

Supplemental Information for “Parametric dependence of hot electron relaxation timescales on electron-electron and electron-phonon interaction strengths”

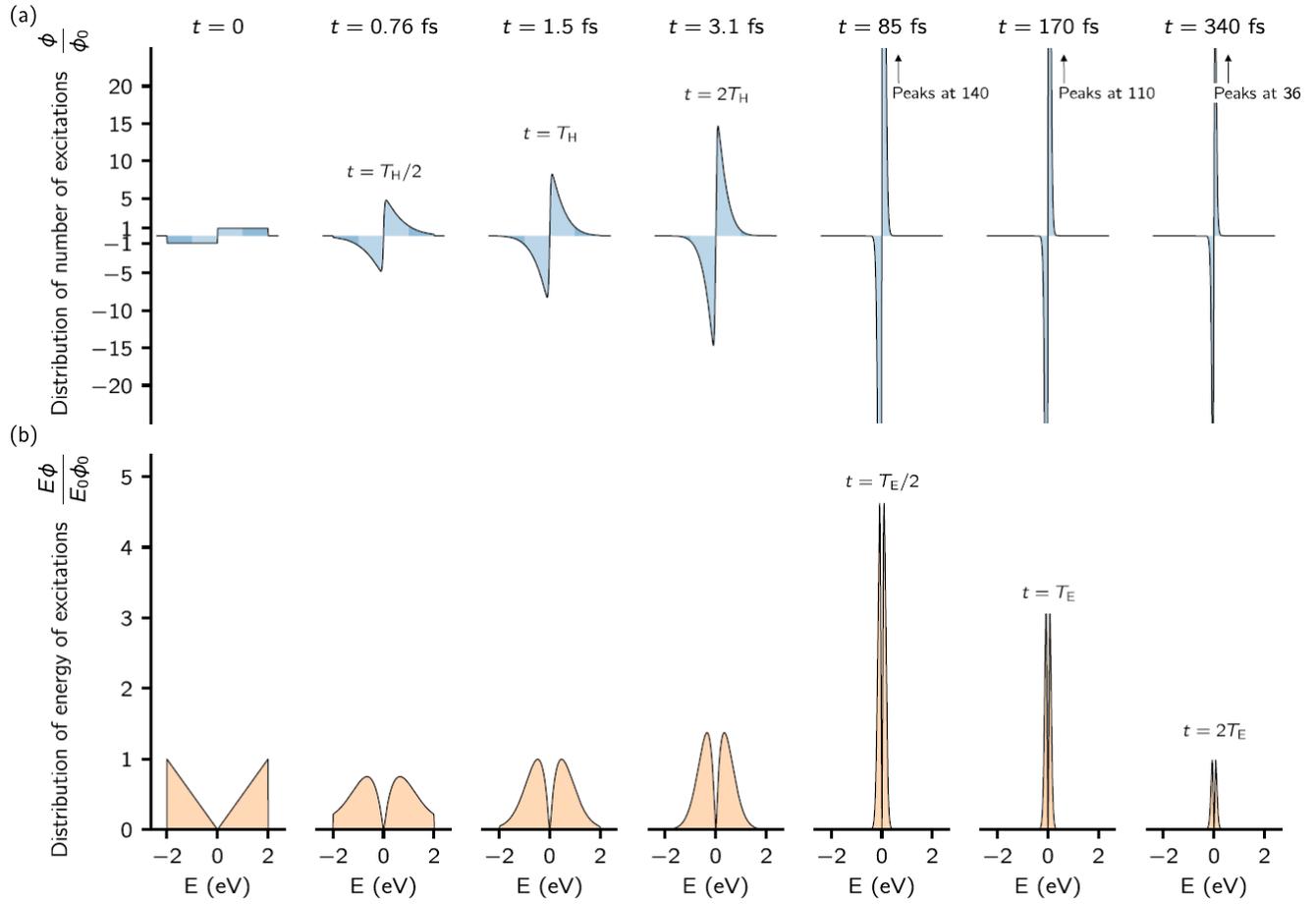
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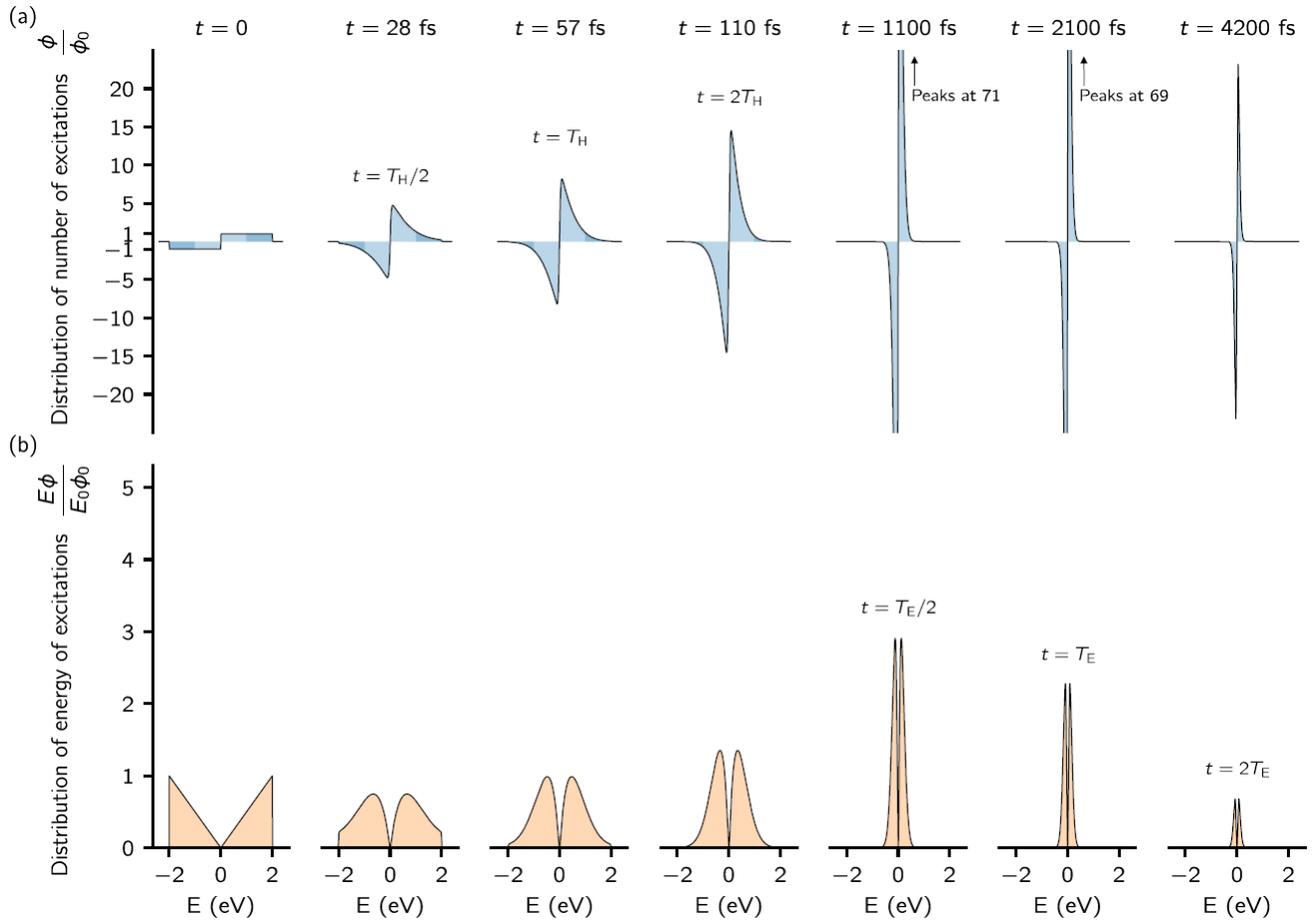
