_2O-OH) complex of -503 ± 7 kJ/mol. From this, we estimate a O-Pt(111) bond enthalpy in adsorbed hydroxyl of 248 ± 7 kJ/mol within this complex. This value is an upper bound, since it assumes that the H-bonding interactions between OH_{ad} and H_2O_{ad} are the same in the complex as in a pure H_2O adlayer, but the very fact that OH_{ad} and H_2O_{ad} combine into a stable 1:1 complex proves they are more stable in the complex. Using the difference in DFT values for the O-Pt(111) bond enthalpies for OH_{ad} of 217 kJ/mol within the (H_2O-OH) complex (estimated with this same assumption) and of 179 kJ/mol for isolated OH_{ad} to approximately correct this assumption gives an estimate of 210 ± 7 kJ/mol for the experimentally measured O-Pt(111) bond strength in isolated OH_{ad} . These revised values are used to estimate reaction enthalpies for the dissociation of adsorbed water and hydroxyl on Pt(111). The DFT value for water is in good agreement, but the DFT value for OH_{ad} dissociation is 27 kJ/mol less endothermic

Table 1. Standard enthalpies of formation at 298 K (ΔH_f^0) of O adatoms, adsorbed hydroxyl and the coadsorbed hydroxyl-water complex (both D and H isotopes) on Pt(111) at the specified coverages, and the corresponding O-Pt(111) bond enthalpies calculated from the corrected enthalpy of O₂ adsorption (TPD-based data in Fig. 1) and the thermodynamic cycle of Figure 5 within ref.⁴. Numbers in italics are the original values reported in ref. ⁴ before correction (which in the case of O_{ad} corresponds to the uncorrected heats originally reported by Fiorin et al.¹). Values for OD_{ad} and OH_{ad} were estimated from the values for the corresponding hydroxyl-water complex, assuming that the water in this complex has the same heat of formation as the most stable structure of a pure water adlayer, as describe in ref.⁴. Conversion of experimental enthalpies, which were all for the D isotope, to the H isotope used the known difference in zero-point energies, as described in text.

Adsorbate	Coverage (ML)	Experimental ΔH_f° (kJ/mol)	O-Pt(111) Bond Enthalpy (kJ/mol)	DFT ΔH_f° (kJ/mol)	DFT O-Pt(111) Bond Enthalpy (kJ/mol)
O_{ad}	0 ML	-109 ± 7 (-150 ± 7)	$358 \pm 7^*$	-119	-362
	0.17 ML	-102 ± 7 (-133 ± 7)	$351 \pm 7^*$	-114	-357
	0.25 ML	-99 ± 7 (-125 ± 7)	$348 \pm 7^*$	-109	-352
$(D_2O-OD)_{ad}$	1/3 ML	-511 ± 7 (-527 ± 7)	-	-	-
$(H_2O-OH)_{ad}$	1/3 ML	-503 ± 7	-	-456	-
OD_{ad} within $(D_2O-OD)_{ad}$ complex	1/3 ML	-210 ± 7 (-226 ± 7)	248 ± 7 (263 ± 7)	-	-
OH_{ad} within $(H_2O-OH)_{ad}$ complex	1/3 ML	-207 ± 7	248 ± 7	-187	217**
D_2O_{ad} High Coverage	$\sim 2/3$ ML	-293 ± 7	51.3 ± 7	-	-
H_2O_{ad} High Coverage	$\sim 2/3$ ML	-288 ± 7	46.2 ± 7	-269	30
H_2O_{ad} Isolated	1/16 ML	$(-268 \pm 7)^{***}$	$(26.2 \pm 7)^{***}$	-249	10
OH_{ad} Isolated	1/16 ML	$(-169 \pm 7)^{***}$	$(210 \pm 7)^{***}$	-149	179**
H_{ad} Isolated	$\sim 1/16$ ML	-36	-	-33	-

* The bond enthalpies listed here for O_{ad} are the entire O-Pt(111) bond enthalpy, which sums the bonding to three Pt atoms since O_{ad} sits in a 3-fold hollow site.²² We use here the known standard heat of formation of O_g of 249.2 ± 0.1 kJ/mol.²³ Bond enthalpies for adsorbed hydroxyl and water to Pt(111) are defined here to include all adsorbate-adsorbate interaction energies.

** This uses the DFT value for $\Delta H_f^\circ(OH_g)$ of 30.3 kJ/mol. (The experimental value is 39.0 kJ/mol)²⁴

*** The experimental values for “isolated” adsorbates are written in parentheses here, since they were estimated by correcting the measured value for the high-coverage case by adding the energy difference between this and the low-coverage limit as estimated by DFT.

Table 2. Reaction enthalpies ($\Delta H_{\text{rxn}}^{\circ}$) on Pt(111) for three reactions involving adsorbed OH, comparing experimental values with those estimated by DFT on Pt(111) terraces. These reaction heats were calculated from the heats of formation of all the adsorbates in two situations with respect to surface coverage: in their lowest-coverage state and in their most stable situation, which for $\text{H}_2\text{O}_{\text{ad}}$ corresponds to the high-coverage pure water adlayer and for OH_{ad} corresponds to its presence in the coadsorbed ($\text{H}_2\text{O-OH}$) complex, assuming that the water in this complex has the same heat of formation as in that most stable pure water adlayer. (Note that this “most stable” case is equivalent to replacing each OH_{ad} in each reaction as written below with $(\text{H}_2\text{O-OH})_{\text{ad}}$, and adding an $\text{H}_2\text{O}_{\text{ad}}$ to the other side of the reaction, which is a more rigorous way to represent these reaction in that case.) The experimental values were only determined in this “most stable” situation. The experimental low-coverage limits are written in parentheses here, since they were estimated by correcting this $\Delta H_{\text{rxn}}^{\circ}$ value for the most stable case by adding the difference in $\Delta H_{\text{rxn}}^{\circ}$ between this and the low-coverage limit as estimated by DFT.

