

# **Light-Induced Relaxation Dynamics in the Ferricyanide Ion Revisited with Ultrafast XUV Photoelectron Spectroscopy**

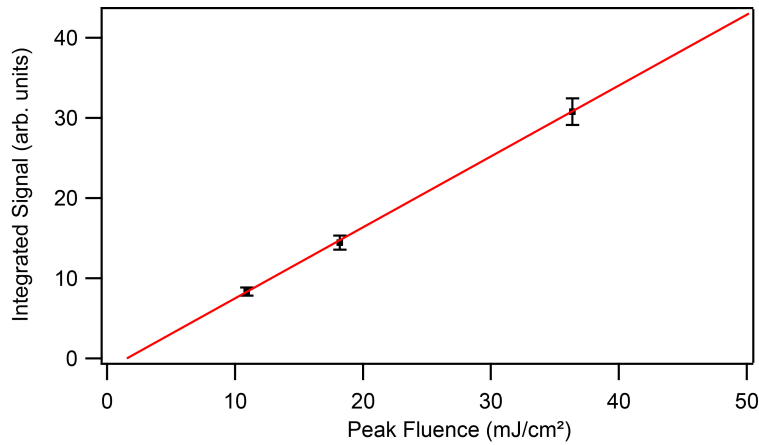
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## **SUPPLEMENTARY INFORMATION**

## Pump intensity study.

In order to verify that the observed dynamics are initiated by absorption of a single pump photon, the transient signal was recorded as a function of the pump beam intensity. The measurements were performed for three values of the pump pulse energy of 1.2, 2, and 4 mJ. These values correspond to a peak energy fluence of 10.8, 18, and 36 mJ/cm<sup>2</sup>, respectively, of the pump beam in the interaction region. The transient signal, recorded at 200 fs time delay and integrated over the binding energy range between 6 and 6.8 eV, is shown in Figure S1, demonstrating a linear dependency on the pump beam intensity. The peak energy fluence of 18 mJ/cm<sup>2</sup> was used during the data acquisition, ensuring that the initial excitation has a one-photon character.



**Figure S1.** Dependency of the transient signal, integrated over the range of binding energies between 6 and 6.8 eV, on the peak energy fluence of the pump beam. The red line depicts the linear dependency.

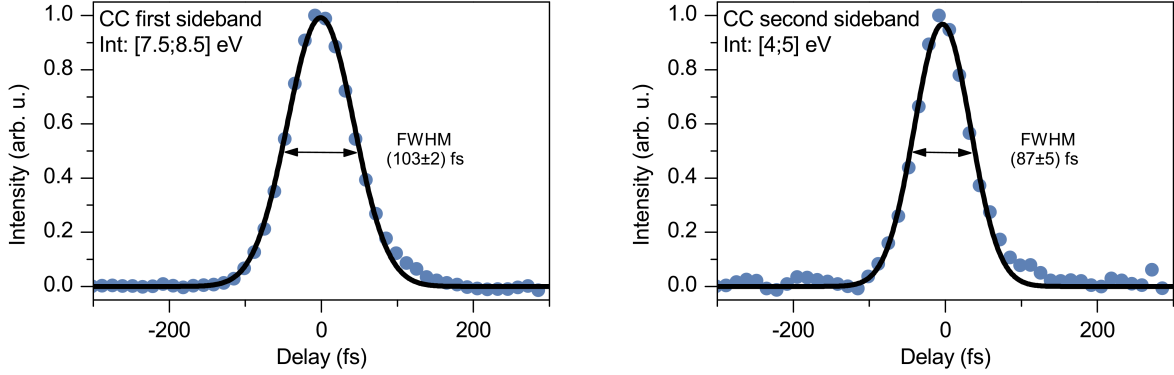
## Cross correlation measurements.

