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Elucidating the Structure and Dynamics of CO Ad-Layers on MgO Surfaces

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I. MODELS WITH DIFFERENT COVERAGE

In the main body of the manuscript we present results for the $c(4\times2)$ ordered phase of CO molecules adsorbed on the MgO (001) surface, a phase characterized by six CO molecules per conventional cell, corresponding to a surface coverage $\theta = 0.75$. This is indeed the equilibrium structure of the monolayer at low temperature consistent with all available experimental data. Therefore, the maximum degree of adsorption for CO molecules on MgO (001) surfaces is 75% (i.e. every four Mg sites in the surface, three are "occupied" by CO molecules and one is free). A coverage of 100% is unstable because of lateral repulsive interactions being dominant against attractive CO-surface interactions.

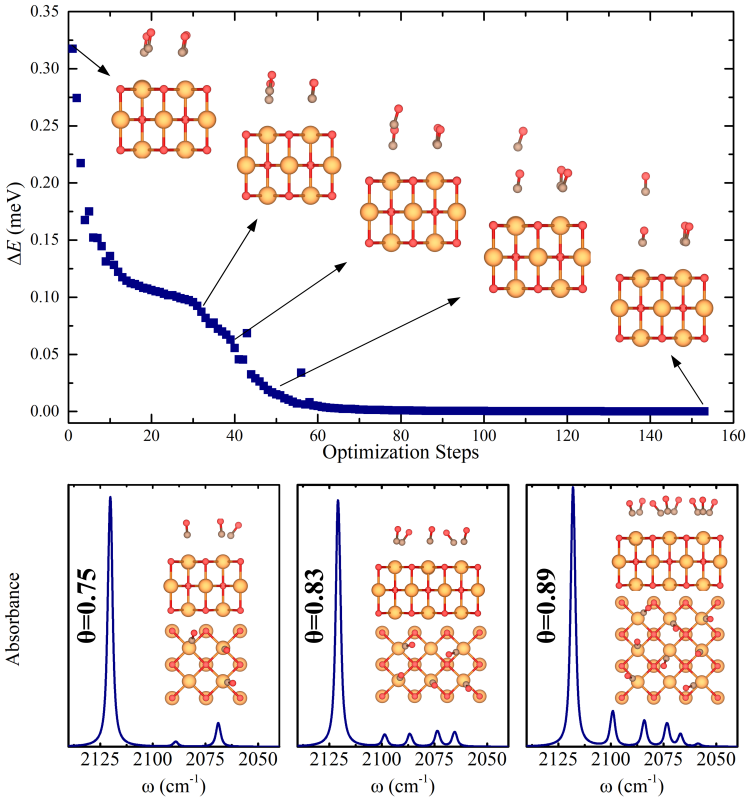

FIG. 1: Top panel: energy profile of a geometry optimization where four CO molecules are initially adsorbed on the four Mg sites of a (2×2) cell (snapshots of the structure during the optimization are also given, which show how one of the four CO molecules is desorbed because of unfavorable lateral interactions). Bottom panels: computed infrared spectroscopic fingerprint of different models for the adsorption of CO on MgO (001) characterized by different coverage and/or periodicity of the monolayer (left: three COs in a (2×2) cell; middle: five COs in a (2×3) cell; right: eight COs in a (3×3) cell).

In order to check whether or not our computational setup was capable of describing in a balanced and reliable way all of the existing interactions, we performed a structural relaxation of an adsorbed monolayer where CO molecules were initially adsorbed on each Mg site at the surface, with a (2×2) cell (i.e. four CO molecules per cell). The energy profile of such structural

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optimization is reported in the top panel of Figure 1, along with snapshots showing how the structure evolves throughout the process. It is clearly seen that, as the optimization goes, one of the four CO molecules is "ejected" from the monolayer because of the repulsive lateral interactions. The resulting monolayer corresponds to $\theta = 0.75$, with three CO molecules per 4 Mg sites.

We have also explored the effect of different degrees of coverage and/or periodicity of the monolayer on the infrared spectroscopic fingerprint of the system. None of the explored configurations produced a spectrum compatible with the experimentally measured one, but the $c(4 \times 2)$ model discussed in the main body of the manuscript. The bottom panels of Figure 1 show some of the explored configurations along with their corresponding infrared spectrum in the region of CO stretching.