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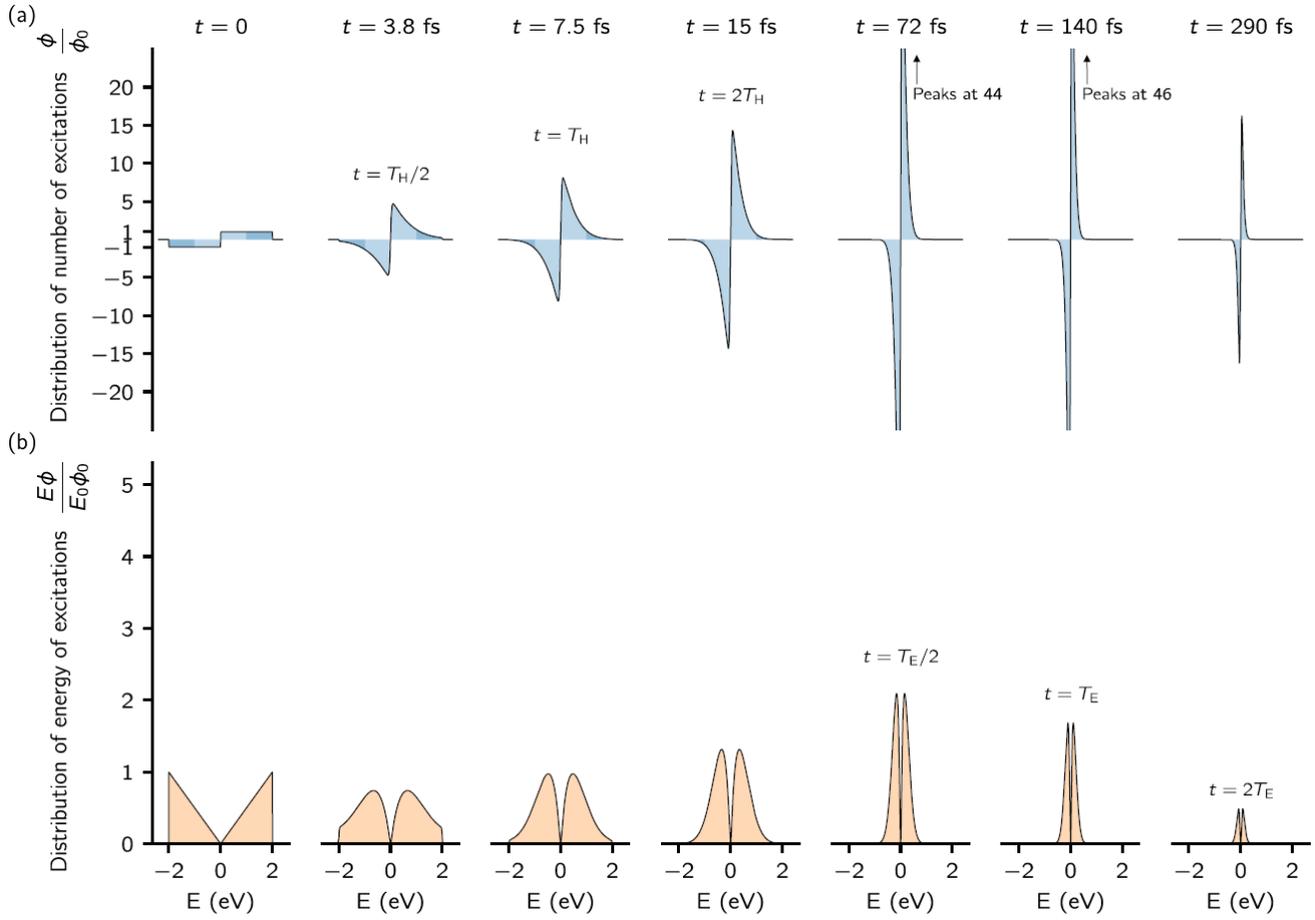
Supplementary Figures