The cross correlation signal in the first- and second-order sidebands of laser-assisted XUV ionization of water was obtained by integrating the transient signal over the energy ranges 7.5–8.5 eV (first sideband) and 4–5 eV (second sideband), respectively. The results are shown in Figure S2, where solid curves represent fitted Gaussian profiles of width  $103 \pm 2$  and  $87 \pm 5$  fs, respectively. The smaller cross correlation width of the second sideband is

consistent with the equation describing the width convolution:

$$\tau^2 = \tau_{\text{XUV}}^2 + \frac{\tau_{\text{pump}}^2}{|N|}, \quad (1)$$

where  $\tau_{\text{pump}}$  and  $\tau_{\text{XUV}}$  are the pulse durations of the pump and probe beams, respectively,  $N$  is the sideband order, and  $\tau$  is the resulting cross correlation width. Using equation (1) and the width values obtained for the first and second sidebands, we find that the pulse duration of the pump beam was approximately 80 fs (FWHM).



**Figure S2.** Cross correlation signal in the first (left panel) and second (right panel) sidebands of laser-assisted XUV ionization of water. Results of fit to Gaussian envelopes are presented by solid lines. The cross correlation widths of 103 and 87 fs, respectively, are obtained from the fit.

## Kinetic models.

**The simple model.** In the simple model, we consider the electron population dynamics of a single excited state  $X_1$ :



where  $P(t)$  is the population rate which is proportional to the pump pulse intensity and  $k_1$  is the decay rate. The differential equation describing the population  $[X_1]$  has the form:

$$\frac{d[X_1]}{dt} = P(t) - k_1[X_1], \quad (3)$$

with the initial condition  $[X_1] = 0$  at  $t \rightarrow -\infty$ . Considering that the pump pulse has a Gaussian time envelope of width  $\sigma$ ,  $P(t) \propto \exp(-t^2/\sigma^2)$ , and that the photoexcitation process is not saturated, equation (3) can be integrated analytically:

$$[X_1](t) = A e^{-k_1 t} (\text{erf}(t/\sigma - \sigma k_1/2) + 1), \quad (4)$$

where  $\text{erf}(x)$  is the error function of argument  $x$ , and  $A$  is a numerical coefficient.

**The extended model.** In the extended model, the electron relaxation dynamics involve an additional state  $X_2$ :



where  $k_2$  denotes the relaxation rate of  $X_2$ . The population of this state is described by the differential equation:

$$\frac{d[X_2]}{dt} = k_1 [X_1] - k_2 [X_2], \quad (6)$$

where  $[X_1](t)$  is given by equation (4), and the initial condition reads  $[X_2] = 0$  at  $t \rightarrow -\infty$ . Equation (6) can be solved analytically:

$$[X_2](t) = B \left( e^{\frac{(k_2^2 - k_1^2)\sigma^2}{4}} e^{-k_2 t} (\text{erf}(t/\sigma - \sigma k_2/2) + 1) - e^{-k_1 t} (\text{erf}(t/\sigma - \sigma k_1/2) + 1) \right), \quad (7)$$

where  $B$  is a numerical constant.

## ***F*-test results.**

In order to compare the results of the models with the measured transient signal, the population of  $X_1$  and  $X_2$  is convoluted with a Gaussian function describing the time envelope of the XUV probe pulse, and the cross correlation yield is included in the fit function. The fit

function, thus, has the form:

$$f(t) = \int_{-\infty}^{+\infty} ([X_1](t') + [X_2](t')) \exp\left(-\frac{(t-t')^2}{\tau_{XUV}^2}\right) dt' + C \exp\left(-\frac{t^2}{\sigma^2 + \tau_{XUV}^2}\right), \quad (8)$$

where  $[X_1](t)$  and  $[X_2](t)$  are given by equations (4) and (7). The numerical constants  $A$ ,  $B$ , and  $C$ , and the decay rates  $k_1$  and  $k_2$  are treated as fit parameters. The second term of the integrand in equation (8) is excluded when fitting results by the simple model.

