Supporting Information: How to extract adsorption energies, adsorbate-adsorbate interaction parameters and saturation coverages from temperature programmed desorption experiments

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SI Note 1: Fitting TPD

The following analysis was applied to obtain all parameters used in **Figure 1** from TPD experiments.

1. Images of TPD curves were taken from Ref [1,2]. Webplotdigitizer[3] was used to convert the images into discrete points.
2. The background signal due to pumping of CO was determined by fitting an exponential function to the "tail" of each TPD curve.

$$\frac{d\theta_{(T)}}{dt} = A\exp(-kT) \tag{1}$$

where A, k, T were obtained from the fit. The curve fitting was done through *scipy.optimize.minimize*[4], where the least square residuals were minimized. In cases where the exponential background generated a negative signal for the terraces, a constant background from the first point was used. Results of the fit and corresponding normalized TPD are shown in **Figure S 1**.

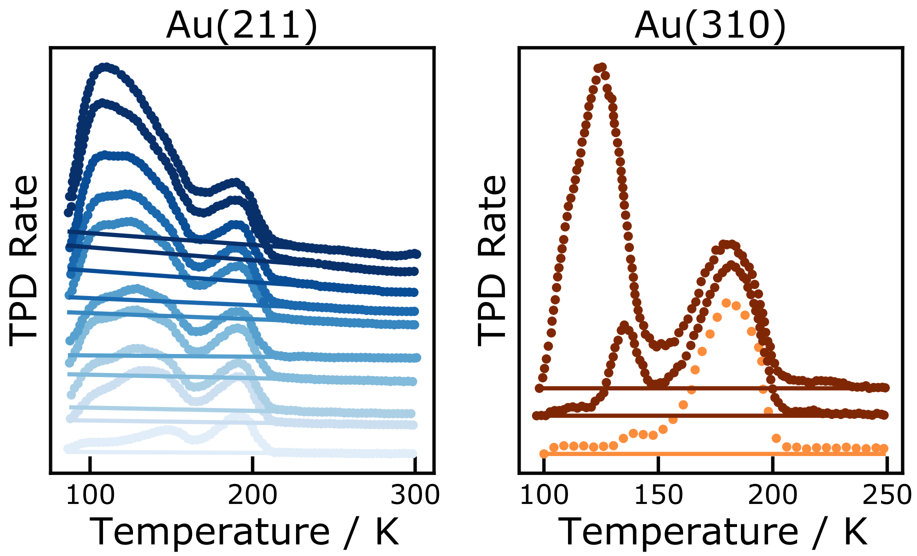

Figure S 1: Fitted background of Temperature Programmed Desorption curves for Au(211) and Au(310) and corresponding normalized TPD curves

3. Relative coverages (θ_{rel}) were obtained by numerically integrating the rate over the TPD temperature range with Eq. (2) of the main text,

$$\theta_{rel(T)} = \frac{\int_{Tmin}^{T} \frac{d\theta}{dT} dT}{\int_{Tmin}^{Tmax} \frac{d\theta}{dT} dT} \qquad (2)$$

Numerical integration was carried out by using the *numpy.trapz*[4] module. The rate of change of coverage with time $\frac{d\theta_{rel}}{dt}$ was determined as a function of the temperature by multiplying the rate with the experimental heating rate β.

4. The desorption energy as a function of the temperature for a first order process such as CO desorption is given by the following equation (rearranged from Eq. 1 in the main text)

$$G_d = -k_B T \log\left(-\frac{\frac{d\theta_{(T)}}{dt}}{\nu\theta_{(T)}} \right) \tag{3}$$

Where ν is the pre-factor for the reaction. Here we assume that the pre-factor is $\frac{k_B T}{h}$.

G_d can be written as follows

$$G_d = \Delta E_{\theta\rightarrow 0} - b\theta_{rel}\theta_{sat} - k_b T \ln\left(\frac{\theta_{rel}\theta_{sat}}{1 - \theta_{rel}\theta_{sat}}\right) \forall\, \theta_{rel} \tag{4}$$

the parameters θ_{sat} and $\Delta E_{\theta\rightarrow 0}$ are fit to G_d values for different exposures. The fitted curves are shown in **Figure S 2** for (211) and (310). The curves for the step sites fit the points well, while there are significant deviations for the terraces. This error in fit is likely due to adsorbate-adsorbate interactions between the CO^* on step and terrace sites. These interactions are missing in the high temperature ranges where CO^* is almost exclusively on the step.

