

**P017** FTIR detection of carboxyl groups in bovine heart cytochrome c oxidase.

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FTIR spectroscopic studies of bovine heart cytochrome c oxidase (CcO) have revealed complex carboxyl group changes linked both to CO dissociation from heme  $a_3$  and to redox changes of heme a. The highly conserved Glu242 is thought to contribute in both cases, consistent with its proposed involvement in an internal proton transfer that is crucial for interhaem electron transfer. Crystallographic data suggest that Asp51 and Asp91, residues located in possible proton transfer pathways, also undergo redox-linked changes. Hence, they might be expected to provide additional carboxyl IR changes. To investigate this further, FTIR difference spectra of bovine CcO were recorded in the presence of  $\text{Ca}^{2+}/\text{Na}^+$  or  $\text{Zn}^{2+}/\text{Cd}^{2+}$ , since these metals have been shown to bind closely to Asp51 and Asp91, respectively, and might be expected to affect any ligand- or redox-linked structural changes that they might undergo. The effects of these metals on CO photolysis- and redox-induced difference spectra will be reported. As an additional means to resolve the multiple carboxyl contributions observed upon CO photolysis from bovine CcO, we have applied time-resolved rapid-scan and step-scan FTIR spectroscopy, with particular attention to the  $1800\text{-}1700\text{ cm}^{-1}$  carboxylic region. Our results will be discussed in terms of specific carboxyl group function in the proton pathway(s) of CcOs.