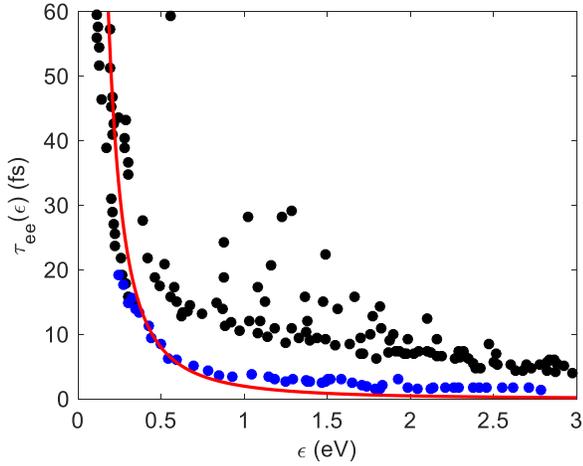
Supplementary Figure 1 | Hot Electron Dynamics in Pt. (a) Hot electron distribution and (b) hot electron energy distribution of Pt at selected times. The ratio of electron-phonon to electron-electron interaction strength for Pt is lower than most metals, $\gamma_{ep} / \beta_{ee} \approx 0.08$.



Supplementary Figure 2 | Hot Electron Dynamics in Au. (a) Hot electron distribution and (b) hot electron energy distribution of gold at selected times. The ratio of electron-phonon to electron-electron interaction strength in Au is typical of most metals, $\gamma_{ep} / \beta_{ee} \approx 0.25$.



Supplementary Figure 3 | Hot Electron Dynamics in Al. (a) Hot electron distribution and (b) hot electron energy distribution of Aluminum at selected times. The ratio of electron-phonon to electron-electron interaction strength in Al is higher than most metals, $\gamma_{ep} / \beta_{ee} \approx 0.6$.



Supplementary Figure 4 | Average lifetime of nonequilibrium electrons in Pd. The red line is the prediction of Eq. (6) in main text using the value for e-e interaction listed in Table 1 in the main text, $\beta_{ee}^{-1} \approx 8$ fs. The black circles are taken from first-principles predictions by Ladstädter et al.¹. The blue circles are experimental values from two-photon photoemission measurements². Fixing the e-e interaction strength based on the 0.5 eV lifetime results in a reasonable prediction for τ_{ee} by our model at energies less than 1 eV. The energy relaxation time, τ_E , is most sensitive to the e-e scattering times of electrons with energies below 1 eV.

Supplementary Notes

Supplementary Note 1.

Here, we derive the electron-phonon collision integral. Consider the electronic states in a metal described by wavevectors \vec{k} and $\vec{k} + \vec{q}$, and energies $\varepsilon(\vec{k})$ and $\varepsilon(\vec{k} + \vec{q})$. There are four types of electron-phonon interactions that cause transitions between state \vec{k} and $\vec{k} + \vec{q}$.

- (1) Absorption of phonon \vec{q} causing an electron to scatter from \vec{k} to $\vec{k} + \vec{q}$.
- (2) Emission of phonon $-\vec{q}$ causing an electron to scatter from \vec{k} to $\vec{k} + \vec{q}$.
- (3) Absorption of phonon $-\vec{q}$ causing an electron to scatter from $\vec{k} + \vec{q}$ to \vec{k} .
- (4) Emission of phonon \vec{q} causing an electron to scatter from $\vec{k} + \vec{q}$ to \vec{k} .

Interactions of type (1) and (2) decrease the occupation of state \vec{k} (out scattering), while (3) and (4) increase its occupation (in scattering). The rate at which phonon \vec{q} is absorbed by an electron is proportional to the phonon occupation N_q . The rate at which phonon \vec{q} is emitted by an electron is proportional to $N_q + 1$, where the N_q accounts for stimulated emission and 1 accounts for spontaneous emission. The rate of change in occupation of state \vec{k} due to a phonon with momentum \vec{q} is

$$\Phi_q = \frac{2\pi}{\hbar} |M_j(\vec{q})|^2 \{ (\Delta_1 + \Delta_4) \delta(\varepsilon(\vec{k}) - \varepsilon(\vec{k} + \vec{q}) + \hbar\omega_j(\vec{q})) + (\Delta_2 + \Delta_3) \delta(\varepsilon(\vec{k}) - \varepsilon(\vec{k} + \vec{q}) - \hbar\omega_j(-\vec{q})) \}, \quad (\text{S1})$$

$$\Delta_1 = -f(\vec{k}) N_q [1 - f(\vec{k} + \vec{q})], \quad (\text{S2})$$

$$\Delta_2 = -f(\vec{k}) [N_q + 1] [1 - f(\vec{k} + \vec{q})], \quad (\text{S3})$$

$$\Delta_3 = [1 - f(\vec{k})] N_q [f(\vec{k} + \vec{q})], \quad (\text{S4})$$

$$\Delta_4 = [1 - f(\vec{k})] [N_q + 1] [f(\vec{k} + \vec{q})]. \quad (\text{S5})$$

Here, $|M_j(\vec{q})|^2$ is the square of the matrix element that governs how strongly phonon \vec{q} in branch j couples the electronic states. The delta functions require the transitions between electronic states conserve energy. The occupation factor $f(\vec{k})$ and $[1 - f(\vec{k})]$ occupation factors account for the fact

that transitions occur from occupied states into empty states. The total rate of change in state \bar{k} due to all electron-phonon interactions is determined by summing Eq. (1) over all phonon branches j and phonon states q ,

$$\left(\frac{\partial f(\bar{k})}{\partial t}\right)_{\text{ep}} = \sum_j \int \frac{d^3q}{(2\pi)^3} \Phi_q. \quad (\text{S6})$$

