How long, and why, do Photoexcited Electrons in a Metal Remain Hot?

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Abstract. Calculations are presented to show how dynamics of photoexcited electrons depend on electron-electron (e-e) and electron-phonon (e-p) interaction strengths. The observed dependence is universal to most metals, and is also somewhat counterintuitive. For example, the time that high energy electron states remain occupied depends only on the strength of e-e interactions, even if e-p interactions are much stronger. Furthermore, even though only e-p interactions can reduce the total energy stored by hot electrons, the time it takes for energy to leave the electronic subsystem is governed by both e-e and e-p interactions. Finally, the effect of e-e interactions on energy-relaxation is largest in metals where e-p interactions are strongest. We report simple expressions that accurately capture the interplay of e-e and e-p interactions on relaxation rates of the hot electron distribution. These findings are important for understanding ultrafast electron dynamics in a diverse range of fields, e.g. ultrafast magnetism, photocatalysis, plasmonics, and others.
Absorption of light by a metal generates a nonthermal distribution of electrons and holes [1-3]. In the femtoseconds to picoseconds after absorption, a complex cascade process emerges from individual electron-electron (e-e) and electron-phonon (e-p) scattering events [4-6]. This cascade process drives the system into a new equilibrium state. We characterize the emergent hot electron cascade process with two time-scales, $\tau_H$ and $\tau_E$. Time $\tau_H$ measures how long the metal contains highly excited electrons with energy comparable to that of the incoming photons, $h\nu$. Somewhat arbitrarily, we define $\tau_H$ as the time for the number of highly excited electrons with energy greater than or equal to $h\nu/2$ to drop by a factor of $1/e$, see Figure 1. Another emergent time scale shown in Figure 1 is $\tau_E$. Time $\tau_E$ is the time required for the total energy stored by all hot electrons to drop by a factor of $1/e$.

Time-scales $\tau_E$ and $\tau_H$ are critical, and distinct, figures of merit for a variety of scientific and engineering endeavors, such as photocatalysis, ultrafast magnetism, and others. Photocatalytic performance of plasmonic metal nanoparticles is often governed by $\tau_H$, as high energy electrons drive chemical reactions [7-10]. On the other hand, ultrafast magnetic phenomena are commonly driven by $\tau_E$ because they depend on how quickly spatial gradients in internal energy are relaxed [11-17]. On time-scales shorter than $\tau_E$, hot electrons transport energy at rates that are 2-3 orders of magnitude faster than is possible after electrons and phonons thermalize [15, 18-21].

Despite the fundamental importance of $\tau_H$ and $\tau_E$, confusion persists over how they depend on the strength of the e-e versus e-p interactions. For example, the time scale, $\tau_H$, is often incorrectly estimated from a simplified Boltzmann rate equation with a Matthiessen’s-like rule [22-25], resulting in $\tau_H^{-1} = \tau_{ee}^{-1} + \tau_{ep}^{-1}$. Here $\tau_{ep}$ is the electron-phonon quasi-particle scattering time. This
treatment leads to the incorrect conclusion that, since e-p scattering rates are stronger than e-e scattering rates, $\tau_H$ depends on the strength of e-p interactions. However, we find that, due to differences in the nature of e-e vs. e-p interactions, $\tau_H$ depends solely on e-e interactions. For photoexcitation with visible light, this is true even if $\tau_{ep}$ is hundreds of times shorter than $\tau_{ee}$. Our finding reconciles the fact that first-principles calculations find similarly strong e-e and e-p interactions in simple metals [22] despite experimental and theoretical studies suggesting that $\tau_H$ is determined by e-e interactions [1, 26].