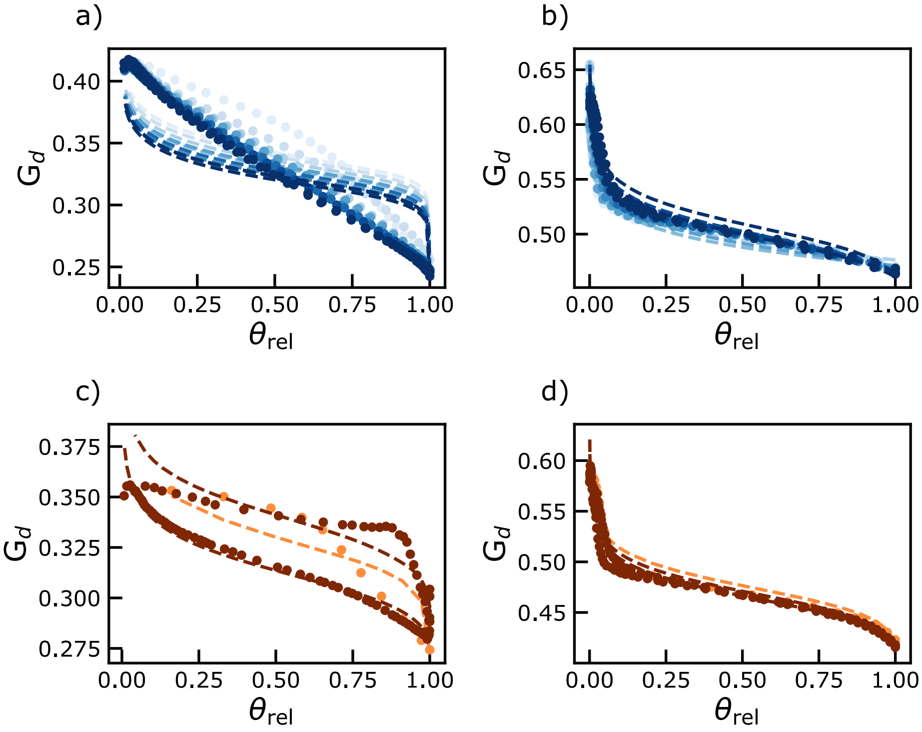

Figure S 2: Fitted desorption energy with relative coverage for a) first peak of (211) TPD b) Second peak of (211) TPD c) First peak of (310) TPD d) Second peak of (310) TPD

The saturation coverage based on the fit are shown in **Figure S 3** for all exposures.

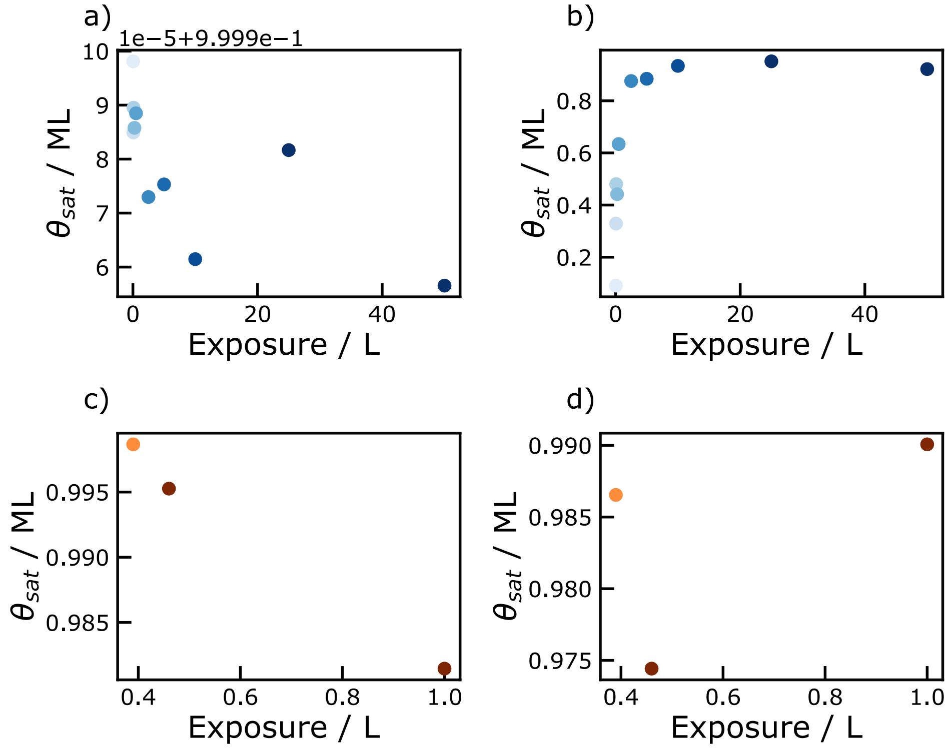

Figure S 3: Fitted saturation coverage for a) first peak of (211) TPD b) Second peak of (211) TPD c) First peak of (310) TPD d) Second peak of (310) TPD

Finally, the equilibrium overage can be determined by adding the entropic contributions to G_d

$$\Delta G_{CO^*(\theta,T)} = -G_{d(\theta,T)} - T\left(S_{CO^*}^{harm} - S_{CO(g)}^{ideal}\right) \quad (5)$$

The frequencies used are tabulated below and entropies are calculated using the Harmonicthermo and IdealGasThermo modules of ASE[5].

