

# Femtosecond Study of Electron Photodetachment from Complex Anions: $\text{Fe}(\text{CN})_6^{4-}$ and $\text{CuBr}_2^-$ in $\text{H}_2\text{O}$

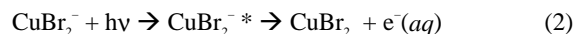
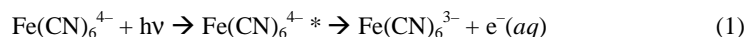
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**Abstract.** The ultrafast dynamics of photoelectron detachment from the molecular anions,  $\text{Fe}(\text{CN})_6^{4-}$  and, for the first time  $\text{CuBr}_2^-$ , are studied in detail by means of pump-multicolor probe spectroscopy and compared to the prototypical  $\Gamma^-$  system.

## 1. Introduction

The development of sub-50 fs UV laser sources allows one to investigate the influence of the solvent environment on very simple chemical reactions in the aqueous phase [1]. Photolysis of the ferrocyanide system has been used as an efficient source of solvated electrons in several recent experiments [2], however the mechanism of photodetachment in complex anions is not well understood. The initial process of the generation of the solvated electron was first observed by Rentzepis with ~2 ps resolution [3], which, however, was not sufficient to observe the electron formation time. In this paper, we present a detailed pump-probe study using a broadband visible/IR probe and explore the effect of excitation into different electronic states of the ferrocyanide ion, as well as the first ultrafast study of another molecular anion,  $\text{CuBr}_2^-$ .



In each case, the initial excited state has been assigned as charge-transfer-to-solvent (CTTS) in analogy to the bands seen in halide ions [4, 5]. However, the existence of overlapping intramolecular electronic bands for these ions may lead to a more involved mechanism for electron detachment. A fascinating possibility exists for reaction (2) that on ultrafast removal of the electron, we will be able to track the neutral  $\text{CuBr}_2$  fragment as it undergoes dissociation or solvolysis – to lead to independent solvated ions.

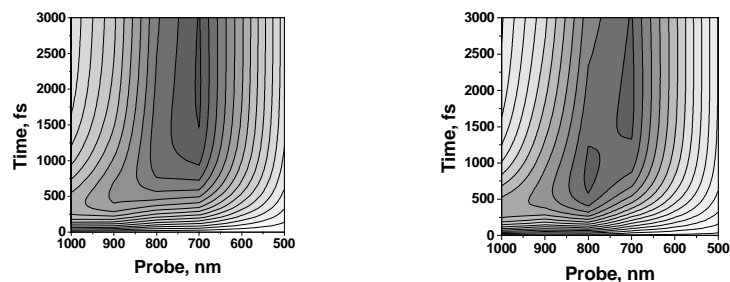
## 2. Experimental Methods

A 200 kHz Ti: sapphire regenerative amplifier producing pulses of 45-50 fs in duration drives a visible-pumped optical parametric amplifier (OPA). Additional 780 nm and 390 nm driven supercontinua are used in our experiment to probe in

the 500-1000 and 350-500 nm spectral range respectively. A 255-300 nm photodetachment pump pulse is generated by temporal-walkoff-controlled second harmonic generation of the OPA signal beam, and is dispersion compensated with pairs of calcium fluoride prisms. At 255 nm, the pump pulse is  $\sim 50$  fs – the pump-probe instrument response throughout is  $\sim 100$  fs. The pump and probe beams are focused into a free flowing jet of the room temperature aqueous solutions containing either 0.04 M  $\text{Fe}(\text{CN})_6^{4-}$  or 0.005 M  $\text{CuBr}_2^-$  ions. In the case of  $\text{Fe}(\text{CN})_6^{4-}$ , the time resolved signal for each probe color has been fitted to an arbitrary multi-exponential function to give an unbiased representation of the data, Figure 1. The transient absorption at 3 ps delay for each probe is normalized to the literature equilibrated hydrated electron spectrum, which is assumed as the only long-time signal carrier over the spectral region displayed. Transient absorption spectra for several pump-probe delays are shown in Figure 2.

### 3. Results and Discussion

The appearance and subsequent time evolution of the electron absorption band subsequent to photodetachment is observed in Figure 1, where it is compared with data for the atomic iodide anion studied in our laboratory [1]. Rise times are fastest

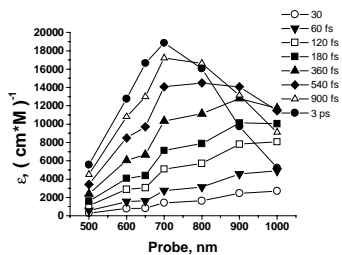


**Fig. 1.** 255 nm pump – multicolor probe experimental data for (left)  $\text{Fe}(\text{CN})_6^{4-}$  in  $\text{H}_2\text{O}$ , (right)  $\text{I}^-$  in  $\text{H}_2\text{O}$ . The thermalization of the ejected electron is faster for  $\text{Fe}(\text{CN})_6^{4-}$ .

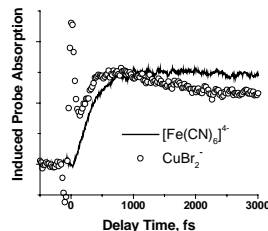
at 1000nm ( 180 fs, compared to 600 fs at 500 nm ), and the band is almost fully developed within 900 fs after resonant photo-oxidation of the  $\text{Fe}^{\text{II}}$  center, Figure 2. The relaxation of the electron is apparently more rapid than in the case of iodide detachment. As we probe further blue than shown in Figure 1, the absorption rise time becomes faster than in the visible ( $\sim 370$ -350 fs at 387 and 400 nm). Both  $\text{Fe}(\text{CN})_6^{3-}$  and the solvated electron absorb in this region. Therefore, results of UV and blue probe experiments, as reported by others [6], are more complex to analyze without separating out the component due solely to the evolution of the ejected electron.

Geminate recombination of the products of reaction (1) is observed over a 100 ps timescale. We find that the recombination yield although small, increases with increasing solution ionic strength over a range of 9 to 20 %. We attribute this to

the fact that  $\text{Fe}(\text{CN})_6^{4-}$  does not exist as a totally dissociated ion in aqueous solution; the fraction of ion pairing with the  $\text{K}^+$  counter ion and thus the effective charge on the geminate recombination target varies with overall solute concentration.



**Fig. 2.** Transient absorption spectra at several delays; 255 nm pump -multi color probe  $\text{Fe}(\text{CN})_6^{4-}$  in  $\text{H}_2\text{O}$ .



**Fig. 3.** 255 nm Photodetachment of  $\text{CuBr}_2^-$  (circles) and  $\text{Fe}(\text{CN})_6^{4-}$  (solid line) with an 800 nm probe, rise times are 140 fs and 350 fs respectively.

The photodetachment of the  $\text{Fe}^{\text{II}}$  center occurs over a wide excitation range with widely varying quantum yield [4]; this is not well understood. To explore the possibility of contrasting ejection pathways on pumping into an intramolecular rather than CTTS state, we have photodetached with well separated pump energies. Surprisingly, pump-probe signals obtained for 255 nm, assigned to a CTTS transition [4], and for 300 nm, an iron  $d-d$  transition [7], are perfectly overlapped for all probe wavelengths recorded. One explanation for the identical electron ejection dynamics is that the poorly resolved CTTS band is in fact very broad and substantially overlaps with the intramolecular electronic transitions.

Finally, the data obtained for electron photodetachment from  $\text{CuBr}_2^-$ , Figure 3, indicate considerably faster electron detachment dynamics than for the multiply-charged ferrocyanide complex ion.

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