Unlike for $\tau_H$, the role of e-e interactions is generally ignored when estimating $\tau_E$ and e-p is assumed to dominate [27]. The most common method for determining $\tau_E$ is the two-temperature model [27-29], which neglects the effects of a nonthermal distribution, and therefore e-e interactions. We find that, because of nonthermal effects, for most metals $\tau_E \approx 2.5 \gamma_{ep}^{-0.75} \beta_{ee}^{-0.25}$ instead of simply $\tau_E \approx \gamma_{ep}^{-1}$ as in the two-temperature model. Here $\gamma_{ep}$ and $\beta_{ee}$ are measures of e-p and e-e interaction strength: $\gamma_{ep}$ is the two-temperature model prediction for the energy relaxation rate [28], and $\beta_{ee}$ is the electron-electron relaxation rate for an electron/hole 0.5 eV above/below the Fermi level. The energy relaxation rate remains sensitive to e-e scattering until $\tau_E$ is at least 2 orders of magnitude larger than $\tau_H$.

The outline of the rest of the paper is as follows. First, we summarize our numerical calculation for the hot electron dynamics following the photoexcitation of a broad distribution of electrons and holes. Second, we detail how relaxation times for the photoexcited electrons depend on e-e vs.
e-p interactions. Finally, we conclude by discussing how our results compare to experiment, and how experimental parameters such as laser fluence and ambient temperature will affect dynamics.

Results

To accurately capture the interplaying effects of electron-electron and electron-phonon scattering on the hot electron dynamics, we solve the equation of motion for the electron distribution function in a simple metal

$$\frac{df(\varepsilon,t)}{dt} = \Gamma_{ee}(f(\varepsilon,t)) + \Gamma_{ep}(f(\varepsilon,t))$$

(1)

Here $\varepsilon$ is electron’s energy, $\Gamma_{ee}$ is the e-e collision integral [30], and $\Gamma_{ep}$ is the e-p collision integral [28]. Unlike the commonly used relaxation-time approximation, Eq. (1) accounts for both increases and decreases in $f(\varepsilon,t)$ due to scattering events. Since we are interested in the time-evolution of the hot electrons, we linearize Eq. (1) by defining the hot electron distribution as $\phi(\varepsilon,t) = f(\varepsilon,t) - f_0(\varepsilon)$. Here $f_0$ is the thermal Fermi-Dirac distribution prior to photoexcitation at 300 K. Further details of our calculation are presented in Supplementary Information.

We evaluate $\phi(\varepsilon,t)$ as a function of e-e and e-p interactions strengths, $\beta_{ee}$ and $\gamma_{ep}$. As a measure of the e-p interaction strength, we use $\gamma_{ep}^{-1} = 3\hbar\lambda\langle\omega^2\rangle/\left(\pi k_B T\right)$. This is the energy relaxation rate that results from Eq. (1) with the assumption that $f$ is a Fermi-Dirac distribution at a temperature above ambient. In other words $\gamma_{ep}^{-1}$ is the $\tau_E$ predicted by the two-temperature model [28]. Here, $\lambda\langle\omega^2\rangle$ is the 2nd frequency moment of the e-p spectral function [28]. To measure the e-e interaction strength, we choose the e-e relaxation time for 0.5 eV excitations. This is the lowest
energy where experimental two-photon emission data for electron lifetimes in metals are commonly available [26]. We want the e-e scattering time to be realistic at low excitation energies because $\tau_E$ is most sensitive to e-e scattering at low energies.

Solving Eq. (1) requires initial conditions. We assume photons with energy $hv$ will excite a flat distribution of electrons and holes with concentration $\phi_0 << 1$ that extends to an energy $hv$ above and below the Fermi level. Our conclusions do not rely on the assumption that a flat distribution is excited; we obtain similar results if we assume photons with energy $hv$ only excite electrons and holes at energy $hv/2$ above and below the Fermi level. We limit our focus to photons in the visible spectrum. Our solution of Eq. (1) for $\phi(e,t)$ yields dynamics that are broadly consistent with prior studies that solved similar rate equations to understand hot electron dynamics in specific metals, e.g. Al, Au, Cu [5, 6, 8, 31-34]. New to our study is explicit consideration of how dynamics evolve across a wide range of e-e and e-p scattering strengths.

