# Comment on "Ultrafast Laser Excitation of CO/Pt(111) Probed by Sum Frequency Generation: Coverage Dependent Desorption Efficiency"

In a recent letter, Fournier *et al.* [1] report a $\sim 10^5$ photodesorption probability increase with coverage for CO on Pt(111) using femtosecond laser pulses. However, this anomalous coverage dependence was inferred in an indirect manner from a steady-state model applied to sum frequency generation spectra, which are sensitive not to the desorbing molecules, but rather to those remaining on the surface. Here, by a direct, quantitative determination of gas-phase CO molecules photodesorbed from the Pt(111) surface, we show that the desorption probability does not vary significantly with coverage. In addition, we provide an alternative explanation for the observations of Fournier *et al.* [1].

We desorb CO from Pt(111) using 140 fs laser pulses at 790 nm with a fluence of $70 \pm 5 \ J/m^2$ (very similar to [1]). Desorbed CO is detected using a quadrupole mass spectrometer. Time-of-flight (TOF) spectra (see left inset of Fig. 1) are recorded for each individual laser shot. To determine the desorption probability, integrated TOF spectra are recorded for ten sequential laser shots, temporally separated by 1 s, at the same position on the platinum crystal. The desorption probability $P_{des}$ at the initial coverage $\theta_{CO}$ is proportional to the signal at the first point (first shot yield, FSY). Figure 1 depicts the results of these experiments for two coverages. As the fluence in our experiments is constant, $P_{des} \propto FSY/\theta_{CO}$, and our results clearly demonstrate that the desorption probability is independent of coverage within a factor of $\sim 3$ (right inset of Fig. 1). Note that although the angular distribution of the desorbed CO may vary with coverage, this cannot explain the discrepancy between our results and [1], as in our setup the detection efficiency varies by only a factor of 4 when going from $cos(\theta)$ to $cos^{20}(\theta)$.

The reason for the anomalously large coverage dependence reported in [1] presumably lies in an omission in the analysis. In their Eq. (1), replenishment of CO desorbed from the laser focus is assumed to occur solely via adsorption of molecules from the gas phase. However, the lateral mobility of CO on the surface is sufficiently large [2] for CO to diffuse into the laser focus from the surrounding saturated monolayer (note that the experiments in [1] were performed under a CO background pressure). Thus, the lateral concentration gradient stabilizes on a time scale of seconds owing to diffusion. Indeed, in analogous experiments on CO/Ru(0001), diffusion was used to redose CO between laser shots [3], since background adsorption alone was insufficient (diffusion of CO is faster on Pt(111) [2] than on Ru(0001) [4]). Hence, an additional term due to diffusion should be added to Eq. (1) of [1], which will be relatively important at low coverages (low background pressures), where redosing from the background gas is slow. The effective redosing rate at
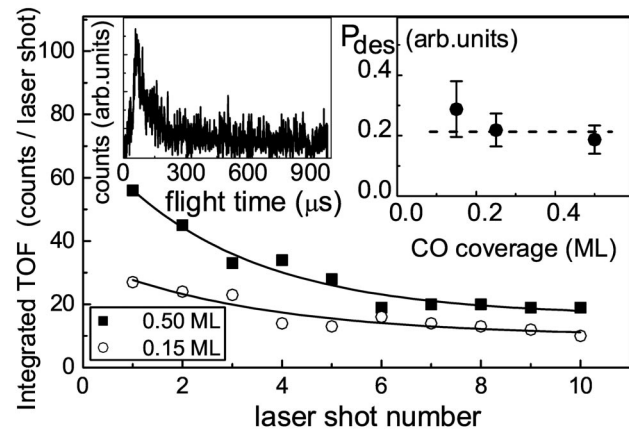


FIG. 1. Depletion curves (CO desorption yield vs shot number) for two coverages (expressed in monolayers, ML) of CO on Pt(111) indicated in the graph. Lines are the results of a model assuming coverage-independent desorption probability. Left inset: CO Flight-time distribution (average of 1000 shots; $\theta_{CO} = 0.5$ ML). Right inset: desorption probability vs coverage for three coverages, directly obtained from the depletion curves. Within the experimental accuracy, the desorption probability is independent of coverage (dashed line).

low coverage will therefore be many times higher than assumed in the model. As a result, *seemingly* less desorption occurs, leading to a gross underestimate of the desorption probability in [1] at low coverage.

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