We turn this into an expression for the occupation of states with energy $\varepsilon(\bar{k})$ by averaging over angles \bar{k} ,

$$\left(\frac{df(\varepsilon)}{dt}\right)_{\text{ep}} = \frac{1}{D(\varepsilon)} \sum_k \frac{df(k)}{dt} \delta(\varepsilon - \varepsilon(k)). \quad (\text{S7})$$

Here, $D(\varepsilon)$ is the electronic density of states at energy ε . Multiplying Eq. (S7) by the integrals $\int d\varepsilon' \delta(\varepsilon(k+q) - \varepsilon')$ and $\int d\omega \delta(\omega(q) - \omega)$, i.e. multiplying Eq. (S7) by unity twice, yields

$$\left(\frac{df(\varepsilon)}{dt}\right)_{\text{ep}} = \int d\varepsilon' \int d\omega \left[\frac{1}{D(\varepsilon)} \sum_k \int \frac{d^3q}{(2\pi)^3} \Phi_q \delta(\varepsilon - \varepsilon(k)) \delta(\varepsilon' - \varepsilon(k+q)) \delta(\omega - \omega(q)) \right]. \quad (\text{S8})$$

Equation (S8) is equivalent to Eq. (S7). This is evident by considering what happens if we evaluate the integrals in Eq. (S8) over $d\varepsilon'$ and $d\omega$. The delta functions will result in ε' becoming $\varepsilon(k+q)$, and ω becoming $\omega(q)$, thereby recovering Eq. (S7). After rearranging the integrals in Eq. (S8), we arrive at

$$\left(\frac{df(\varepsilon)}{dt}\right)_{\text{ep}} = 2\pi \int d\varepsilon' \int d\omega Q(\omega, \varepsilon, \varepsilon') \left[\delta(\varepsilon - \varepsilon' + \hbar\omega) H_a(\varepsilon, \varepsilon', \omega) + \delta(\varepsilon - \varepsilon' - \hbar\omega) H_e(\varepsilon, \varepsilon', \omega) \right]. \quad (\text{S9})$$

Here, the functions H_a and H_e contain the information in Δ_1 , Δ_2 , Δ_3 , and Δ_4 , but averaged over angles \bar{k} :

$$H_a(\varepsilon, \varepsilon', \omega) = -f_e(\varepsilon) N_p(\omega) [1 - f_e(\varepsilon')] + [1 - f_e(\varepsilon)] [N_p(\omega) + 1] f_e(\varepsilon'), \quad (\text{S10})$$

$$H_e(\varepsilon, \varepsilon', \omega) = -f_e(\varepsilon) [N_p(\omega) + 1] [1 - f_e(\varepsilon')] + [1 - f_e(\varepsilon)] [N_p(\omega)] f_e(\varepsilon'). \quad (\text{S11})$$

In Eq. (S9), we have introduced the electron-phonon spectral function

$$\alpha^2 F(\omega, \varepsilon, \varepsilon') = \frac{1}{\hbar D(\varepsilon)} \sum_k \sum_q |M_j(q)|^2 \delta(\varepsilon - \varepsilon') \delta(\varepsilon' - \varepsilon(k+q)) \delta(\omega - \omega(q)). \quad (\text{S12})$$

The electron-phonon spectral function contains all the useful information regarding the electron-phonon interaction in metals³. We follow Kabanov et al.⁴ and assume the e-p spectral-function will be independent of electron energy $\alpha^2 F(\omega, \varepsilon, \varepsilon') = \alpha^2 F(\omega)$. With the assumption that $\alpha^2 F(\omega)$ is independent of ε , we execute the integral in Eq. (S9) over ε' to get

$$\left(\frac{df(\varepsilon)}{dt}\right)_{\text{ep}} = 2\pi \int d\omega \alpha^2 F(\omega) [H_a(\varepsilon, \varepsilon + \hbar\omega, \omega) + H_e(\varepsilon, \varepsilon - \hbar\omega, \omega)]. \quad (\text{S13})$$

