## Supporting Information

# Chemical and Structural In-Situ Characterization of Model Electrocatalysts by Combined Infrared Spectroscopy and Surface X-Ray Diffraction

Olaf Brummel[1,*], Leon Jacobse[2,§], Alexander Simanenko[1], Xin Deng[1,2], Simon Geile[2],
Olof Gutowski[3], Vedran Vonk[2], Yaroslava Lykhach[1], Andreas Stierle[2,4], Jörg Libuda[1]

[1]Interface Research and Catalysis, ECRC, Friedrich-Alexander-Universität Erlangen-Nürnberg,
Egerlandstraße 3, 91058 Erlangen, Germany

[2]Centre for X-ray and Nano Science CXNS, Deutsches Elektronen-Synchrotron DESY,
Notkestraße 85, 22607 Hamburg, Germany

[3]Deutsches Elektronen-Synchrotron DESY, Notkestraße 85, 22607 Hamburg, Germany

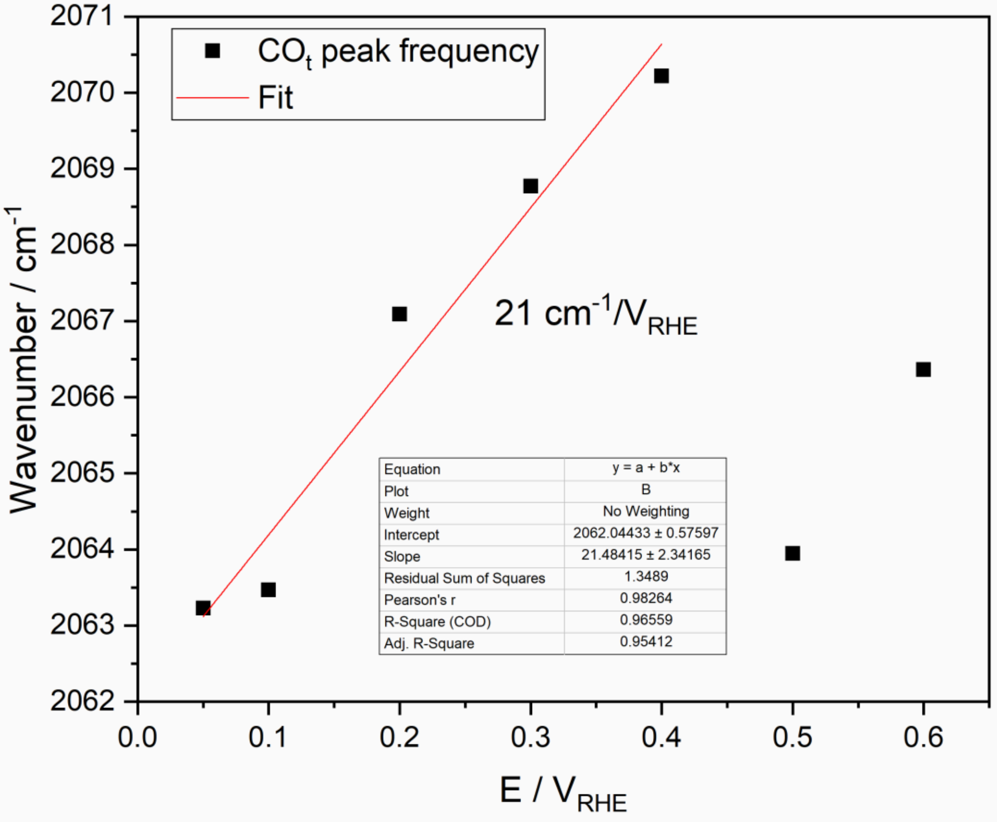
[4]Fachbereich Physik, Universität Hamburg, Jungiusstraße 11, 20355 Hamburg, Germany

Email: olaf.brummel@fau.de

[§]Current address: Department of Interface Science, Fritz Haber Institute of the Max Planck
Society, Berlin, Germany

## 1. Determination of the Stark slope

We observe a potential dependent frequency shift in the CO bands, which can be attributed to the change in electric field (Stark effect). For the most intense and sharp $CO_t$ band we determined the Stark slope by plotting the wavenumber against the applied potential (**Figure S1**). The Stark slope is 21 $cm^{-1} \cdot V^{-1}$, which is in good agreement with the literature.[1]



| | |
|---|---|
| Equation | y = a + b*x |
| Plot | B |
| Weight | No Weighting |
| Intercept | 2062.04433 ± 0.57597 |
| Slope | 21.48415 ± 2.34165 |
| Residual Sum of Squares | 1.3489 |
| Pearson's r | 0.98264 |
| R-Square (COD) | 0.96559 |
| Adj. R-Square | 0.95412 |

