Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information: Adsorption, surface relaxation and electrolyte structure at Pt (111) electrodes in non-aqueous and aqueous acetonitrile electrolytes.

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S1. Discussion on model selection for non-aqueous MeCN data.

Figures S1 and S2 shows the specular CTR zoomed in to highlight the area most affected by the scattering from ordered electrolyte (close to the first anti-Bragg position), different models are indicated. The O_2 data is presented as an example but the situation was the same for the data measured in the absence of O_2. Reduced χ^2 values for the fits are shown in brackets and these are for the whole data set (i.e. including non-specular CTR which is not shown). Some fits did not converge, or the coverage of an ad-layer went to zero giving another one of the fits already shown. In Figure S3 the ratio of the two data sets are shown. What is clear is that the models that considered no electrolyte ordering or only one ad-layer (but no error function) were insufficient to model the data. Small improvements to the fits to the data presented in the paper could be obtained by adding more layers (i.e. parameters) to the structural model. The corresponding electron density profiles are shown in Figures S4 and S5, in each case the position of the first layer and error function are consistent with the

simpler model. We therefore decided to select this model as overfitting the data is possible.

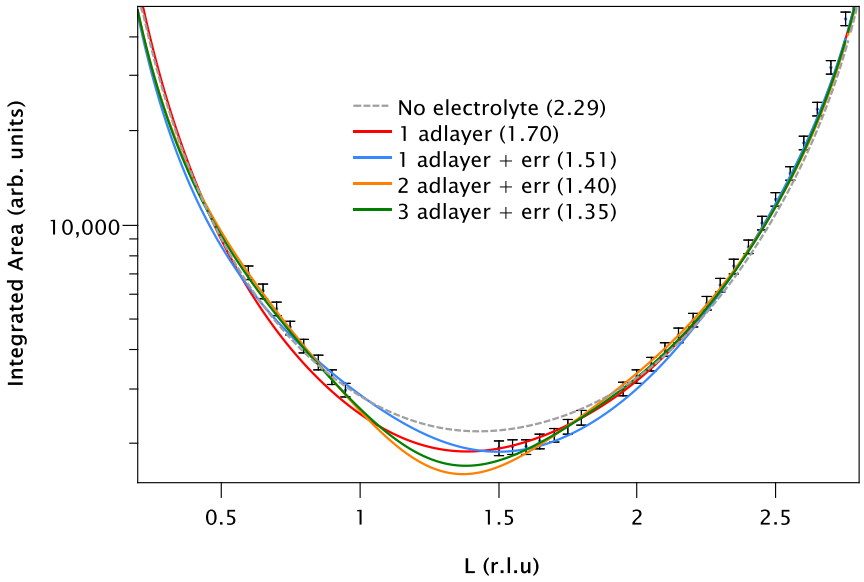

Figure S1: A section of the specular CTR measured at -1.1 V in MeCN saturated with O_2. Various models that were used to fit the data are indicated.