For the simple model, the fit yields the lifetime of the excited state  $X_1$  of 466 fs (calculated as inverse value of the decay rate,  $k_1^{-1}$ ). When the extended model is fitted, the lifetimes of 170 and 730 fs are obtained for the state  $X_1$  and  $X_2$ , respectively. The reduced  $\chi^2$  values obtained from the fit of the simple and extended models are 1.5 and 1.07, respectively. To provide a solid comparison between the two models, the  $F$  statistics are calculated, given by

$$F = \frac{(\text{RSS}_s - \text{RSS}_e) (n - p_e)}{\text{RSS}_e (p_e - p_s)}, \quad (9)$$

where  $\text{RSS}_s = 0.079$  and  $\text{RSS}_e = 0.055$  are the residual sums of squares obtained from the fit of the simple and extended models, respectively,  $p_s = 3$  and  $p_e = 5$  are the corresponding numbers of fit parameters, and  $n = 84$  is the number of data points. Using these parameters and numbers, we obtain  $F = 17.5$  for the  $F$  statistic. The smaller RSS value extracted for the extended model is statistically significant if the  $F$  statistics exceed a critical value  $F_c$  defined by the F-distribution function,  $F_c = F(p_e - p_s, n - p_e)$ . In the present case we have  $F_c = F(2, 79) = 3.1$ . Thus, the  $F$  statistic significantly exceeds the critical value and the simple model can be rejected with a confidence larger than 99.9%.

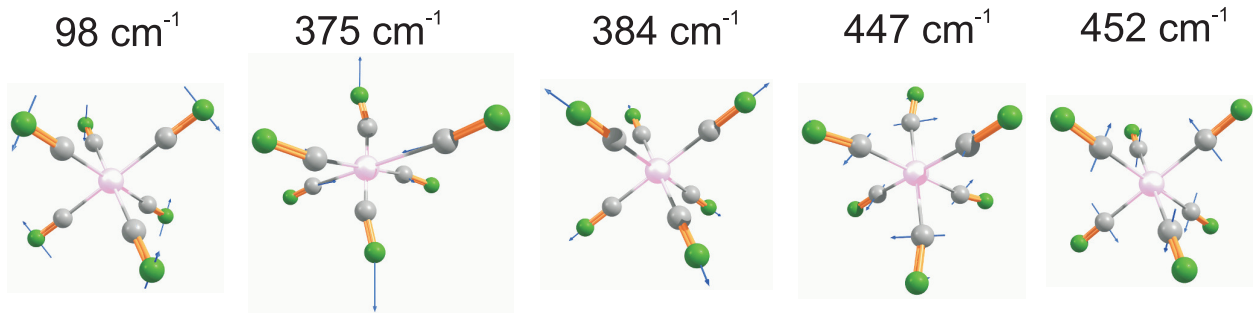
## Calculated Huang-Rhys factors

To indicate the tuning and coupling modes which are responsible for the photophysics of  $[\text{Fe}(\text{CN})_6]^{3-}$  in the lowest excited states, the Huang-Rhys factors have been calculated based on the model of the shifted harmonic oscillators. The results of this analysis are presented

in Table S1 and the modes themselves are shown in Figure S3. Note that large values of Huang-Rhys factors evidence strong anharmonic character of the vibrations and were used here only to select the active modes. All tuning modes as well as coupling modes correspond to the qualitatively similar potential energy cuts. The mode with a ground state frequency of  $384\text{ cm}^{-1}$  has been chosen for illustration purpose (see Figure 5(a) in the main article) because it corresponds to the largest shift between the LMCT doublet and ligand-field quartet states.

**Table S1:** The Huang-Rhys factors for active tuning modes for different states with respect to the ground state. The coupling modes corresponding to pseudo-Jahn-Teller effect are also presented. The ground-state harmonic frequency is denoted by  $\omega$ . Besides symmetry, the states are labeled according to their numerical order:  $D_{3-5}$  are the lowest absorbing doublet LMCT states,  $D_{6,7}$  are the lowest doublet ligand-field states, and  $Q_1$  is the lowest quartet ligand-field state.