**Figure S1:** Band position of $CO_t$ on Pt(111) as a function of the electrode potential.

## 2. Diffusion of CO from the bulk solution into the thin layer

In the thin layer configuration, diffusion between the bulk solution and the thin layer is strongly hindered.[1] To analyze this effect in more detail, we set up the thin layer configuration at 0.05 $V_{RHE}$, then purged the bulk solution with CO and measured time-resolved IR spectra (1 spectrum in 5 min) over 115 min. During this time we observed the formation of a $CO_t$ band at 2065 $cm^{-1}$ (**Figure S2**), reaching an intensity of $\Delta R/R = 0.29\%$. This is 28% of the $CO_t$ intensity observed in the $CO_t$ oxidation experiment ($\Delta R/R = 1.03\%$) discussed in the manuscript. The results indicate that only traces of CO enter the thin-layer within the experimental time.

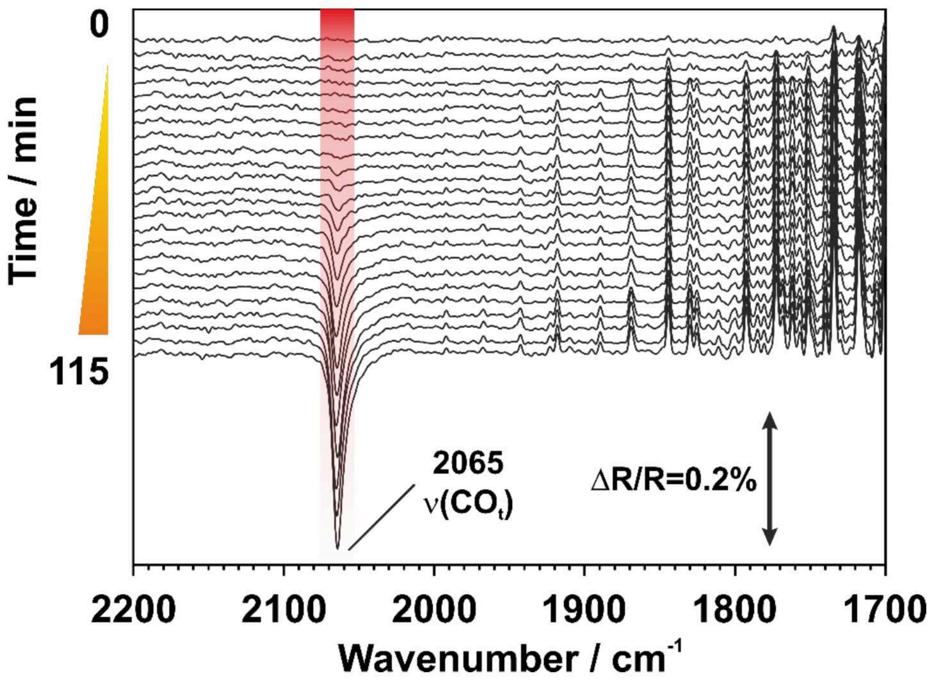


**Figure S2:** EC-IRRA spectra of CO diffusion from the bulk solution into the thin layer and adsorption on the Pt(111) surface. The spectra were measured at 0.05 $V_{RHE}$ for 115 min with one spectrum measured each 5 min. The background spectrum was measured after the thin layer configuration was established.

## 3. Fitting parameters

We summariezed the parameters used to fit the SXRD data in **Table S1.**

**Table S1:** Fitting parameter values: Overview of the occupancies, vertical displacements, and Debye-Waller factors obtained with the PE model without mass conservation. The errors represent the results of the least square fit, whereas the real uncertainties may be larger.