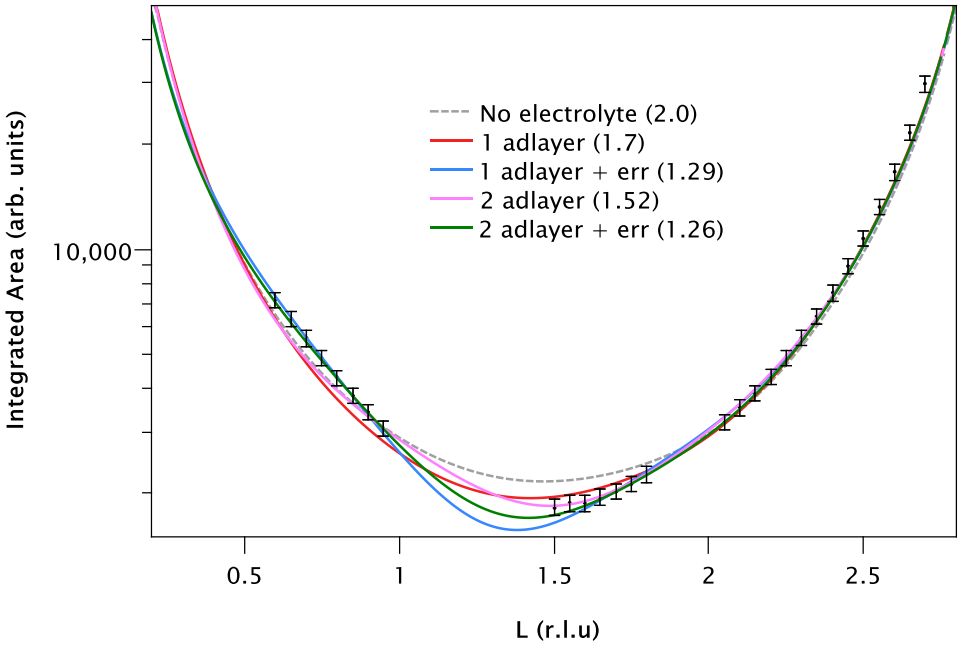

Figure S2: A section of the specular CTR measured at 0.4 V in MeCN saturated with O_2. Various models that were used to fit the data are indicated.

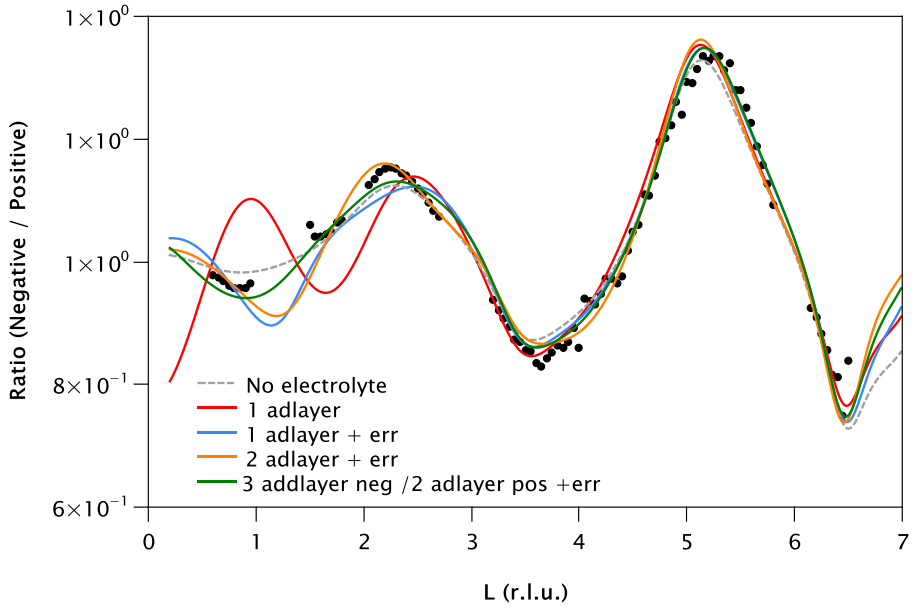

Figure S3: The ratio between the two CTRs measured in MeCN saturated with O_2, the ratio between the best fits of various models are also indicated.

