Understanding the photoinduced desorption and oxidation of CO on Ru(0001) using a neural network potential energy surface

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The study of ultrafast photoinduced dynamics of adsorbates on metal surfaces requires thorough investigation of laser-excited electrons and, in many cases, the highly excited surface lattice. While ab initio molecular dynamics with electronic friction and thermostats (T_e, T_l)-AIMDEF [1] addresses such complex modeling, it imposes severe computational costs, hindering quantitative comparison with experimental desorption probabilities. In order to bypass this limitation, we utilize the embedded atom neural network method to construct a potential energy surface (PES) for the coadsorption of CO and O on Ru(0001). Our results demonstrate that this PES not only reproduces the ab initio dynamics but it is also able to yield statistically significant data for long lasting trajectories that correlate well with experimental findings. Furthermore, the analysis of the dynamics reveals the existence of a dynamic trapping state that acts as a precursor for CO desorption. Altogether, our results validate the underlying theoretical framework, providing a robust support for the description of not only the photoinduced desorption but also the oxidation of CO in terms of nonequilibrated but thermal hot electrons and phonons.

References

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[2] Funk,Stephan. "Ultraschnelle Reaktionsdynamik an Oberflächen: Desorption und Oxidation von CO auf Ru (001) induziert durch Femtosekunden-Laserpulse." PhD diss., 1999.

[3] Tetenoire, Auguste, Christopher Ehlert, J. I. Juaristi, Peter Saalfrank, and M. Alducin. "Why Ultrafast Photoinduced CO Desorption Dominates over Oxidation on Ru (0001)." *The Journal of Physical Chemistry Letters* 13, no. 36 (2022): 8516-8521.

Figures

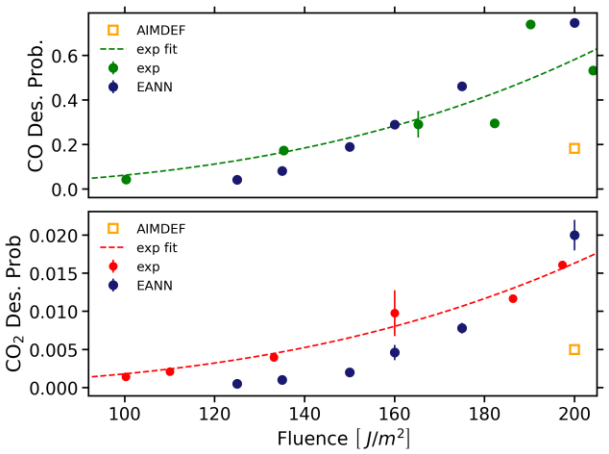

Figure 1. Fluence dependence of CO (top panel) and CO_2 (bottom panel) desorption probabilities upon irradiating the CO/2O/Ru(0001) surface with a 800 nm laser pulse of FWHM 110 fs. Green (top panel) and red (bottom panel) circles are the experimental results shown in ref. [2] for CO and CO_2 desorption, respectively. Dashed lines in both panels are obtained by fitting the experimental data and should be used to guide the eye. Blue circles and error bars (the latter masked in many cases by the symbol size) are the results of our NNPES-based (T_e, T_l)-MDEF simulations. Open orange squares are the (T_e, T_l)-AIMDEF results for F=200 J/m^2 [3]

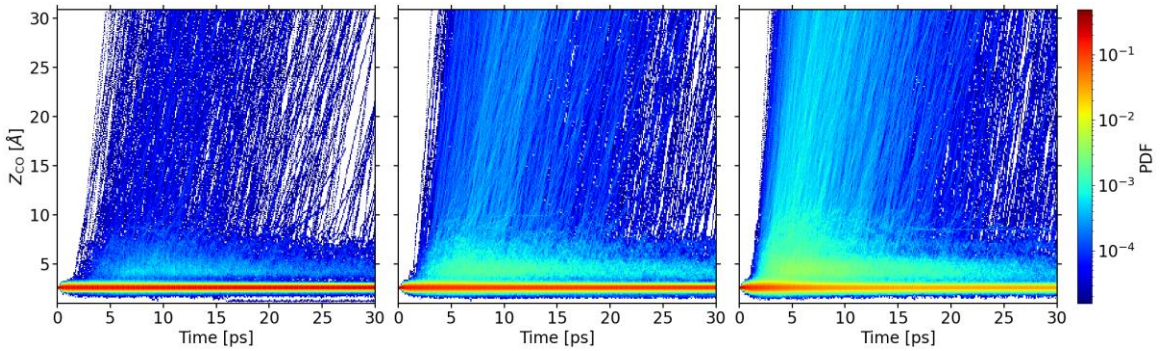

Figure 2. Normalized probability density of the CO center of mass height Z_{CO} as a function of time for three different absorbed laser fluences: 120 J/m^2 (left), 160 J/m^2 (middle), 200 J/m^2 (right). Z_{CO} is measured from the mean position of the Ru topmost layer