In Eq. (S13) $H_a(\varepsilon, \varepsilon + \hbar\omega, \omega)$ describes all e-p interactions that link electronic states with energy ε to energy $\varepsilon + \hbar\omega$, while $H_e(\varepsilon, \varepsilon - \hbar\omega, \omega)$ describes interactions that link $\varepsilon - \hbar\omega$ to ε . Next, we introduce our definition for the nonequilibrium electron distribution function $f(\varepsilon) = f_0 + \phi(\varepsilon)$. We also Taylor series expand $f(\varepsilon')$ and $\phi(\varepsilon')$ terms out to second order in ω . With this approximation, Eq. (S10) and Eq. (S11) for yields

$$H_a(\varepsilon, \varepsilon + \hbar\omega, \omega) + H_e(\varepsilon, \varepsilon - \hbar\omega, \omega) \approx N_p(\omega) (\hbar\omega)^2 \frac{\partial^2 \phi}{\partial \varepsilon^2} + \left(-2 \frac{\partial f_0}{\partial \varepsilon} \hbar\omega\right) \phi(\varepsilon) + (1 - 2f_0(\varepsilon)) \hbar\omega \frac{\partial \phi}{\partial \varepsilon} + \frac{1}{2} (\hbar\omega)^2 \frac{\partial^2 \phi}{\partial \varepsilon^2} \quad (\text{S14})$$

The terms that describe the effects of spontaneous phonon emission are largest, therefore spontaneous phonon emission is the most important type of e-p interaction for nonequilibrium dynamics.

Plugging the expression for $H_a + H_e$ in Eq. (S14) into Eq. (S13) yields

$$\left(\frac{df(\varepsilon)}{dt}\right)_{\text{ep}} \approx 2\pi \int d\omega \alpha^2 F(\omega) \times \left\{ \left[-2 \frac{df_0(\varepsilon)}{d\varepsilon} \hbar\omega\right] + \hbar\omega \frac{\partial \phi(\varepsilon)}{\partial \varepsilon} [1 - 2f_0(\varepsilon)] + \frac{1}{2} (\hbar\omega)^2 \frac{\partial^2 \phi(\varepsilon)}{\partial \varepsilon^2} [2N_p(\omega) + 1] \right\}, \quad (\text{S15})$$

Only one term in Eq. (S15) contains $N_p(\omega)$, meaning the e-p collision integral depends only weakly on temperature. Evaluating the integral over ω for all terms in Eq. (S15) that do not contain $N_p(\omega)$ yields

$$\left(\frac{df(\varepsilon)}{dt}\right)_{\text{ep}} \approx \pi \hbar \lambda \langle \omega^2 \rangle \left[\left(-2 \frac{df_0}{d\varepsilon}\right) \phi(\varepsilon) + (1 - 2f_0) \frac{\partial \phi(\varepsilon)}{\partial \varepsilon} \right] + \chi \frac{\partial^2 \phi(\varepsilon)}{\partial \varepsilon^2}, \quad (\text{S16})$$

$$\chi = \pi\hbar \left[2\hbar \int d\omega N_p(\omega) \omega^2 \alpha^2 F(\omega) + \hbar \frac{\lambda \langle \omega^3 \rangle}{2} \right]. \quad (\text{S17})$$

Here, the terms of the form $\lambda \langle \omega^n \rangle$ are the n th frequency moments over the Eliashberg function, as defined in Eq. (4) of the main text. As a final simplification, we take the high temperature limit for the phonon occupation function, i.e. $\chi \approx k_B T \pi \hbar \lambda \langle \omega^2 \rangle$. With this substitution, Eq. (S16) is equivalent to Eq. (5) in the main text.

Our study is concerned with electron dynamics at room temperature. To confirm that using the high temperature approximation for χ won't affect our conclusions, we consider the dynamics of Al. Al has the highest frequency phonons of all the metals we are considering. If assuming $\chi \approx k_B T \pi \hbar \lambda \langle \omega^2 \rangle$ does not cause considerable error in our predictions for Al, we conclude it is a reasonable approximation for all the metals we consider. We take $\alpha^2 F(\omega)$ from Waldecker et al.⁵ and find τ_E for Al changes by less than 2% if we use χ as defined in Eq. (S17) instead of $\chi \approx k_B T \pi \hbar \lambda \langle \omega^2 \rangle$. The change in τ_E is small because the dynamics are not sensitive to χ .