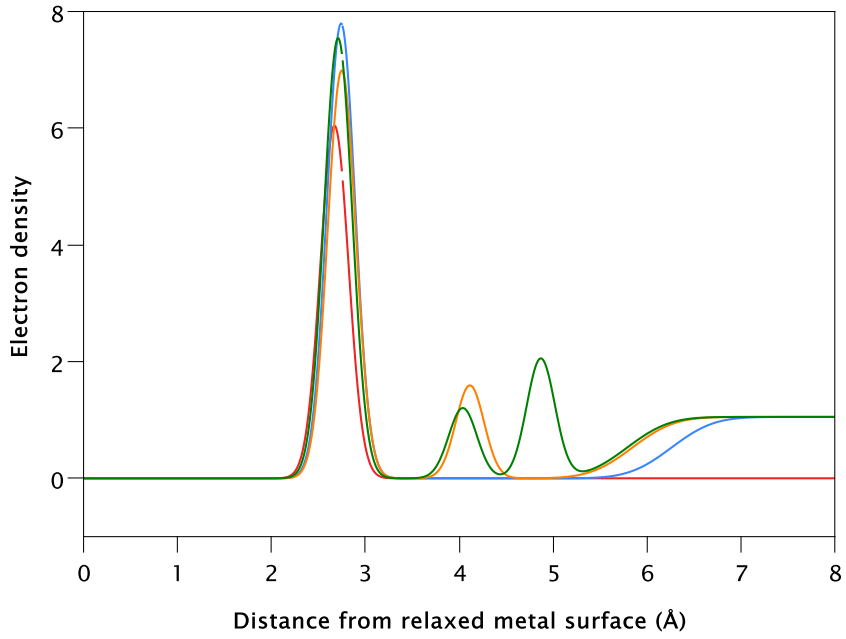

Figure S4: Electron density profiles calculated from best fits to the CTRs measured at -1.1 V in MeCN saturated with O_2. Various models that were used to fit the data are indicated.

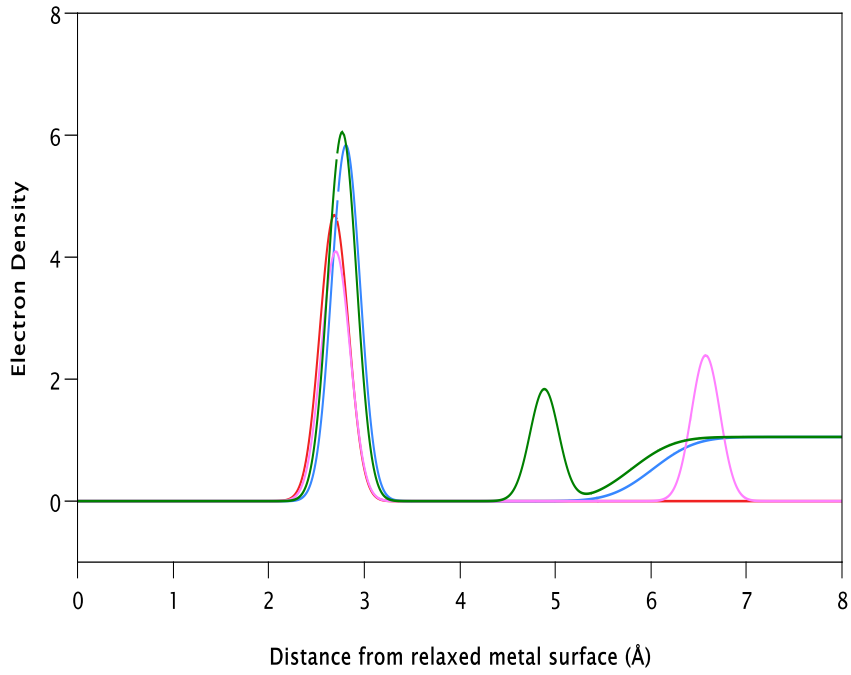

Figure S5: Electron density profiles calculated from best fits to the CTRs measured at 0.4 V in MeCN saturated with O_2. Various models that were used to fit the data are indicated.

S2. CTR data and discussion on model selection for aqueous MeCN data.

Figures S6 and S7 show the best fits to the CTRs at various concentrations of MeCN at both 0 V and 0.85 V, the ratios of the given each CTR with the 0.01 M CTR are shown in Figure 8 of the manucscript as are the calculated electron density profiles in Figure 9. Various models were used to fit the data and by inspecting how well the models fit the ratio of data sets (the ratio itself was not actually fitted-each CTR data set was fitted independely) a model was selected. Figure S8 shows several of the models tried for two of the CTRs. The model that consistently fit all the datasets consisted of two adlayers and an error function, the best fit parameters are given in Table S1.

