

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 Simanenko¹, Xin Deng^{1,2}, Simon Geile²,
Olof Gutowski³, Vedran Vonk², Yaroslava Lykhach¹, Andreas Stierle^{2,4}, Jörg Libuda¹

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

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

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

⁴Fachbereich 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·V⁻¹, which is in good agreement with the literature.¹

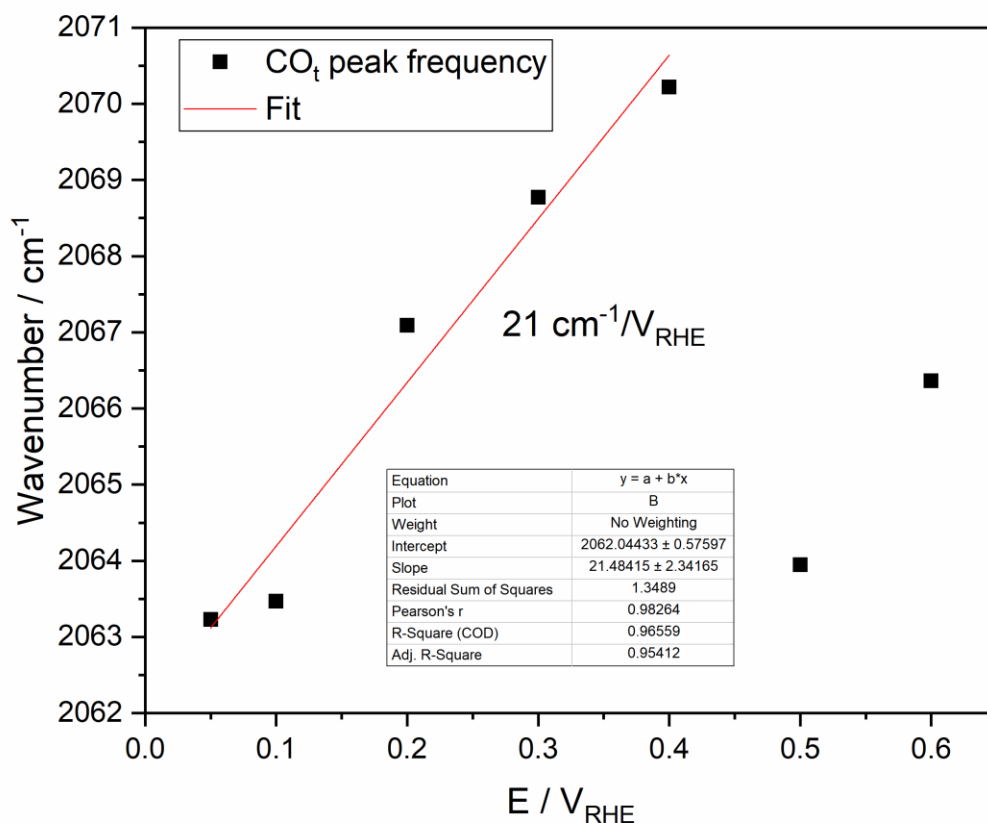


Figure S1: Band position of CO_t on Pt(111) as a function of the electrode potential.

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 ΔR/R = 0.29%. This is 28% of the CO_t intensity observed in the CO_t oxidation experiment (ΔR/R = 1.03%) discussed in the manuscript. The results indicate that only traces of CO enter the thin-layer within the experimental time.