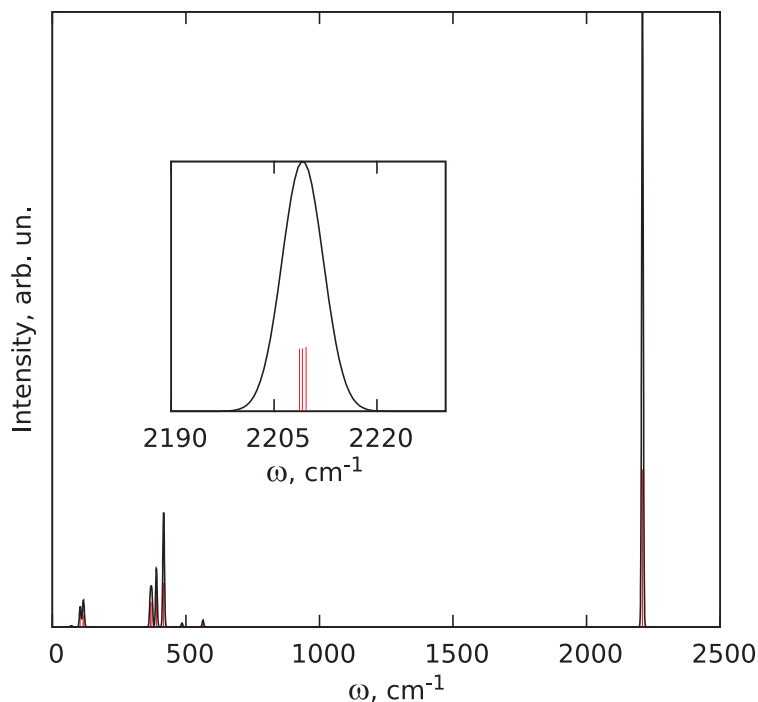
| $\omega, \text{cm}^{-1}$ | Assignment    | Symmetry | Huang-Rhys factors |                  |                  |                 |
|--------------------------|---------------|----------|--------------------|------------------|------------------|-----------------|
|                          |               |          | $D_3(^2A_{2u})$    | $D_{4,5}(^2E_u)$ | $D_{6,7}(^2E_u)$ | $Q_1(^4B_{1g})$ |
| Tunning modes            |               |          |                    |                  |                  |                 |
| 98                       | def(NC–Fe–CN) | $a_{1g}$ | 3.69               | 4.35             | 0.28             | 0.41            |
| 384                      | str(Fe–CN)    | $a_{1g}$ | 1.57               | 1.55             | 12.65            | 16.10           |
| 452                      | rock(CN)      | $a_{1g}$ | 2.29               | 1.96             | 0.21             | 0.21            |
| Coupling modes           |               |          |                    |                  |                  |                 |
| 375                      | str(Fe–CN)    | $e_g$    |                    |                  |                  |                 |
| 447                      | rock(CN)      | $e_g$    |                    |                  |                  |                 |



**Figure S3.** Tuning and coupling normal modes of  $[\text{Fe}(\text{CN})_6]^{3-}$  responsible for the transitions between states considered in the present work.

## Calculated IR spectrum

The IR spectrum of  $[\text{Fe}(\text{CN})_6]^{3-}$  in the ground electronic state of  $D_{3d}$  equilibrium configuration is shown in Figure S4. A Gaussian broadening of  $7\text{ cm}^{-1}$  (FWHM) is applied to the calculated stick spectrum. The broadening width is chosen in accordance with the experimental value reported in Ref. 19. One can see that the C–N stretching normal modes are not degenerate, which is in contrast to octahedral symmetry. However, the splitting between transitions is notably smaller than the line width (see inset). One should also note that the spectrum is obtained in harmonic approximation and the vibrational frequencies are not scaled. Naturally, they are overestimated with respect to the experiment.



**Figure S4.** The IR spectrum of  $[\text{Fe}(\text{CN})_6]^{3-}$  in the ground electronic state of  $D_{3d}$  point group symmetry calculated in the frame of harmonic approximation. A Gaussian broadening of  $7\text{ cm}^{-1}$  (FWHM) is applied. The inset shows the region of C–N stretching vibrations which were in focus in Ref. 19.