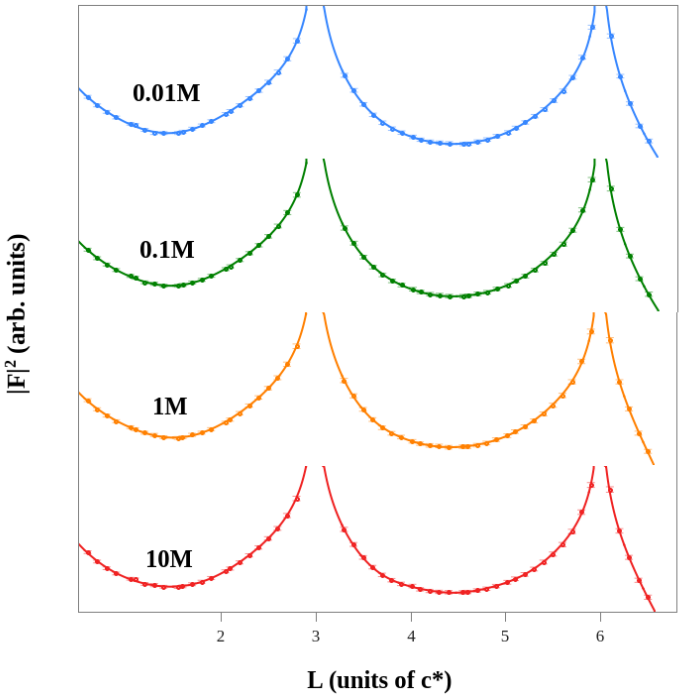

Figure S6: Fits to crystal truncation rods measured at 0.85 V for Pt (111) / 0.1 M $HClO_4$ + x M MeCN, where x is the concentration indicated in the Figure.

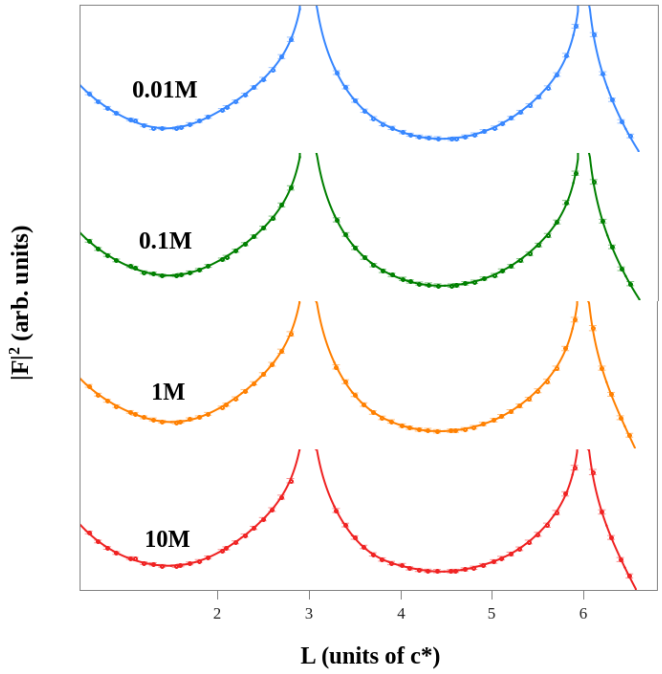

Figure S7: (a) Fits to crystal truncation rods measured at 0.85 V for Pt (111) / 0.1 M $HClO_4$ + x M MeCN, where x is the concentration indicated in the Figure.

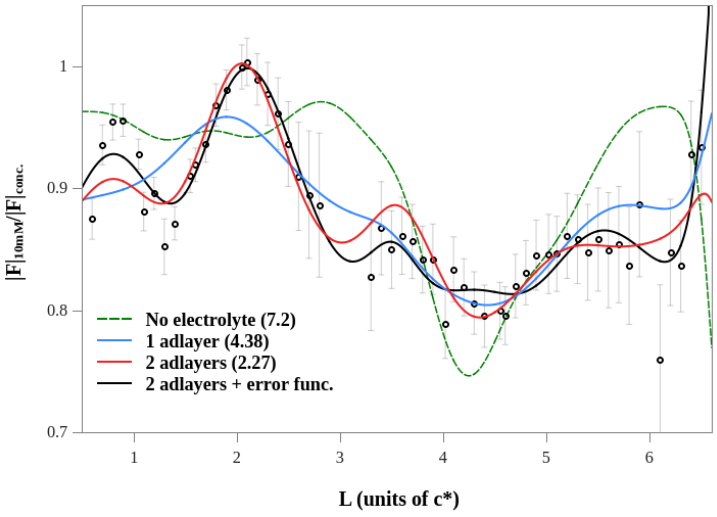

Figure S8. Data measured at 0 V in 10 M MeCN normalised to that measured in 10 mM. The ratios of the best fits achieved with different models to the CTRs are shown.

