

Supporting Information

Maréchal and Rich 10.1073/pnas.1019419108

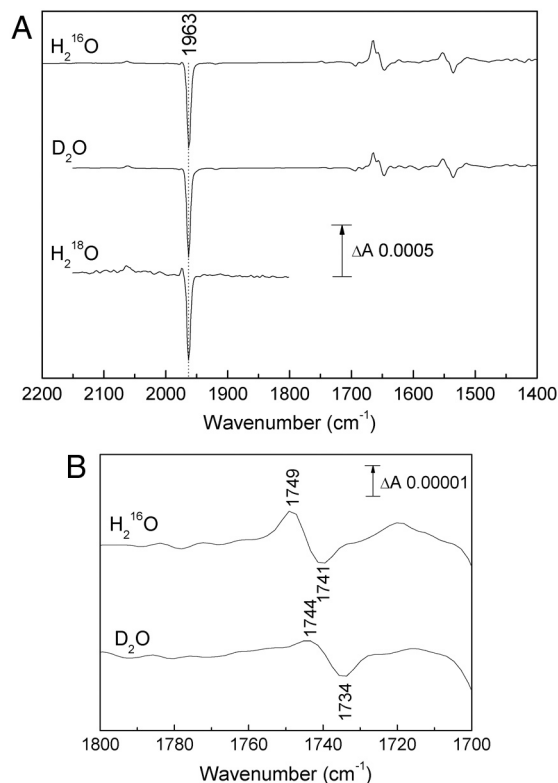


Fig. S1. Light-induced CO photolysis transmission FTIR difference spectra of fully reduced bovine CcO-CO. (A) FTIR difference spectra were recorded in H_2^{16}O (top trace, average of 7,500), D_2O (middle trace, average of 10,000), and H_2^{18}O (lower trace, average of 650) media. All data were normalized to their CO band intensities at 1963 cm^{-1} . (B) Expanded $1,800\text{--}1,700\text{ cm}^{-1}$ region showing protonated carboxyl group shifts. The signals at $1,749$ (+) and $1,741$ (–) in H_2^{16}O are shifted down to $1,744$ (+) and $1,734$ (–) in D_2O .

Table S1. Frequencies of the Gaussian components used for fitting to the experimental CO photolysis transmission FTIR difference spectra of Fig. 2 in H_2^{16}O (top trace) and H_2^{18}O (lower trace) media in the $3,700\text{--}3,560\text{ cm}^{-1}$ range. All bands were fixed to the same FWHM of 6 cm^{-1}

	Frequency, cm^{-1}														
H_2^{16}O	3,680(+)	3,669(–)	3,654(–)	3,645(+)	3,640(+)	3,630(+)	3,619(–)	3,615(–)	3,609(+)	3,601(+)	3,594(–)	3,581(–)	3,576(+)	3,569(+)	3,560(–)
D_2O	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
H_2^{18}O	3,665(+)	3,657(–)	3,638(–)	3,632(+)	3,623(+)*	—	3,613(–)	3,605(–)	3,599(+)	3,591(+)	3,576(–)	3,569(–)	3,564(+)	ND [†]	ND [†]
$\Delta\nu^{18}\text{O-}^{16}\text{O}$	–15	–12	–16	–13/–8	–17/–7	—	–6	–10	–10	–10	–18	–12	–12	—	—

ND, not determined.

*Whereas three components were required to fit the data in the $3,645\text{--}3,630\text{ cm}^{-1}$ region in H_2^{16}O , only two equivalent components were evident in H_2^{18}O . Hence their band equivalencies and $\Delta\nu^{18}\text{O-}^{16}\text{O}$ values are uncertain.

[†]The filter cut off data below $3,560\text{ cm}^{-1}$