Table S1: Vibrational frequencies for gas phase and adsorbed species

Species	**Vibrational Frequencies (cm^{-1})**
$CO_{(g)}$	2121.52, 39.91, 39.45
CO^* on $Au(111)$	2084.8, 201.7, 110.3, 110.2, 70.7, 70.8
CO^* on $Au(211)$	2044.1, 282.2, 201.5, 188.5, 38.3, 11.5

$CO^{*}on\ Au(100)$	1886.5, 315.2, 273.4, 222.2, 152.7, 49.8
$CO^{*}on\ Au(110)$	2054.5, 262.9, 183.4, 147.3, 30.9, 30.

In comparison, the Redhead equation requires only the peak position of the TPD. However, it provides no information on coverage dependence of adsorption energy. For a given peak temperature T_p, the desorption energy, $\Delta E_{\theta\rightarrow 0}$ can be written as,

$$\Delta E_{\theta\rightarrow 0} = k_B T_p \ln\left(\frac{\nu T_p}{\beta} - 3.64\right)$$

The peak temperature for Au(211) was reported as 197 K, which means $\Delta E_{\theta\rightarrow 0} = 0.58$ eV

Finally, we test if our assumption of linear adsorbate-adsorbate interaction strength is reasonable in the context of CO* on gold. Instead of Equation 3 in the main text we use the following non-linear expression

$$G_d(\theta, T) \approx \ \Delta E_{\theta\rightarrow 0} - b_1\theta - b_2\theta^2 - k_b T \ln\left(\frac{\theta}{1-\theta}\right)$$

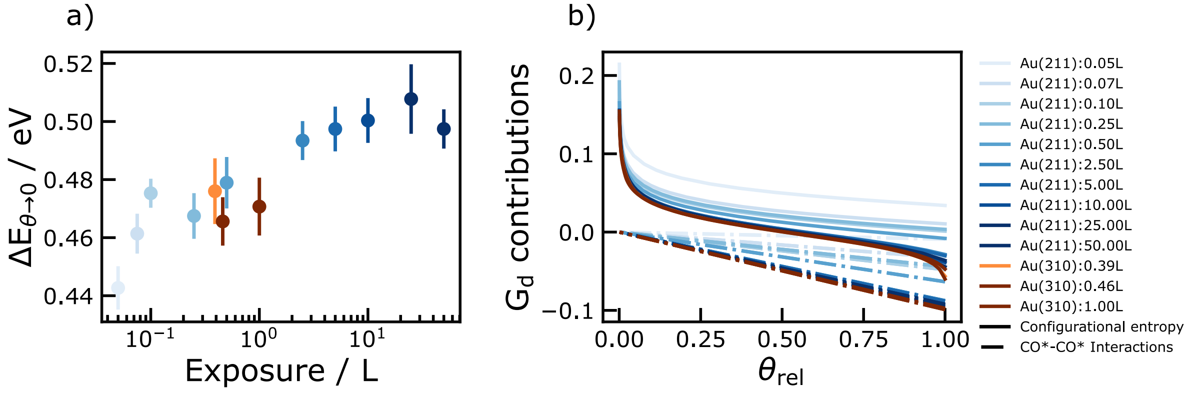

Figure S 4: Components of the free energy obtained using a non-linear energy dependence with coverage

Comparing **Figure 2** with **Figure S 4**, we find that there is little change in the numerical value of all the parameters. Furthermore, the CO*-CO* interaction parameters resembles linear behavior. The only change that we see between the two figures is lowering of the error bars associated with the fitting, which is simply due to the addition of one extra free parameter. Based on this test, we believe that the simple way of including just linear adsorbate-adsorbate interactions is justified in our case.

SI Note 2: CO adsorption under atmospheric conditions

***Energetics of CO desorption*:** Desorption energies were estimated from the Temperature Programmed Desorption (TPD) experiments under the assumption that the transition state for CO desorption was very similar to $\mathrm{CO}_{(g)}$ in vacuum. To evaluate this assumption, we examine the energy along the reaction path for the desorption of a $\mathrm{CO}_{(g)}$ to Au(211). Geometries were obtained using Climbing-Image Nudged Elastic Band (ci-NEB) calculations[6], as implemented within VASP. Forces on the climbing image were considered converged if they are lower than $0.05 \mathrm{eV\AA^{-1}}$.