		0.01M	0.1M	1M	50% (~10M)
0.0V	ε_{23} (Å)	0.012 ± 0.001	0.015 ± 0.002	0.017 ± 0.002	0.016±0.003
	ε_{12} (Å)	0.078 ± 0.001	0.082 ± 0.001	0.086 ± 0.002	0.089 ± 0.002
	σ_{Pt1} (Å^{-1})	0.089 ± 0.006	0.110 ± 0.009	0.12 ± 0.01	0.12 ± 0.01
	θo1	1.50 ± 0.05	1.60 ± 0.04	1.64 ± 0.05	1.83 ± 0.06
	d_{o1} (Å)	2.22 ± 0.01	2.15 ± 0.03	2.09 ± 0.03	2.06 ± 0.04
	θ_{o2}	0.53 ± 0.02	0.42 ± 0.04	0.36 ± 0.05	0.3 ± 0.1
	d_{o2} (Å)	3.33 ± 0.05	3.25 ± 0.06	3.23 ± 0.06	3.27 ± 0.08
	d_{err} (Å)	4.1 ± 0.1	3.7 ± 0.1	3.6 ± 0.1	3.2 ± 0.3
	r-χ^2	**0.13**	**0.11**	**0.11**	**0.20**
0.85V	ε_{23} (Å)	0.011 ± 0.002	0.012 ± 0.002	0.014 ± 0.002	0.013±0.002
	ε_{12} (Å)	0.062 ± 0.002	0.064 ± 0.002	0.073 ± 0.003	0.075 ± 0.003
	σ_{Pt1} (Å^{-1})	0.12 ± 0.01	0.13 ± 0.01	0.14 ± 0.01	0.14 ± 0.01
	θo1	1.30 ± 0.06	1.40 ± 0.06	1.57 ± 0.07	1.75 ± 0.08
	d_{o1} (Å)	2.12 ± 0.04	2.07 ± 0.04	2.01 ± 0.04	2.01 ± 0.04
	θ_{o2}	0.72 ± 0.06	0.63 ± 0.05	0.56 ± 0.06	0.60 ± 0.08
	d_{o2} (Å)	3.28 ± 0.04	3.31 ± 0.05	3.36 ± 0.06	3.38 ± 0.07
	d_{err} (Å)	4.1 ± 0.1	4.1 ± 0.1	4.0 ± 0.2	3.2 ± 0.3
	r-χ^2	**0.14**	**0.18**	**0.22**	**0.28**

Table S1 Parameters obtained from best fits to specular CTRs for different concentrations of MeCN.

S3. Fits to CTRs for aqueous electrolytes

In Figure S9 fits to CTR data of the Pt (111) / 0.1 M $HClO_4$ interface are shown. The CTRs were measured at 0.0 V and 0.72 V. A small improvement to the fits was gained by including an electrolyte in the model but this was not statistically significant enough to warrant the inclusion of the extra parameters, therefore the fits presented only model the metal electrode. The parameters that gave the best fit are shown in Table S2. In Figure S10 the ratio between the data measured at 0 V and 0.72 V is presented, from which it is clear that the best fits to the CTRs do a reasonable job of modelling any change between the potentials (the change being dominated by surface relaxation).

The full CTRs measured in H_2SO_4 and KOH electrolytes were only available at 0 V, which means that ratios are not available. However, we are confident that fits to the three CTRs available (Figure S11) do a reasonable job of modelling the electrode surface, the results of which are presented in Table S3. We think in the future these measurements should be revisited using more modern synchrotron beamlines and detectors. By making a series of measurements with increasing electrolyte concentration on the same electrode it should be possible to get reliable electron density profiles across the double layer region as a function of electrode potential.