| Potential [$V_{RHE}$] | $Occ_{sur}$ [ML] | $Occ_{PE}$ [ML] | $\Delta z_{base}$ [Å] | $\Delta z_{sur}$ [Å] | $\Delta z_{PE}$ [Å] | $DW_{base}$ | $DW_{sur}$ | $DW_{PE}$ | χ2 (norm.) |
|---|---|---|---|---|---|---|---|---|---|
| 0.1 | 0.82 ±0.02 | 0.04 ±0.02 | 0.004 ±0.004 | 0.052 ±0.004 | 0.15 ±0.07 | 0.61 ±0.05 | 0.4 ±0.2 | 0 ±4 | 4.1 |
| 0.2 | 0.80 ±0.02 | 0.10 ±0.02 | -0.002 ±0.004 | 0.033 ±0.004 | -0.58 ±0.04 | 0.59 ±0.05 | 0.1 ±0.1 | 4 ±2 | 4.2 |
| 0.3 | 0.86 ±0.02 | 0.04 ±0.02 | 0.001 ±0.003 | 0.024 ±0.003 | 0.15 ±0.06 | 0.70 ±0.04 | 0.9 ±0.1 | 0 ±3 | 3.6 |
| 0.4 | 0.79 ±0.02 | 0.09 ±0.02 | -0.010 ±0.005 | -0.007 ±0.004 | -0.50 ±0.04 | 0.62 ±0.06 | 0.1 ±0.1 | 0 ±1 | 6.6 |
| 0.5 | 0.81 ±0.02 | 0.06 ±0.02 | -0.004 ±0.005 | -0.009 ±0.005 | -0.35 ±0.08 | 0.44 ±0.05 | 0.1 ±0.1 | 0 ±2 | 6.6 |
| 0.6 | 0.81 ±0.01 | 0.07 ±0.02 | -0.003 ±0.004 | -0.014 ±0.004 | -0.11 ±0.05 | 0.54 ±0.04 | 0.3 ±0.1 | 0 ±2 | 4.8 |
| 0.7 | 0.80 ±0.03 | 0.10 ±0.03 | -0.017 ±0.006 | -0.021 ±0.007 | -0.23 ±0.07 | 0.52 ±0.08 | 0.1 ±0.3 | 0 ±2 | 11.9 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 0.8 | 0.85 ±0.02 | 0.04 ±0.02 | 0.005 ±0.004 | -0.007 ±0.004 | 0.14 ±0.06 | 0.65 ±0.05 | 0.7 ±0.1 | 0 ±2 | 4.2 |
| 0.9 | 0.80 ±0.02 | 0.05 ±0.02 | 0.005 ±0.004 | -0.011 ±0.004 | 0.01 ±0.05 | 0.65 ±0.05 | 0.4 ±0.2 | 0 ±3 | 3.0 |
| 1.0 | 0.82 ±0.01 | 0.06 ±0.01 | 0.016 ±0.004 | -0.012 ±0.004 | 0.94 ±0.04 | 0.64 ±0.05 | 0.4 ±0.1 | 0 ±1 | 4.6 |
| 1.1 | 0.81 ± 0.02 | 0.08 ± 0.02 | 0.004 ± 0.004 | -0.022 ± 0.004 | -0.02 ± 0.04 | 0.66 ± 0.05 | 0.6 ± 0.2 | 0 ± 2 | 4.6 |
| 1.2 | 0.73 ± 0.02 | 0.12 ± 0.02 | 0.001 ± 0.003 | -0.062 ± 0.004 | -0.13 ± 0.03 | 0.75 ± 0.07 | 1.0 ± 0.3 | 0 ± 1 | 4.8 |
| 1.3 | 0.73 ± 0.03 | 0.17 ± 0.02 | 0.009 ± 0.006 | -0.092 ± 0.008 | -0.14 ± 0.03 | 0.86 ± 0.07 | 3.9 ± 0.4 | 0 ± 1 | 5.4 |
| 1.4 | 0.61 ± 0.03 | 0.14 ± 0.02 | -0.00 ± 0.01 | -0.04 ±0.01 | -0.12 ± 0.03 | 0.85 ± 0.08 | 2.8 ± 0.4 | 0 ± 1 | 6.7 |
| 1.5 | 0.28 ± 0.02 | 0.09 ± 0.02 | -0.01 ± 0.02 | 0.05 ± 0.04 | -0.02 ± 0.05 | 1.0 ± 0.1 | 0.1 ± 0.6 | 0 ± 2 | 6.4 |

## 4. Simulated CTRs in the presence and absence of a CO adlayer

We simulated the (10) and (11) CTRs in the presence (red) and the absence (blue) of a 2x2-3CO adlayer. We placed the CO molecules at a distance of 1.85 Å with a C-O bond length of 1.15 A.[2]

