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Free Energy Relationships for the Outer-Sphere Anion–Anion and Anion–Cation Optical Electron Transitions Involving Common Cyanometalate (II) and (IV) Donors: Evidence for the Frequency-Distorted Reorganization Dynamics

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Abstract

This work is an extension of the research project on the outer-sphere optical charge transfer (CT) initiated by Prof. R.R. Dogonadze at the Laboratory founded by him in Tbilisi, Georgia. We report the band deconvolution procedures and accomplished free energy relationships for recently observed novel outer-sphere anion–anion and anion–cation optical electron transitions involving common cyanometalate II and IV ions, viz. $[M(CN)_x]^{4-}$, M = Fe, Ru, Os (x = 6) and M = Mo, W (n = 8) as electron donors, and $[Fe^{III}(CN)_6]^{3-}$ and $[Ru^{III}(NH_3)_6]^{3+}$ as electron acceptors, respectively. The CT band maximum vs. the redox asymmetry

free energy relationships, constructed through the consideration of spin-orbit splitting effects, exhibit linear character with slopes close to unity as predicted theoretically, and fully confirm the assignment of these transitions to outer-sphere optical electron transitions as outlined in the preceding works. The preliminary comparative analysis of presented relationships based on the contemporary charge transfer theory and recent differential *DO-D* stretching overtone data strongly suggests the essential redox asymmetry for the reorganization free energy increments attributed to first solvating shells of cyanometalate ions involved.

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