

# Supporting Information for Publication

## Reverse Spillover Dominating CO Adsorption on Single Cobalt Atoms in Graphene di-Vacancies

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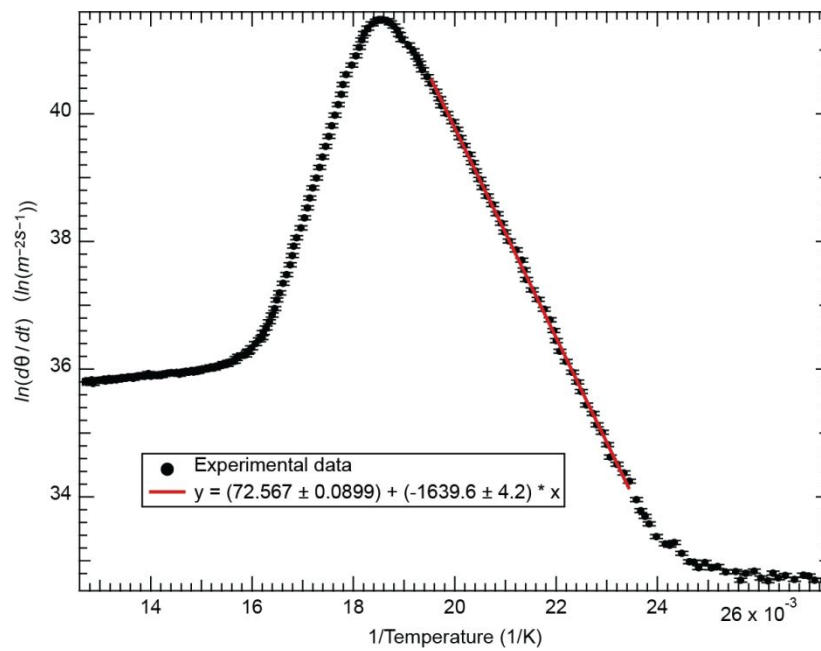


Figure S1. CO TDS spectrum of the Gr/Ni(111) sample acquired after dosing 1.0 L of CO at 30 K (heating rate 1 K/s). The desorption peak is attributed to CO desorption from pristine Gr. In the graph we plot the natural logarithm of the desorption rate ( $\ln(d\theta/dt)$ ) as a function of  $1/T$ . From the linear fit (red line), performed in the low-temperature part of the peak, it is possible to extrapolate the attempt frequency ( $\nu_{0,d}$ ) and desorption energy ( $E_d$ ):  $\ln\left(\frac{d\theta}{dt}\right) = \ln(\nu_{0,d}\theta^0) - \frac{E_d}{k_B}\left(\frac{1}{T}\right)$ .  $\theta^0$  is the CO coverage on pristine Gr at  $t = 0$ .  $E_d = (141 \pm 1)$  meV;  $\nu_{0,d} = (7.1 \pm 0.4) \times 10^{12}$  Hz

