

VIBRATIONAL MODE COUPLING TO REVERSE ELECTRON TRANSFER IN $(\text{CN})_5\text{FeCNRu}(\text{NH}_3)_5^-$ IN SOLUTION

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(Received 7 April 1997)

We present charge transfer absorption, resonance Raman and time-resolved infrared spectral data for $(\text{CN})_5\text{FeCNRu}(\text{NH}_3)_5^-$ in various solvents. The transient infrared spectra and anisotropies reveal both non-equilibrium vibrational populations of high frequency modes *and* local solvent heating.

Keywords: Electron transfer; resonance Raman; infrared spectra; transient spectra

The static CT (electronic) absorption spectra (peak frequency and width) of $(\text{CN})_5\text{FeCNRu}(\text{NH}_3)_5^-$ in various solvents are strongly solvent coupled. Analysis of the bands indicates that H_{AB} (electronic mixing) is large, but not strongly solvent dependent. The static IR spectra lead us to conclude that the *trans*-CN stretch (found at ca 2018 cm^{-1} in D_2O), which exhibits strong intensity, is strongly solvent coupled, and shifts to higher frequency with stronger H-bonding (*N*-methylformamide *vs.* Formamide *vs.* D_2O). On the other hand, the *cis*-CN (found at ca 2047 cm^{-1} in D_2O), which exhibits strong intensity, is sharp, and not strongly solvent dependent. The bridging-CN exhibits weak intensity, is sharp and not strongly solvent coupled.

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We have also collected static resonance Raman spectra CT band. The *cis*-CN stretch was not observed. The *trans*-CN was observed, but the intensity was strongly solvent dependent. The bridge-CN stretch exhibited large intensity, a modest solvent effect, and a small frequency shift.

The transient IR spectra seen in Figure 1 may be summarized as follows: Within 1 ps there is a strong bleach of *cis*-CN, a strong induced absorbance of *trans*-CN, which is shifted to lower frequency. With a ca 6 picosecond $1/e$ time there is decay of *trans*-CN induced absorbance, and an associated shifting to higher frequency. Also with about a 6 ps $1/e$ time, there is recovery of *cis*-CN bleach.

The electron transfer occurs in ca 100 fs [1]. Therefore, we interpret these transient IR data in D₂O as follows: Solvent heating induces principal spectral changes. The extent of early time frequency shift suggests H-bond breaking and subsequent reforming at *trans*-CN. The transient IR data also show evidence of non-equilibrium vibrational states induced by the electron transfer process itself. We have simulated these states from the resonance Raman and static IR spectra [2].

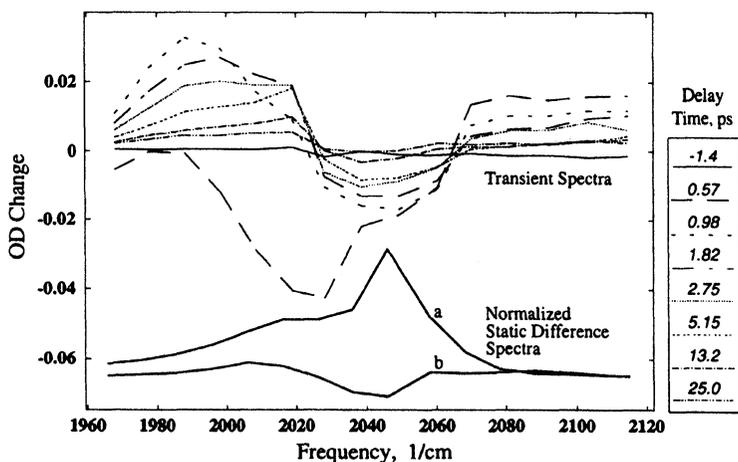


FIGURE 1 Fe-Ru in D₂O. Top: Transient IR spectra at various delay times. Bottom: a, solution minus D₂O difference spectrum; b, further difference spectrum, 90°C minus 26°C.

References

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