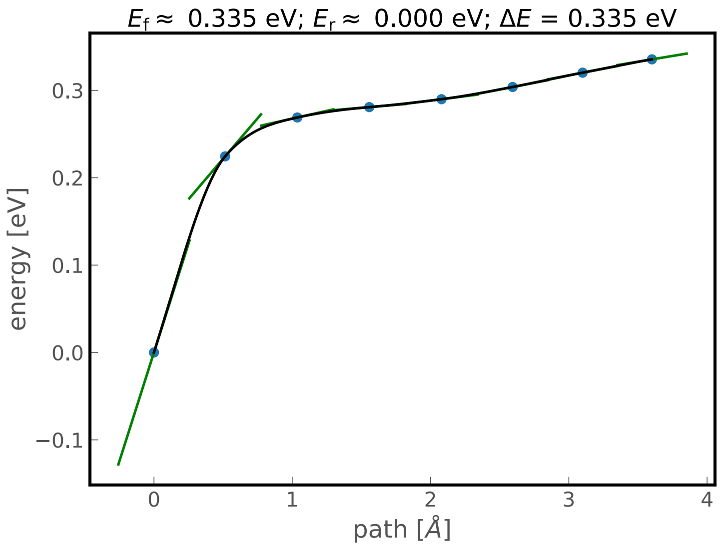

Figure S 5: Climbing image NEB for CO adsorption for Au(211)

The final state was chosen as CO far away from the surface and the intial state was CO bound to the top site of Au(211). **Figure S 5** shows that there was no discernable transition state associated with this process. Initially, there is by a jump in energy associated with CO bonding to the surface, followed by there is a long Van-der-Waals region associated with a change in energy of 0.1eV. We have therefore assumed in our TPD analysis, that the electronic energy of the desorbed CO in gas phase, $E_{\mathrm{CO(g)}}$ to be equivalent to $E_{\mathrm{CO^{TS}}}$

Free energy contributions in differential free energy: We describe here how to convert from differential energy to the differential free energy as was done in **Figure 4b.**

$$\Delta G_{\mathrm{diff}} = \Delta E + \Delta ZPE - T\left(S_{CO^*}^{harm}(\theta_2) - S_{CO^*}^{harm}(\theta_1)\right) - T(S_{\mathrm{config}}(\theta_2) - S_{\mathrm{config}}(\theta_1))$$

Where $S_{CO^*}^{harm}$ was approximated using frequencies in **Table S1.** The integral configuration entropy can be written as[7]

$$S_{config}^{integral} = -k\ln\left(\frac{\theta}{1-\theta}\right) - \frac{k}{\theta}\ln(1-\theta)$$

References

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Note 3: Supplementary Tables

Table S2: Fit parameters for low temperature range of Au(211)

Exposure (L)	**Temperature Range (K)**	**$\Delta E_{\theta\rightarrow 0}$ (eV)**	**Residual (eV)**	**b (eV)**
0.05	[0, 170]	0.34	0.096	0.16
0.075	[0, 170]	0.34	0.085	0.15
0.1	[0, 170]	0.34	0.084	0.16
0.25	[0, 170]	0.33	0.089	0.16
0.5	[0, 170]	0.33	0.084	0.16
2.5	[0, 170]	0.32	0.089	0.16
5.0	[0, 170]	0.33	0.089	0.17

10.0	[0, 170]	0.32	0.092	0.16
25.0	[0, 170]	0.32	0.091	0.17
50.0	[0, 170]	0.32	0.091	0.16

Table S3: Fit parameters for high temperature range of Au(211)

Exposure (L)	**Temperature Range (K)**	$\boldsymbol{\Delta E_{\theta\to 0}}$ **(eV)**	**Residual (eV)**	**b (eV)**
0.05	[170, 250]	0.44	0.009	0.13
0.075	[170, 250]	0.46	0.017	0.12
0.1	[170, 250]	0.48	0.018	0.13
0.25	[170, 250]	0.47	0.021	0.12
0.5	[170, 250]	0.48	0.027	0.12
2.5	[170, 250]	0.49	0.032	0.14
5.0	[170, 250]	0.5	0.03	0.13
10.0	[170, 250]	0.5	0.036	0.14
25.0	[170, 250]	0.51	0.037	0.14
50.0	[170, 250]	0.5	0.034	0.14

Table S4: Fit parameters for low temperature range of Au(310)

Exposure (L)	**Temperature Range (K)**	**$\Delta E_{\theta \to 0}$ (eV)**	**Residual (eV)**	**b (eV)**
0.46	[0, 150]	0.34	0.038	0.05
1.0	[0, 150]	0.31	0.034	0.07

Table S5: Fit parameters for high temperature range of Au(310)

Exposure (L)	**Temperature Range (K)**	$\boldsymbol{\Delta E_{\theta \to 0}}$ **(eV)**	**Residual (eV)**	**b (eV)**
0.46	[150, 240]	0.47	0.043	0.13
1.0	[150, 240]	0.47	0.045	0.13