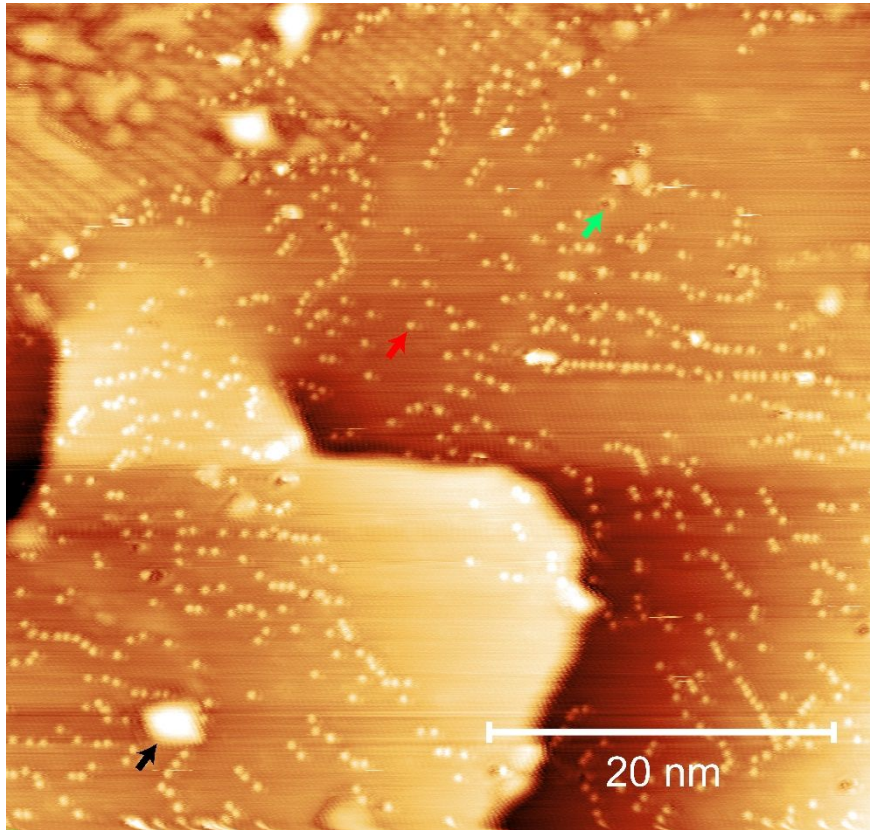


Figure S2. : Room temperature STM image representative of the Gr/Ni(111) sample. Both aligned (center-bottom) and rotated domains (top left) are visible, together with Ni@Gr (red arrow, 1.6 % ML) and dark depression (green arrow), attributed to graphene carbon vacancies. Bigger protrusions (black arrow) are associated to Gr bubbles. In rotated domains, the lower Gr-Ni interaction allows carbon segregation from the bulk. The formation of  $\text{Ni}_2\text{C}$  at the interface lifts the Gr sheet, which becomes almost freestanding.<sup>1,2</sup>