The rate equation for hot electron dynamics (Eq. 1) predicts a cascade process. We summarize the dynamics in Figure 2 by plotting the predictions of Eq. 1 for the total number of hot electrons vs. time. For realistic values of e-e scattering and e-p scattering strengths, e.g. $\gamma_{ep} / \beta_{ee} \approx 0.25$, e-e scattering increases the number of hot electrons by about a factor of 5 on a $\tau_E$ time-scale. Alternatively, if e-e scattering were infinitely strong, the energy stored in the initial nonthermal distribution would instantly redistribute into a thermal distribution. A thermal hot electron distribution has $\sim 16x$ as many hot electrons as are initially excited.

From $\phi(e,t)$ predicted by Eq. (1), we determine relaxation times for the dynamics as a function of e-p and e-e scattering strengths. Figure 3 shows how $\tau_H$ (time for high energy electrons to
decay into lower energy electrons) and \( \tau_E \) (time for energy of the hot electrons to be transferred to the lattice) depend on \( \gamma_{ep} / \beta_{ee} \). As can be seen from Figure 3, in nearly all metals, \( \gamma_{ep} / \beta_{ee} \) is such that \( \tau_H \) depends only on e-e, while \( \tau_E \) is determined by both e-e and e-p.

We now discuss the origins for the dependence of \( \tau_E \) and \( \tau_H \) on \( \beta_{ee} \) and \( \gamma_{ep} \). For most metals, high energy electrons decay with \( \tau_H \approx C \beta_{ee}^{-1} \), where \( C \approx 0.8 \text{ eV}^2 / (h \nu)^2 \) with our model assumptions. In general, \( C \) will depend on \( \phi(\varepsilon, t = 0) \) and the energy dependence of the e-e scattering times. The dependence of \( \tau_H \) on only e-e interactions can be rationalized as follows. A single electron-phonon interaction will, on average, change the electron’s energy by \( \hbar \langle \omega \rangle \). Here, \( \hbar \langle \omega \rangle \) is the average phonon energy of the metal, which is much smaller than photon energies in the visible range. If all electron-phonon scattering events could move hot electrons towards equilibrium, we would expect energy transfer to the lattice at a rate of \( \hbar \langle \omega \rangle \tau_{ep}^{-1} \) per hot electron, and the quasiparticle e-p scattering time \( \tau_{ep} \) would need to be 50-100x smaller than \( \beta_{ee}^{-1} \) to govern \( \tau_H \). However, this simple analysis overestimates the effect of e-p interactions on \( \tau_H \). Not all phonon scattering events relax the nonthermal hot electron distribution towards equilibrium. Phonon emission decreases the average energy per electron, while phonon absorption increases it. Eq. 1 predicts that the net effect of electron-phonon interactions on dynamics is a decrease in energy per electron at a rate of \( \pi^2 k_B T \gamma_{ep} / (3h) \), which is less than \( \hbar \langle \omega \rangle \tau_{ep}^{-1} \).

The approximation \( \tau_H \approx C \beta_{ee}^{-1} \) breaks down in the limit of strong e-p interactions, e.g. \( \gamma_{ep} / \beta_{ee} \gg 1 \). For metals where literature data is available for both \( \gamma_{ep} \) and \( \beta_{ee} \), we could find
no examples where $\gamma_{ep}/\beta_{ee} \gg 1$. However, metallic compounds with exceptionally strong e-p interactions, such as Be, VN and MgB$_2$ with $\lambda \langle \omega^2 \rangle \approx 2000$ meV$^2$, do not have data available for e-e lifetimes. If these metals possessed weak e-e interaction strengths, e.g. $\beta_{ee}^{-1} > 50$ fs, then $\tau_H$ would be sensitive to the e-p interaction strength.

In contrast to $\tau_H$, $\tau_E$ is sensitive to both e-e and e-p scattering so long as $\gamma_{ep}/\beta_{ee} > 0.05$. While it is obvious the time-scale for energy transfer from electrons to phonons should depend on e-p scattering strength, the importance of e-e scattering is less straightforward. Unlike e-p scattering, e-e interactions do not change the total energy in the electronic subsystem. Instead, e-e interactions alter how energy is distributed across the electronic subsystem. Electron-electron scattering events turn a single electron into three electrons, see Fig. 2. Three electrons transfer energy to the phonons three times as fast as one electron because they will spontaneously emit phonons three times as often. As a result, both e-e and e-p interactions determine $\tau_E$ if electronic interactions don’t rapidly thermalize the electronic subsystem.

