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Supporting Information for Publication:

Ultrafast Pump-Probe Spectroscopy of Neutral Fe_nO_m Clusters (n, m < 16)

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The ion signal prior to pulse overlap was confirmed to be a combination of the individual beams. The fluence of the pump and probe beams are adjusted to minimize ion production when either the pump or the probe beam is individually present. Due to the large intensity of certain clusters, some signal was observed with either the pump or probe beam. At negative time delays (the 800 nm beam serves as the pump laser), the signal intensity is equal to the summation of the two beams. At positive time delays, the total signal exceeds the summation of the individual beams. This confirms that 400 nm beam excited the cluster to a state with an appreciable lifetime such that the 800 nm beam could ionize and enhance the signal. Figure S1 shows the enhancement for $FeO_{n=1-5}$.

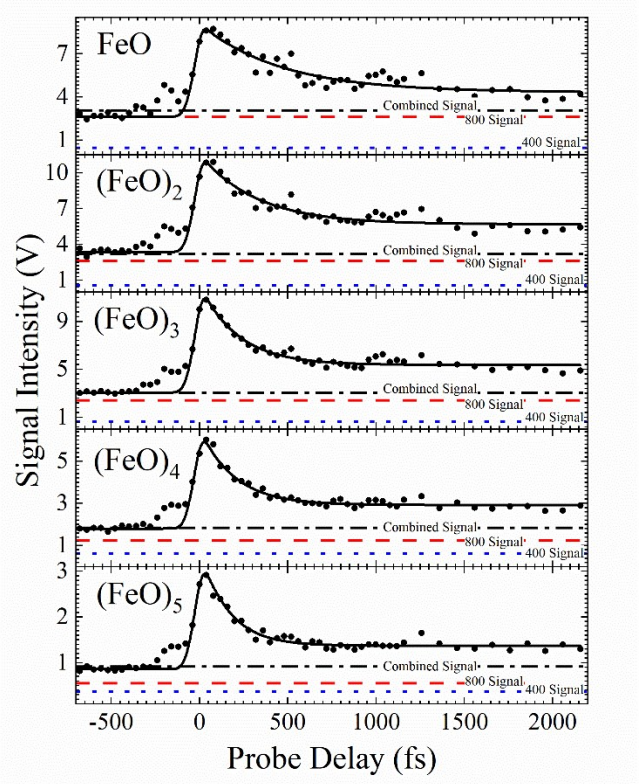

Figure S1. Transients of $(FeO)_n$ ($n < 6$) showing the contribution of the 400 nm (blue short dash), 800 nm (red long dash), and combined signal value (black dot dash) as well as the total ion signal and fit (black solid).

According to first order perturbation theory, the ionization rate, W, of a non-resonant process is proportional to the laser intensity to the power of N as shown in Equation 1:

$$W = \sigma_N I^N, \tag{1}$$

with σ_N representing the laser pulse cross section and N number of photons required involved. This equation can be rearranged to produce a straight line on a log-log plot of signal intensity vs laser intensity, where the slope shows the number of photons involved in ionization:

$$\log_{10}(W) = N\log_{10}(I) + \log_{10}(\sigma_N), \tag{2}$$

This model predicts that the slope will match to integer numbers showing the minimum number of photons required for ionization. However, noninteger values for the slope may suggest resonant intermediate states, fragmentation, or the onset of strong-field ionization which is common with femtosecond laser pulses. Further, this model is developed rigourously for application with single laser beams, and we show here that it can still be applied to obtain reasonable estimates to the photon order for a combination of overlapping laser beams in this experiment. By holding one beam at the flunece used in the pump-probe experiment and scanning the other laser beam, the signal dependence on the varying beam's intensity was analyzed. At temporal overlap, before the molecule has had time to undergo significant relaxation, the power of each beam was individually scannned to determine its photon order on ionization (Figure S2). The slopes are rounded to the nearest integer values. For $FeO_{n=1-3}$, the number of 400 nm photons was determined to be 1, and the number of 800 nm photons required for ionization was determined to be 4 which is in agreement with their ionization potentials as described in the main text.