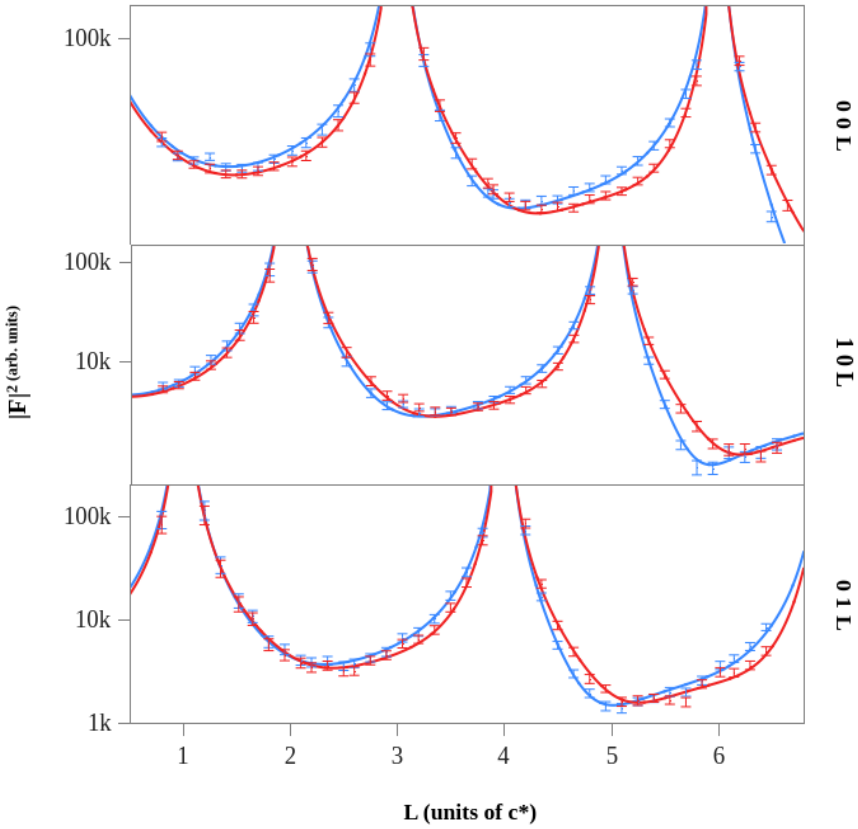

Figure S9: Fits to CTRs measured at the Pt (111) / 0.1 M HClO4 interface. 00l, 10L and 01L CTRs were all fit simultaneously. The two potentials measured at 0.0 V and 0.72 V are shown in blue and red respectively.

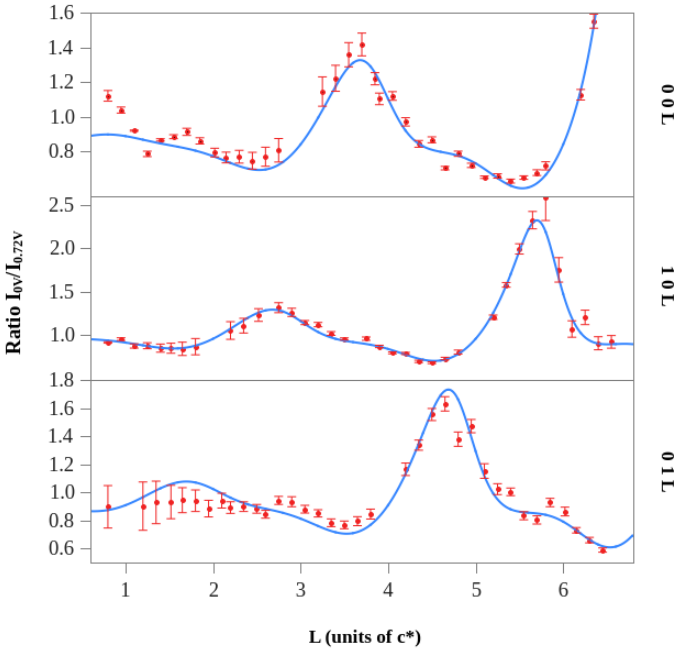

Figure S10 (b). Data at 0 V normalised to that at 0.72 V for three different CTRs. measured at the Pt (111) / 0.1 M HClO4 interface

	0.00 V	0.72 V
ε_{12}(Å)	0.058(2)	0.014(1)
σ_2(Å)	0.062(5)	0.044(7)
σ_1(Å)	0.094(5)	0.071(6)
χ^2_{red}	1.17 (1.03)	0.90 (1.00)
R-Factor	0.083	0.074

