# The Balance of Independent and Correlated Electron Dynamics in Transition Metals

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Attosecond transient absorption spectroscopy is now a proven method for the investigation of ultrafast electron and phonon dynamics in optically excited solids. In previous work, we found that changes to the local-field effect induced by the near-infrared pump pulses play a characteristic and often dominant role in the transient response of transition metals [1,2] - even if they form part of a compound [3]. This contrasts with simple nearly-free electron metals, such as Al [4], for which the early response is dominated by electron-gas heating, or semiconductors, such as GaAs [5], where the early signal following pump-probe overlap is dominated by state-filling. The dynamics of the latter systems can be accurately described in an independent-electron approach, whereas the local-field effects intrinsically require the inclusion of electron correlations. Nevertheless, state-filling and heating also play a role in transition metals and their compounds. Here, we provide a systematic overview of the electronic response of optically excited transition metals from the few-femtosecond to the many-picosecond timescales and put it into context of prior studies. We will put particular emphasis on how the dynamical balance between state-blocking dynamics and local-field effect depends on the position in the periodic table of elements.

In our experiments, we use extreme ultraviolet (XUV) attosecond pulse trains generated via high-harmonic generation in an argon gas jet and a few-femtosecond near-infrared pump pulse. The broadband high-harmonic spectra probe states around the Fermi level from potentially multiple (shallow) core levels. Electron dynamics are excited in thin-film transition metals, free-standing or evaporated onto 20 nm thick silicon nitride substrates.

For first-row and second-row transition metals Ti and Zr, the influence of the local-field effect was found to follow the pump fluence and instantaneously cancel out the NIR induced state-blocking dynamics [1]. The third-row transition metal $\beta$-W, however, showed a slower rise of the absorption change signal and the balance between state-blocking dynamics and local-field effect changed dynamically due to electron-phonon thermalization [2]. The contrast between these responses was ascribed to a difference in $d$-orbital density of states around the Fermi level and the more delocalized character of the outer $5d$ valence orbitals of $\beta$-W, compared to the $3d$ and $4d$ orbitals of Ti and Zr, respectively..

For the description of the dynamics during electron-electron and electron-phonon relaxation, the influence of an excited electron population on the local-field effect needs to be considered, which typically leads to a broadening of the absorption resonances of transition metals. For the balance between population dynamics and the local-field effect it is found that for first-row transition metals the local-field effect typically compensates a decrease in absorption above the Fermi energy, which is caused by a pump-induced increase in electron population at these energies. Due to the more delocalized nature of their outer orbitals, the induced change in the local-field effect is not strong enough for third-row transition metals to fully compensate for state-blocking dynamics above the Fermi energy. Even though its effect is less pronounced for the more delocalized orbitals, by comparing experimental spectrograms with time-dependent density functional theory, it is found that the local-field effect still needs to be considered to explain the resulting signal on the femtosecond timescale.

In our presentation, we review recent findings from attosecond transient absorption experiments on transition metals and provide a systematic overview of their electronic and phononic response. The influence of the excited electron population on the modification of the local-field effect is found to decrease as the initial state orbitals become more delocalized.

## References


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