Our treatment of e-p interactions is similar to other theoretical studies on nonequilibrium electron dynamics that numerically solved the Boltzmann rate equations, e.g. Del Fatti *et al.*⁶, and Rethfeld *et al.*⁷. Del Fatti *et al.* assumed a Debye-like phonon dispersion, and assumed a constant value for the electron-phonon matrix element M . They then fixed the value of the constant by fitting pump/probe data. Rethfeld *et al.* followed a similar procedure as Del Fatti, but with a simple functional form for the e-p matrix element taken from Ashcroft and Mermin. Making these assumptions result in different values for $\lambda \langle \omega^2 \rangle$ than what we used, and so their assumptions result in different predictions for τ_E .

Once Eq. (S16) is solved, it is straightforward to calculate the energy dynamics as a function of time.

$$E_{tot}(t) = \int_{-\infty}^{\infty} (\varepsilon + \varepsilon_f) D(\varepsilon) \phi(\varepsilon) d\varepsilon. \quad (\text{S18})$$

Here, $D(\varepsilon)$ is the electron density of states, and ε_f is the Fermi-energy.

Supplementary Note 2

In our calculations, we made three assumptions that are only rigorously valid if the electronic density of states does not have significant energy dependence. We discuss why these assumptions are reasonable here, and how we expect them to affect our results.

First-principles calculations suggest the strength of e-p interactions vary in transition metals by as much as a factor of five within 2-3 eV of the Fermi-level⁸. 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 τ_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 τ_H is determined by e-e interactions. Second, τ_E is sensitive to the strength of e-p interactions at electron energies that are occupied on τ_E time-scales. On τ_E time scales, nearly all nonequilibrium electrons are within a few hundred meV of the Fermi level, see Fig. 2b in main text. Assuming a constant e-p interaction across energy scales of a few hundred meV is reasonable, even in most transition metals. 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, we performed first-principles calculations for the value of $\lambda \langle \omega^2 \rangle$ at the Fermi-level vs. 0.5 eV above the Fermi-level. These calculations suggest $\lambda \langle \omega^2 \rangle$ varies by a factor of two from ~ 120 to 60 meV^2 . Therefore we expect our model to underestimate τ_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 ε^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. Transition metals do not display an ε^2 energy dependence away from the Fermi-level, partly due to interband transitions. We show this in Supplemental Figure 4 by comparing our model's predictions for $\tau_{ee}(\varepsilon)$ to first principles based predictions by Ladstädter *et al.*¹. This oversimplification will cause a small error for τ_E , because sensitivity to e-e interactions is small. A factor of two change in the in e-e scattering time at all energies will cause a $\sim 20\%$ change in our model's predictions for τ_E . Alternatively, τ_H is entirely determined by the e-e scattering time of high energy excitations, and therefore the error will be larger. A factor of two decrease in the e-e scattering times of high energy electrons, i.e. those with $\varepsilon > hv/2$, would lead to a factor of two decrease in the value of τ_H .

We assumed the photoexcitation of a metal with photons of energy hv results in an initial occupation of electrons and holes that is independent of energy within hv of the Fermi level. This assumption will affect τ_H , but not τ_E . τ_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, τ_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.

Supplementary Note 3

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. We arrived at these phenomenological expressions by fitting curves to the numerical results to Eq. (1) for τ_E and τ_H . They are not analytically derived.

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

$$\tau_E \gamma_{ep} \approx 1 + A \left\{ 1 - \tanh \ln \left[B \left(\frac{\gamma_{ep}}{\beta_{ee}} \right)^{-0.42} \right] \right\} + C \left\{ \operatorname{sech} \ln \left(D \left(\frac{\gamma_{ep}}{\beta_{ee}} \right)^{-0.42} \right) \right\}^2, \quad (\text{S-17})$$

With $A = -0.34 + 2.3(h\nu / eV)$, $B = 1.5(h\nu / eV)^{1.2}$, $C = -0.25 + 0.53(h\nu / eV)^{1.1}$, and $D = 0.63(h\nu / eV)$.

Alternatively, the lifetime of high energy electrons is well approximated as

$$\tau_H \beta_{ee} (h\nu)^2 \approx E \left\{ 1 + \tanh \ln \left[F \left(\frac{\gamma_{ep}}{\beta_{ee}} \right)^{-0.47} \right] \right\}, \quad (\text{S-18})$$

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

Supplementary References

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