The energy relaxation times in Figure 3 are well approximated as $\tau_E \approx 2.5 \cdot \beta_{ee}^{-0.25} \gamma_{ep}^{-0.75}$ provided $0.05 < \gamma_{ep}/\beta_{ee} < 2$. Alternatively, $\tau_E \approx \gamma_{ep}^{-1} + 1.8 \gamma_{ep}^{-1} \left[ 1 - \tanh \left( -0.35 \ln \left[ 0.6 \gamma_{ep}/\beta_{ee} \right] \right) \right]$ is a good approximation for all $\gamma_{ep}/\beta_{ee} < 2$. A survey of literature values for e-e and e-p interaction strength suggest nearly all metals fall in the range of $0.05 < \gamma_{ep}/\beta_{ee} < 2$, see Fig 3. For these metals, the two-temperature model estimate of $\tau_E$ is off by a factor ranging from 1.3 to 3, depending on the ratio $\gamma_{ep}/\beta_{ee}$. 
In the limit of strong e-e scattering, \( \gamma_{ep} / \beta_{ee} < 0.05 \), the predictions of Eq. 1 converge to the two-temperature model prediction, \( \tau_E \approx \gamma_{ep}^{-1} \). In this limit, hot electron relaxation occurs in a two-step process. The first step is e-e scattering drives electrons into a distribution that is nearly thermal. The second step is the near-thermal distribution of hot electrons transferring energy to the lattice on a \( \gamma_{ep}^{-1} \) time-scale. Of the metals where literature values were available for both \( \gamma_{ee} \) and \( \beta_{ee} \), only Rb and Cs had sufficiently weak e-p interactions for the two-temperature model to be valid. Alternatively, due to strong e-e interactions, Pd and Pt are close to meeting the \( \gamma_{ep} / \beta_{ee} < 0.05 \) criteria for two-temperature model validity.

While the two-temperature model will lack predictive power in most systems made up of only one metal, \( \gamma_{ep} / \beta_{ee} < 0.05 \) is easier to satisfy in bilayer systems composed of different types of metals. In a bilayer, if one metal has strong e-e interactions, while the other has weak e-p interactions, e.g. Pt with Au [19, 35], then photoexcited electrons in these systems will relax via a two-step process similar to the one described above for two-temperature behavior [19, 21]. First hot electrons will thermalize in the layer with strong e-e scattering. Second, a now thermalized distribution of hot electrons will exchange energy with phonons in the metal layer with weak e-p interactions. Several recent experimental studies have observed two-step dynamics in metal bilayer systems [19, 21, 35].

Now we compare our model predictions for \( \tau_E \) for Au and Al with the available experimental values. While a variety of experimental studies are sensitive to the cooling rates of photoexcited electrons [29], interpretation of such experiments is not straightforward [8, 36, 37]. Time-resolved measurements of changes in optical properties, e.g. time-domain thermoreflectance or time-
domain transient absorption, are common methods for studying hot electron dynamics [1, 27, 29, 38-40]. However, optical properties depend on the excited electron distribution in a complex way. Therefore, deducing $\tau_E$ from decay-rates of thermoreflectance or transient absorption signals is not trivial [8]. Two recent experimental studies on hot electron dynamics in Au account for this complexity by modeling of how the hot electron distribution correlates to changes in the dielectric function of Au. Both studies conclude hot electrons transfer energy to phonons on a 2-3 ps time-scale. This time-scale is reasonably consistent with time-resolved measurements of thermal diffuse electron scattering of photoexcited Au films [41]. The scattering experiments suggest energy transfer between hot electrons and zone-edge phonon modes occurs in 2 to 3 ps. We conclude our model’s prediction for Au of $\tau_E \sim 2$ ps is in good agreement with experiment. Alternatively, our model prediction for Al of $\tau_E \sim 0.14$ ps agrees less well with the best experimental values available. Tas and Maris estimate $\tau_E \sim 0.23$ ps in Al based on picosecond acoustic measurements that are sensitive to hot-electron diffusion [5]. Time-resolved electron-diffraction measurements of Bragg peaks in Al thin films suggest phonons take $\sim 0.3$ ps to heat up after photoexcitation of the electrons [36].

