DYNAMICS OF METAL CYANIDES

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Time resolved IR spectroscopy was used to characterize the vibrational energy relaxation (VER) dynamics of the CN stretching bands of aqueous molecular metal cyanides and networked metal cyanides, such as Prussain Blue, in reverse micelles. The vibrational and rotational relaxation dynamics of the CN stretching bands near 2000 cm^{-1} for aqueous molecular cyanides $Au(CN)_2^-$, $Ni(CN)_4^{2-}$, $Pt(CN)_4^{2-}$, $Co(CN)_6^{3-}$, $Mn(CN)_4^{2-}$, and $Ru(CN)_6^{4-}$ have been investigated using ultrafast pump-probe spectroscopy. While the spectra and dynamics of $Ru(CN)_6^{4-}$ are similar to those previously reported for ferrocyanide, VER times are significantly longer (>30 ps) in the other molecules. $Mn(CN)_6^{3-}$ represents an intermediate case with a relaxation time of about 15 ps in water. The VER dynamics extend and reinforce the established trends of metal cyanide CN band frequencies and intensities. Prussian Blue and its ruthenium analog were also studied using visible pump-IR probe and IR pump-IR probe spectroscopy. The VER dynamics are similar to the monometal cyanides and there is evidence for CN band excitation following back electron transfer based on the comparison of visible and infrared pump results.