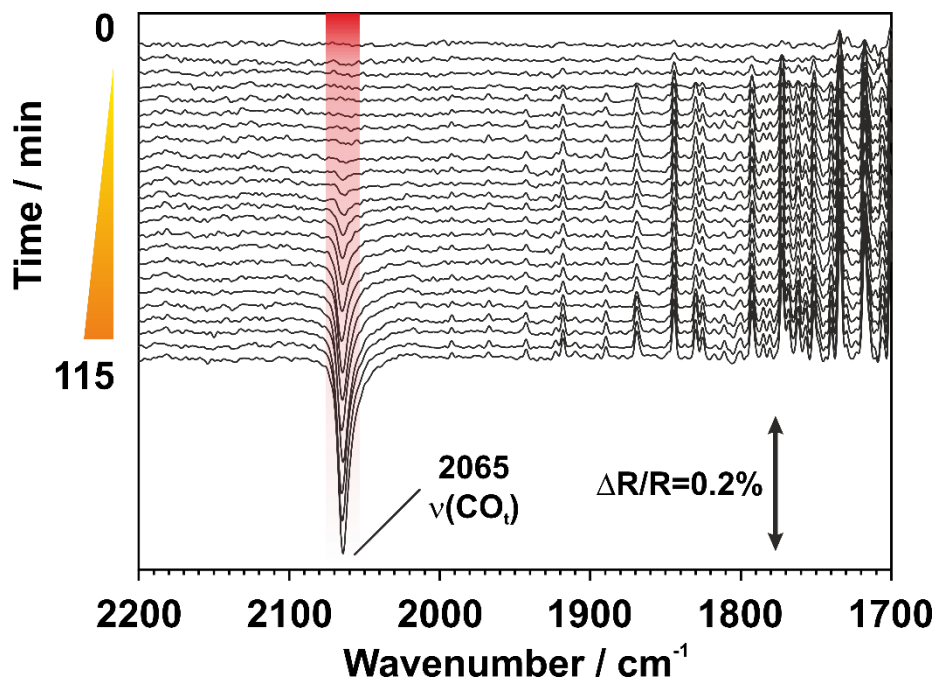


Figure S2: EC-IRRA spectra of CO diffusion from the bulk solution into the thin layer and adsorption on the Pt(111) surface. The spectra were measured at 0.05 V_{RHE} for 115 min with one spectrum measured each 5 min. The background spectrum was measured after the thin layer configuration was established.

3. Fitting parameters

We summarized 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]	Δz _{base} [Å]	Δz _{sur} [Å]	Δz _{PE} [Å]	DW _{base}	DW _{sur}	DW _{PE}	χ ² (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 \pm 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 \pm 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 \pm 1	4.6
1.1	0.81 \pm 0.02	0.08 \pm 0.02	0.004 \pm 0.004	-0.022 \pm 0.004	-0.02 \pm 0.04	0.66 \pm 0.05	0.6 \pm 0.2	0 \pm 2	4.6
1.2	0.73 \pm 0.02	0.12 \pm 0.02	0.001 \pm 0.003	-0.062 \pm 0.004	-0.13 \pm 0.03	0.75 \pm 0.07	1.0 \pm 0.3	0 \pm 1	4.8
1.3	0.73 \pm 0.03	0.17 \pm 0.02	0.009 \pm 0.006	-0.092 \pm 0.008	-0.14 \pm 0.03	0.86 \pm 0.07	3.9 \pm 0.4	0 \pm 1	5.4
1.4	0.61 \pm 0.03	0.14 \pm 0.02	-0.00 \pm 0.01	-0.04 \pm 0.01	-0.12 \pm 0.03	0.85 \pm 0.08	2.8 \pm 0.4	0 \pm 1	6.7
1.5	0.28 \pm 0.02	0.09 \pm 0.02	-0.01 \pm 0.02	0.05 \pm 0.04	-0.02 \pm 0.05	1.0 \pm 0.1	0.1 \pm 0.6	0 \pm 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 Å.²