While the present study considers the regime of low laser fluence, we expect that at larger fluence the type of dynamics, and relaxation times, will be different. At higher fluence, the dynamics will be closer to the two-step process described by the two-temperature model. This change occurs because a higher laser fluence requires fewer e-e scattering events to relax photoexcited electrons to a Fermi-Dirac thermal distribution. To understand why, consider an absorbed fluence of 10 mJ m$^{-2}$ in a 10 nm thick Au film. This energy density spread across a thermal distribution of electrons corresponds to 60 meV per hot electron, much less than eV scale energies of photoexcited
electrons. Alternatively, an absorbed fluence of 10 J m$^{-2}$ spread across a thermal distribution of electrons corresponds to ~0.5 eV per hot electron, which is comparable to the energy of photoexcited electrons. Therefore, a distribution excited by a high fluence laser pulse requires fewer e-e scattering events to evolve to a Fermi-Dirac distribution.

Our calculations were carried out at 300 K, but the results are similar at other temperatures provided $T \ll T_D$, where $T_D$ is the metals Debye temperature. The rate of energy relaxation will increase at lower temperatures because of decreases in electronic heat capacity, i.e. changes in $f_0(\varepsilon,T)$. Changes to e-p scattering rates due to changes in ambient temperature are relatively unimportant. This is because the rate of energy transfer from hot electrons to phonons depends primarily on stimulated phonon emission, which is temperature independent. The effect of temperature is included in our simple approximation for $\tau_E$ via the $\gamma_{ep}$ term.

In conclusion, we have numerically solved the Boltzmann rate equation to quantify how hot electron relaxation rates depend on e-e and e-p interactions. For most simple metals, the rate of energy transfer is sensitive to both e-e scattering and e-p scattering due to cascade dynamics. The energy relaxation time is well approximated as $\tau_E \approx 2.5 \cdot \beta_{ee}^{-0.25} \gamma_{ep}^{-0.75}$, where $\gamma_{ep}$ is the electron-phonon energy relaxation rate predicted for a thermal electron distribution, and $\beta_{ee}$ is e-e scattering rate of an electron or hole 0.5 eV away from the Fermi level. In the limit that $\gamma_{ep} / \beta_{ee} < 0.05$, e-e scattering is effective at establishing a thermal distribution of electrons before significant energy transfer to lattice. In this limit, the two-temperature model is a valid approximation. We can identify only a few metals that meet this
criterion: Rb and Cs. These findings are important for understanding ultrafast electron dynamics in a diverse range of fields, e.g. ultrafast magnetism, photocatalysis, plasmonics, and others.

Figures

**Figure 1.** Time-scales for relaxation of photoexcited distribution of electrons in Au. (a) After excitation with energy $hv$, the occupation states where $|\varepsilon - \varepsilon_f| \geq hv/2$ decays with time $\tau_H$ due to e-e interactions. (b) The photon energy absorbed by the electrons remains in the electronic subsystem for time $\tau_E$, which is 35 times greater than $\tau_H$. 
Figure 2. Time-evolution of the number of hot electrons after excitation with photons of energy $h\nu = 2\, \text{eV}$. Curves are shown for three different values of e-e scattering strengths, $\gamma_{ep}/\beta_{ee} \approx 0.25$ (realistic e-e), 0.05 (strong e-e), and 0 (infinite e-e). For the case of infinitely strong e-e scattering, the initial distribution evolves instantaneously into a thermal distribution, which increases the number of hot electrons by a factor of ~16.