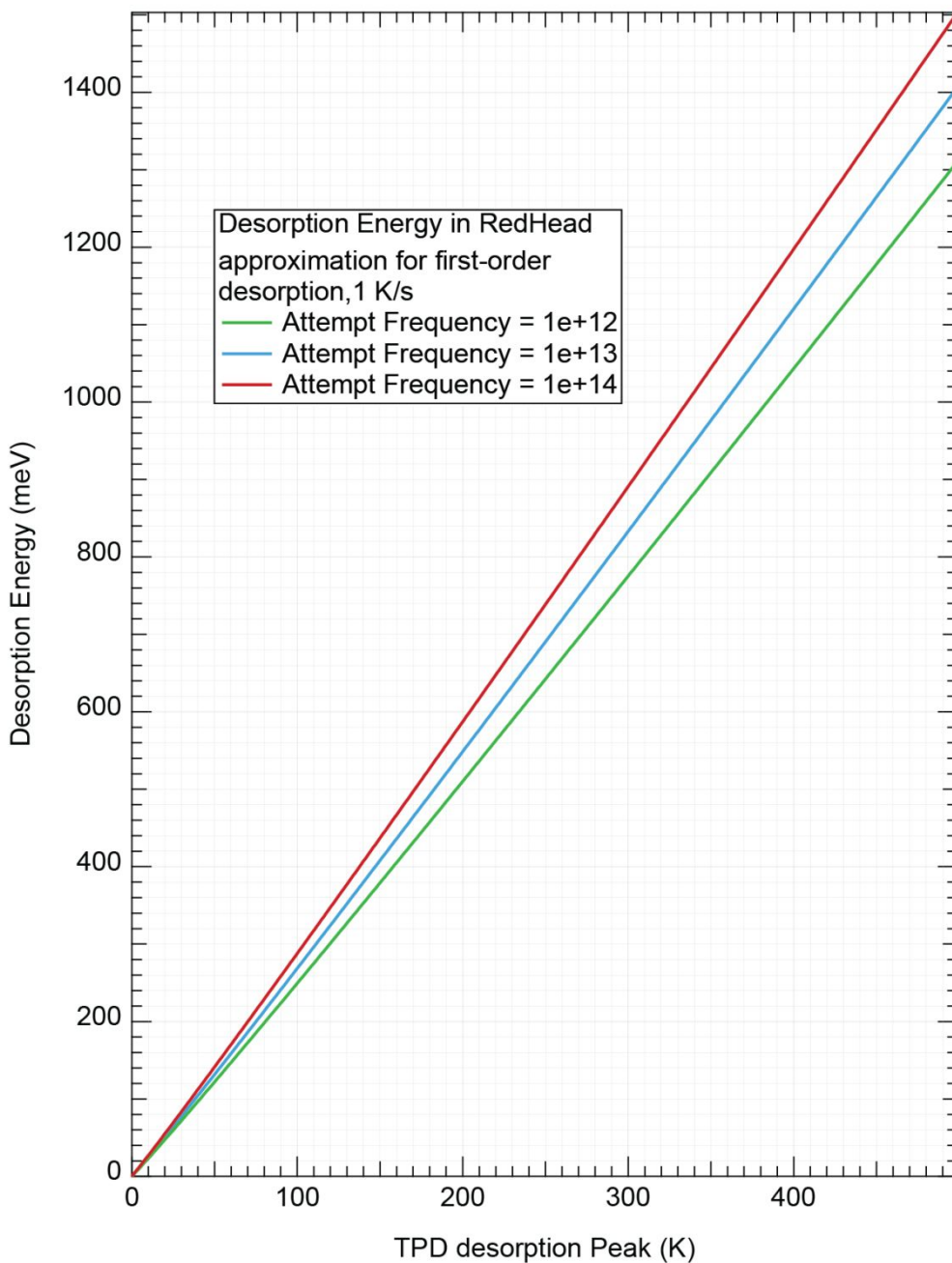


Figure S3. : The graph shows the relationship between the temperature of a first order desorption peak ( $T_m$ ) in a TDS experiment (i.e., corresponding to the maximum desorption rate) and the desorption energy ( $E$ ) determined by solving the Redhead approximation given below.<sup>3</sup> This solution is obtained numerically, for a heating rate of  $\beta = 1$  K/s, pre-exponential factors of  $\nu = 10^{12}, 10^{13}$ , and  $10^{14}$  Hz, and assuming the desorption energy and pre-exponential factor being independent of coverage.

Redhead approximation:

$$\frac{E}{RT_m^2} = \frac{\nu}{\beta} e^{-E/RT_m}$$

## Supporting Discussion 1: Sniffer Calibration

In this section, the calibration procedure for the Sniffer is described, for both gas dosing and TDS-spectra-to-coverage conversion. These procedures depend on the sample–Sniffer nose distance, which, for the experiments reported in this manuscript, is fixed to  $100\pm 5\ \mu\text{m}$ .

For a TDS experiment, the conversion of the ion current, as read by the QMS, into absolute coverage is conducted as follows:

- i. The clean surface of Ni(111) is saturated by dosing approximately 10 L CO at 30 K;
- ii. The integral of the desorption profile has been set equal to 0.57 ML, according to previous studies.<sup>4</sup>

Once the above procedure is completed, to calibrate the amount of CO exposure the following procedure has been followed:

1. A primary calibration is performed by closing the Sniffer pumping and introducing a certain pressure of Ar inside the main chamber. This ensures that the pressure in the latter (read by a hot-filament ionization gauge) is the same as in the Sniffer's QMS;
2. With clean Ni(111) in the measurement position, 0.1 L of CO are nominally dosed, according to the calibration in step 1.;
3. The TDS area is converted to absolute coverage based on the calibration described in step ii.;
4. By using the low coverage approximation of the Langmuir equation:  $\theta = \frac{DS_0}{\sqrt{2\pi m_{CO} k_B T_{CO}}}$  ( $D$  = CO dosage in Pa·s) and assuming unitary sticking probability ( $S_0 = 1$ ), the actual CO dosage can be derived and compared with the nominal 0.1 L.
5. The correction factor is applied to calibration of step 1.

## REFERENCES

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