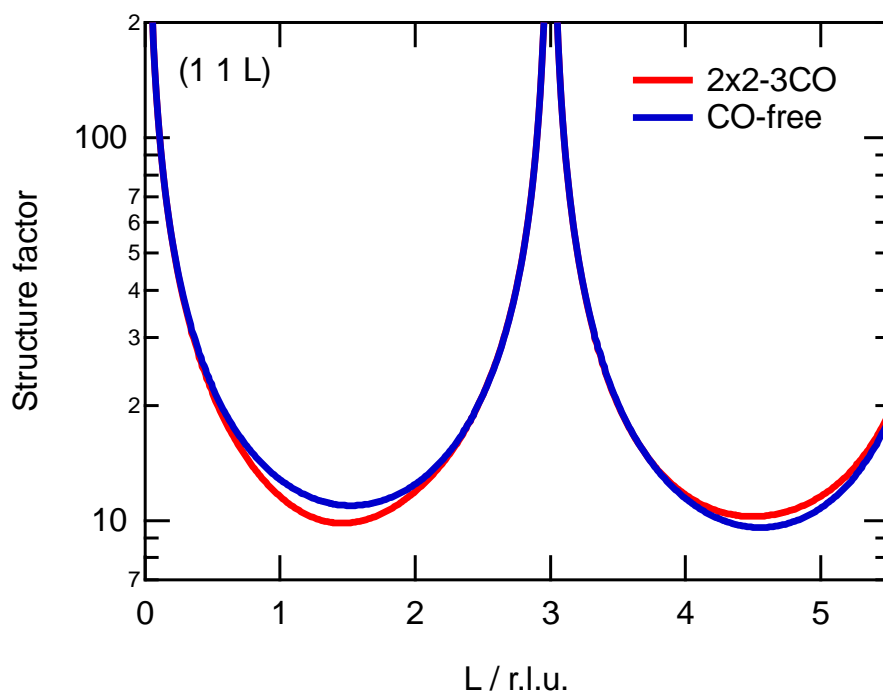


Figure S3: Simulated (11) CTRs in the presence (red) and absence (blue) of a 2x2-3CO adlayer.

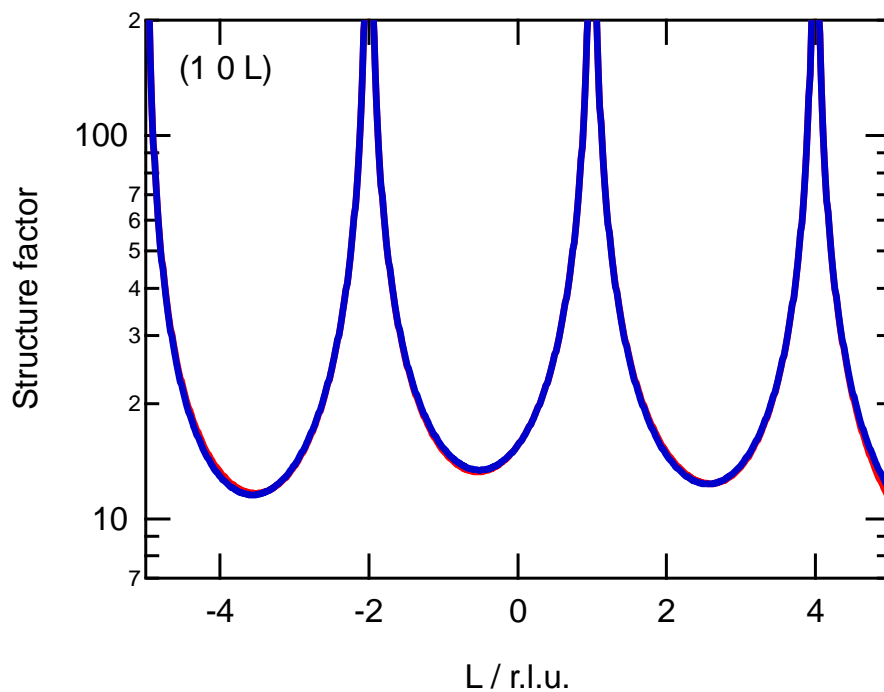


Figure S4: Simulated (10) CTRs in the presence (red) and absence (blue) of a 2x2-3CO adlayer.

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

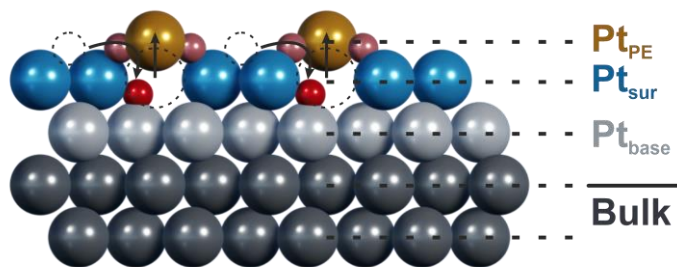


Figure S5: Ball model illustrating the place-exchange mechanism.

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