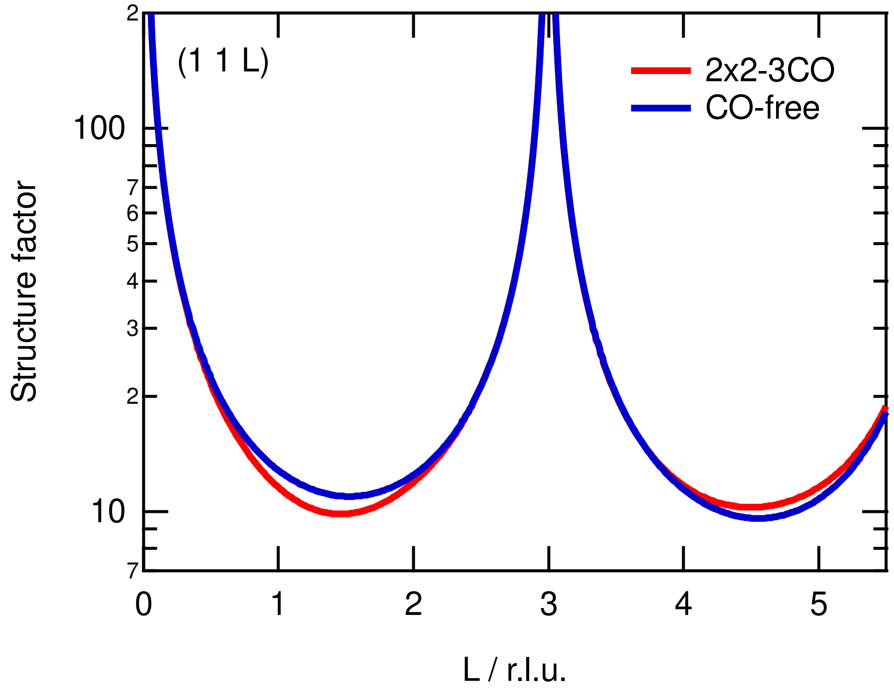


**Figure S3:** Simulated (11) CTRs in the presence (red) and absence (blue) of a 2x2-3CO adlayer.

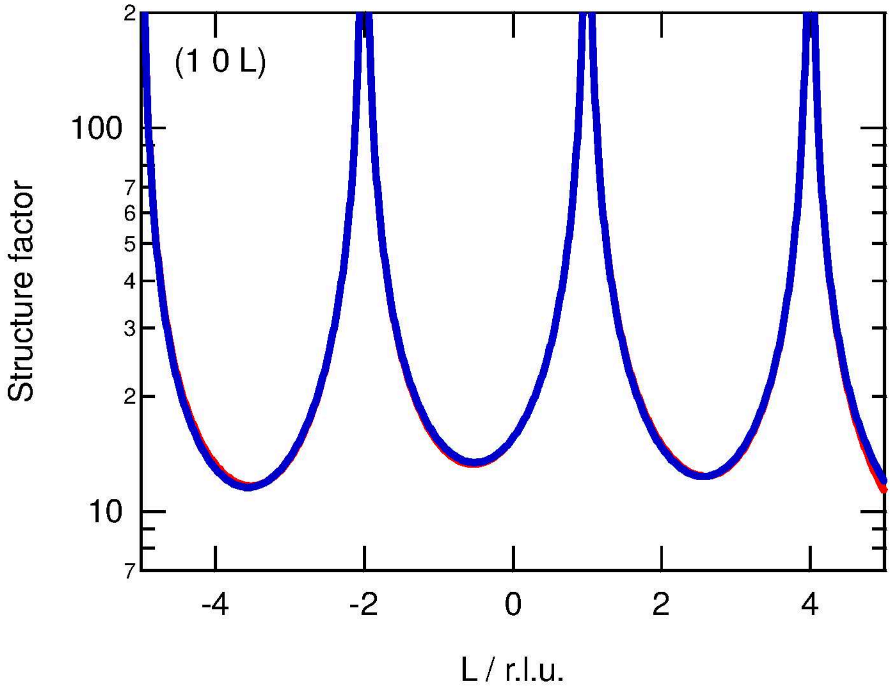


**Figure S4:** Simulated (10) CTRs in the presence (red) and absence (blue) of a 2x2-3CO adlayer.

## 5. Place-exchange mechanism

The oxidation of Pt occurs via a place-exchange (PE) mechanism, which we illustrated in **Figure S5**. In the PE process, Pt surface atoms are vertically displaced from the surface by approximately a single Pt(111) step height.[3-7]

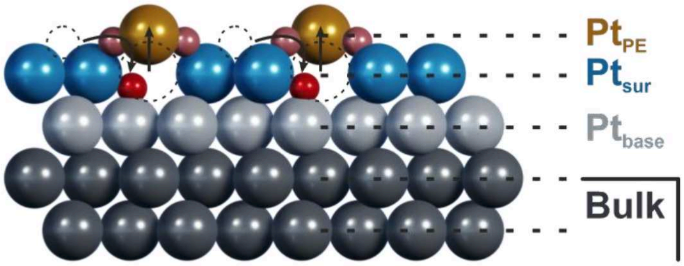


**Figure S5:** Ball model illustrating the place-exchange mechanism.

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