Figure 3. Dependence of relaxation times $\tau_H$ and $\tau_E$ on e-e and e-p interaction strengths. For realistic values of e-e vs. e-p scattering strength, $\tau_H$ depends only on $\beta_{ee}$, while $\tau_E$ depends on both.
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Supplementary Information

Model Details

The numerical calculations are based on the rate equation

\[
\frac{df(\varepsilon,t)}{dt} = \Gamma_{ee}(f(\varepsilon,t)) + \Gamma_{ep}(f(\varepsilon,t)),
\]

(S1)

The electron-phonon collision integral can is approximated as

\[
\Gamma_{ep}(\phi(\varepsilon,t)) \approx \pi h \lambda \langle \omega^2 \rangle \left[ -2 \frac{df_0(\varepsilon)}{d\varepsilon} \phi(\varepsilon) + \left[ 1 - 2f_0(\varepsilon) \right] \frac{\partial \phi(\varepsilon)}{\partial \varepsilon} + k_B T \frac{\partial^2 \phi(\varepsilon)}{\partial \varepsilon^2} \right].
\]

(S2)

Here, \( \lambda \langle \omega^2 \rangle \) is the second frequency moment of the Eliashberg function \( \alpha^2 F(\omega)\omega^{-1} \),

\[
\lambda \langle \omega^2 \rangle = 2 \int d\omega \alpha^2 F(\omega)\omega.
\]

(S3)

We use the analytic solution for the electron-electron collision integral derived in Ref. [S1] for Fermi liquids

\[
\frac{d\phi}{dt} = -\phi(\varepsilon) + \frac{2\beta_{ee}}{\tau_{ee}(\varepsilon)} \left( \frac{1}{(0.5 \text{ eV})^2} \right) \int_{-\infty}^{\infty} d\varepsilon' \phi(\varepsilon') \cosh \left( \frac{\varepsilon'}{2k_B T} \right) \times \left[ \left( \frac{\varepsilon - \varepsilon'}{2k_B T} \right) - \left( \frac{\varepsilon + \varepsilon'}{2k_B T} \right) \right]
\]

(S4)

where
Here, $\varepsilon_f$ is the Fermi energy, and $T$ is the temperature. We show examples of the time-evolution of the occupation vs. energy, $\phi(\varepsilon)$, and energy-distribution vs. energy, $\varepsilon\phi(\varepsilon)$, in Supplemental Figure 1. We show dynamics for Cs, Au, and Li, because the metals represent the whole range of dynamics metals will display. The ratio of interaction strengths, $\gamma_{ep}/\beta_{ee}$, is small, normal, and large in Cs, Au, and Li, respectively.

We have made the following assumptions in our modelling of hot electron dynamics. Eq. 1 assumes the distribution function depends only on energy and time, thereby neglecting variation in angles of the wavevector. When solving Eq. 1 we neglect any rise in internal energy of the lattice, i.e. we assume the heat-capacity of the phonons is infinite. We linearize Eq. (1) by assuming a low fluence for the photoexcitation, $\phi(\varepsilon,t) = f(\varepsilon,t) - f_0(\varepsilon) << 1$, and keeping only terms linear in $\phi(\varepsilon,t)$. We neglect the dependence of the e-p spectral function on electron energy. We neglect the energy dependence of the electronic density of states and the energy dependence of the electron-electron scattering matrix element. By setting the initial distribution to $\phi(\varepsilon,t = 0) = \phi_0$ at all energies within $\hbar\nu$ of the Fermi-level, we are assuming an energy independent joint-density of states. These latter three assumptions are all related to the energy dependence of the electronic density of states. We discuss these latter three assumptions in more detail below.

