Electronic Supplementary Material for PCCP

Redox-linked protein dynamics of cytochrome c probed by time-resolved surface enhanced infrared absorption spectroscopy

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Content:

Electric field strength at the protein/SAM interface

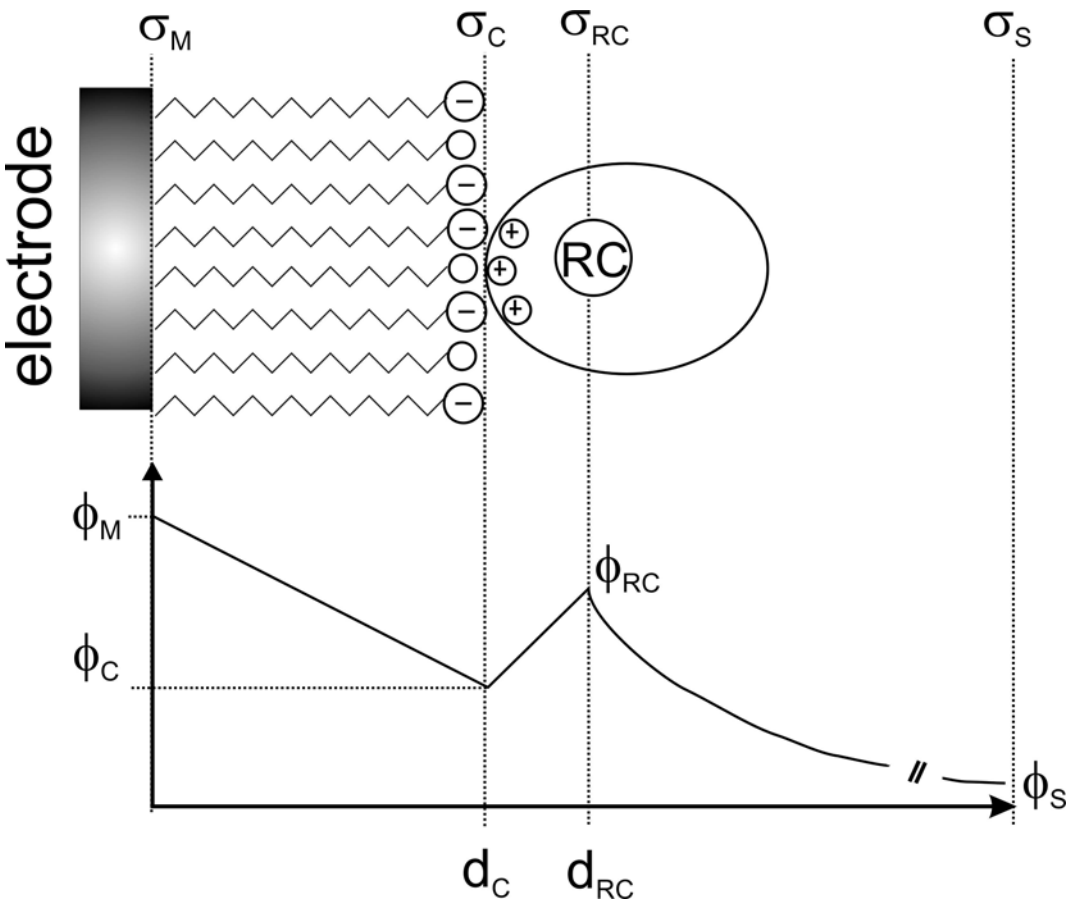

Fig. S1. Schematic representation of the potential distribution across the electrode/SAM/protein/solution interfaces.

Within the electrostatic model for the interfacial potential drops (Fig. S1), the electric field strength at the protein/SAM interface E_{EF} is given by

(S1) $$E_{EF} = \frac{\sigma_M}{\varepsilon_0 \varepsilon_c}$$

or, with

(S2) $$\sigma_M + \sigma_C + \sigma_{RC} + \sigma_S = 0$$

(S3) $$E_{EF} = -\frac{\sigma_C + \sigma_{RC} + \sigma_S}{\varepsilon_0 \varepsilon_c}$$

where σ_M, σ_C, σ_{RC}, and σ_S are the charge densities on the metal, on the SAM, at the reaction site (heme), and in the solution, respectively (§ref). The quantities ε_0 and ε_S refer to the permittivity and the dielectric constant in the SAM, respectively. Linearisation of the Gouy-Chapman expression for σ_S allows rewriting Eq. S3 to

$$\text{(S4)}\quad E_{EF} = -\frac{\sigma_C + \sigma_{RC} - \varepsilon_0 \varepsilon_S \kappa E_{RC}}{\varepsilon_0 \varepsilon_c}$$

where ε_S and κ are the dielectric constant and the Debye length in solution. E_{RC} denote the potential drop at the redox site which can be expressed by

$$\text{(S5)}\quad E_{RC} = \frac{\sigma_C \varepsilon_P d_C + \varepsilon_o \varepsilon_P \varepsilon_C (E - E_{pzc}) + (d_C \varepsilon_P + d_{RC} \varepsilon_C)\sigma_{RC}}{\varepsilon_o \left[\varepsilon_C \varepsilon_P + (d_C \varepsilon_P + d_{RC} \varepsilon_C)\varepsilon_S \kappa\right]}$$

Here ε_P is the dielectric constant in the protein and d_C and d_{RC} are the thickness of the SAM and the distance between the SAM/protein interface and the reaction site, as defined in Fig. S1. The quantities E and E_{pzc} refer to the electrode potential and the potential of zero charge, respectively. Inserting Eq. S5 into Eq. S4 one obtains

$$\text{(S6)}\quad E_{EF} = \frac{-\sigma_C \left[\varepsilon_C \varepsilon_P + d_{RC} \varepsilon_C \varepsilon_S \kappa\right] - \sigma_{RC} \varepsilon_C \varepsilon_P + \varepsilon_0 \varepsilon_S \varepsilon_C \varepsilon_P \kappa \left(E - E_{pzc}\right)}{\varepsilon_o \varepsilon_C \left[\varepsilon_C \varepsilon_P + (d_C \varepsilon_P + d_{RC} \varepsilon_C)\varepsilon_S \kappa\right]}$$

Since at pH values around 7, $|\sigma_C| >> |\sigma_{RC}|$ and furthermore $\varepsilon_C \varepsilon_P << d_{RC} \varepsilon_C \varepsilon_S \kappa$, Eq. S6 simplifies to

$$\text{(S7)}\quad E_{EF} = \frac{-\sigma_C d_{RC} + \varepsilon_0 \varepsilon_P \left(E - E_{pzc}\right)}{\varepsilon_o (d_C \varepsilon_P + d_{RC} \varepsilon_C)}$$