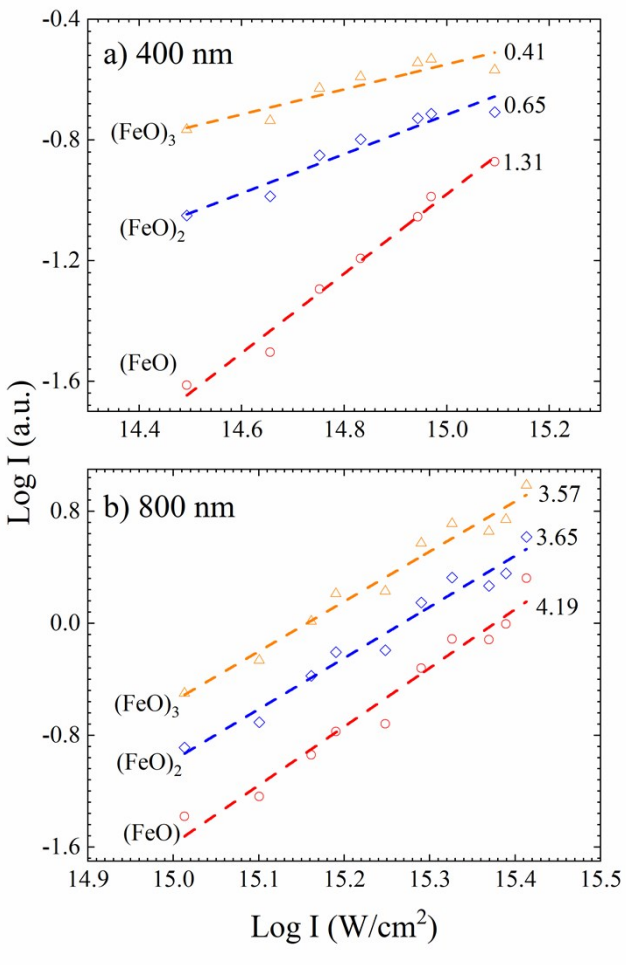

Figure S2. Power dependence of Fe and $(FeO)_n$ ($n < 4$) as a function of a) 400 nm pump and b) 800 nm probe power.

Pump probe scans for the larger clusters are provided here under identical experimental procedures as provided in the main text. Although the noise is increased due to low signal intensity for the larger clustsers, their lifetimes are evaluated and observed to be similar across the cluster size. Figure S3 shows the transient data for the $(FeO)_{9\text{-}12}$ and $(FeO)_{9\text{-}15}O$ clusters.

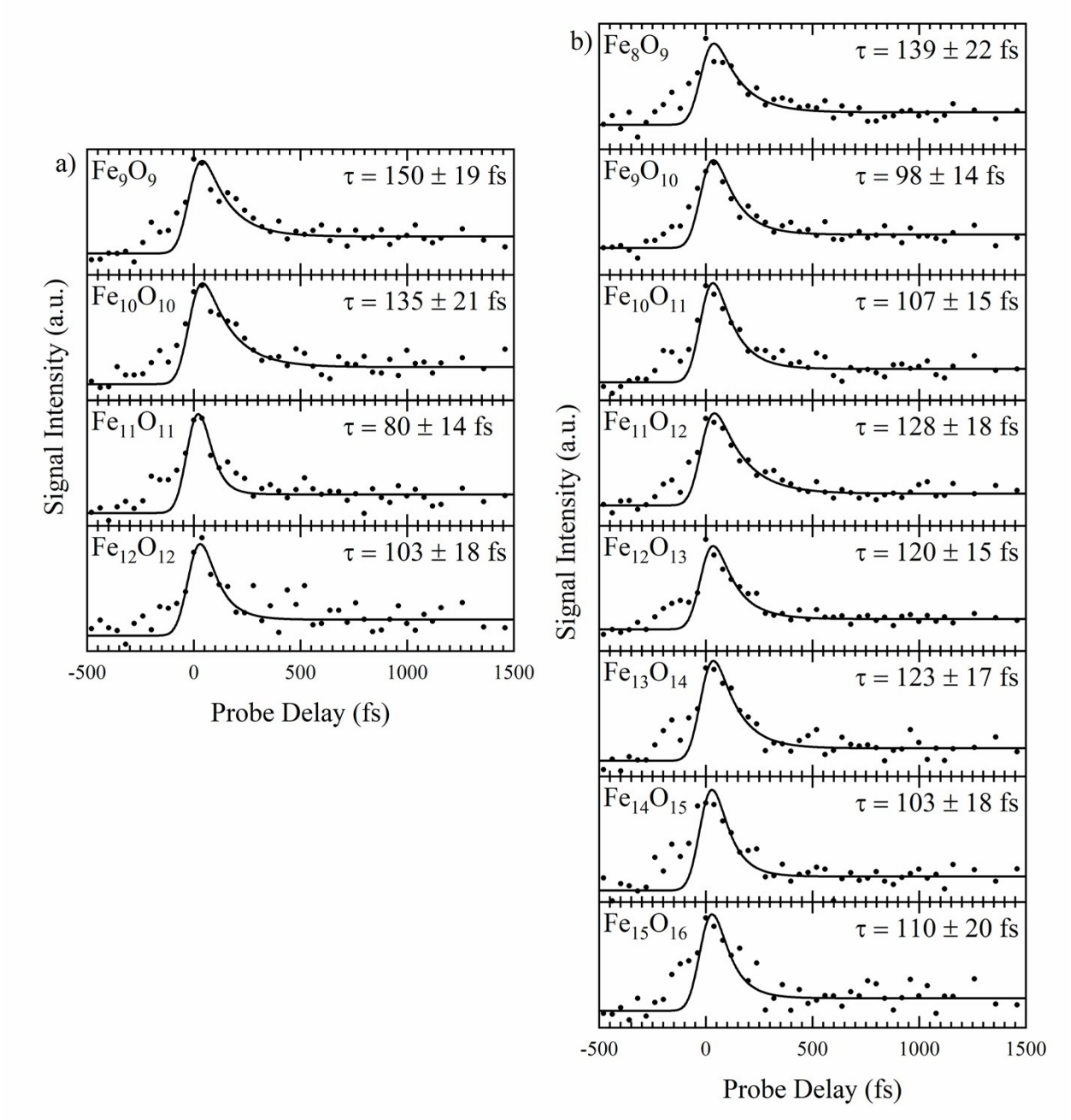

Figure S3. Transient signals and best fit lines of a) $(FeO)_n$ (n = 9-12) and b) $(FeO)_nO$ (n = 8-15)