First-principles calculations suggest the strength of e-p interactions vary can vary by as much as a factor of five within 2-3 eV of the Fermi-level [S2]. We neglect this energy-dependence in our
calculation. This assumption is reasonable for the following reasons. First, electron-phonon interactions don’t have a significant influence on $\tau_H$ in most metals, even if the e-p interaction strength is multiplied by a factor of 5. Therefore, this assumption will not influence our conclusion that $\tau_H$ is determined by e-e interactions. Second, the value of $\tau_E$ is sensitive to the strength of e-p interactions at electron energies that are occupied on $\tau_E$ time-scales. On $\tau_E$ time scales, most hot electrons and holes are within a few hundred meV of the Fermi level. Assuming a constant e-p interaction across energy scales of a few hundred meV is more reasonable than a few eV. We expect our assumption to introduce the most error in metals with peaks in the density of states near the Fermi level, e.g. Pt, and Pd. For example, in Pt, the value of $\lambda \left< \omega^2 \right>$ at the Fermi-level vs. 0.5 eV above the Fermi-level varies by a factor of two from ~120 to 60 meV$^2$. Therefore we expect our model to underestimate $\tau_E$ for metals such as Pt and Pd with an error on the order of 50%.

Equations (4) and (5) are an overly simplistic description of the energy dependence of e-e scattering. By assuming an $\epsilon^2$ dependent e-e scattering time, and setting the curvature based on the lifetime of 0.5 eV excitations, we are overestimating the electron-electron scattering rate for higher energy excitations in most transition metals. Transistion metals do not display an $\epsilon^2$ energy dependence away from the Fermi-level. This oversimplification will cause a small error for $\tau_E$, because the sensitivity to e-e interactions is small. For example, a factor of two error in e-e scattering time at all energies will cause only a 20% error in $\tau_E$. Alternatively, $\tau_H$ is entirely determined by the e-e scattering time of high energy excitations, and therefore the error will be larger.

We assumed the photoexcitation of a metal with photons of energy $hv$ results in an intial
occupation of electrons and holes that is independent of energy within $h\nu$ of the Fermi level. This assumption will effect $\tau_H$, but not $\tau_E$. $\tau_H$ is a weighted average of the electron-electron scattering times for high energy excitations. If different states are excited, the weighted average will be different. Alternatively, $\tau_E$ is not sensitive to whether the initial distribution is broad or narrow because e-e scattering quickly relaxes the initial distribution into a nonthermal distribution with states occupied closer to the Fermi level.

**Approximate Expressions for Time-Scales of the Dynamics**

In the main text we provided simple expressions that work for the e-e and e-p interaction strengths observed for most metal systems. Here we present more complicated expressions that work across the entire range of e-e and e-p scattering strengths provided $h\nu$ is greater than 0.5 eV.

The energy relaxation time for $\gamma_{ep}/\beta_{ee} < 10^5$ is

$$\tau_{E/\gamma_{ep}} = 1 + A \left(1 - \tanh \left[ B \left( \frac{\gamma_{ep}}{\beta_{ee}} \right)^{-0.42} \right] \right) + C \left( \sech \ln \left[ D \left( \frac{\gamma_{ep}}{\beta_{ee}} \right)^{-0.42} \right] \right)^2,$$

With $A = -0.34 + 2.3h\nu$, $B = 1.5(h\nu)^{1.2}$, $C = -0.25 + 0.53(h\nu)^{1.1}$, and $D = 0.63h\nu$. Alternatively, the lifetime of high energy electrons is well approximated as

$$\tau_{H/\beta_{ee}}(h\nu)^2 = E \left(1 + \tanh \left[ F \left( \frac{\gamma_{ep}}{\beta_{ee}} \right)^{-0.47} \right] \right),$$

with $E = 0.39$, and $F = 0.11 + 1.9(h\nu)^{1.4}$.

**Literature Values for Interaction Strengths**

The values of e-e and e-p interaction strengths we found in the literature for various metals are reported in Supplemental Table 1. The values for $\lambda \left(h^2\omega^2\right)$ were taken from a compilation of
values reported by Phil Allen in Ref. [S3]. While it is not an input into our model calculations, we include values for $\tau_{ep}$ in Supplemental Table 1 for comparison. We estimate these using the formula $\tau_{ep} \approx \hbar / \left(2\pi \lambda k_B T\right)$. The values for the e-e scattering time of the alkali metals was taken from a theory calculation by MacDonald in Ref. [S4]. With the exception of Pt and Tb, the remaining values of e-e scattering times were taken from experimental two-photoemission measurements of electron lifetimes [S5]. The e-e scattering times for Pt and Tb were assumed to be equivalent to Pd and Gd, respectively. We don’t list values for $\tau_H$ for the transition and rare-earth metals in Supplemental Table 1, because we expect $\tau_H$ in these metals to be different than what our model predicts due to our model assumptions described above.