Table S2 Parameters giving best fits to $HClO_4$ data

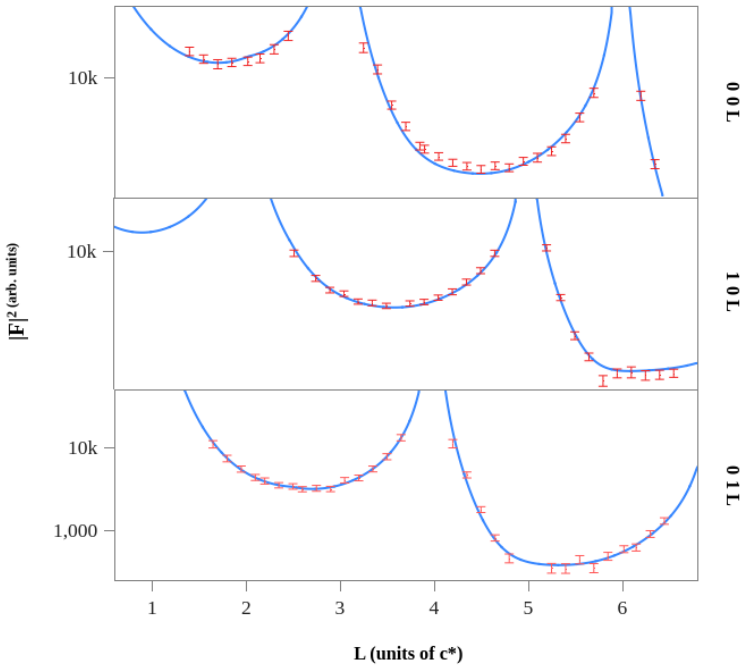

Figure S11 Best fits to CTRs measured at the Pt (111) / 0.1 M H_2SO_4 interface. 00l, 10L and 01L CTRs were all fit simultaneously

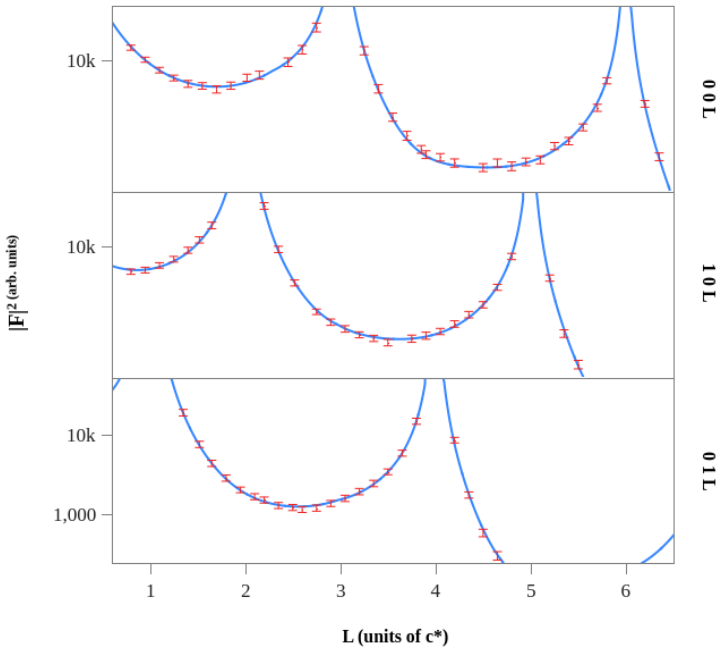

Figure S12 Best fits to CTRs measured at the Pt (111) / 0.1 M KOH interface. 00l, 10L and 01L CTRs were all fit simultaneously

	KOH (0.0 V)	H_2SO_4 (0.0 V)
ε_{21}(Å)	0.005(1)	0.008(3)
ε_{12}(Å)	0.058(1)	0.061(3)
σ_2(Å)	0.070(5)	0.04(1)
σ_1(Å)	0.100(6)	0.07(1)
χ^2_{red}	0.44	2.15
R-Factor	0.058	0.11

Table S3 Parameters giving the best fits to KOH and H_2SO_4 CTR data at 0 V.