Reaction	Coverage	Experimental ΔH_{rxn} (kJ/mol)	DFT ΔH_{rxn} (kJ/mol)
$\text{H}_2\text{O}_{\text{ad}} \rightarrow \text{OH}_{\text{ad}} + \text{H}_{\text{ad}}$	Low-Coverage Limits	(63)	67
	Most Stable Adsorbates	45	49
$\text{OH}_{\text{ad}} \rightarrow \text{O}_{\text{ad}} + \text{H}_{\text{ad}}$	Low Coverage Limits	(24)	-3
	Most Stable Adsorbates	62	35
$2\text{OH}_{\text{ad}} \rightarrow \text{O}_{\text{ad}} + \text{H}_2\text{O}_{\text{ad}}$	Low-Coverage Limits	(-39)	-70
	Most Stable Adsorbates	17	-14

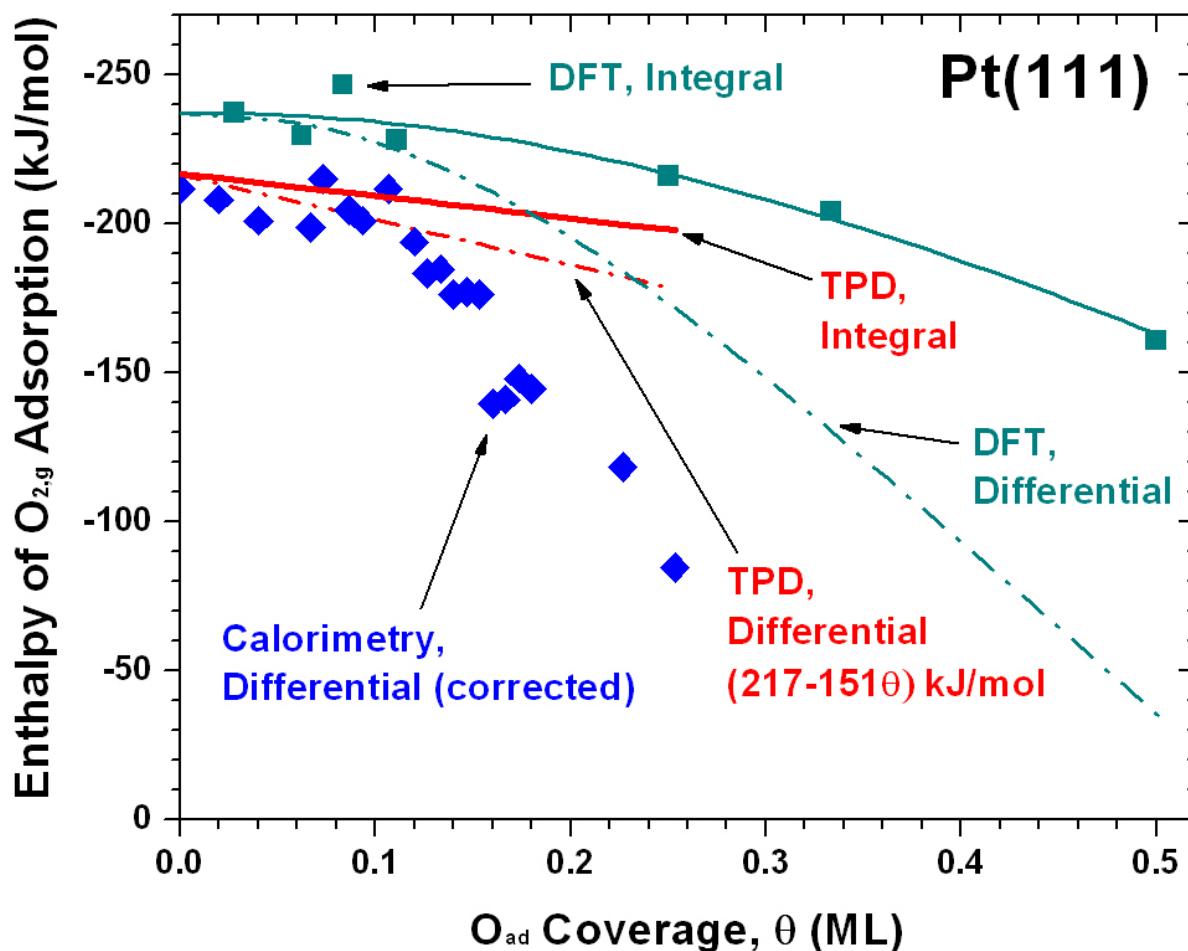


Figure 1. The enthalpy of $O_{2,g}$ adsorption on Pt(111) versus O_{ad} coverage measured by Fiorin et al. using single crystal adsorption calorimetry¹, after correction for an error in reflectivity as described in text (filled diamonds) compared to that determined from the TPD experiments of ref² and ³ (solid line). We have averaged the TPD measurements of ref² and ³ and added $\frac{1}{2} RT$ for direct comparison to adsorption enthalpies, as described in text, giving $\Delta H_{ads} = (217-151\theta)$ kJ/mol, where θ is the coverage. Also presented is the integral heat of adsorption calculated by DFT as a function of coverage (filled squares) and, for comparison, the integral heat of adsorption from TPD (dashed line). The inset focuses on the region from 0 to 0.25ML of O_{ad} coverage, which is the maximum coverage reached in most ultrahigh vacuum experiments.

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