Supplemental References

[S1] V. V. Kabanov, A. Alexandrov, PRB 2008, 78, 174514.
[S2] M. Bernardi, J. Mustafa, J. B. Neaton, S. G. Louie, Nat. Comm. 2015, 6.
[S3] P. B. Allen, PRB 1987, 36, 2920.
[S4] A. H. MacDonald, R. Taylor, D. Geldart, PRB 1981, 23, 2718.
[S5] M. Bauer, A. Marienfeld, M. Aeschlimann, Progress in Surface Science 2015, 90, 319.
Table S1. Literature values for the electron-electron and electron-phonon interaction strengths of various metals. We also include the predictions of Equations S1-S5 for $\tau_E$ of each metal, and $\tau_H$ of the free-electron like metals.

| Metal | $\lambda \langle h^2 \omega^2 \rangle$ (meV²) | $\tau_{ep}$ (fs) | $\gamma_{ep}^{-1}$ (fs) | $\beta_{ee}^{-1}$ (fs) | $\gamma_{ep}/\beta_{ee}$ | $\tau_E$ (fs) | $\tau_H$ (fs) |
|-------|---------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Li    | 160                             | 12             | 110            | 230            | 2              | 330            | 42             |
| Na    | 13                              | 29             | 1400           | 350            | 0.25           | 2500           | 68             |
| K     | 3.4                             | 37             | 5200           | 550            | 0.1            | 7400           | 110            |
| Rb    | 1.8                             | 27             | 9900           | 330            | 0.03           | 10600          | 64             |
| Cs    | 0.85                            | 25             | $2.1 \cdot 10^4$ | 240            | 0.01           | 3050           | 47             |
| Ta    | 190                             | 4.6            | 93             | 17             | 0.2            | 150            |                |
| Mo    | 240                             | 13             | 74             | 57             | 0.8            | 173            |                |
| Fe    | 280                             | 12             | 63             | 7.5            | 0.11           | 92             |                |
| Rh    | 420                             | 10             | 42             | 12             | 0.3            | 77             |                |
| Ni    | 230                             | 13             | 77             | 14             | 0.2            | 130            |                |
| Pd    | 160                             | 8.6            | 110            | 8              | 0.07           | 140            |                |
| Pt    | 170                             | 6.1            | 100            | 8              | 0.08           | 130            |                |
| Cu    | 57                              | 31             | 310            | 160            | 0.5            | 660            | 31             |
| Ag    | 26                              | 34             | 680            | 300            | 4.4            | 920            | 51             |
| Au    | 15                              | 27             | 1200           | 300            | 0.25           | 2100           | 58             |
| Al    | 300                             | 9.4            | 59             | 40             | 0.7            | 140            | 8              |
| Gd    | 90                              | 6              | 200            | 28             | 0.14           | 306            |                |
| Tb    | 90                              | 6              | 200            | 18             | 0.1            | 270            |                |
**Figure S1.** Hot electron distribution (top row) and hot electron energy distribution (bottom row) of cesium at selected times. \(E\)-\(p\) interactions in Cs are much weaker than \(e\)-\(e\) interactions.

**Figure S2.** Hot electron distribution (top row) and hot electron energy distribution (bottom row) of gold at selected times. The ratio of \(e\)-\(p\) to \(e\)-\(e\) interaction strength in Au is typical of most metals.
Figure S3. Hot electron distribution (top row) and hot electron energy distribution (bottom row) of lithium at selected times. The ratio of e-p to e-e interaction strength in Li is higher than most metals.